## RM_MWGL Regional Meeting 1

### Capping and passivation of aluminum nanoparticles with epoxy-alkenes

***Brandon J Thomas***[1], *bthoma21@slu.edu, Katherine Wentz*[2], *Elena Guliants*[3], *Christopher E Bunker*[4], *Sophia E Hayes*[2], *Paul A Jelliss*[1], *Steven W Buckner*[1]. *(1) Department of Chemistry, Saint Louis University, Saint Louis, Missouri 63103, United States (2) Department of Chemistry, Washington University, Saint Louis, Missouri 63130, United States (3) Department of Electrical & Computer Engineering, University of Dayton Research Institute, Dayton, Ohio 45469, United States (4) Propulsion Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States*

Aluminum nanoparticles (AlNPs) have applications in small-scale hydrogen production & high-density energy storage. However, production of air stable AlNPs has proved challenging as Al readily reacts with $O_2$ & $H_2O$. This leads to formation of a 2-6 nm $Al_2O_3$ layer on the AlNP surface. For particles on the order of 20 nm in diameter, this oxide layer can comprise a huge percentage of the particle's mass (> 70%). Our goal is to produce air-stable core-shell aluminum nanostructures that are resistant to reactions with $H_2O$. We report on the synthesis of AlNPs capped & passivated with 1,2-epoxy-9-decene. Epoxides have proven to be an effective capping agent for AlNPs as the epoxide functionality can readily react with Al. By also inducing polymerization of the terminal alkene functionality of the epoxide, we produce AlNPs with long-term air stability on the order of 6 weeks. These nanostructures are embedded in an interconnected hydrophobic polymer matrix, preventing penetration of the Al core by water. Raman Spectroscopy and Solid-State NMR results are presented to confirm alkene polymerization. We also present results from PXRD, ATR-FTIR, DSC/TGA, & titrimetric analysis to confirm the presence of active aluminum. TEM images are presented to determine particle sizes.

---

## RM_MWGL Regional Meeting 2

### Nanoneedles and Nanowires of superconducting FeSe encapsulated by carbon nanotubes

*Dr. Manashi Nath, **Sukhada Patil**, scpcq5@mail.mst.edu. Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65401, United States*

Iron chalcogenides have attracted considerable attention due to their novel electronic and magnetic properties which make them useful in magnetic semiconductor and spintronic devices. Recently iron selenide, crystallizing in the tetragonal phase, has been in the center of attraction after sudden discovery of superconductivity ($T_C$ = 8K). We have synthesized FeSe nanowires encapsulated inside carbon nanotubes by a simple CVD reaction at 800°C from the volatile precursors, iron acetylacetonate and elemental Se. The core-shell FeSe/C nanotubes were grown on Au-coated Si substrates. The diameters of the nanotubes were 30-50 nm while the length exceeded

several µm. The FeSe filling length could be varied by modifying the reaction conditions. In some cases the FeSe filling was pronounced and hollow at the tip and tapered down towards the tube interior forming a nanoneedle. The core-shell nanotubes were characterized by powder x-ray diffraction, SEM, HRTEM, EDAX, SAED with elemental mapping and magnetic measurements.

**RM_MWGL Regional Meeting 3**

## Aniline capped gold colloids by solvated metal atom dispersion method

***Yijun Sun**, kuailenv@ksu.edu, Kenneth J Klabunde. Department of Chemistry, Kansas State University, Manhattan, KS 66502, United States*

Thoils were found to be very efficient ligands for the digestive-ripening process, during which a colloidal suspension in a solvent is refluxed at the solvent boiling temperature in the presence of a capping ligand to convert a highly polydisperse colloid into a nearly monodisperse one. Lots of work has been done by using thiols as the capping ligands to form gold colloids in our group. Apart from thiols, we are also interested in using amines, which were also found to have similar efficiency for this purpose. We want to differentiate between thiols and amines as the ligands in gold colloids. Our method is based on the solvated metal atom dispersion technique (SMAD), which is very suitable for preparation of large amounts of metal colloidal solutions. We prepared aniline capped Au colloids in butanone using our SMAD method and these colloids were characterized using electron microscopy and spectroscopic techniques such as UV-visible, NMR, FT-IR etc. The details about our findings towards aniline capped Au colloids would be discussed in the presentation.

**RM_MWGL Regional Meeting 4**

## Effects of the potential energy landscape on exciton delocalization in single 1-d quantum wires

***Virginia L Wayman**[1,2], vlwayman@wustl.edu, Robert A Burnett[1,2], Benjamin S Hoener[1,2], P J Morrison[1,2], Fudong Wang[1,2], William E Buhro[1,2], Richard A Loomis[1,2]. (1) Department of Chemistry, Washington University, St Louis, MO 63130, United States (2) Center for Materials Innovation, Washington University, St Louis, MO 63130, United States*

Due to their one-dimensional (1-D) character, semiconductor quantum wires (QWs) have been considered for use in opto-electronic devices that implement charge-transport techniques. The potential energy landscape of a QW is not uniform due to varying surface passivation and structural defects. A photogenerated exciton in a QW will likely encounter a potential minima (or trap site), thus hampering its ability to behave as a free wave in a 1-D cylinder. In this work, we have modified the potential energy landscape of a single QW to investigate the quantum-mechanical behavior of excitons. Delocalization of bound excitons has been observed over an entire CdSe QW, with

distances up to 10 microns. The role of subtle potential energy fluctuations in the landscape of a QW on exciton dynamics has been studied by performing temperature-dependent studies at 4 K.

## RM_MWGL Regional Meeting 5

## Effect of doping transition metal ions on silica and titania aerogel systems

***Manindu N Weerasinghe****, manindu@ksu.edu, Kenneth J Klabunde.Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Transition metals and their respective ionic species show various properties depending on the number of *d* electrons available on their outermost electronic shell. There are a large number of reports on transition metal ions doped systems for catalytic, environmental remediation as well as in photo-catalytic water splitting studies. It is very interesting to study the effects of the doped transition metal ions and the host materials on textural, optical, and catalytic properties.

We have synthesized a novel silicon dioxide ($SiO_2$) and titanium dioxide ($TiO_2$) based systems doped with different transition metal ions such as cobalt, chromium and vanadium ions using well-known aerogel synthesis method. These samples were characterized with X ray photoelectron spectroscopy, BET surface area analysis, X-ray diffraction studies and Diffuse reflectance UV-Vis spectroscopic measurements. Catalytic and photocatalytic activities were determined using acetaldehyde as a model pollutant. According to the kinetic studies chromium doped systems showed very high visible light photocatalytic activity while cobalt doped systems show dark catalytic activity towards acetaldehyde decomposition. Moreover, silica based systems tend to show higher catalytic activities compared to titania based systems.

Oxygen absorption studies are currently carrying out in our lab to determine the ability of these catalysts to bind with oxygen and create reactive oxygen species. Detailed study of the catalysts will be carried out to understand the mechanisms of catalytic/photocatalytic activities of the systems.

## RM_MWGL Regional Meeting 6

## Coaxial silicon coating on vertically aligned carbon nanofibers for high-performance lithium-ion batteries

***Steven Arnold Klankowski***[1]*, sklank@k-state.edu, Jun Li*[1]*, Ronald Rojeski*[2]*.  (1) Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States  (2) 200 Carlyn Avenue, Suite C, Catalyst Power Technologies, Campbell, CA 95008, United States*

Improving the energy capacity, charging/discharging speed, and lifetime of Lithium-ion batteries is critical for their broader applications in portable electronics and hybrid

electrical vehicles. We report a study on the development of a three-dimensional core-shell nanowire architecture anode for high-performance Li-ion batteries. This unique anode comprises of an amorphous silicon layer coaxially coated on a forest-like nanostructure of vertically aligned carbon nanofibers (VACNFs) that is grown on a substrate of 0.0033 inch thick Copper foil. The highly conductive VACNFs are firmly attached to the substrate and provide a good electron-conducting pathway while mechanically supporting the silicon coating upon charge/discharging cycling. The freedom in radial expansion also accommodates Silicon's large volume expansion upon lithiation (up to 300%) and thus improves the cycle stability. This nanostructured anode was characterized against a Lithium metal electrode with cyclic voltammetry and galvanostatic charging/discharging measurements to determine energy storage capacity, capacity retention, coulombic efficiency, and cycle lifetime.
Our results demonstrated that the silicon coating with the nominal thickness of 500 nm and 1500 nm presents a Lithium storage capacity of ~3,000 to 3,500 mAh/g at C/2 power rate, close to the theoretical capacity of 4,200 mAh/g, and greater than 96% coulombic efficiency. This capacity is about an order of magnitude larger than that of commercial graphite anodes (~370 mAh/g). Besides the loss at initial cycling owing to the formation of solid electrolyte interface, the capacity remains relatively stable in following charging/discharging processes. The Silicon thickness and the carbon nanofiber length are currently being optimized to improve cell life and increase storage capacity.

**RM_MWGL Regional Meeting 7**

## Characterizing the excitation-energy dependence of photoluminescence quantum yields in quantum nanostructures

***Jessica Hoy***[1,2]*, jhoy@wustl.edu, Yi-Hsin Liu*[1]*, Lindsey Steinberg*[1,2]*, William E Buhro*[1,2]*, Richard A Loomis**[1,2]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63105, United States (2) Center for Materials Innovation, Washington University in St. Louis, St. Louis, Missouri 63105, United States*

We have characterized the photoluminescence (PL) efficiency of room-temperature CdSeZnS core-shell quantum dots (QDs) and CdTe quantum wires (QWs). We have measured PL quantum yields (QYs) as high as 72% and 15% for the QDs and QWs, respectively. Although photons can be absorbed for wide ranges of energies above the band-edge energy of the quantum nanostructures, emission only occurs near the band edge. The excess energies with which the excitons (electron-hole pairs) are prepared do strongly influence the PL QYs as non-radiative pathways compete with relaxation to the band edge. Subtle differences between the excitation-energy dependences of the PL quantum yields measured for the QDs and QWs are justified by considering the dimensionalities, electronic energies, and possible exciton translational kinetic energies associated with the nanostructures.

**RM_MWGL Regional Meeting 8**

### Tuning titanium dioxide nanomaterials for renewable energy applications

***Xiaobo Chen**, chenxiaobo@umkc.edu. Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110, United States*

The rapid depletion of the fossil fuel reserves, the increase of green-house gas emissions and other environmental pollutions, bring up an urgent need for the development of renewable and clean energy sources. The ability to use sunlight to produce fuels such as $H_2$ and electricity from abundant, non-toxic resources, and to decompose environmental pollutions with benign catalysts, would improve our livings. Here, I would like to present our research on how to turn white titanium dioxide into yellow and black titanium dioxide, in order to efficiently remove pollutions and generate hydrogen from water. The fundamental materials and physiochemical characterizations will be discussed in details.

**RM_MWGL Regional Meeting 9**

### Hybrid titanium dioxide nanomaterials for dye-sensitized solar cells

***Hongshan He**, hongshan.he@sdstate.edu, Yihan Zhong, Mukul Dubey, Maheshwar Shrestha, Liping Si. Center for Advanced Photovoltaics, South Dakota State University, Brookings, SD 57007, United States*

$TiO_2$ nanoparticles (NPs) have very high surface area, which allows for their sufficient dye loading for efficient dye-sensitized solar cells (DSCs). However, electrons from dyes have to migrate between $TiO_2$ NPs to the fluorine-tin-oxide (FTO) semiconductor

layer underneath to the external circuit. During this process, severe electron recombination occurs, lowering electron collection efficiency and thereby limiting the efficiency of devices. One way to minimize electron recombination in DSCs is to apply $TiO_2$ nanotubes ($TiO_2$ NT). One disadvantage of $TiO_2$ NTs is their low surface area. A simple calculation shows that total surface area of $TiO_2$ NTs is only ~18% of that of $TiO_2$ NPs with same thickness and projected area on FTO glass. Therefore it is critical to develop method to increase their surface area. In this report, a novel and low-cost in situ methods to hybrid $TiO_2$ NPs into $TiO_2$ NTs will be reported. The resulting nanostructures were characterized by scanning electron microscope (SEM) and atomic force microscope (AFM). The resulting materials were fixed on FTO glass and their performance was tested in the dye-sensitized solar cells. A significant photovoltaic enhancement was observed, which could have dramatic impact on the development of high efficiency solar cells.

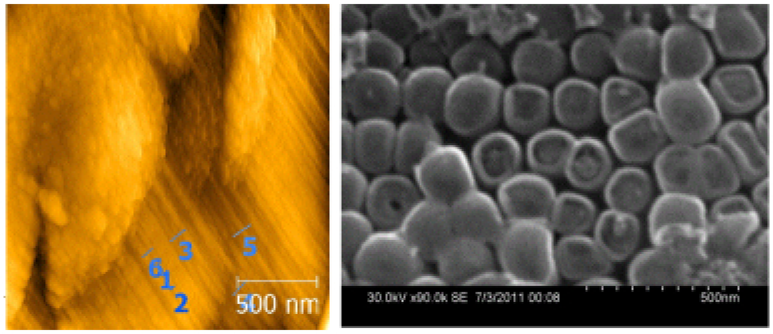


Figure 1. AFM (Left) and SEM (right) of hybridized $TiO_2$ nanostructure

---

## RM_MWGL Regional Meeting 10

### $TiO_2$ compact layers prepared by low temperature colloidal synthesis and deposition for high performance dye-sensitized solar cells

***Curtiss S Kovash***, *curtiss.kovash@sdstate.edu, Brian A Logue.Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, United States*

Compact layers are used in dye-sensitized solar cells (DSSCs) to passivate transparent conducting oxides (TCOs). TCO passivation increases DSSC performance by reducing electrical loss from recombination at the TCO-electrolyte interface and by improving electrical contact between the TCO and $TiO_2$ photoelectrode. A novel process for synthesis of colloidal $TiO_2$ compact layer particles (4.0±1.0 nm diameter) via acid hydrolysis of titanium isopropoxide was developed. DSSCs fabricated with the colloidal $TiO_2$ compact layer, with no compact layer, and those with an RF-sputtered compact layer were evaluated. Relative to a DSSC with no compact layer, the colloidal compact layer improved the short-circuit current density, fill factor, and solar energy-to-electricity conversion efficiency by 17.6%, 4.44%, and 25.3%, respectively. Relative to the sputtered compact layer, the colloidal compact layer improved the short-circuit current density and solar energy-to-electricity conversion efficiency by 5.47% and 5.32%,

respectively, with no significant change in the fill factor. The improved DSSC characteristics were attributed to increased shunt resistance due to decreased electrolyte reduction at the TCO-electrolyte interface and decreased series resistance due to improved electrical contact between the TCO and the $TiO_2$ photoelectrode.

## RM_MWGL Regional Meeting 11

## Design of MspA-based solar cells

***Ayomi Perera***, *ayomee@ksu.edu, Sebastian Wendel, Hongwang Wang, Stefan H. Bossmann.Chemistry, Kansas State University, Manhattan, Kansas 66506-0401, United States*

MspA is a very stable mycobacterial porin. We are utilizing MspA to create a precisely defined geometry in the light-absorbing layer of a solar cell to prevent recombination of charge carriers due to disorder. The Shockley-Queisser efficiency limit describes the theoretical limit of solar cells; a Grätzel cell type solar cell can reach up to 32% efficiency. However, the efficiency that has been reached was of the order of only 15%. Recombination processes account for the difference between the theoretical threshold and the efficiency that has been observed in optimized cells. It is our paradigm that MspA will provide the missing ordering factor that will lead to increased efficiency. We will discuss the purification of MspA, the synthesis and attachment of ruthenium(II)polypyridyl-type sensitizers, and the photophysical results obtained with these “nano solar cells”. Strategies for large-scale solar cell production will be presented.

## RM_MWGL Regional Meeting 12

## Solution-based synthesis of crystalline titanium disulfide nanobelts

***Vladimir V. Plashnitsa***, *Vladimir.Plashnitsa.1@nd.edu, Pornthip Tongying, Galina Krylova, Masaru K. Kuno.Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, United States*

Layered titanium dichalcogenides ($TiX_2$, where X = S, Se) are typical representative members of an extended family of quasi two-dimensional (2D) 3d–5d metal dichalcogenides that exhibit anisotropic physical properties. This arises from strong covalent M–X intralayer bonding in comparison to weak interlayer van der Waals bonding. In recent years, there has been a renaissance in studying nanostructured titanium disulfide, $TiS_2$, because of its different physical-chemical properties in comparison to the bulk. Namely, while bulk $TiS_2$ is a semimetal, nanostructured $TiS_2$ falls into a category of narrow-gap semiconductors, where the band gap can be tuned by changing nanostructure morphology.

Crystalline $TiS_2$ thin films have been conventionally prepared using chemical vapor deposition (CVD). In general, this entails decomposing different titanium and sulfur

precursors at temperatures above 500 $^{o}$C. More recent studies, however, have revealed the possibility to obtain $TiS_2$ nanostructures using wet chemical syntheses. In the present study, we demonstrate a facile approach for preparing nanostructured, belt-like $TiS_2$ using solution chemistry. Low and high resolution transmission electron microscopy (TEM) images reveal the formation of ultra-thin crystalline belt-like $TiS_2$ nanostructures with an average length of 400-500 nm and with widths of 10-25 nm. Additional studies have focused on the physical/chemical properties of these obtained $TiS_2$ nanobelts. This includes possible photocatalytic hydrogen generation under visible light irradiation. The preliminary UV-Vis measurements have indicated the presence of a broad absorption between 580 – 610 nm, which suggests the existence of an apparent band gap.

**RM_MWGL Regional Meeting 13**

## Synthesis of hybrid arylene ethynylene macrocycles via alkyne metathesis depolymerization

***Dustin E Gross**, degross@illinois.edu, Jeffrey S Moore.Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

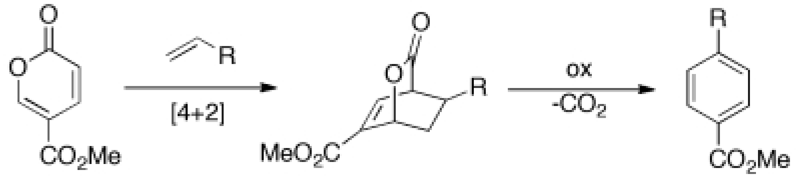
Arylene-ethynylene macrocycles (AEMs) are an interesting class of molecules due to their ability to self-assemble into multi-dimensional supramolecular nanostructures. Recently we reported the thermodynamically controlled macrocyclization using a highly active molybdenum alkylidyne catalyst and functionalized diyne monomers. We also extended this methodology to the depolymerization of arylene ethynylene polymers. Using this method we have been able to synthesize discrete macrocycles from homopolymers in good yield on a preparatively useful scale. We have now broadened the scope of this technique to create a combinatorial library of hybrid AEMs from the depolymerization of arylene ethynylene copolymers.

**RM_MWGL Regional Meeting 14**

## Aromatics from pyrones: 4-Substituted alkyl benzoates from alkenes, coumalic acid and methyl coumalate

***Sean J Riley**[1,2], srile y@iastate.edu, George A Kraus[1,2]. (1) Center for Biorenewable Chemicals, Ames, IA 50011, United States (2) Department of Chemistry, Iowa State University, Ames, IA 50011, United States*

The Diels–Alder reaction of either coumalic acid or methyl coumalate with unactivated alkenes provides only para-substituted adducts in good yield. It proceeds via a bicyclic intermediate followed by a decarboxylative aromatization reaction facilitated by catalytic palladium on carbon. This represents one of the few methods of producing aromatic compounds from biobased starting materials, and is a potential route towards the preparation of terephthalic acid.

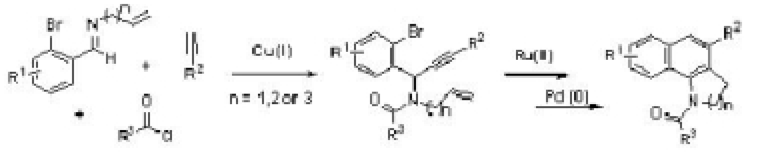


## RM_MWGL Regional Meeting 15

## Modular syntheses of tetrahydro benzoquinolines and dihydro benzoindoles via sequential copper, ruthenium and palladium catalyzed reactions.

***Sandeep N Raikar***[2], *snraikar@ku.edu, Helena Malinakova*[1]. *(1) Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States (2) Department of The Center for Chemical Methodologies and Library Development, University of Kansas, Lawrence, Kansas 66047, United States*

Transition metals efficiently catalyze carbon-carbon bond forming reactions. We have been investigating the use of sequences of different metal catalyzed reactions in the synthesis of heterocycles. Herein we report our studies on a strategic sequence of Copper, Ruthenium and Palladium catalyzed reactions for the synthesis of tetrahydro benzoquinolines and dihydro benzoindoles. The efforts towards the design of a one pot protocol based on this methodology will be presented



## RM_MWGL Regional Meeting 16

## Reaction pairing: A modular approach to diversity-oriented synthesis of benzofused sultams

***Joanna K Loh***, *joannaloh@ku.edu, Thiwanka B Samarakoon, Alan Rolfe, Sun Young Yoon, Paul R Hanson*. Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States*

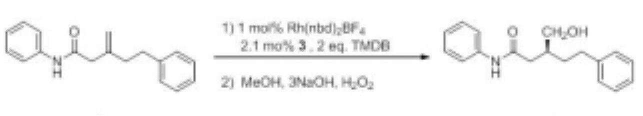
A reaction pairing strategy focused on the utilization of a collection of reactions (sulfonylation, $S_NAr$ addition and Mitsunobu alkylation) to generate skeletally diverse benzofused sultams is reported. The pairing of sulfonylation and $S_NAr$ reactions rapidly generates tricyclic, bridged benzofused sultams. The addition of the Mitsunobu reaction in a sulfonylation–Mitsunobu–$S_NAr$ sequence allows access to benzo-oxathiazocine-1,1-dioxides, while a simple change in combination to sulfonylation–$S_NAr$–Mitsunobu affords structurally distinct tricyclic, bridged benzofused sultams. With these scaffolds in hand, two 40-member libraries were efficiently prepared via a microwave-assisted intermolecular $S_NAr$ diversification reaction.

## RM_MWGL Regional Meeting 17

## Carbonyl-directed catalytic asymmetric hydroboration of 1,1-disubstituted alkenes

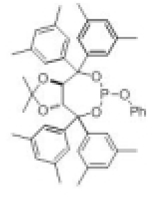
***Mohammad Odeh Bani Khaled**, mohammad@huskers.unl.edu, sean smith, Gia Hoang, James M Takacs. Department of Chemistry, University Of Nebraska-Lincoln, Lincoln, Nebraska 68588, United States*

The efficient asymmetric hydroboration of 1,1-disubstituted alkenes remains as an unsolved problem with the exception of a few recent examples. We find that simple chiral monophosphite and -phosphoramidite ligands in conjunction with $Rh(nbd)_2BF_4$ serve as highly effective catalysts for the carbonyl-directed catalytic asymmetric hydroboration (CAHB) of a small series of 1,1-disubstituted alkenes within a *β*,*γ*-usaturated phenyl amide molecular framework. For example, CAHB of phenyl amide **1** with TMDB and $Rh(nbd)_2BF_4$ in combination with (xTADDOL)POPh (**3**) affords γ-hydroxyamide **2** in excellent enantiomeric purity (**72**%, **94**% ee) **.**This talk will discuss the efficiency of directed catalytic Asymmetric Hydroboration of 1,1–disubstituted alkene.



1

2



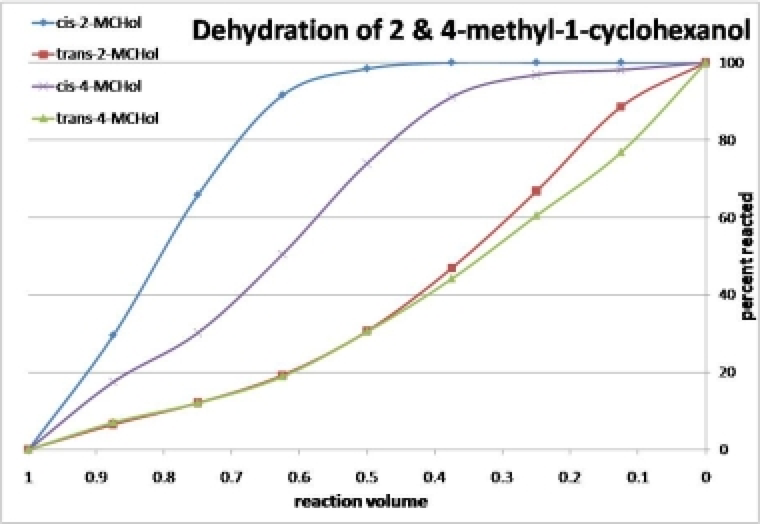
3

## RM_MWGL Regional Meeting 18

### Dehydration of 3 and 4-methyl-1-cyclohexanols: A study of reaction rates and product distributions

***Nicola Toritto***, *jbfriesen@dom.edu, J. Brent Friesen. Department of Physical Sciences, Dominican University, River Forest, Illinois 60305, United States*

The product distribution and kinetics of the mineral acid catalyzed dehydration of cis and trans-2-methyl-1-cyclohexanols have been systematically investigated. However, comparatively little is known about the analogous dehydration of 3 and 4-methyl-1-cyclohexanols which also exist in the form of
cis and trans diastereomers. A series of kinetic experiments for 2, 3, and 4-methyl-1-cyclohexanol were performed to monitor the disappearance rates of the each diastereomer by gas chromatography with a flame ionization detector (GC-FID). For all three methylcyclohexanols the less stable diastereomer, in which both ring substituents cannot be simultaneously equatorial, reacts faster than the more stable diastereomer. Among the three less stable isomers, cis-2-methyl-1-cyclohexanol reacts faster than trans-3-methyl-1-cyclohexanol and cis-4-methyl-1-cyclohexanol.



In this study, the distribution of 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 4-methyl-1-cyclohexene, ethylidenecyclopentane, and
methylenecyclohexane dehydration products were monitored with GC-FID and NMR at regular intervals. Generally, the less stable diastereomers react to give predominantly a single alkene as the product. By comparison, the more stable diastereomers yield a more varied assortment of alkenes. The implications of these findings for the dehydration mechanism will be presented.

## RM_MWGL Regional Meeting 19

### Predicting DNA-intercalator binding: The development of an arene-arene stacking parameter

***Laura K.E. Hardebeck**, lhardebe@slu.edu, Charles A. Johnson, Yi Ren, Tyler Zahrli, Brent M. Znosko, Michael Lewis. Department of Chemistry, Saint Louis University, Saint Louis, Missouri 63103, United States*

The synthesis of a series of substituted napthalimides, along with their intercalation into one sequence of DNA, will be presented as well as two QSAR analyses. First, a two-parameter QSAR analysis, incorporating one electronic parameter and one dispersion/polarizability parameter, was performed to generate a theoretical $\Delta T_m$ value, which was then correlated to an experimentally determined $\Delta T_m$ value. Secondly, a one-parameter QSAR analysis was performed utilizing a novel arene-arene stacking parameter, $\prod^{\pi}$, developed in our group. The $\prod^{\pi}$ parameter was developed from computationally determined binding energies of parallel stacked benzene-substituted benzene dimer systems. The results of this study indicate that a one parameter analysis using the $\prod^{\pi}$ parameter produce correlations equal to or exceeding that of the two parameter analysis, which incorporated commonly used QSAR descriptors.

## RM_MWGL Regional Meeting 20

### Enhancing photoreactivity of co-crystals by utilizing molecular pedal motion in the organic solid state

***Ryan H. Groeneman**[1], rgroenem@jeffco.edu, Elizabeth Elacqua[2], Leonard R. MacGillivray[2]. (1) Department of Chemistry, Jefferson College, Hillsboro, MO 63050, United States (2) Department of Chemistry, University of Iowa, Iowa City, IA 52242, United States*

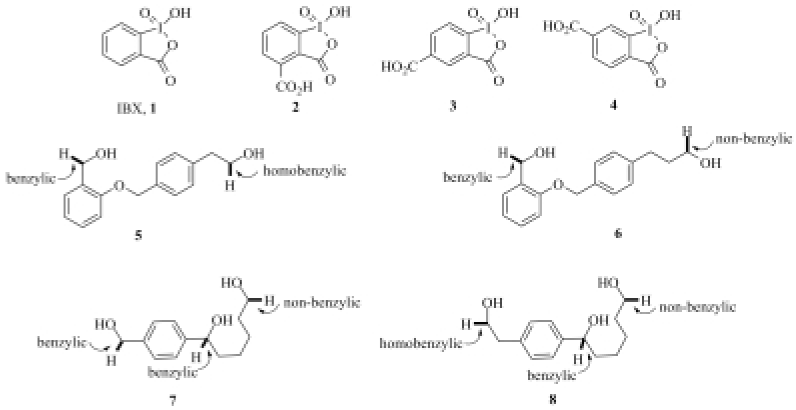
It has been demonstrated that organic molecules based on stilbenes and azobenzenes will undergo a pedal motion in the solid state. The ability to convert from one conformation to another can change the overall chemical and physical properties of a crystal. In an investigation to study the [2+2] cycloaddition reaction involving various ester-containing olefins in the solid state, we have discovered an enhanced reactivity of stilbene-like compounds over smaller ligand systems. We believe the enhanced reactivity is a result of the olefin undergoing a change in conformation due to pedal motion. In this lecture, we will report a series of resorcinol based co-crystals with two different olefins that demonstrate varying photochemical reactivity. The structures of the co-crystals as well as the cyclobutane based-photoproducts will be discussed as well as the photochemical conditions that are required for this type of reaction. This work is generously supported by the National Science Foundation and PRISSM.

## RM_MWGL Regional Meeting 21

### New insights into an alternate mechanism for oxidation of alcohols using iodine (V) reagents

*Balaram Raya, Kishor K Madne, Savithri Jajam, **Thottumkara K. Vinod**, mftkv@wiu.edu. Department of Chemistry, Western Illinois University, Macomb, IL 61455, United States*

Hypervalent iodine (V) reagents, *o*-iodoxybenzoic acid (IBX, **1**) prominent among them, have become reagents of choice for a wide range of selective oxidative transformations in synthetic organic chemistry. The currently accepted mechanism of oxidation of alcohols by IBX in polar aprotic solvents is the well-established ligand exchange mechanism. We have recently reported the synthesis of three new water-soluble IBX derivatives, **2**-**4**, as user-friendly substitutes for the DMSO soluble parent reagent, IBX. While the ease and selectivity of oxidation of alcohols using the new IBX derivative parallel that of IBX in polar aprotic solvents, the selectivities observed in the oxidation of diol and triol substrates, **5-8** in aqueous solvent mixtures allude to an alternate oxidation mechanism. The observed selectivities are explained using a mechanism involving an initial H-atom abstraction followed by a single electron transfer (SET) step and correlated to the bond dissociation energies of the benzylic, homobenzylic and non-benzylic αC-H bonds involved in the initial H-atom abstraction step.

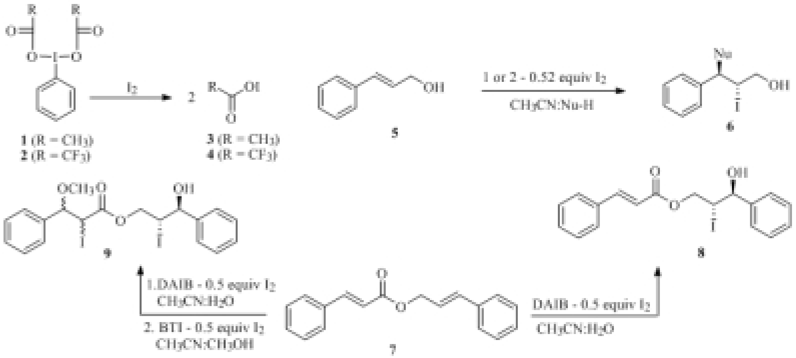


## RM_MWGL Regional Meeting 22

## Iodine atom economic co-iodination of alkenes: Selective and differential functionalization of the two double bonds in dienes

*Himabindu Gottam, Madhumitha Kistammagiri, Sonali R. Pandey, **Thottumkara K. Vinod**, mftkv@wiu.edu. Department of Chemistry, Western Illinois University, Macomb, IL 61455, United States*

In-situ generation of acetyl hypoiodite, **3**, and trifluoroacetyl hypoidite, **4**, from the oxidation of elemental iodine using diacetoxyiodobenzene (DAIB, **1**) and bis(trifluroacetoxy)iodobenzene (BTI, **2**) respectively and the subsequent use of these hypoiodite reagents in co-iodination of alkenes is reported. The observed 100% iodine atom economy in the reaction is mechanistically justified and unequivocally demonstrated by 1H NMR investigation. Synthetic utility of this new procedure for the co-iodination of alkenes is highlighted by the use of a diverse array of nucleophilic components in the reaction for rapid assembly substituted alkanes from alkenes. Selective co-iodination of the electron rich double bond in dienes is observed when **1** is the electrophilic iodine source in the reaction, while the use of **2** results in exhaustive functionalization of both double bonds in dienes. Careful choice of the hypervalent iodine oxidants and the nucleophilic components in the reaction allows for selective and sequential functionalization of the two double bonds of dienes as shown below in the conversion of **7** to **8** and **9** respectively. These and other selective co-iodination of alkenes will be discussed.



**RM_MWGL Regional Meeting 23**

## From sewage sludge to ebooks: An academician's ventures into the small business world

***Stanley E Manahan***, ManahanS@missouri.edu. *Department of Chemistry, University of Missouri, Columbia, MO 65201, United States*

In 1968 the author shifted his research and academic endeavors to environmental chemistry. In 1971 he wrote a textbook on environmental chemistry that is now in its 9th edition, which was followed by a number of related books through a succession of publishers. His subsequent research on coal gasification led to the development of a process for gasification of wastes and the establishment along with a faculty colleague from another campus of a small company to attempt to commercialize the waste gasification process. Two SBIR contracts, a U. S. Department of Energy contract, and several other grants were obtained to support the development and commercialization of the waste gasification process, which resulted in the construction and operation of a pilot-scale gasifier and development of successful methods for the treatment of a variety of wastes including low-level radioactive wastes, refractory organics, sewage sludge, and other materials and included two patents. Unfortunately, the means were never found to commercialize the process. Throughout, the author maintained his interest in book publishing and the name of the company set up to treat wastes lives on as a

nameplate for several ebooks currently published in environmental science, green chemistry, and sustainability science and technology.

## RM_MWGL Regional Meeting 24

## So, you want to be a consultant? Here's how to do it.

***David Webster**, david.webster1@sbcglobal.net.ddw2, LLC, Fishers, IN 46038, United States*

Today's biotechnology, chemical, and pharmaceutical, companies have a steady stream of consultants - contract individuals - knocking on their door. How do they get in and sell their products and services, i.e., land a contract? A successful consultant must be ready with credentials (not a resume), an understanding of the client's needs, knowledge of the important variables of each opportunity, and be prepared to sell his/her persona to the decision maker. Customers also expect intangibles: the “jello”, which is “Does it feel right to everyone?” If any reservations arise, you are history and better re-group and move on to the next potential client. The customer has the final say and the bottom line is “Can these consultants cut our costs and improve our revenue and profits?” Each consultant offers a different product/service mix, analytical support, and subcontractors. What is best for you? Learn how one can position yourself, with some basic principles and tools, to be your own boss and land consulting contracts.

## RM_MWGL Regional Meeting 25

## NUtech Ventures: Catalyzing startup success

***Jane Garrity**, jgarrity@nutechventures.org. NUtech Ventures, Lincoln, NE 68508, United States*

NUtech Ventures is a nonprofit affiliate of the University of Nebraska that helps university researchers partner with the private sector to commercialize technologies based on their pioneering research – or in some cases, to join the private sector through entrepreneurship. Technology Agent Jane Garrity will discuss how NUtech Ventures works with prospective entrepreneurs to turn their inventions into successful businesses. This may involve finding technical or business partners, developing a patent strategy, reviewing a business plan, or identifying funding opportunities. Examples will be provided of successful Nebraska spinout companies. Dr. Garrity will also discuss NUtech Ventures' upcoming programs for entrepreneurship education and proof-of-concept funding.

## RM_MWGL Regional Meeting 26

## Terminated to terminator

***Jerry Jost**, jerry.jost@jostchemical.com. Jost Chemical Company, Saint Louis, MO 63114, United States*

This is the story of Jost Chemical Company: 25 years ago, an undercapitalized, start-up chemical manufacturing company with one full-time and two part-time employees that today has grown to 150 employees. It's a story of a great bunch of people (the right people on the bus) taking a company from ground zero to an Ernst and Young Entrepreneurial Company 2010 national finalist in 25 years. The growth of Jost Chemical Co has been an amazing average of 27% per year over the company's 25-year history. Learn what Jost did right and what they would do-over to make it even better.

**RM_MWGL Regional Meeting 27**

## Chemistry in the pharmaceutical industry, part one

***Todd M Stark**, todd.m.stark@gmail.com. Johnson Matthew Pharma Services, Devens, MA 01434, United States*

We will explore synthetic, analytical and physical chemistry throughout the drug discovery and development process. In part one, the focus will be on discovery from initial screening for activity, medicinal chemistry, pre-clinical testing, to filing an IND.

**RM_MWGL Regional Meeting 28**

## Synthesis of fluorophores that reveal dynamic aspects of physiology in vivo in *C. elegans*

***Blake R Peterson**[1], brpeters@ku.edu, Zachary R Wodziak[1], Aaron M Bender[2], Liqiang Fu[1], Michael Branden[1], Nora M Wallace[1], Zhenguo Zhou[1], Mashesh Visvanathan[1], Gerald H Lushington[1], Brian D Ackley[2]. (1) Department of Medicinal Chemistry, University of Kansas, Lawrence, KS 66045, United States (2) Department of Molecular Biosciences, University of Kansas, Lawrence, KS 66045, United States*

Animal cells sense and precisely control intracellular and extracellular pH for cell survival, maintenance, and defense against pathogens. Disregulation of this process is known to contribute to inflammation, cancer proliferation, and cardiovascular disease. In the nematode model organism *C. elegans*, previous studies of fluorophores quenched by acid have revealed that the pH of the lumen of the intestine of this animal sharply oscillates during the defecation motor program (DMP), a process controlled by calcium-mediated signaling in intestinal cells. As a new approach to visualize and quantify dynamics of acidification of tissues in vivo, we synthesized novel rhodamine-derived fluorophores termed “Kansas Reds” that become fluorescent upon protonation. Feeding these compounds to living *C. elegans* animals revealed a dynamic wave of high acidity, unrelated to mechanical pumping of fluid, that propagates from the posterior intestine to the anterior intestine and back over a period of ~10 seconds during the DMP. By

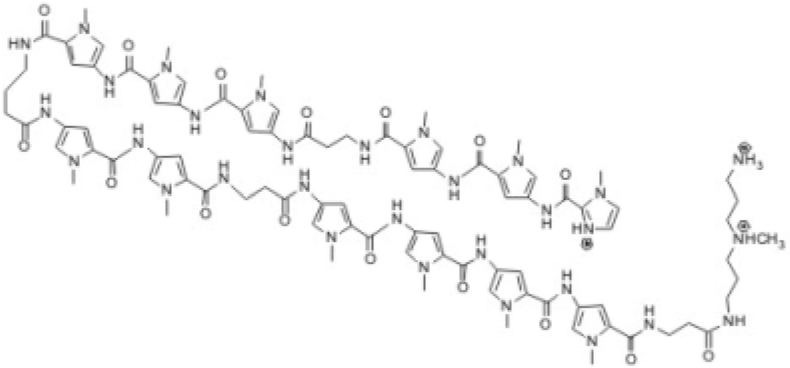
precisely tuning the pKa values of these fluorophores, we created ratiometric sensors that allowed mapping of this dynamic pH gradient and detection of small molecules and mutations that affect this process. Acid-activated fluorophores with rapid response kinetics and appropriately matched pKa values have unique potential for the discovery of modulators of targets controlling dynamic changes in pH in vivo.

## RM_MWGL Regional Meeting 29

### Pyrrole-imidazole Polyamides active against Human Papillomavirus (HPV) in cell and tissue culture

***James K. Bashkin***, *bashkinj@umsl.edu. Department of Chemistry & Biochemistry/Center for Nanoscience, University of Missouri - St. Louis and Nanovir, LLC, St. Louis, MO 63121, United States*

We recently reported[1] the potent antiviral activity of certain polyamides designed against HPV. An example structure is shown below, where the counterions are TFA. This presentation will describe the chemical design, characterization and biological activity of this class of potent anti-HPV compounds.



(1) Edwards, T. G.; Koeller, K. J.; Slomczynska, U.; Fok, K.; Helmus, M.; Bashkin, J. K.; Fisher, C. *Antivir. Res.* **2011**, *91*, 177-186.

## RM_MWGL Regional Meeting 30

### Chemistry in the pharmaceutical industry, part two

***Todd M Stark***, *todd.m.stark@gmail.com. Johnson Matthey Pharma Services, Devens, MA 01434, United States*

We will explore synthetic, analytical and physical chemistry throughout the drug discovery and development process. In part two, the focus will be on development from cGMP manufacture, clinical trials Phases 1-3, formulation, to final approval.

### RM_MWGL Regional Meeting 31

## ConocoPhillips Wood River CORE project

***Jeff Burkinshaw***, *Jeffrey.R.Burkinshaw@conocophillips.com, Kent Peccola.Wood River Refinery, Conoco-Phillips Company, Roxana, IL 62084, United States*

Wood River Refinery, jointly owned by ConocoPhillips and Cenovus Energy, is in the process of expanding the refining capacity, improving the ability to process Canadian crude, and increasing the yield of clean fuels, ultimately enhancing the U.S. energy supply and improving economic security.

This expansion project is referred to as CORE – COker and Refinery Expansion. Operational startup is anticipated in fourth quarter of 2011. Once complete, the project will increase crude oil refining capacity from 306 MBPD to 356 MBPD, more than double heavy crude oil refining capacity from 95 MBD to 225 MBD, and increase by 5 percent the yield of clean products such as gasoline, diesel and jet fuel. Other products will include petrochemical feedstocks, asphalt and coke. The increased fuels volume is expected to be sold into the Midwest U.S. market.

### RM_MWGL Regional Meeting 32

## R&D phoenix: new labs arising from the ashes

***John K Borchardt***, *jkborchardt@hotmail.com. Southhaven Communications, Houston, TX 77083, United States*

Many large, modern laboratories in the Great Lakes and Midwest regions each employing thousands of people have been closed. The trend is most pronounced in the pharmaceutical industry. These closures have resulted in many highly educated, high income professionals losing their jobs. However, the same attractions that led to these laboratories being opened in specific localities remain: an educated workforce, area colleges and universities, good pre-college education systems and quality of life. As a result, a new trend has developed. Local governments and universities have taken over these expensive labs and begun renting them as multi-user facilities to existing large, medium and small-sized companies as well as startups. So one can have mini-companies in mega-laboratory sites.

### RM_MWGL Regional Meeting 33

## Tech transfer & commercialization: Applied research and gap funding

***Rick Silva**, Rick.Silva@cu.edu.Technology Transfer Office, University of Colorado-Denver, Aurora, CO 80010, United States*

In order to augment the maturation of early technology at the University of Colorado (CU), the CU Proof-of-Concept Program (POC Program) was deployed by the CU Office of Technology Transfer in 2004. Five different funding modalities have been used to support commercialization at CU and within startup companies based on CU IP. The POC Program was modeled, in part, upon the funding disciplines of the Deshpande Center for Technological Innovation at the Massachusetts Institute of Technology. The POC Program has been productive by most accounts. The POC Program has deployed over $11.5M into over 139 commercially relevant research and feasibility projects in order to advance CU intellectual property. Over 44 projects have resulted in exclusive license or option transactions including 8 new companies spun out of the University of Colorado. POC Program investments have helped induce over $53M in follow-on grant funding and $173M in venture investment.

**RM_MWGL Regional Meeting 34**

## Divergence: From startup to acquisition, a success story

***Derek Rapp**, derek.k.rapp@monsanto.com. Monsanto Company, Saint Louis, MO 63167, United States*

Divergence, Inc., began operations in 1999 as a genomics-based company looking to identify pathways to control and prevent parasitic infections. Divergence's strategy and business positioning changed over a decade as opportunities arose and as Divergence's technology evolved. When Divergence was acquired by Monsanto Company in early 2011, the company had a collection of assets that were valuable – both proprietary products in development and novel research platforms that were the source of Divergence's products and could be utilized to make many more discoveries over time.

While Divergence began as a genomics company, arguably the company's strongest assets at the time of acquisition were in the area of chemistry. The company developed a research platform (trademarked as Harvest) and had discovered multiple molecules that were at different stages of development (most notably a nematicide that continues to show great promise).

In order to succeed, Divergence had to grow its team, put in place a great number of relationships with companies and academic institutions, and ensure that its strategy was consistent with its capabilities and with the opportunities presented by the markets in which the company was hoping to introduce products over time. To accomplish these tasks, the company had to raise tens of millions of dollars despite times of general economic recession, weak capital markets, and questions as to how privately-held, thinly-capitalized, illiquid companies could provide attractive returns to their shareholders.

In his talk, Derek will reflect on his experiences over the ten years and share key learnings. He would very much like to see more entrepreneurs move their ideas from concepts to successful companies.

## RM_MWGL Regional Meeting 35

### Innovators turning into entrepreneurs: How to get started

***Daniel J Broderick**, dbroderick@biogenerator.org.Biogenerator, Saint Louis, MO 63108, United StatesGlobal Agtech Investor Network, Saint Louis, MO 63132, United States*

The Midwest and Great Lakes regions of the United States are home to some of the finest scientists and research organizations in the country. Innovation and invention at these institutions occurs on a daily basis. Increasingly scientists are also entrepreneurs with a desire to start their own company. However, most lack the knowledge of how to get started and where to find the capital to fund their company until revenue begins to support the business. This session will present information about resources and contacts to help get a company started and financed in the Midwest. It will also present statistics about the productivity and the investment activity of the region.

## RM_MWGL Regional Meeting 36

### Designing ice cream quality with the aid of a microscope

***H. Douglas Goff**.Dept of Food Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada*

The texture of ice cream is one of its most important quality attributes. Optimal texture results from optimizing the structure of its components. Ice cream manufacture begins by assembling a mix, which is comprised of water, fat, protein, sugars, minerals and vitamins that are derived from the dairy and other ingredients that are used. The mix is heated and homogenized to form a fat emulsion. Some of the proteins and minerals are dispersed as colloidal particles, others are dissolved in water along with the sugar. After aging the mix to crystallize the fat, the mix is frozen while being agitated, which has the three-fold effect of freezing some of the water to ice minute crystals (the smaller the better for optimal texture, a function of freezing rate; some of the water remains unfrozen due to the dissolved solutes according to Raoult's Law), whipping in air to create a foam (up to half of the volume of ice cream is air; the smaller the bubbles the better for optimal texture) and partially-coalescing the fat emulsion to form fat structure (which has a great impact on mouthfeel and shape retention). So it is important that manufacturers design and implement both formulations and processes that develop optimal structure of ice, air and fat, which ultimately leads to the best eating properties. Structure has been extensively studied by a combination of microscopic techniques that give valuable insight into the effects of ingredients and processing.

**RM_MWGL Regional Meeting 37**

# Valence-bond determination of bond lengths of polycyclic aromatic hydrocarbons

***Jerry R Dias**, diasj@umkc.edu.Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110-2499, United States*

Pauling's valence-bond method for determining bond lengths is compared to recent experimental and theoretical results and is shown to still be a viable procedure. His method only requires computation of the number of Kekulé and Dewar structures of conjugated hydrocarbons. Both alternant and nonalternant polycyclic aromatic hydrocarbons including essentially disconnected and non-Kekuléan systems have bond lengths that are easily determined by this method.

Table 1. Bond lengths of perylene.

| Bond | X-ray (Å) | Pauling, unexcited (Å) | Bond No. | Pauling, 1st excited (Å) | Bond No. | Herndon (Å) |
|---|---|---|---|---|---|---|
| 1-2 | 1.415 | 1.423 | 1.3333 | 1.412 (1.412) | 1.391 (1.390) | 1.422 |
| 2-3 | 1.369 | 1.370 | 1.6667 | 1.380 (1.379) | 1.591 (1.610) | 1.381 |
| 3-3a | 1.398 | 1.423 | 1.3333 | 1.421 (1.421) | 1.342 (1.339) | 1.422 |
| 6a-6b | 1.471 | 1.504 | 1.0 | 1.470 (1.470) | 1.120 (1.120) | 1.464 |
| 6a-6a[1] | 1.428 | 1.423 | 1.3333 | 1.424 (1.427) | 1.328 (1.322) | 1.422 |
| 6-6a | 1.394 | 1.370 | 1.6667 | 1.386 (1.386) | 1.549 (1.558) | 1.381 |
| 3a-3a[1] | 1.421 | 1.423 | 1.3333 | 1.428 (1.427) | 1.304 (1.322) | 1.422 |

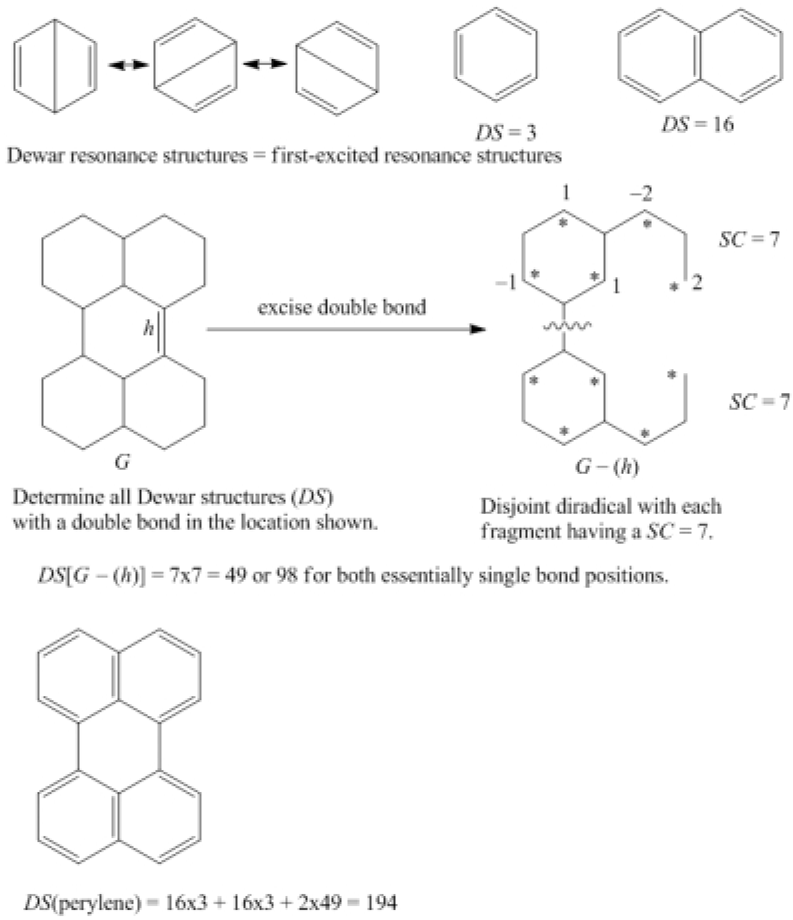


Figure 2. Determination of the number of Dewar structures ($DS$) of perylene and its subgraph generated by localizing a double bond on its essentially single bond $h$.

## RM_MWGL Regional Meeting 38

### In search for natural tau fibrillization inhibitors: Preliminary evaluation of horse apple fruit extract

*Saad Awan[1], Aida Abraha[2], **Ehab A Abourashed**[1], eabouras@csu.edu. (1) Department of Pharmaceutical Sciences, Chicago State University, Chicago, IL 60628, United States (2) Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628, United States*

The intracellular precipitation and formation of neurofibrillary tangles of tau protein in the human brain is one of the major etiological factors of Alzheimer's disease (AD). At present, no causative treatment exists for AD. However, inhibition of tau protein fibrillization represents a viable target for the discovery and development of potential anti-AD drugs. Estrogens have been found to inhibit the extracellular formation of amyloid beta protein, the other major etiological factor of AD. Since isoflavones have

structural similarity to estrogens, they may also have the potential to inhibit the formation of AD-specific plaques, mainly amyloid beta and tau proteins. In this work, an isoflavone-rich extract of the fruit of horse apple (hedge apple, osage orange, *Maclura pomifera*) was prepared and evaluated in vitro for its ability to inhibit the fibrillization of full-length tau protein (HT40). Tau fibrillization was monitored by Static Laser Scattering (SLS) and Transmission Electron Microscopy (TEM). Although results of SLS were inconclusive, visual examination of the TEM samples clearly showed inhibition of tau fibrillization in comparison to the negative control. The obtained results warrant further investigation of the extract as well as its major isoflavones, osajin and pomiferin, which have been isolated and characterized during the course of this study.

**RM_MWGL Regional Meeting 39**

### RNA CoSSMos: Characterization of Secondary Structure Motifs- A searchable database of secondary structure motifs in RNA three dimensional structures

***Pamela L. Vanegas****, pvanegas@slu.edu, Graham A. Hudson, Amber R. Davis, Shannon C. Kelly, Charles C. Kirkpatrick, Brent M. Znosko. Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, United States*

RNA secondary structure is important for designing therapeutics, understanding protein-RNA binding, and predicting tertiary structure of RNA. Several databases and downloadable programs exist that specialize in the three-dimensional structure of RNA, but none focus specifically on secondary structural motifs such as internal, bulge, and hairpin loops. The RNA Characterization of Secondary Structure Motifs (RNA CoSSMos) Database is a freely accessible and searchable online database and website of three dimensional characteristics of secondary structure motifs. To create the RNA CoSSMos Database, 2,010 PDB files were searched for internal, bulge, and hairpin loops, and each loop's structural information, including sugar pucker, glycosidic linkage, hydrogen bonding patterns, and stacking interactions, were included in the database. False positives were defined, identified, and reclassified or omitted from the database to ensure the most accurate results possible. Users can search via general PDB information, experimental parameters, sequence, and specific motif and by specific structural parameters in the subquery page after the initial search. Returned results for each search can be viewed individually or a complete set can be downloaded into a spreadsheet to allow for easy comparison. The RNA CoSSMos Database is automatically updated weekly and is available at http://cossmos.slu.edu.

**RM_MWGL Regional Meeting 40**

### Chemical synthesis of α-deuterated amino acid, biosynthesis of *Clostridium symbiosum* glutamic dehydrogenese (*cs*-GDH) and study of kinetic isotope effect of dehydrogen reaction of glutamic acid catalyzed by *cs*-GDH

***Xueyi Chen**, xchen@kumc.edu, Steven J. Maniscalco, Harvey F. Fisher. Department of Biochemistry and Molecular Biology, University of Kansas-Medical Center, Kansas City, Kansas 66160, United States*

α-Deuterated amino acids are the key substrates for the study of kinetic isotope effect of enzymatic dehydrogenize reactions. In this study, we present a convenient synthesis of α-Deuterated amino acids using deutoxide and acetyl anhydride. More than 98% isotope purity is achieved within two deuteration cycles and it was characterized by $^1$H NMR. *cs*-GDH was synthesized by using bioreactor i.e. genetically modified *Escherichia coli* (*E-coli*) and it was purified on a Remazol dye column. The transient-state kinetic approach reveals the formation of intermediate complex in real time course. Time dependent kinetic isotope effect was also determined.

## RM_MWGL Regional Meeting 41

## Time-averaging approximation in the interaction picture for absorption line shape and vibrational energy transfer in liquid water

***Mino Yang**[1], minoyang@hotmail.com, James L. Skinner[2]. (1) Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 361-763, Republic of Korea (2) Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States*

The time-averaging approximation (TAA), originally deveolped to calculate vibrational line shapes for coupled chromophores using mixed quantum/classical methods, is reformulated. Time-averaging was performed for the full one-exciton Hamiltonian in the original version of theory, while herein the time-averaging is performed on the coupling (off-diagonal) Hamiltonian in the interaction picture. As a result, the influence of the dynammic fluctuations of the transition energies is more accurately described. We compare numerical predictions of the two versions of the TAA with numerically exact results for the vibration absorption line shape of the OH stretching modes in neat water. It is shown that the TAA in the interaction picture yields theoretical line shapes that are in better agreement with exact results.

## RM_MWGL Regional Meeting 42

## Control of surface functionality via photopatterning: Self-assembled monolayers for small molecule and protein attachment

***Matthew Hynes**, mjhynes@go.wustl.edu, Joshua Maurer. Department of Chemistry & Center for Materials Innovation, Washington University in St. Louis, St. Louis, MO 63130, United States*

Self-assembled monolayers (SAMs) are an efficient method for functionalizing surfaces on the microscopic and nanoscopic scale with spatially defined surface chemistries. This research presents a new technique that was developed for patterning alkane thiols

on gold. This methodology began with the synthesis of a glycol monomer. This monomer has three distinct regions; a thiol head group, a long alkane chain, and a glycol tail. The thiol head group covalently binds to gold coated substrates while the long alkane chains self assemble through Van der Waals forces producing a well-defined surface with functional groups oriented for interfacial reactions. The tail group was composed of a tetraethylene glycol unit which has been shown to resist nonspecific protein adhesion. By utilizing a commercially available direct write photolithography system, a gradient of proteins was produced by oxidizing the underlying monolayer, which created sites for the proteins to adhere. This pattern was characterized both fluorescently and with surface plasma resonance imaging.

Another advantage of using the direct write photolithography system was its capability to cleave photoprotecting groups that absorb at 325 nm. As a result, a novel nitroveratryl monomer was synthesized to explore this functionality, which had a nitroveratryl protected carboxylic acid added onto the glycol tail. The nitroveratryl group was then site-selectively cleaved on the surface producing a carboxylic acid. Two different amine compounds were then coupled to the surface in successive fashion producing a circle in a box pattern. The pattern was characterized by matrix assisted laser desorption ionization (MALDI) imaging. This patterning technique was more versatile than microcontact printing methods of patterning SAM because photopatterning allows for multiple rounds of deprotection/coupling resulting in a variety of molecules being patterning on a surface as opposed to microcontact printing which only allows for a single pass.

**RM_MWGL Regional Meeting 43**

## Contribution of core/shell and core/shell/shell lattice interfaces on the optical properties of quantum dots?

***Bernard O Omogo**[1], bomondi@uark.edu, Mourad Benamara[2], Colin D Heyes[1]. (1) Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, United States (2) Institute for Nanoscale Materials Science and Engineering, University of Arkansas, Fayetteville, AR 72701, United States*

Quantum Dots (QDs) are promising components in a range of optical applications because of their high photo-stability, broad absorption spectrum and easily tunable emission. In particular, they have become widely used as fluorescence probes in ultrasensitive biomedical imaging due to their advantages over other probes. In order to use QDs in such applications, it is preferable to isolate the QD core from the biological environment with a shell, comprising of less-toxic material with a higher band gap. Thus, the biological system is protected from the more toxic core while the fluorescent core is protected from the effects of the biological environment.

Since the shell has different lattice parameters to the core, a lattice mismatch is introduced which can affect the lattice parameters by introducing a charge-carrier trap states. One solution to reduce the lattice strain is to use core/shell/shell approach, where the internal shell has a smaller mismatch with the core than the outer shell, but this introduces an additional interface that can also affect the optical properties.

In order to investigate the effects of adding this additional interface, we have synthesized CdSe/ZnS Core/Shell and CdSe/CdS Core/Shell as well as CdSe/CdS/ZnS Core/Shell/Shell QDs. We have characterized the structural properties of these QDs with high resolution electron microscopy and one particle elemental analysis, and the optical properties by ensemble and single QDs Spectroscopy. We have studied the effect of the shell material and thickness on the quantum yield, fluorescence lifetime and blinking- a phenomenon in which the QDs switches between the bright and dark states under constant illumination. These results will contribute to the understanding of the origin of the trap states that are known to cause non-radiative decay pathways and hence blinking in core/shell and core/shell/shell systems and consequently improve their biomedical imaging as well as other optoelectronic applications

**RM_MWGL Regional Meeting 44**

## Expression, purification and oligomer formation of amyloid beta(1-42) associated with Alzheimer's disease

***Chi Zhang**, czz76@mail.umkc.edu, Nathan Oyler. Department of Chemistry, University of Missouri Kansas City, United States*

Alzheimer's Disease(AD), is the most common type of senile dementia, which is the seventh-leading cause of death in United States. Recent findings suggest that soluble Aβ oligomers have more cytotoxicity in brain than Aβ fibrils which were considered to be the neurotoxins resulting in the degeneration of brain cells before. The long term objective of our proposal is to explore the secondary and tertiary structure of Aβ oligomers by applying SSNMR analytical method. In pursuit of that goal, we are studing the methods to produce uniformly $^{13}C$ and $^{15}N$ labeled amyloid beta oligomers. The methods and current progress in amyloid beta expression, purification and oligomer formation are presented.

**RM_MWGL Regional Meeting 45**

## Characterization of arsonic acid self-assembled monolayers (SAMs): A new class of monomers

***Natalie A LaFranzo**, nalafran@wustl.edu, Joshua A Maurer. Department of Chemistry, Washington University in St. Louis, Saint Louis, MO 63130, United States*

Self-assembled monolayers (SAMs) are composed of tightly-packed organic molecules on a substrate that form a well-ordered structure. Typically, the “head group” of the organic monomers of the monolayer covalently attaches to a substrate, and monolayer order and self-assembly is achieved through van der Waals interactions between the long alkyl chains of the monomer “tail groups”. Monolayers containing “head groups” consisting of thiols, siloxanes and phosphonates have been demonstrated on gold, glass and metal oxides, respectively. Phosphonates that interact with oxide surfaces in a polydentate fashion are more stable than the thiol monolayers, which have a monodentate interaction with gold. Modeled after the ability of long alkyl chain phosphonic acid monolayers to assemble onto metal-oxide surfaces, a hexadecyl arsonic acid monomer has been synthesized to generate a new class of SAMs. The monomer was prepared in a one-pot multi-step synthesis starting from arsenic trichloride. Similar to phosphonate monomers, arsonate monomers are capable of polydentate attachment. Well-ordered arsonic acid monolayers have been successfully prepared using a straight-forward soaking technique on titanium oxide and borosilicate glass substrates. Surfaces were characterized by contact angle, IR spectroscopy, MALDI mass spectrometry and atomic force microscopy. While phosphonate SAMs are readily prepared on titanium oxide surfaces under identical conditions, phosphonate monolayers have not been shown to form on glass. This suggests increased reactivity of the arsonate head group relative to the phosphonate head group, which may allow for unique applications of these SAMs. Additionally, cell-culture studies with CHO-K1 cells demonstrate that the organoarsenic species is non-toxic in the monolayer.

**RM_MWGL Regional Meeting 46**

## Mineral Levels in Mature Soybean Seed Are Not Altered by Glyphosate Treatment or the Glyphosate Tolerance Trait

***Denise R Lundry***[1], *denise.r.lundry@monsanto.com, Robert M Alba*[2], *Angela Hendrickson Culler*[1], *Marian S Bleek*[1]. *(1) Department of Regulatory, Monsanto Company, St. Louis, MO 63167, United States (2) Department of Ag Technology, Monsanto Company, Chesterfield, MO 63198, United States*

Glyphosate-tolerant soybeans (GTS) represent more than 90% of soybean grown in the U.S., and are the predominant biotech crop planted globally. Despite 15 years of safe and efficacious glyphosate use over GTS, and increased yields associated with GTS adoption, debate continues on the potential for unintended effects associated with glyphosate treatment over GTS. An area of particular interest has been the effect of glyphosate treatment on mineral levels in soybean. This study compared levels of calcium, copper, iron, magnesium, manganese, potassium, phosphorus, and zinc in the seed of a glyphosate-treated GTS variety to that of an untreated near-isogenic conventional soybean control. The untreated GTS variety was also compared with the near-isogenic conventional soybean control to assess any potential impacts of the GTS trait itself. As mineral levels in seed demonstrate considerable variability based upon soil fertility, environment, and location, data were generated from seed harvested at multiple geographically separate sites throughout the US. A total of 16 different untreated conventional soybean varieties were also included to provide further information on natural variability in mineral ranges. The comparisons confirmed that both glyphosate treatment and the GTS trait had no substantial or consistent impact on the levels of minerals in soybean seed as there were no meaningful differences in

mineral levels in the seed of treated and untreated GTS, when compared to a genetically similar conventional soybean, and a range of diverse soybean germplasms.

## RM_MWGL Regional Meeting 47

### Self-assembly and dynamics in pore formation by amphiphilic heptapeptides

***Saeedeh Negin**, saeedehnegin@gmail.com. Chemistry and Biochemistry, Center for Nanoscience, University of Missouri-St. Louis, St. Louis, missouri 63121, United States*

We have shown that ion transport by amphiphilic tryptophan-containing heptapeptides (Synthetic Anion Transporters or SATs) is affected by self-assembly of the monomers in the bulk aqueous phase and within the bilayer. The mechanism of ion transport was confirmed by planar bilayer conductance studies. Ion transport in these systems was found to be sensitive to change in the *C*-terminal portion of the heptapeptide sequence. A significant difference in transport was observed when L-Trp was replaced by D-Trp in the same position.

## RM_MWGL Regional Meeting 48

### $^{19}$F NMR studies reveal pH susceptibility of domain 2 of anthrax PA

***Fatemeh Chadegani**, nazych@gmail.com, Jim Bann.Chemistry, Wichita State University, Wichita, Kansas 67260, United States*

*Bacillus anthracis* is a gram-positive bacterium and is the causative agent of anthrax. Anthrax secretes a three component toxin called the anthrax toxin which composed of three proteins including lethal factor (LF), edema factor (EF), and protective antigen (PA).

PA transfers LF and EF into the host cytosol through a membrane spanning pore, which forms within low pH endosomes. Once EF and LF have entered the cytosol, the enzymatic activities block processes important to the host immune response. The two identified receptors are capillary morphogenesis protein 2 (CMG2) and tumor endothelial marker 8 (TEM8) which are required for endocytosis.

According to previous studies monomeric PA consists of four domains and domain 2 and 4 of PA are involved in pore formation. The large 2β2–2β3 loop of domain 2, a chymotrypsin-sensitive loop (residues 302-325) which is disordered in the monomer, will form the transmembrane portion of β-barrel in the pore by structural rearrangement and relocation. This loop is connected to the pH sensitive loop in the Greek Key motif of domain 2 by 2β3–2β4 strands (residues 343-350). Based on PA crystallographic data, residues in the pH sensitive loop are ordered at pH 7.4 and disordered at pH 6.

We biosynthetically labeled all seven tryptophans in the PA with 5-fluorotryptophan to examine the structure of protective antigen, using $^{19}$F NMR spectroscopy (W65, W90,

W136, W206, W226, W346 and W477). We carried out temperature and binding studies with the goal of assigning these residents. We also have accomplished NMR experiments as a function of pH to study pH vulnerability of domain2 of anthrax toxin. Our data show that with decreasing the pH from 8 to 5, W346 peak intensity will decline and interestingly, it will disappear at pH 5 which suggest that W346 residue is pH sensitive and allows susceptibility of domain 2 and pore formation.

## RM_MWGL Regional Meeting 49

### Free Energy Changes and the Vibrational Partition Function

*Paul E Smith, **Shu Dai**, daishu@ksu.edu.Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

Many quantum mechanical effects are absent in classical simulations, especially of those of biomolecular systems. One such effect involves the contribution of intramolecular and intermolecular vibrations to the vibrational partition function (Qvib). In this study, contributions from Qvib to the total free energy change are investigated for several systems and processes in solution including: the free energy of solvation, protein folding, and the activities of a series of solutes in aqueous solution, and the enthalpy of mixing. It is determined that the contributions of Qvib can be significant (10-35%) but usually difficult to evaluate, especially for protein folding. It is argued that these contributions can be, or have been, included in classical force fields by the use of effective intermolecular interactions. However, this requires the use of experimental and simulated free energy (or enthalpy) changes which have not been corrected for changes in Qvib during the parametrization process. Even then, an effective interaction approach is not expected to fully reproduce the temperature dependent properties of real system.

## RM_MWGL Regional Meeting 50

### Photophysical Properties and Electronic Structure of Stable, Tunable Synthetic Bacteriochlorins: Extending the Features of Native Photosynthetic Pigments

***Eunkyung Yang**[1], Christine Kirmaier[1], Michael Krayer[2], Masahiko Taniguchi[2], Han-Je Kim[2], James R Diers[3], David F Bocian[3], Jonathan S Lindsey[2], Dewey Holten[1]. (1) Department of Chemistry, Washington university in St.Louis, Missouri 63130-4889, United States (2) Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States (3) Department of Chemistry, University of California, Riverside, California 92521-0403, United States*

Bacteriochlorins, which are tetrapyrrole macrocycles with two reduced pyrrole rings, are Nature's near-infrared (NIR) absorbers (700-900 nm). The strong absorption in the NIR region renders bacteriochlorins excellent candidates for a variety of applications including solar light harvesting, flow cytometry, molecular imaging, and photodynamic therapy. Natural bacteriochlorins are inherently unstable due to oxidative conversion to the chlorin (one reduced pyrrole 18 ring) or the porphyrin. The natural pigments are also

only modestly amenable to synthetic manipulation, owing to a nealy full complement of substituents on the macrocycle. Recently, a new synthetic methodology has afforded access to stable synthetic bacteriochlorins wherein a wide variety of substituents can be appended to the macrocycle at preselected locations. Herein, the spectroscopic and photophysical properties of 33 synthetic bacteriochlorins are investigated. The NIR absorption bands of the chromophores range from ~700 to ~820 nm; the lifetimes of the lowest excited singlet state range from ~2 to ~6 ns; the fluorescence quantum yields range from ~0.05 to ~0.25; and the yield of the lowest triplet excited state is ~0.5. The spectroscopic/photophysical studies of the bacteriochlorins are accompanied by density functional theory (DFT) calculations that probe the characteristics of the frontier molecular orbitals. The DFT calculations indicate that the impact of substituents on the spectral properties of the molecules derives primarily from effects on the lowest unoccupied molecular orbital. Collectively, the studies show how the palette of synthetic bacteriochlorins extends the properties of the native photosynthetic pigments (bacteriochlorophylls). The studies have also elucidated design principles for tuning the spectral and photophysical characteristics as required for a wide variety of photochemical applications.

### RM_MWGL Regional Meeting 51

## Theoretical studies on the optoelectronic properties of *N*-fused quinazoliniminiums

***Olajide Alawode***, *sundeep@ksu.edu, Sundeep Rayat. Kansas State University, United States*

Bridgehead-nitrogen containing fused heterocycles have received a great deal of attention as highly efficient chromophores for the development of Organic Light Emitting Diodes. The presence of N-atom at the ring fusion is known to impart unique photophysical properties to these compounds for device fabrication, such as excellent luminescence and easily tunable emission colors. We are interested in evaluating the scope of a unique class of phenanthridine-fused quinazoliniminiums for applications in OLED technology. In this paper, we utilized density functional theory and time-dependent density functional theory at 6-311+G* basis set to investigate the electronic and optical properties of a series of a phenanthridine-fused quinazoliniminiums containing a variety of different substituents.
Our results the HOMOs, LUMOs, energy gaps, ionization potentials, electron affinities and the reorganization energies can be finely tuned by varying the substituents on these chromophores.

### RM_MWGL Regional Meeting 52

## Synthesis of potent inhibitors of YopH in *Yersinia pestis*: Pathogen responsible for the Black Death

***Mahesh P Paudyal**, mpp2nf@mail.umsl.edu, Christopher D Spilling. Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

Yersinia is the pathogenic bacteria causing human diseases ranging from gastrointestinal syndromes to bubonic plague.[1] Yersinia pestis, one of the three species of genus Yersinia, is responsible for the bubonic plague. Also known as the Black Death, bubonic plague killed millions of people in the 15th century. The number of people killed by this bacterium during the course of human history approaches 200 million.[2] Moreover, this pathogen could be misused as a biological weapon and an agent for mass destruction in warfare.

The pathogenicity of Yersinia depends on the activity of a bacterial virulence factor known as Yersinia outer protein H (YopH).[3] YopH is homologous to eukaryotic protein tyrosine phosphatase (PTP) with potent tyrosine phosphatase activity.[4] PTPs constitute a large family of signaling enzymes. YopH disrupts signal transduction pathways by removing a phosphate group (dephosphorylation) from a variety of proteins including PTPs. This deregulates the PTP activity increasing the risk of numerous diseases including diabetes, cancer, and immune system dysfunction, amongst others.

It has already been shown that blocking the protein tyrosine phosphatase YopH of this bacterium can render it avirulent. Thus the design and synthesis of potent and selective YopH inhibitors are of prime importance to serve as anti-plague agents. The cytotoxicity of YopH inhibitors developed so far are limited to the micro-molar range. Based on our previous results,[5] we have designed a series of salicylic acid derived ligands. These bidentate ligands are aimed to achieve higher binding affinity and specificity and thus are expected to increase the inhibitory activity approaching the nano-molar range. The strategy involves the synthesis of four heterocyclic building blocks which will be coupled to a wide variety of amines using parallel chemistry to finish up the synthesis of YopH inhibitors. Herein, we report the progress towards the synthesis of these inhibitors.

**RM_MWGL Regional Meeting 53**

## Morphology-controlled synthesis of nanosize cuprite ($Cu_2O$)

***Khadga M. Shrestha**, khadga@ksu.edu, Kenneth J. Klabunde. Department of Chemistry, Kansas State University, Mahattan, Kansas 66506, United States*

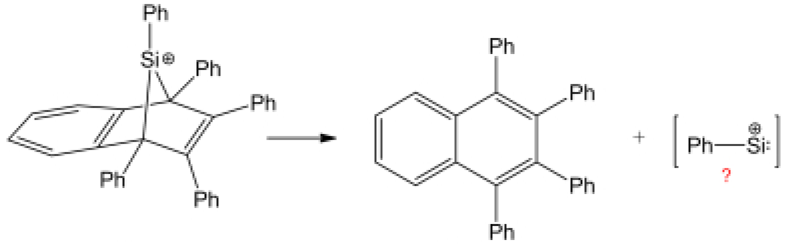
$Cu_2O$ nanomaterials were synthesized with different copper precursors. The precursors were reduced with glucose and ethylene glycol. First, an aqueous solution of copper (II) acetate was reduced with glucose at three different conditions to investigate the effects on the morphology. Furthermore, the copper acetate was also reduced with ethylene glycol. In addition to copper acetate, copper (II) sulfate was also used for the synthesis of $Cu_2O$ material. Indeed, copper sulfate was used to prepare Benedict's solution, and it was reduced with glucose. All these materials were characterized with powdered X-ray diffraction (XRD) patterns, SEM, EDX, BET measurements, and UV-vis absorption spectra. XRD patterns show that $Cu_2O$ materials were formed in all cases; however, when the acetate solution was reduced with ethylene glycol, a small amount of CuO also appeared in addition to $Cu_2O$. SEM images showed some interesting and unique morphologies; hexapods, octahedra, hollow spheres and flower-like structure were found. It was found that the change in conditions and precursors greatly affected the morphologies to give different morphologies. Specific surface areas of these materials were found to be relatively low as these materials were prepared in solution phase. We found few differences in the absorption of UV-vis absorption among these materials with the change in morphologies; however, we found significant differences in UV-vis absorption of these materials from that of commercial $Cu_2O$.

## RM_MWGL Regional Meeting 54

## Computational investigation of the extrusion of PhSi:$^+$ from a 7-phenyl-7-silanorbornadienyl cation in solution

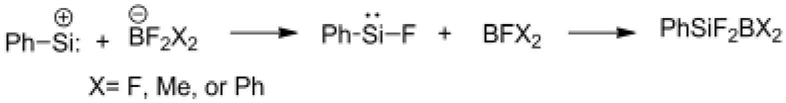
***Sophia E. White***, *swhite@go.wustl.edu, Peter P. Gaspar. Department of Chemistry, Washington University, Saint Louis, MO 63130, United States*

The synthesis of phenylsilyliumylidene, Ph-Si:$^+$, is explored computationally. This type of four-valence electron reactive intermediate has the potential to react as a "supersilylene," and form as many as three bonds in concert![1] In 2001, Müller and coworkers found that the 2,3-benzo-1,4,5,6,7-pentaphenyl-7-silanorbornadienyl cation (1) rapidly decomposes to form tetraphenylnaphthalene (2), unless it is rapidly trapped.[2]



(1) (2)

We believe that PhSi:$^+$ is formed as a highly reactive intermediate upon the fragmentation of (1) and can be trapped by fluorine containing borates.


$$Ph-\overset{\oplus}{Si}: + \overset{\ominus}{B}F_2X_2 \longrightarrow Ph-\ddot{Si}-F + BFX_2 \longrightarrow PhSiF_2BX_2$$

X= F, Me, or Ph

We have investigated computationally several trapping reactions involving $BF_2X_2^-$ and PhSi:$^+$ and the step-wise reaction, shown above, is predicted to occur with low barriers.[3]

[1] Gaspar, P.P.; Liu, X.; Ivanova, D.; Read, D.; Prell, J.S.; gross, M.L. *ACS Symposium Series*, **2006**, *917*, 52-65.
[2] Schuppan. J.; Herrschaft, B.; Müller, T. *Organometallics*, **2001**, *20, 4584-4592.*
[3] This research was supported in part by the National Science Foundation through TeraGrid resources provided by the National Center for Supercomputing Applications (NCSA), under grant number TG-CHE070050N

## RM_MWGL Regional Meeting 55

## In situ generation of bromine for micelle-assisted bromination and oxidation

***Archana Mishra**, axmishra1@wichita.edu, Zifan Wang, Doug S English, Erach Talaty. Department of Chemistry, Wichita State University, Wichita, KS 67208, United States*

This poster describes our recent work in which CTAB (cetyltrimethylammonium bromide) micelles are used as catalytic platforms for performing bromination and oxidation reactions in water at room temperature. The bromide counter ion is used to prepare $Br_2$ in situ which is subsequently employed as a brominating and oxidizing agent. In this process the bromide is rapidly oxidized to bromine using BPO (benzoic peroxyanhydride). The reaction is facilitated by the micelle which improves the BPO solubility and its proximity with $Br^-$. Several example reactions are discussed including micelle-assisted bromination of cholesterol and methyl styrene along with an example of mild oxidation of benzyl alcohol to form benzaldehyde. These examples illustrate how the bromine formed in situ, can be used as a mild oxidizing agent and also as a brominating agent. Kinetic studies of $Br_2$ formation and cholesterol bromination are also presented. The use of aqueous CTAB as a catalytic platform for bromine-based chemistry provides a promising approach for green chemistry since it avoids the use of caustic brominating agents and organic solvents and is efficient at room temperature.

## RM_MWGL Regional Meeting 56

## Reaction of hemiacetals with Pd π-allyls: Stereoselective synthesis of cyclic ethers

***Surendra Dawadi**, sd88f@umsl.edu, Christopher D. Spilling. Department of Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, MO 63121, United States*

Tetrahydrofuran (thf) and tetrahydropyran (thp) moieties are found in many biologically active natural products. Consequently, new methods for the construction of these fragments are of considerable importance. Palladium(0) catalyzed cyclization of primary alcohol (R', R'' = H) with allylic diacetate leads to the formation of 2-substituted cyclic ethers.[1] This widely studied reaction proceeds via a Pd π-allyl complex. On the other hand, aldehydes and ketones in methanol form hemiacetals (R' = OMe, R'' = H, $CH_3$) in the equilibrium mixture, which, although they are weak nucleophiles, react with Pd π-allyl to give 2,5 and 2,6 disubstituted thf and thp, respectively. Chiral ligands like (*R,R*)-DACH-phenyl Trost ligand is employed for non-racemic cyclizations.[2] The vinyl acetate (R', R'' = H) thus obtained was treated with ozone followed by reductive workup with sodium borohydride to produce tetrahydrofurfuryl alcohol. Specific rotation of this alcohol was measured and compared with the literature values to determine absolute configuration at C-2 of the ring. It was found that (*R*)-tetrahydrofurfuryl alcohol was obtained by employing the (*R,R*)-DACH-phenyl Trost ligand. The stereocontrolled formation of chiral cyclic ethers is thus achieved from olefinic alcohols and hemiacetals.

(1) Muzart, J. *Tetrahedron* **2005**, 61, 5955-6008

(2) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, 39, 747-760

**RM_MWGL Regional Meeting 57**

## AFM imaging analysis of pUC19 DNA on modified mica

***Nadia Nezamabadi**, nnezama@siue.edu, Jenna C. Goeckner, Chin-Chuan Wei, Eric J. Voss. Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026-1652, United States*

The supercoil structure of DNA is thought to play a key role in the genetic process in cells. Microscopy has the potential to explain the detailed structure of the supercoiled DNA when the resolution of the microscope is high enough to observe DNA strands. One of the most useful techniques for imaging DNA in air and in aqueous solution is atomic force microscopy (AFM), which has the possibility to image the dynamics of DNA at the nanoscale. Since this microscope generates an image by probing the surface of the sample with a sharp tip attached to the end of a flexible cantilever, it is essential that the sample is adsorbed onto an ultra-flat surface. Modification of the mica surface allows reliable and reproducible imaging of supercoiled pUC19 DNA. The growth, isolation, and purification of pUC19 DNA will be reported, as well as AFM imaging of pUC19 DNA on modified mica. This project was supported by National Science Foundation grant DUE-0633186.

**RM_MWGL Regional Meeting 58**

## NMR observations of optical pumping events in si-GaAs and GaAs quantum wells

***Dustin Wheeler***[1], *dwheeler@wustl.edu, Erika Sesti*[1], *Wieland Worthoff*[2], *Christopher Stanton*[3], *Sophia E Hayes*[1]. *(1) Department of Chemistry, Washington University in Saint Louis, Saint Louis, Missouri 63130, United States (2) Fakulät Physik, Technische Universität Dortmund, Dortmund, Germany (3) Department of Physics, University of Florida, Gainesville, Florida 32611, United States*

Semiconductors play an increasingly dominant role in the electronics used in day-to-day life. In our research, we strive to understand how semiconductor structure and defects in the material interact with electrons. One technique that offers insight into the electronic structure of a material is optically pumped nuclear magnetic resonance (OPNMR). By optically exciting electrons using light, we create situations where the NMR signals change because of those electrons.

Our recent work has involved changing the energy of the light and observing how it results in electron orientation in a sample of bulk GaAs. Simulations of experimental results involve incorporation of the energy dependent electron orientation to simulate the nuclear spin polarization within the material. These simulations predict signal intensity changes in the OPNMR signal based on optically populated electronic states.

Important investigations on quantum wells of AlGaAs/GaAs (materials present in many cd players, bar code scanners, etc.) have been made through OPNMR. Our current measurements involve the evolution of OPNMR signal intensity as a function of photon energy. Experimental investigations of these quantum wells show unique behavior when compared to non-quantum-confined samples.

**RM_MWGL Regional Meeting 59**

## Elucidating the energy-transfer mechanisms at the interface between the chlorosome and FMO protein in green sulfur bacteria

***Gregory S. Orf***[1], *gregory.s.orf@wustl.edu, David Bina*[1], *Robert E. Blankenship*[2]. *(1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Departments of Chemistry and Biology, Washington University in St. Louis, St. Louis, MO 63130, United States*

The light harvesting complexes in green bacteria have been heavily studied and are of particular interest to the areas of biohybrid nanomaterials and photovoltaics. In green sulfur bacteria, the cytoplasmic Fenna-Matthews-Olson (FMO) protein acts as a wire to funnel excitations generated by solar photons in the chlorosomes to the membrane-bound reaction center (RC). The chlorosome, FMO protein, and RC have been individually studied in depth but the specifics of the interface between the chlorosome and FMO protein are still under debate. It is proposed that, *in vivo,* the CsmA "baseplate" protein-pigment complex of the chlorosome interacts with the FMO protein and serves as the energy-transfer bridge. This work seeks to uncover the exact energy-transfer mechanisms and structure of this interface using an *in vitro* reconstitution of the CsmA-FMO interaction from *C. tepidum* using both solution and surface methods. The

reconstituted complex will be probed with spectroscopic, fluorescence, and crystallographic techniques. Insights gleaned from these findings will be beneficial to constructing more efficient bio-inspired photovoltaics that incorporate photosynthetic machinery or synthetic analogs.

## RM_MWGL Regional Meeting 60

### Spectroelectrochemical investigations of metalloporphyrin carbonyl and nitrosyl complexes

***Michael J. Shaw**, michsha@siue.edu, Krishna Sharmah-Gautam, Kenneth W Rodgers, Christopher Felchlia, Amin Daryaei, Pearl Ashitey. Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, Illinois 62026, United States*

The preparation and characterization of a series of [M(NO)(por)($CO_2$Fc)] complexes (M = Ru, Fe; por = tetraphenylporphryin, tetratolylporphyrin, tetraanisolylporphyrin; Fc = ferrocenyl) is described. These complexes undergo multiple, reversible oxidation events which can be based at the M-NO unit, the porphyrin, or the ferrocenyl unit. Cyclic voltammetry and fiber-optic-IR spectroelectrochemical investigations are used to determine the primary site(s) of electron transfer for each redox event.

## RM_MWGL Regional Meeting 61

### Prospecting for NMR Structures with Sparse, Unassigned Data

***Anna E. Nesbitt**, anesbitt@scs.uiuc.edu, Ming Tang, Michael C Brothers, Krisitin M. Nuzzio, Gemma Comellas, Lindsay J. Sperling, Chad M. Rienstra. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States*

Traditionally, *ab initio* protein structure prediction methods have relied on the needle-in-a-haystack approach of building an expansive set of model structures with borrowed “@home” CPUs to identify comparatively few structures built within 2 Å of the native fold. Recently, advanced methods for sampling protein fold space (i.e. fragment assembly) have hastened the pace of building convergent structures, and many of these improved methods make use of simultaneous advancements in chemical shift prediction (CHESHIRE/SPARTA). For instance, interjecting chemical shifts into the fragment selection and model evaluation facets of ROSETTA has expanded the protein size limit for CS-ROSETTA significantly by decreasing the CPUs required to populate the 2-5 Å space with model structures. Although such hybrid methods often make use of partial chemical shift assignments and/or unassigned NOE data, they do not yet incorporate unassigned 2D spectra. By surveying various object matching and pattern recognition algorithms, we have identified a method for comparing unassigned spectra to spectra predicted for a candidate structure. We test this method against a pool of models built by comparative modeling and with ROSETTA3.1, and rigorously benchmark it against several available structure validation methods. Ultimately we seek

to test whether models populating the 3-7 Å range can be identified via unassigned NMR data, from which the successful subset of fragments and/or comparative modeling templates may be culled to expedite structural refinement. Obtaining a crude structure in the early stages of NMR data analysis has enormous potential to accelerate data analysis, since the chemical shift predictions could serve as a first approximation to the assignments. Of particular note is the utility of SHIFTX2 or SPARTA+ predicted $^{13}C$ shifts, which are considerably more accurate than $^{1}H$ or $^{15}N$ shifts; the relative ease of $^{13}C$ chemical shift predictability opens a unique window of opportunity for $^{13}C$ detected SSNMR experiments.

## RM_MWGL Regional Meeting 62

## Preparative Studies of Re(I)-Terpyridine Complexes

***Daniel R Black**, daniel.black@my.und.edu, Sean E Hightower. Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58201, United States*

Over the past 40 years to rhenium(I) diimine tricarbonyl complexes have received considerable attention in part due to their rich excited-state chemistry and luminescent properties associated with the metal-to-ligand charge transfer (MLCT) excited state. These rhenium(I) diimine tricarbonyl complexes have applications as photo-sensitizers, photo-catalysts, and luminescent sensors and probes. While these rhenium (I) diimine tricarbonyl complexes have been extensively investigated, no tris-chelated rhenium(I) complexes have been explored.

Recent work conducted by our group has opened a synthetic route to the meridionally tris-chelated *cis*-$Re(\eta^3\text{-tpy})(CO)_2Cl$ complex. This complex absorbs throughout the visible spectrum with a reversible oxidation potential that is +0.85V (vs. SCE) less oxidizing relative to *fac*-$Re(\alpha,\acute{\alpha}\text{-diimine})(CO)_3Cl$ type complexes. In addition, the reactivity of *cis*-$Re(\eta^3\text{-tpy})(CO)_2Cl$ mirrors (or tracks) that of well-established *fac*-$Re(\alpha,\acute{\alpha}\text{-diimine})(CO)_3Cl$ complexes which has allowed complexes of the type *cis*-$[Re(\eta^3\text{-tpy})(CO)_2L]^{n+}$ (L = $NCCH_3$, $PPh_3$, Py, and $PR_3$; n = 1) to be prepared and characterized.

## RM_MWGL Regional Meeting 63

## Tether-Mediated Ring-Closing Metathesis Studies

***Soma Maitra**, smaitra@ku.edu, Rambabu Chegondi, Jana Markley, Paul R. Hanson*. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

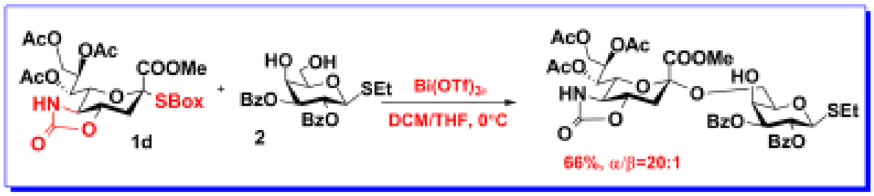
Ring-Closing metathesis (RCM) has emerged as one of the most powerful and efficient methodologies in small molecule and natural product synthesis. Temoporary phosphate tether mediated diastreoselective ring-closing metathesis will be discussed probing other parameters such as ring-size, stereochemistry and conformation. This method is being further extended to the synthesis of complex bioactive natural products.

## RM_MWGL Regional Meeting 64

### Selective sialylations by the use of C-5 modified S-benzoxazolyl sialyl donors

***Chase Gobble***, *cgobble@siue.edu, Cristina De Meo, Matthew Stark, Payal Patel, Ben Harris.Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026, United States*

Sialic acid is always expressed at the terminal position of glycoconjugates and its biological functions range from cell-cell adhesion and mobility, to oncogenesis and recognition by viruses and bacteria. Thus, the synthesis of sialic acid-containing glycoconjugates (sialosides) is an important tool for a better understanding of their biological roles and for designing sialotherapeutics. However, the chemical synthesis of these important natural products is often plagued with low yields and/or stereoselectivities. Previously we reported that the use of S-benzoaxoyl (SBox) as leaving group can allow selective sialylations in the presence of a thioethyl galactosyl acceptor. Unfortunately, the desired disaccharide was obtained with no stereoselectivity, limiting therefore the applicability of this methodology. Herein, we report that the investigation of C-5 modified S-benzoaxoyl donors in selective sialylation and a dramatic improvement of the methodology by the use of oxazolidinone modified SBox donor in the presence of bismuth triflate. This combination allowed the synthesis of the desired target with complete stereoselectivity.



## RM_MWGL Regional Meeting 65

### Electronic structure of platinum fluoride, PtF, by intracavity laser absorption spectroscopy

***Kaitlin A. Womack***[1], *kwomack@siue.edu, Leah C. O'Brien*[1], *James J. O'Brien*[2]. *(1) Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652, United States (2) Department of Chemistry and Biochemistry, University of Missouri, St. Louis, MO 63121-4499, United States*

Three vibrational bands of a new electronic transition of PtF have been recorded at high resolution by intracavity laser absorption spectroscopy. The gas phase PtF molecules were produced in a Pt-lined hollow cathode plasma of approximately 0.5 A, with an argon support gas at 2 torr and a trace amount of $SF_6$. Bandheads at 13078.9, 12523.4, and 11946.4 $cm^{-1}$ were observed, and based on the isotopologue structure these are assigned as the (1,0), (0,0), and (0,1) vibrational bands of a new electronic transition. Vibrational intervals are determined for the two states involved in the transition: $\Delta G_{1/2}'$= 555.5 $cm^{-1}$, and $\Delta G_{1/2}''$= 577.0 $cm^{-1}$. Analysis of the rotational structure is in progress and will be presented.

## RM_MWGL Regional Meeting 66

## Spectral analysis of the three major isotopologues of PtC

*Jasmine Raskas[1],* ***Dylan Schultz**[1]*, *obrien@jinx.umsl.edu, James J O'Brien[2], Leah C O'Brien[3]. (1) Clayton High School, Clayton, MO 63105, United States (2) Department of Chemistry and Biochemistry, University of Missouri-St Louis, Saint Louis, MO 63121, United States (3) Department of Chemistry, Southern Illinois University-Edwardsville, Edwardsville, IL 62025, United States*

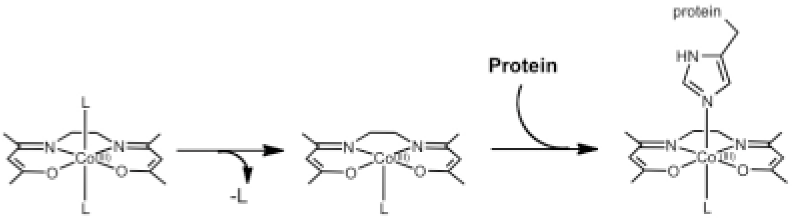
Intracavity laser absorption spectroscopy was used to record at high resolution several vibrational bands of the $A''^1\Sigma^+ - X^1\Sigma^+$ and $A'^1\Pi - X^1\Sigma^+$ electronic transitions of PtC. Individual rotational lines of the three major isotopologues ($^{194}$PtC, $^{195}$PtC and $^{196}$PtC) were identified. Molecular constants for the A", A' and X states will be presented.

## RM_MWGL Regional Meeting 67

## Cobalt(III) Schiff base complexes as zinc finger transcription factor inhibitors

***Marie C Heffern***, *marieheffern@u.northwestern.edu, Allison S Harney, Natsuho Yamamoto, Thomas J Meade. Department of Chemistry, Northwestern University, Evanston, IL 60201, United States*

Advances in the understanding of metal-protein binding interactions have stimulated the development of metal-based inhibitors of proteins involved in disease progression. To this end, Co(III) Schiff base complexes (Co-sb) have been developed that inhibit the activity of histidine-containing proteins through a dissociative exchange mechanism of the labile axial ligand. Target selectivity is achieved by conjugation of an oligonucleotide or peptide with high affinity for the protein of interest. This strategy has been successfully demonstrated in the inhibition of zinc finger transcription factors implicated in cancer metastasis.



We are trying to understand the discrete components of Co-sb complexes that influence inhibitory activity. The interaction between Co-sb and zinc finger (ZF) peptide fragments are studied with spectroscopic techniques to elucidate how Co-sb binds to the ZF motif and elicits structural disruptions. The dynamics of the interaction are measured and evaluated by isothermal titration calorimetry and mass spectrometry. Further, by implementing fluorescent imidazoles as axial ligands for Co-sb, we are developing self-reporting pH-responsive Co-sb prodrugs. In this construct, the axial ligand will selectively dissociate from the Co(III) center in acidic environments and changes in fluorescent intensity or spectral shifts will be observed. These investigations will enhance our understanding of Co-sb as protein inhibitors to allow for greater regulation of inhibitor activity towards the development of therapeutic complexes.

**RM_MWGL Regional Meeting 68**

## Reductive Photoelimination of Bromine from a Pt(IV) Perylene Complex

***Mehdi Masjedi**, mehdimasjedi@yahoo.com, Alice Raphael Karikachery, Paul R. Sharp. Department of Chemistry, University of Missouri, Columbia, Columbia, Missouri 65211, United States*

Efficient photolytic conversion of solar energy into stored energy of chemical bonds is an important goal. In contrast to production of hydrogen through water splitting, which is a difficult route because of four electron oxidation of water, hydrogen halide (HX) splitting is a more facile two electron process resulting in formation of molecular hydrogen and halogens. Accordingly, a potential key step in a transition metal catalyzed process is the photoelimination of halogen from a dihalide complex. Bromine photoelimination from several organoplatinum(IV) complexes containing different ring systems such as corannulene, phenanthrene, naphthalene, benzotrifluoride or aniline, has been observed by our group.

Herein, we report the synthesis, characterization and single crystal X-ray studies of a Pt(IV) perylene complex with high quantum yield efficiency for bromine elimination in the visible region.

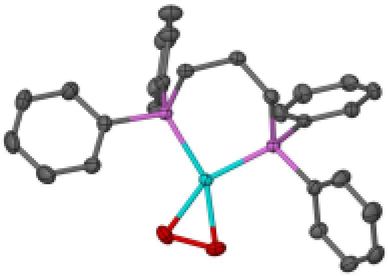
**RM_MWGL Regional Meeting 69**

## Synthesis and reactivity of bidentate phosphine platinum(II) peroxo compounds

***Morgan A. Moody**, mamc05@mail.mizzou.edu, Paul R. Sharp. Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States*

The synthesis and characterization of several bidentate phosphine platinum(II) peroxo compounds, $Ph_2P(CH_2)_nPPh_2$ (n= 1-4), was developed. Metathesis of the dichloroplatinum phosphine compounds with potassium superoxide in dimethylformamide, presumably followed by disproportionation, produced the titled compounds. Isolation of the $dpppPtO_2$, n = 3, product was achieved and crystallized in

the monoclinic space group $P2_1/c$ with a = 9.982(3) Å, b = 14.098(4) Å, c = 19.102(5), and β = 90.087(3) ° with Z = 4 (T = -100°C), R1 = 0.0181. The compound has an O-O bond length of 1.523(3) Å. The reactivity of these compounds has been studied with small molecules, including CO, $CO_2$, and $SO_2$.

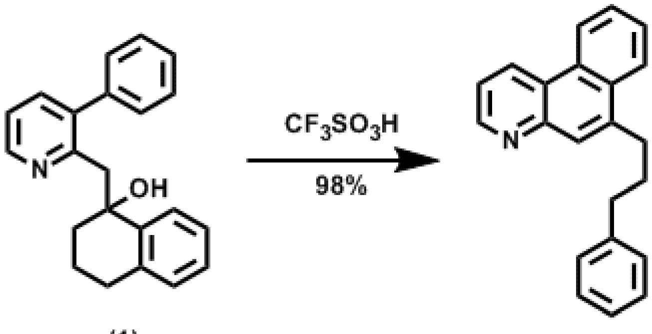


## RM_MWGL Regional Meeting 70

## Triflic acid promoted synthesis of various azapolycyclic aromatic compounds

***Anila Kethe***, *akethe@niu.edu, Ang Li, Rajashekara Reddy Naredla, Douglas A Klumpp*.Department of Chemistry and Biochemistry, Northern Illinois University, Dekalb, IL 60115, United States*

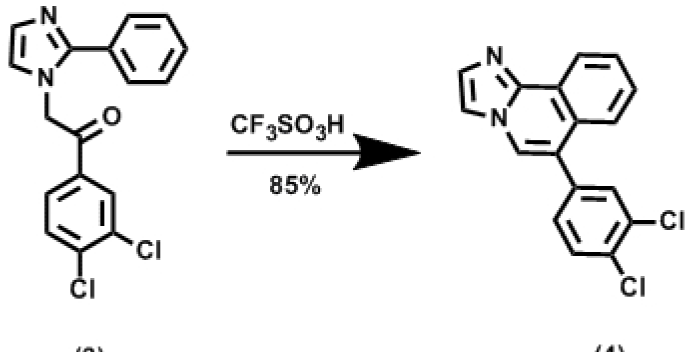
(I) Aza-polycyclic compounds have important biological and material science applications. Using our superacid promoted reactions, a series of heterocyclic alcohols like **(1)**were reacted to yield corresponding functionalized aza-polycyclic aromatic compounds like **(2)** though a series of ring closing and opening cascades involving dicationic intermediates



(1)

(2)

(II) Selective Estrogen Receptor Modulators (SERMs) are a class of compounds that interact with subsets of estrogen receptors.
Well known examples of this class of compounds are the marketed drugs, Tamoxifen and Raloxifen. Using our chemistry of superelectrophilic dehydrative cyclizations we made a few nitrogen containing like **(4)** from heterocyclic ketones like **(3)** in excellent yields.



(3) (4)

**RM_MWGL Regional Meeting 71**

## Assignment of proton resonances for damaged DNA using two-dimensional nuclear magnetic resonance

***Stephen P Kramer**, Kramer17@live.missouristate.edu, Brianna Medrano, Gary Meints. Department of Chemistry, Missouri State University, Springfield, MO 65897, United States*

The Dickerson sequence of self complementary DNA, ds(C-G-C-G-A-A-T-T-C-G-C-G)$_2$, has been thoroughly characterized via two-dimensional NMR, as well as other techniques. We have used this sequence as a frame of reference to map chemical shift changes caused by inclusion of a single lesion base. Due to errors in transcription, damage to the DNA, or carcinogenic substances, single base legions such as uracil, etheno-dA, or abasic sites occur and can result in mutagenic or cytotoxic effects. These errors arise in different ways. Cytosine is unstable and has been known to change into uracil via spontaneous deamination, abasic sites arise due to cleavage of the glycosidic bond, and the etheno adduct can be created as a product of lipid peroxidation or alkylation by metabolites of vinyl chloride.

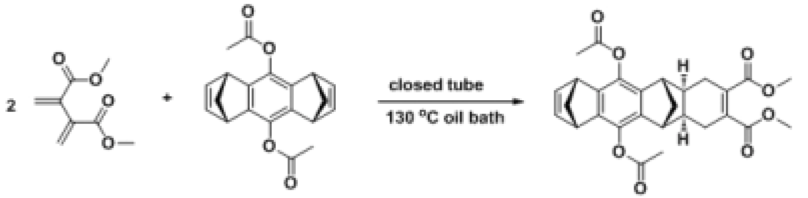
Several damaged Dickerson sequences were analyzed using NMR and the chemical shifts compared to those of the undamaged Dickerson sequence. The sequences studied were two uracil substituted sequences **U3** [ds(C-G-**U**-G-A-A-T-T-C-G-C-G)$_2$] and **U9** [ds(C-G-C-G-A-A-T-T-**U**-G-C-G)$_2$], one sequence with an abasic site **S5** [ds(C-G-C-G-**S**-A-T-T-C-G-C-G)$_2$], and an etheno substituted sequence **edA5** [ds(C-G-C-G-**edA**-A-T-T-C-G-C-G)$_2$]. By mapping the chemical shifts of the damaged DNA sequences and comparing them against the Dickerson sequence, it was possible to determine the impact of the lesion on the chemical shifts. Preliminary results indicate that structural changes manifest locally, primarily at the site of the lesion and its base pairing partner.

## RM_MWGL Regional Meeting 72

## Synthesis toward molecular “tweezers”

***Tamara R. Bowen**, trbowen@eiu.edu, Zhiqing Yan. Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, United States*

Molecular curvature and a certain degree of structural rigidity are essential for the construction of molecular containers. We show here the synthesis toward a “tweezer-shaped” molecule. The curvature of the molecule as well as the rigidity are achieved by two bicyclo[2.2.1]heptane motifs. The bicyclic structure has been constructed by two Diels-Alder reactions between dicyclopentadiene and benzophenone. The second Diels-Alder reaction generated a mixture of both syn- and anti-isomers in a ratio of 3:1. The desired syn-isomer was isolated by multiple recrystallizations from ethyl acetate. A third Diels-Alder reaction was then used to extend the “arms” of the molecular tweezers. During the first attempt of this step, 1,3-butadiene-2,3-dicarboxylic acid was used as the diene, but was unsuccessful, presumably due to the instability of the diacid. When using the dimethyl ester derivative, an unsymmetrical exo-product was obtained. The structure of this crystalline product was determined by both $^1$H NMR and X-ray.



## RM_MWGL Regional Meeting 73

## Nanorattles: Silver nanoparticles entrapped in porous polymer nanocapsules

***Sergey N. Shmakov**, sshmakov@memphis.edu, Eugene Pinkhassik. Department of Chemistry, Saint Louis University, St Louis, MO 63103, United States*

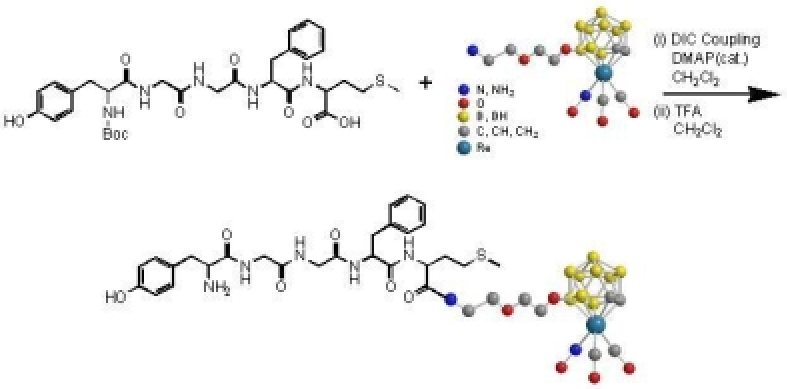
Hollow polymer nanocapsules that entrap simultaneously formed silver nanoparticles were prepared via a one-step synthesis. Bilayer of phospholipid liposomes was used as temporary scaffold for templating of hollow polymer nanocap-sules (NCs). Addition of pore forming template allowed controllable formation of nano-sized pores in the walls of NCs. Metal nanoparticles (NPs) demonstrated tremendous promise in many applications, such as catalysis, medical imaging, and development of new analytical methods. Hence, the entrapment of nanoparticles in hollow nanocapsules may offer several advantages. Free radical photoinitiator facilitated both polymerization within the bilayer and formation of metal nanoparticles in the aqueous core. Metal NPs in solution are unstable without stabilizing agent and have a tendency to aggregate. Walls of nanocapsules prevent NPs from aggregation. Based on sizes of nanocapsules and nanoparticles, it was calculated that less than 5% of NC volume is occupied by a nanoparticle and more than 95% of NC volume is available for co-entrapment of other species (e.g., drugs) or for allowing unhindered flow of analytes or substrates and products. We anticipate that this method of producing of nanorattles may be adapted to a broad range of metals and monomers.

**RM_MWGL Regional Meeting 74**

## Synthesis and functionalization of Rhenacarboranes as drug-delivery vehicles

***Daniel Pruitt**, dpruitt1@slu.edu, Paul Jelliss. Department of Chemistry, Saint Louis University, St. Louis, MO 63180, United States*

Rhenacarboranes and their derivatives provide an attractive area of research due to their ability to cross over the blood-brain barrier (BBB). As potential drug-delivery vehicle candidates, an array of these rhenacarboranes can be synthesized and functionalized via coupling to various amino acids and polypeptides. Our foremost objective is to synthesize a rhenacarborane complex functionalized with a pendant polyether side-chain containing a terminal target functional group (-OH/$NH_2$) that will be able to bind with the desired polypeptide Met-enkephalin. Met-enkephalin is commonly known as opioid growth factor (OGF) and is present in biological systems in the central nervous system (CNS). OGF can then bind to opioid growth factor receptors (OGFr) which can lead to suppression. When connected to the rhenacarborane, OGF could be transported past the BBB and then biologically cleaved off the vehicle, allowing for distribution into the CNS. During synthesis, all complexes and intermediates were characterized by IR and NMR spectroscopy.

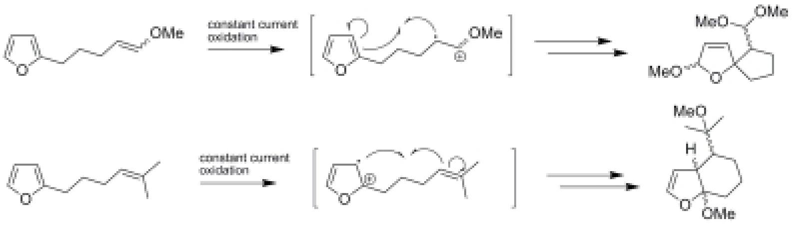


## RM_MWGL Regional Meeting 75

## Studies towards the electrooxidative coupling of heterocycles to olefins

***Jake A Smith***, *jake.a.smith@go.wustl.edu, Kevin D Moeller. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Furans substituted at the three position behave as effective substrates for electrooxidative olefin coupling reactions, and this reactivity has been taken advantage of en route to complex targets such as (-)-Alliacal A and the Arteannium ring structure. Expanding from this previous work, the reactivity of furans substituted at the two position was examined. While proving synthetically nonviable, these substrates did provide an insight into the nature of the radical cation intermediate, as illustrated in the associated figure. Moving forward, the viability of oxazoles and imidazoles as coupling substrates will be examined, the products of which could yield Robinson annulation-type enones when subjected to acid hydrolysis, and applied to the synthesis of Aberrarone.



## RM_MWGL Regional Meeting 76

## New cucurbitane analogs: Potential anticancer candidates for the treatment of prostate cancer

***Nichole Rice***, *nichole.rice@sdstate.edu, Fathi Halaweish. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, United States*

Cucurbitacins (Cu) have been used as natural product remedies, for centuries. Cu are traditionally used for their anti-inflammatory and hepataprotective properties, but are also effective against different cancer types (prostate, breast, colon, pancreatic). Their activity towards cancer is partly due to their anti-inflammatory properties, inhibition of COXII, iNOS/NF-kβ. In the USA Prostate Cancer (PCa) is the second leading cause of death in men. Androgens play an important role in the development of PCa. Androgen-ablation therapy (AAT) is one of the current treatments used for PCa. AAT works by blocking the AR, but can push PCa from an androgen-dependent state to an androgen-independent state. Cu have been shown to inhibit the AR and may also interact with Hsp90. Hsp90 is a molecular chaperone known to interact with the AR, helping it to remain active in the non-favorable conditions often associated with cancer. Molecular modeling (OpenEye®) was used to guide our synthesis of new potential PCa analogs. Modeling shows Cu binding to the AR, Hsp90, COXII, and iNOS/NF- kβ. *In vitro* data for several new Cu analogs derived from Cu B and Cu D will be presented. *In vitro* data has been done using two cell lines, PC-3 and MDA PCa 2b. The data indicates sub-micromolar $IC_{50}$ values for synthetically modified Cu towards PC-3 and MDA PCA 2b PCa cell lines. Synthetic Cu show lower $IC_{50}$ as well as increases affinity towards molecular targets than Cu B or D.

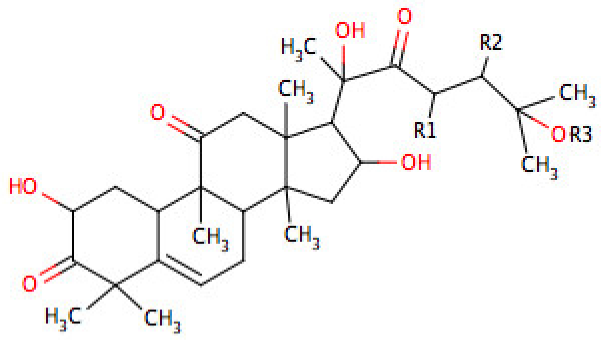


Figure 1: General Structure of Cu analogs

**RM_MWGL Regional Meeting 77**

## Optimization of synthesis toward the development of an anion binding molecule

***Andrew Dawson**, adawson4@slu.edu, Christina Bagwill, Samuel Garvey, Elizabeth Sullivan, Michael Lewis. Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

Intermolecular interactions of aromatics play a significant role in chemistry and biology, and the π-electron density of aromatics has been shown to interact with cations, anions, and other aromatics. Anion-π interactions of aromatics have received increasing attention in recent years. Computational work in our group has suggested that ion-substituent interactions are important in anion-π interactions. In order to substantiate these claims, this work focuses on the initial steps in the synthetic development of an anion binding molecule.

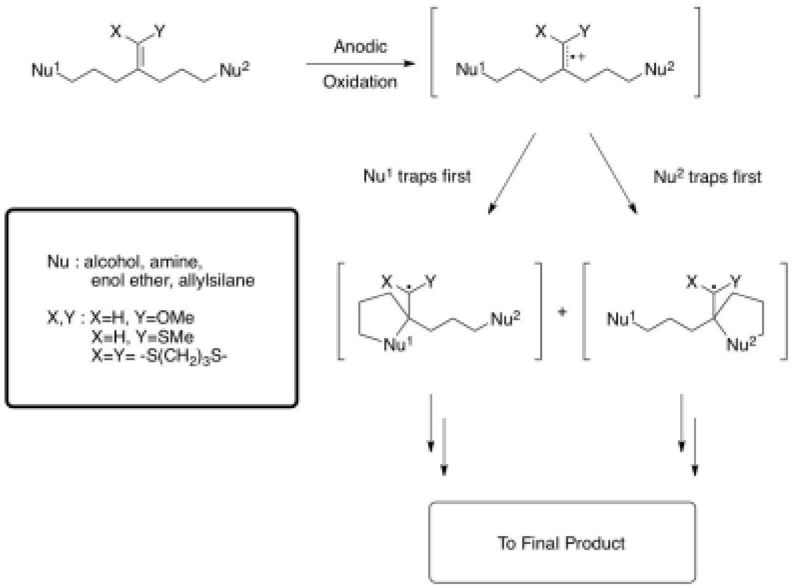
Previously in our group the first three steps of this synthesis included protection of the primary alcohols, N-acylation of the secondary amine, followed by deprotection of the alcohol functional groups. Utilizing the Duck-Hee method, N-acylation of diethanolamine can now be accomplished in one step with fewer by-products and higher yields. It is believed that the coordination of MgO to the primary alcohols is a major contributing factor in the success of this method. Reactions were monitored and purified using standard chromatographic techniques and confirmation was obtained using LCMS. Comparisons of results will be presented between the prior and current synthetic routes. Future work will concentrate on the last step of the reaction involving the formation of the macrocyclic cryptand.

**RM_MWGL Regional Meeting 78**

## Anodic olefin coupling reactions: Probing reaction mechanisms and relative reaction rates via competition experiments

***John M Campbell***[1]*, campbelljm@go.wustl.edu, Hai-chao Xu*[2]*, Kevin D Moeller*[1]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States (2) Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States*

Electron-rich olefins may be oxidized electrochemically to generate radical cations. These reactive intermediates have been known to react intramolecularly with a variety of nucleophiles, including alcohols, amines, enol ethers and allylsilanes to form cyclic compounds. We have found that the reactivity of the radical cation intermediate—and possibly the mechanism of the cyclization—may be tuned by controlling the substituents on the olefin (X and Y in the scheme below). This reactivity may be explored by tethering two different nucleophiles to the same electron-rich olefin, and observing the products formed upon electrolysis. Results gleaned from these so-called “competition studies” allow relative reaction rates for the reaction of a radical cation with various nucleophiles to be determined. Thus, this research allows for the appropriate selection of the X and Y substituents, depending upon the identity of the desired nucleophile, with the continued goal of improving our understanding of anodic olefin coupling reactions for use in organic synthesis.



## RM_MWGL Regional Meeting 79

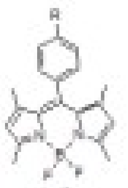
### New BODIPY based fluorescent indicator for elective detection of Pb$^{2+}$ ions in living cells

***Mukulesh Baruah***, *mukulesh.baruah@sdstate.edu, Eric Huntimer, Salama Mahmoud, Adam Hoppe, Fathi Halaweish. Department of Chemistry and Biochemistry, South Dakota State University, United States*

In the environment, lead is a potent threat to life as it accumulated ~1000 fold above than its natural level from the result of human activity. Center for Disease Control and Prevention reported approximately 250 000 young children in the U.S. have blood levels of lead more than 10 ug/dL and is the toxic range. Low-level lead exposure can lead to a number of adverse health effects.

Among other techniques, fluorescence is the most sensitive technique used in analytical chemistry for detection of biologically important ions and molecules. There are only few fluorescent probes for selective detection of lead ions has been reported. Therefore, development of better fluorescent probe for selective Pb$^{2+}$ion detection is interesting for elucidation of lead toxicity in-vivo.

Herein, we wish to report a novel fluorescent probe (Fig-1) for selective detection of Pb$^{2+}$ that is synthesized by linking 4, 4-difluoro-4-bora-3a, 4a-diaza-s-indacene dye as fluorophore covalently through its 8th position to a dicarboxylic acid possessing pseudocrown ether, as ionophore. The indicator shows a large increase of the fluorescence upon increasing lead ion concentration (Fig-2) but no significant changes to the presence of other bivalent ions. The ground state dissociation constant $K_d$ in 20 mM HEPES buffer at pH 7.4 for the complex between lead and the probe was found to be ~18 mM. The probe is also applied to monitor Pb2+ in living cells. (Fig-3)



1

Fig 1: BODIPY lead probe, R is the ionophore

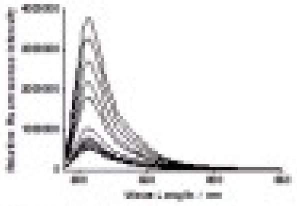


Fig 2: Fluorescence Spectra of 1 upon increasing $[Pb^{2+}]$.

Fig 3: Cells stained with probe without and with $Pb^{2+}$

References:

## RM_MWGL Regional Meeting 80

# Protease-activated receptor (PAR)-1 inhibiting nanoparticles for modulation of vascular inflammatory signaling

***Bhaswati Sinha***[1], *bsinha@dom.wustl.edu, Hua Pan*[1]*, Clay F Semenkovich*[2]*, Samuel A Wickline*[1]*. (1) Department of Internal Medicine, Center for Translational Research in Advanced Imaging and Nanomedicine (C-TRAIN), Washington University in St.louis, Saint Louis, MO 63108, United States (2) Division of Endocrinology, Metabolism and Lipid Research, Washington University in St.Louis, Saint Louis, MO 63110, United States*

The aim of this research is to develop therapeutic nanoparticles, targeting protease-activated receptors (PARs) as potential antithrombotic, antiatherosclerotic and antiinflammatory agents. Since the discovery of PARs in 1990s, there has been a great interest in developing PAR-antagonists as novel antithrombotic agents. Cell penetrating peptides derived from the intracellular loop 3 of PAR 1 and/ or 4, also called pepducins, have demonstrated in vitro platelet aggregation in response to thrombin and specific PAR agonist peptides.[1] One of these pepducins, PAL-12, a PAR1 selective antagonist was chosen as the lead therapeutic component to develop into stable perfluorocarbon (PFC) based nanoparticles (NP). The PAL-12 peptide was successfully synthesized using solid phase peptide synthesis procedure and purified using reversed phase preparative HPLC. A stable PFC nanoparticle emulsion was then formulated by incorporating the PAL-12 onto the nanoparticles and was characterized based on their particle size (258.6 nm) and zeta potential (18.91 mV). To establish the utility of these nanoparticles as PAR1 signaling inhibitor, Human Umbilical Vein Endothelial Cells (HUVEC) were incubated with the PAL-12 NP in presence or absence of known PAR1 selective agonist peptide, SFLLRN-$NH_2$. The objective was to demonstrate if the Pal-12 NP were able to inhibit the activation of transcription factor NF-kB (p65 translocation), involved in one of the downstream signaling pathways of PAR-1. Initial results based on immunohistochemical staining and fluorescence microscopy experiments are promising as there was 61% inhibition of translocation of p65 by NP, indicating inhibition of NF-KB activation. Quantitative experiments on signal pathway mediator responses are currently under way to support the observations that PAR-1 inhibiting PFC nanoparticles are useful constructs for modulation of important mechanisms of vascular inflammation.

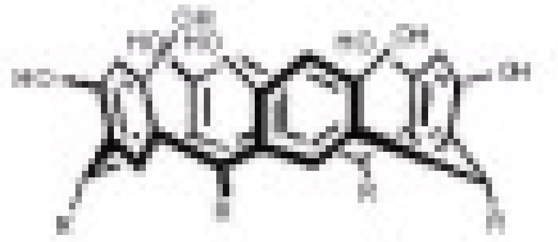
This research was supported by Diabetes and Related Metabolic Diseases Training grant (5 T32 DK007120).

## RM_MWGL Regional Meeting 81

## Amphiphilic Behavior of Alkyl-chained Resorcinarenes

***Priyanka Ogirala***, *priyanka.ogirala@gmail.com. Center for Nanoscience and Department of Chemistry and Biochemistry, University of Missouri-St.Louis, St. Louis, Missouri 63121, United States*

A suite of resorcin[4]arenes (see structure) that vary in headgroups and sidechains have been studied to determine their amphiphilic and self-assembly properties. Self-assembly was assessed for monolayers at the air-water interface using the Langmuir trough. Planar bilayer experiments using the voltage clamp technique revealed that these resorcinarenes do not show ion transport activity. The trough results showed that these compounds form a highly stable monolayer films. Brewster angle microscopy was employed to observe the solid domains that these compounds form on a water surface. The results of these studies and the structural and dynamic inferences drawn from them will be presented.

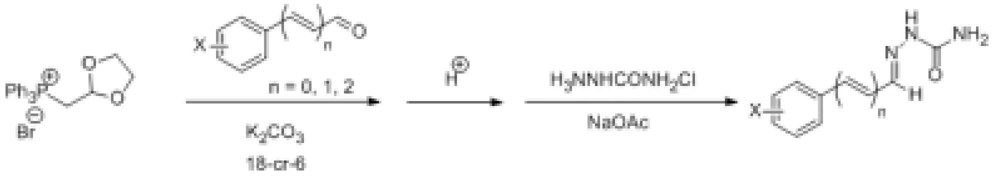


## RM_MWGL Regional Meeting 82

## Synthesis and photochromicity of extended cinnamaldehyde derivatives from phosphorous ylides

***John M Saathoff***, *jmsaathoff@eiu.edu, Stacy M Fortin, Edward M Treadwell. Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920, United States*

This study seeks to expand I.M. Heilbron et al.'s report of the solid state reversed photochromicity of cinnamaldehyde semicarbazones. They reported that ortho and para methoxy derivatives showed enhanced photochromicity, while the meta substituted was not photochromic. By altering the substituents off the phenyl ring as well as the length of the conjugated system we are systematically looking at the ability to tune the photochromicity in this class of compounds. Reacting the known Wittig ((1,3-dioxolan-2-yl)methyl)triphenylphosphonium bromide with mono-, di-, and tri-methoxy benzaldehydes and cinnamaldehydes, as well as vanillin and isovanillin, produced conjugated acetals in 53 % - 88 % yields. The condensation reaction afforded a mixture of cis-trans isomers as seen by $^1H$ NMR spectroscopy, but upon purification by silica gel chromatography extensive isomerization to the trans isomer occurred. Hydrolysis produced the conjugated aldehydes, which were converted to their semicarbazone derivatives. The photochromicity of these compounds, in relationship to their UV-Vis and molecular orbital properties, will be discussed.



## RM_MWGL Regional Meeting 83

## Hydrogen atom abstraction from rhodium hydrides by nitroxyl radicals and generation of $LRh^{2+}$

*__James F Dunne__, jfdunne@iastate.edu, Andreja Bakac. Department of Chemistry, Iowa State University, Ames, IA 50011, United States*

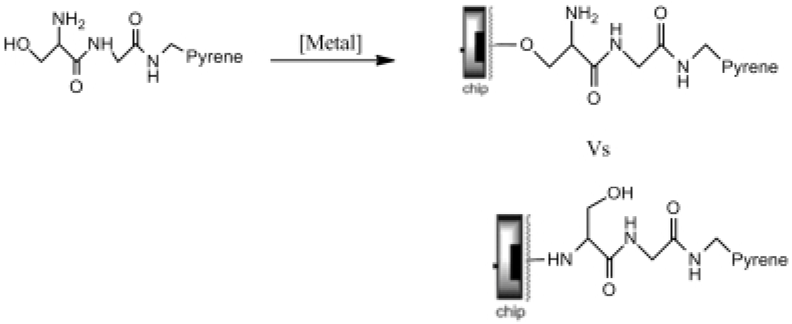
We are interested in accurately determining the metal hydride bond dissociation energies of LRh–H (L = $(NH_3)_4$, [14]ane$N_4$). These hydrides are excellent precursors for highly reactive superoxo, hydroperoxo, and nitrosyl complexes. Thus, an accurate knowledge of the metal hydride bond strength would allow for greater mechanistic understanding of the formation of these compounds, as well as enable a more rational prediction of their reactivity with organic molecules. In this work, we examined the reaction between $[(NH_3)_4(H_2O)RhH^{2+}]$ and 4-hydroxy-TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine 1-oxyl) under acidic conditions. The reaction generates the corresponding hydroxylamine, and a transient $(NH_3)_4(H_2O)Rh^{2+}$ which can be effectively trapped with oxygen to produce the superoxo complex. The reaction of HO-TEMPO with the hydride is first in both $(NH_3)_4(H_2O)RhH^{2+}$ and 4-OH-TEMPO with a rate constant k = 0.216 ± 0.008 $M^{-1}s^{-1}$. The deuteride $(NH_3)_4(H_2O)RhD^{2+}$ reacts more slowly, k = 0.10 ± 0.01 $M^{-1}s^{-1}$, leading to a kinetic isotope effect $k_H/k_D$ = 2.15 ± 0.01, consistent with the breaking of the Rh–H bond in the rate-determining step. ([14]ane$N_4$)$(H_2O)RhH^{2+}$ also reacts with 4-OH-TEMPO but the kinetics were too slow for precise measurements.

## RM_MWGL Regional Meeting 84

## Microelectrode array-based chemistry

*Jennifer Bartels, __Sakshi Uppal__, suppal@wustl.edu, Kevin D. Moeller. Department of Chemistry, Washington University in St.Louis, St.Louis, Missouri 63112, United States*

The placement of biological ligands on microelectrode arrays offers an opportunity to monitor ligand-receptor binding events in “real time”.
But how does one place a molecule on a microelectrode array? We have been developing transition metal routes to accomplish this task. Recently, we have been exploring whether the ligand control of organometallic reactions that governs solution phase chemistry also operates on an array. Our findings along these lines will be discussed.



**RM_MWGL Regional Meeting 85**

## Redox profiling and protein characterization via MS to investigate thiol-based regulatory mechanisms induced by oxidative stress in plants

***Leslie M Hicks***[1], *lhicks@danforthcenter.org, Joseph M Jez*[2], *Sophie Alvarez*[1], *Ashley Galant*[2], *Zhenjiu Liu*[1]. *(1) Proteomics & Mass Spectrometry Facility, Donald Danforth Plant Science Center, Saint Louis, MO 63132, United States (2) Department of Biology, Washington University, Saint Louis, MO 63130, United States*

In many organisms the general role of redox environment as a regulatory factor in cellular processes is only beginning to be examined in detail. In response to changes in cellular redox environment, the formation of disulfide bonds provides a mechanism for rapidly modulating protein function. Although the generation of reactive oxygen species and alteration of cellular redox state can lead to changes in disulfide bond formation in redox-sensitive proteins, the actual number and types of these proteins in plants remain largely unknown. In plants, oxidative regulation and redox signaling occur in photosynthesis, translation, transcription, apoptosis, and seed development, but ongoing efforts to identify proteins using thiol-based redox switches promise to expand the redox proteome. Therefore, our lab has focused on the development of gel- and liquid-based proteomics methods to profile redox responsive proteomes, as well as mass spectrometry approaches to site-specifically characterize reactive sites in the identified targets. Methodological considerations as well as results from our efforts focused on analysis of the redox state of proteins following treatment with either exogenous $H_2O_2$ or buthionine sulfoximine, which depletes glutathione to cause accumulation of endogenous $H_2O_2$, will be presented.

## RM_MWGL Regional Meeting 86

### Functional proteomics in *Arabidopsis* G-protein signaling in response to ABA

***Sophie Alvarez***, *salvarez@danforthcenter.org, Leslie M Hicks, Sona Pandey. Donald Danforth Plant Science Center, Saint Louis, MO 63132, United States*

Quantitative proteomics with the advances in sample preparation and in mass spectrometric instrumentation allows the quantification of abundance changes in the majority of cellular proteins with concentrations range spanning several orders of magnitude. LC-based proteomics approaches are commonly used for proteome profiling and characterization because identification and quantification are done simultaneously. A labeling LC-based quantitative proteomics approach using 4-plex iTRAQ (AB Sciex) was selected to characterize proteins involved in abscisic acid (ABA)-regulated and G-protein mediated signaling pathways in roots of *Arabidopsis*. Heterotrimeric G-proteins have been shown to participate in multiple signaling pathways in *Arabidopsis*, including many that are regulated by ABA, notably seed germination and early seedling development, gene expression changes and guard cell signaling. The Gα subunit of the trimer undergoes a signal-dependent transition from an inactive GDP-bound form to active GTP-bound form, integrating signal perception by a G-protein coupled receptor (GPCR) to downstream effectors. Mutants of the Gα subunit (*gpa1*) and more recently identified GPCR-Type G-proteins, GTG1 and GTG2, (*gtg1gtg2*) undergoing ABA treatment were used to evaluate (i) how the absence of GPA1 and GTG proteins affect protein abundances in *Arabidopsis* roots and whether it can shed light on the role of GPA1 and GTG1/2 in additional, non-ABA related pathways, and (ii) the effect of ABA on the *Arabidopsis* root proteome and the extent of its dependence on the presence of a functional GPA1 and GTG1/2, which might provide important clues to the mechanism of ABA-regulation of G-protein signaling.

## RM_MWGL Regional Meeting 87

### Integrated metabolomics provides novel insight into legume natural product biosynthesis

*Dong Sik Yang, John H Snyder, David V Huhman, Vered Tzin, Stacey Allen, Yuhong Tang,* ***Lloyd W Sumner***, *lwsumner@noble.org.The Samuel Roberts Noble Foundation, Ardmore, OK 73401, United States*

Legumes are fundamental sources of nutrition for most global cultures due to their high protein content achieved through unique symbioses with nitrogen-fixing bacteria collectively known as rhizobia. Legumes also produce a wide array of natural products including flavonoids, isoflavonoids, lignin, anthocyanins, and triterpene saponins. These compounds serve critical roles in plant defense, plant-microbe interactions, symbiosis,

and human and animal health. These natural products also influence the utility of plants as sources of renewable bioenergy, neutraceuticals and pharmaceuticals. *Medicago truncatula* is a close relative of the premium and global forage legume, alfalfa (*Medicago sativa*), and it is an ideal model species for the study of legume biology due to the availability of a genome sequence, commercial Affymetrix GeneChips® for gene expression analyses, and available mutant populations. Unfortunately, the application of genomics resources alone to the study of plant secondary metabolism is currently limited by deficient and/or inaccurate annotation of many secondary metabolic enzymes and by the incomplete knowledge of the full secondary metabolic composition of plants. However, many of these limitations can be circumvented through the use of integrated metabolomics which is a powerful approach for the discovery of novel biosynthetic genes and hypothesis driven assessment of metabolic networks. This presentation will introduce the model legume *Medicago truncatula* and provide an overview of our metabolomics technologies. The presentation will also provide specific examples of how we are exploiting integrated metabolomics and metabolic diversity within natural populations for the discovery and characterization of novel genes/enzymes that are involved in the biosynthesis of triterpene saponins.

**RM_MWGL Regional Meeting 88**

## Mass spectrometry based protein footprinting: the fourth pillar of proteomics

***Michael L Gross**, mgross@wustl.edu, Don Rempel, Jiawei Chen, Brian Gau, Hao Zhang, Richard Huang, Carl Frieden, Kanchan Gerai. Departments of Chemistry and Biochemistry/Biophysics, Washington University, Saint Louis, MO 63130, United States*

MS offers means of determining protein interactions, folding, and unfolding by using chemical footprinting. Driving this approach is the wide availability of mass spectrometers that can be used for footprinting as well as for analytical proteomic. To this end, we are developing fast photochemical oxidation of proteins (FPOP) and implementing HD exchange and other covalent modification approaches to interrogate protein interactions, interfaces, and dynamics of folding/unfolding. A significant advantage of FPOP is its speed, owing to the use of free radicals. Radical generation occurs in low ns, and the radical reactions are complete in 1 microsec. Only a single conformation of the protein exists during the footprinting because the distribution of oxidation products follows a Poisson distribution. Besides OH radicals, other radicals are possible including, the sulfate and carbonate radical anions and the iodine radical. FPOP can also be the probe in a classic, two-laser "pump-probe" experiment whereby a temperature-jump perturbation is produced as a pump by one laser and a second laser initiates FPOP as the probe. Subsequent analysis is by MS. This experiment is capable of probing protein structural dynamics at the sub-millisecond level with improved sensitivity and more detailed structural resolution than any physical chemical method. Better understanding of folding will emerge from this approach, which is more informative than ultrafast mixing, temperature-jump or pressure-jump coupled with time-resolved fluorescence, UV-Raman, IR, nuclear magnetic resonance and circular dichroism. In this lecture, we will use the characterization of various isoforms of ApoE to

illustrate an application of protein footprinting for a biomedically important protein with implications in Alzheimer's disease.

### RM_MWGL Regional Meeting 89

## The use of hydrogen/deuterium exchange-mass spectrometry in VDR modulator development

***Jun Zhang****, zhanggun@wustl.edu. Department of Chemistry, Washington University, Saint Louis, MO 63130, United States*

The vitamin D receptor (VDR) is a ligand-dependent transcription factor and a member of the nuclear receptor (NR) superfamily that classically functions as a heterodimer with retinoid X receptor a (RXRa) to control expression of genes. VDR mediates transcriptional activity upon binding to ligands and altering the receptor conformation. Conformational changes on the receptor may selectively regulate gene transactivation through their differential impact on the co-activator recruitment and correspondingly drive biological response.

VDR is a potential therapeutic target for a range of human disorders and diseases, such as osteoporosis, obesity, autoimmune disease and cancer. VDR natural ligand 1α,25-dihydroxyvitamin $D_3$ (1,25-D3) and its analogs have been used for the treatment of these diseases; however, the therapeutic applications are limited due to hypercalcemic side effects. Therefore, synthetic VDR modulators with reduced side effects are required. A crystal structure of drug target protein/ligand complex is the basis of structure-based drug design. However, not all complexes involving drug targets are crystallizable, and such work is time consuming. Hydrogen/deuterium exchange coupled with mass spectrometry (H/DX-MS) has been demonstrated as a useful method to complement x-ray crystallography. Here, we applied H/DX-MS to probe the conformational dynamics of the ligand binding domain (LBD) of the VDR upon binding its natural ligand 1,25-D3, and two analogs, alfacalcidol and ED-71, to better understand the molecular mechanism of VDR modulators with different observed pharmacological profiles. H/DX revealed that subtle differences in the chemical structure of VDR ligands can elicit distinct interactions within the receptor. So H/DX study of the protein-ligand interactions would be very helpful to guide the structure-activity-relationship study and thereby improve potency and selectivity of modulators. To this end, we further extended H/DX study to lead optimization of selective VDR modulators.

### RM_MWGL Regional Meeting 90

## Formation of Hydrogen-Bonded Nanostructures through the Self-Assembly of Mixed Macrocycles

***Constance R. Pfeiffer**, crpb8c@mail.missouri.edu, Andrew K. Maerz, Drew A. Fowler, Miten Mistry, Charles L. Barnes, Jerry L. Atwood. Department of Chemisty, University of Missouri-Columbia, Columbia, Missouri 65211, United States*

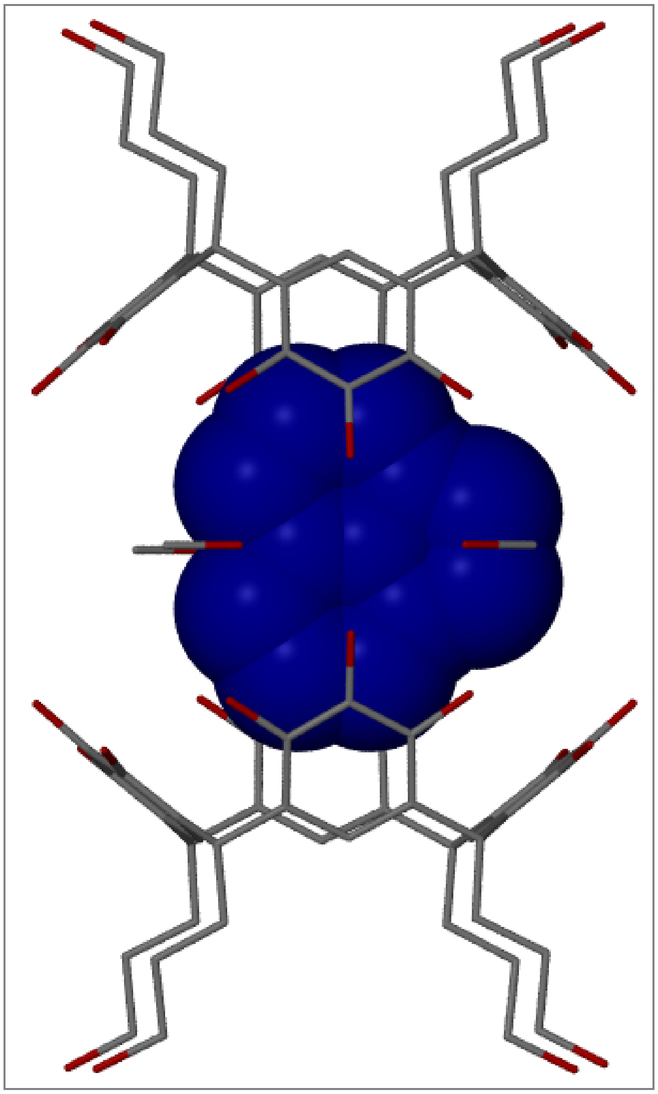
Calix[4]resorcinarenes, as well as the related pyrogallol[4]arenes, have shown to be useful building blocks in supramolecular chemistry. However, the synthesis of mixed macrocycles is a sparse topic in the research of these calixarene family macrocycles. The use of a mixture of resorcinol and pyrogallol in the acid-catalyzed condensation with an aldehyde yields macrocycles with varying ratios of resorcinol and pyrogallol moieties in the product mixture. These “mixed macrocycles” have shown to be useful in the self-assembly of larger entities similar to the parent macrocycles. The previously reported assembly of a hydrogen-bonded hexameric capsule was accomplished by crystallization in diethyl ether of the mixed macrocycle consisting of a 1:3 resorcinol: pyrogallol ratio. Upon further investigation it has been found that crystallization from different solvent systems can result in the formation of other supramolecular entities. Dimeric capsules are formed when the mixed macrocyle is recrystallized in ethanol whereas nanotubes are formed when recrystallized in a mixture of acetone and water. Continued research is focused on the synthesis of new architectures isolated from a broader range of solvent systems.

**RM_MWGL Regional Meeting 91**

## Encapsulation of Fluorescent Reporter Molecules within Hydrogen-Bonded Dimeric Pyrogallol[4]arene Nanocapsules

***Drew A. Fowler**[1], daf58c@mail.missouri.edu, Katrina K. Kline[1], Sheryl A. Tucker[2], Jerry L. Atwood[1]. (1) Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, United States (2) Oklahoma State Universtiy, Stillwater, Oklahoma, United States*

The bowl-shaped pyrogallol[4]arene macrocycles capacity to act as host molecules has been investigated with a number of fluorescent reporter molecules. Pyrogallol[4]arenes have exhibited the ability to form a wide range of supramolecular systems including hydrogen-bonded capsular, bilayer, and nanotube-like motifs in the solid state. The twelve upper-rim hydroxyl groups of these macrocycles aid in the ability of these molecules to form a wide range of hydrogen-bonded systems with numerous cocrystallizing agents. Previous studies have succeeded in the incorporation of guest molecules within the interior of hydrogen-bonded hexameric capsules of *C*-alkylpyrogallol[4]arenes. These guest molecules include the fluorescent reporter molecules pyrene, butyric acid, and pyrene butanol. More recently, the encapsulation of the fluorescent reporter molecule acenapthene within a hydrogen-bonded dimeric capsule, has been reported.



The capsule is seamed through eight hydrogen bonds between two *C*-propan-3-ol pyrogallol[4]arene ($PgC_3OH$) macrocycles and four solvent methanol molecules. Initial results suggest that the presence of the guest molecule aid in the formation of the hydrogen-bonded dimer. This conclusion is based on the preference of $PgC_3OH$ to form bilayer type stuctures with the solvent used in the cocrystallization experiments. Further investigation has shown that a number of guest molecules can reside within the void space of the dimeric nanocapsule.

**RM_MWGL Regional Meeting 92**

## Nanocapsules with programmed nanopores

***Eugene Pinkhassik****, epinkhas@slu.edu. Department of Chemistry, Saint Louis University, St Louis, MO 63103, United States*

We use lipid bilayers as supramolecular self-assembled scaffolds for directed assembly of functional nanomaterials. Recently, we reported a simple method for controlling size, chemical environment, and density of nanopores spanning nanometer-thin membranes. These membranes are characterized by tunable molecular weight cut-off, extremely fast mass transfer, and long-term structural stability. Vesicle-templates polymer nanocapsules can retain medium-sized molecules such as pH-sensitive indicator dyes while providing uninhibited access for small molecules to the capsule interior. Nanocapsules showed no cytotoxicity.

In one application, we entrap catalysts within nanocapsules to combine high efficiency of homogeneous catalysts with ease of separation from reaction products. In another application, we embed dye-loaded nanocapsules in permeable hydrogels to create robust fast-acting optical sensors.

**RM_MWGL Regional Meeting 93**

## Liposome-templated polymer nanocapsules: from synthetic methods to smart containers

***Sergey A Dergunov***[1,2]*, sdrgunov@gmail.com, Mariya D Kim*[1,2]*, Ernö Lindner*[2]*, Eugene Pinkhassik*[1,2]*. (1) Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States (2) Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States*

Liposomes bilayers are used as self-assembled scaffolds for directed assembly of functional nanomaterials. In our previous work [1,2], we reported a simple method for controlling size, chemical environment, and density of nanopores spanning nanometer-thin membranes. These membranes are characterized by tunable molecular weight cut-off, extremely fast mass transfer, and long-term structural stability [2, 3]. Vesicle-templates polymer nanocapsules can retain medium-sized molecules such as pH-sensitive indicator dyes while providing uninhibited access for small molecules to the capsule interior [3, 4]. In this contribution we report on a novel optical sensing platform that utilizes dye loaded, porous nanocapsules embedded in a low density polymer matrix for pH sensing. The wall of the porous nanocapsules is so thin (~ 0.8 nm) that it does not slow the flux of hydronium ions in and out of the capsules. Consequently a free and an encapsulated dye changes its color at the same rate upon pH changes in the solution [3].

1. Dergunov S.A., Pinkhassik E. *Angew. Chemie Inter. Ed.,* 2008, 47, 7036-7039.
2. Dergunov, S.A., et al. *Macromolecules,* 2010, 43, 7785-7792.
3. Dergunov, S.A.; et al. *Chem. Commun.*, 2010, *46*, 1485-1487.
4. Shmakov, S.N., Dergunov, S.A., Pinkhassik, E. *Chem. Commun.,* 2011, **47**, 8223–8225.

**RM_MWGL Regional Meeting 94**

## Controlled Polymer Property Manipulation via Nano and Other Technologies

***Daniel E. Bowen III**, dbowen@kcp.com, Eric A. Eastwood. Honeywell FM&T, Kansas City, MO 64141, United States*

New applications can be found for existing polymer matrixes via the controlled manipulation of a polymer's fundamental properties. Careful examination of the structure property relationships leads to an understanding of the mechanism by which such changes occur. Our research has focused on the application of two ridged, molecular “nanofillers”; 2-dimensional asphaltenes (and other polycyclic aromatic hydrocarbons) and 3-dimensional boron cage compounds (BCCs). Although a few isolated cases serve as precedent, the isolation or synthesis, polymerization and copolymerization, and blending/compounding of these materials in a variety of host polymer matrixes has not been systematically examined. The properties of the resulting nanocomposites have been examined via rheology, and physical and thermal methods. In some cases, this work has lead to the controlled manipulation of a given host polymer's physical properties, although not all the important property changes are brought about via the presence of a nanofiller. This research has also provided important clues regarding the mechanism by which some of these changes take place. (Patent Pending, Serial #'s 12/816,555 filed on 06/16/10, 12/859,658 filed on 08/19/10, 13/118,090 filed on 05/27/11, 13/210,985, filed on 08/16/11,and 13/212,783 filed on 08/18/2011)

**RM_MWGL Regional Meeting 95**

## Polymeric “single molecule magnet” nanoparticle as a magnetic resonance imaging contrast agent

***Dipanjan Pan**, dipanjan@wustl.edu, Benjamin Kim, Anne H Schmieder, Allan J Stacy, Samuel A Wickline, Gregory M Lanza. Internal Medicine, Washington University in St Louis, St Louis, MO 63108, United States*

Single-molecule magnets (SMM) are a class of metallo-organic molecules that exhibit para- and superparamagnetic behavior at the molecular scale showing magnetic hysteresis of purely molecular origin. $Mn_{12}O_{12}(OOCR)_{16}$ ($Mn_{12}$) derivatives, a heavily studied class of SMMs, provides a large ground spin (S) state and magnetic anisotropy resulting from parallel alignment of eight $Mn^{III}$ Jahn–Teller axes. However, the major drawback in terms of their potential uses as a MRI contrast agents is their poor stability and solubility in water. We directly address this problem and assess the feasibility of using $Mn_{12}$ clusters as a contrast agent for MRI in combination with a polymeric micellar nanoparticle. We hypothesize that the induced magnetic moment of $Mn_{12}$ clusters in the applied field can dramatically accelerate the relaxation of surrounding water protons.

Irregular-shaped micelles were synthesized from a co-self assembly of polystyrene-*b*-polyacrylic acid (PS-*b*-PAA) and surfactant polyoxyethylene (80) sorbitan monooleate at 50 °C. Dynamic light scattering measurements revealed the particle hydrodynamic diameter as 17±4 nm with low electrophoretic values (-10mV). The discrepancies in hydrophobic chain lengths between the amphiphilic polymer and the polysorbate presumably determined the nature of the micelles. $Mn_{12}O_{12}(OOCR)_{16}$ oxo clusters were attached to the polymeric particles by a ligand-exchange protocol and purified by exhaustive dialysis against infinite sink of water. Pre and post $Mn_{12}$ modified nanoparticles were characterized TEM, AFM, SEM and EDX and ICP-OES. Magnetic resonance images of the nanoparticles in suspension and particles targeting to human fibrin plasma clots were acquired using T1-weighted (3T) gradient echo images. MR imaging of nanoparticles targeted to fibrin clot phantoms showed clear contrast enhancement, while control clots (non-targeted and targeted no metal) had no ($p<0.05$) contrast change. $Mn_{12}$-labeled irregular micelles represent a novel, high relaxivity, non-gadolinium, agents that offers sensitive noninvasive MR imaging approach for molecular imaging application.

## RM_MWGL Regional Meeting 96

## Morphology control of cadmium selenide nanocrystals: Insights into the roles of di-*n*-octylphosphine oxide (DOPO) and di-*n*-octylphosphinic acid (DOPA)

***Fudong Wang***, *fwang@wustl.edu, William E Buhro. Department of Chemistry, Washington University, St. Louis, MO 63130, United States*

Di-*n*-octylphosphine oxide (*n*-octyl$_2$P(O)H, DOPO) and di-*n*-octylphosphinic acid (*n*-octyl$_2$P(O)OH, DOPA), as two of impurities found in commercial tri-*n*-octylphosphine oxide (*n*-octyl$_3$PO, TOPO), can generate significant differences in the outcomes of CdSe nanocrystal syntheses. Here we report the first systematic study of the roles of DOPO and DOPA in the growth kinetics and morphology control of CdSe nanocrystals. The CdSe nanocrystals are synthesized in the presence of either *n*-tetradecylphosphonic acid (*n*-tetradecylP(O)(OH)$_2$, TDPA) or oleic acid (OA) as the main acid, with DOPO or DOPA added as an additive, to dissolve CdO to form the Cd precursor. In the presence of TDPA, DOPO assists the growth of quantum dots (QDs), whereas DOPA enhances the growth of quantum rods (QRs). When OA is present, both DOPO and DOPA assist the growth of QDs. The QDs produced with DOPA exhibit larger sizes and size distributions than those produced with DOPO. $^{31}$P NMR analyses of the reaction mixtures reveal that DOPO has been converted into DOPA in the course of Cd-precursor preparation. The origin of such puzzling differences in the growth kinetics and shape control of CdSe nanocrystals in the presence of DOPO and DOPA is elucidated.

## RM_MWGL Regional Meeting 97

## Characterization of protein immobilization on nanoporous gold using atomic force microscopy and scanning electron microscopy

***Yih Horng Tan***[1], *tanyh@umsl.edu, Alexei V. Demchenko*[2], *Keith Stine*[1]. *(1) Chemistry and Biochemistry and Center for Nanoscience, University of Missouri - Saint Louis,* *Saint Louis, MO 63121, United States (2) Department of Chemistry and Biochemistry, University of Missouri - Saint Louis, Saint Louis, MO 63121, United States*

Immobilization of proteins from solution onto functionalized surfaces has attracted tremendous amounts of attention, primarily due to the great interest in the development of biosensor devices. Nanoporous gold (NPG), made by dealloying low carat gold alloys, is a relatively new nanomaterial finding application in catalysis, sensing, and as a support for biomolecules. In this study, we use scanning electron microscopy (SEM) and atomic force microscopy (AFM) to characterize a highly efficient approach for protein immobilization on NPG using N-hydroxysuccinimide (NHS) ester functionalized self-assembled monolayers on NPG with pore sizes in the range of tens of nanometers. Comparison of coupling under static versus flow conditions suggests that BSA and IgG can only be immobilized onto the interior surfaces of free standing NPG monoliths with good coverage under flow conditions. Access to the interior surface of NPG for AFM imaging is achieved using a special procedure for cleaving NPG. Furthermore, we expanded the investigation to NPG covered with a-mannose terminated self-assembled monolayers and investigated its use as a biomimetic platform for binding concanavalin A. An understanding of the effect of chemical and physical modification of NPG, in terms of variations in pore size, surface modification, and identity of the adsorptive, will undoubtedly contribute to enhancing suitable sensor applications, particularly in biomaterials/bioanalytical contexts.

**RM_MWGL Regional Meeting 98**

## Pseudocapacitive behavior of electrodeposited nickel hydroxide films on laser ablated nickel electrodes

***Thomas G. Smith***[1]*, thomasgsmith@huskers.unl.edu, Craig Zuhlke*[2]*, Troy Anderson*[2]*, Dennis Alexander*[2]*, Rebecca Y. Lai*[1]*. (1) Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, United States (2) Department of Electrical Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588, United States*

Here we report the electrochemical fabrication and characterization of nickel hydroxide-based pseudocapacitors. In this study, nickel hydroxide was electrodeposited onto nickel foils roughened by various methods, including emery paper roughening and various laser ablation processing methods. We find that a 5-sec electrodeposition of nickel hydroxide is adequate for optimal pseudocapacitive performance. Our preliminary data also suggest that the laser ablated nickel foils display specific capacitance values that are ~1.5 to 3 times higher than the previously reported value for an emery paper roughened nickel foil. With proper optimization, these laser ablated materials could potentially be used in the fabrication of electrochemical supercapacitors.

**RM_MWGL Regional Meeting 99**

## Balancing stability and the SERS activity of caged nanoparticles

***Muriel Konne***, *muriel-konne@uiowa.edu, Marie Pierre, Amanda J Haes. Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States*

Internally etched silica-coated gold nanoparticles are synthesized for the direct detection of 2-naphthalenethiol (2-NT) and 4-aminothiophenol (4-ATP) using surface enhanced Raman scattering (SERS). These “caged” nanoparticles are synthesized using a three step process: (1) bare gold nanoparticles are prepared via citrate reduction, (2) silica shells are grown on and used to promote electromagnetic isolation of their metal cores, and (3) silica membranes are formed around these silica coated gold nanostructures using selective etching of the silica layers near the gold cores. The resulting encapsulation of the gold nanoparticles cores prevents electromagnetic coupling between adjacent metal cores while facilitating molecular diffusion toward the metal for subsequent SERS detection. The target molecules, 2-NT and 4-ATP are monitored as a function of time and concentration. Correlation between SERS signals, extinction spectra, and TEM images indicates that silica etching occurs near the gold core thereby facilitating the direct detect of target molecules using these solution phase nanostructures.

**RM_MWGL Regional Meeting 100**

## Synthesis of $Fe/Fe_3O_4/Au$ core/shell nanoparticles for magnetic hyperthermia and MRI application

***Hongwang Wang***[1], *hongwang@ksu.edu, Tej B Shrestha*[2], *Matthew T Basel*[2], *Raj K Dani*[1], *Leila Maurmann Maurmann*[1], *Viktor Chikan*[1], *Deryl L Troyer*[2], *Stefan H Bossmann*[1]. *(1) Department of Chemistry, Kansas State Universuty, Manhattan, KS 66502, United States (2) Department of Anatomy and Physiology, Kansas State University, Manhattan, KS 66502, United States*

Here we wish to report the synthesis and characterization of $Fe/Fe_3O_4/Au$ core/shell nanoparticles and the application of this material as AC-magnetic hyperthermia agent and stable MRI contrast agent for cancer treatment and diagnosis. The $Fe/Fe_3O_4$ nanoparticles were synthesized by thermal decomposition of $Fe(CO)_5$ in high boiling point solvent with oleylamine as stabilization ligand followed by controlled oxidation. The as-synthesized $Fe/Fe_3O_4$ nanoparticles were further coated with Au in a mild reducing condition, and the thickness of the Au coating was finely controlled. Various characterizations, including TEM, DLS, and Zeta potential, revealed that the nanoparticles are composed of mono-dispersed 10-15 nm spherical core/shell nanostructures. The presence of Au shell was evidenced by UV-vis spectroscopy and further quantified by ICP measurement. The application of this material as AC-magnetic hyperthermia and MRI agent for cancer treatment and diagnosis will be presented.

**RM_MWGL Regional Meeting 101**

## Approaches to Tetrahydrofuran-Containing Natural Products

***Christopher D. Spilling**, cspill@umsl.edu. Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

Tetrahydrofurans (thf) and tetrahydropyrans (thp) are important structural motifs in many biologically active natural products, such as polyether antibiotics, acetogenins, and C-glycosides. Several approaches to the synthesis of tetrahydrofurans will be presented. In particular, one strategy involves the cross-metathesis of hydroxy alkenes and acrolein-derived phosphono allylic carbonates giving substituted phosphonates. Stereospecific Pd(0)-catalyzed cyclization yields thf and thp containing vinyl phosphonates, allowing access to both *cis* and *trans* 2,5-disubstituted tetrahydrofurans and 2,6-disubstituted tetrahydropyrans. The cross metathesis/cyclization strategy induces a high level of diastereoselectivity in the formation of both *cis* and *trans* isomer, which is particularly advantageous over existing methods. The various strategies will be illustrated in the synthesis of centrolobine, the 2,5-disubstituted-3-oxygenated tetrahydrofuran (thf) ring containing epoxy lipids from southern Australian alga *Notheia anomala*, the thf fragments of amphidinolide C.

**RM_MWGL Regional Meeting 102**

## Semi-synthetic opiods from diene natural products

***Tony Mannino**, manninoa@msx.umsl.edu. Covidien/Mallinckrodt Pharmaceutical, Saint Louis, MO, United States*

The plant Papaver somniferum is a source of medicinally important opiods such as morphine and codeine. Opiods are crucial tools in the treatment of pain and anesthesia. This botanical source also provides important starting compounds which are chemically converted to both opiods agonist and antagonist. Two important starting molecules found in the poppy are oripavine and thebaine. These two compounds contain a 1,3-diene as part of their molecular architecture. The diene has been used to synthetically produce both agonist such as oxymorphone and antagonist such as naltrexone. The semi-synthetic route used in the production of Buprenorphine, an agonist, and the process development involving the first two steps of the synthesis will be discussed.

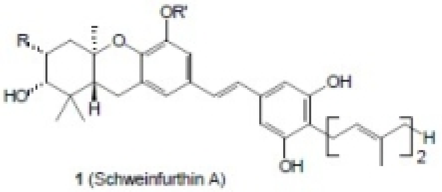
**RM_MWGL Regional Meeting 103**

## Natural product synthesis through tandem cationic reactions

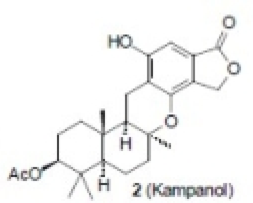
***David F. Wiemer**, david-wiemer@uiowa.edu. Department of Chemistry, University of Iowa, Iowa City, IA 52242-1294, United States*

Cationic cyclization reactions are a topic of intense current interest, although almost all recent work has focused on new strategies to initiate this process. At least as much potential may yet be revealed through studies of novel strategies for termination of the cationic reaction cascade. During the course of our research, we have discovered cascade reactions that occur in high yield under mild conditions when initiated by

epoxide opening and terminated by reaction with methoxymethyl (MOM) “protected” phenols. In some cases, the group released during this process can be utilized in electrophilic aromatic substitution, resulting in an additional carbon-carbon bond formation. Some applications of this tandem process will be presented, including a total synthesis of schweinfuthin A (**1**) and approaches to related compounds such as kampanol (**2**).



1 (Schweinfurthin A)



2 (Kampanol)

## RM_MWGL Regional Meeting 104

## Phosphate tether-mediated protocols for natural product synthesis

***Paul R. Hanson****, phanson@ku.edu. Department of Chemistry, University of Kansas, Lawrence, KS 66045-7582, United States*

The development of phosphate tethers for small molecule synthesis has revealed their use as removable, functionally active tethers that are fundamentally different from widely used silicon-based variants. These tethers are capable of multipodal coupling and multivalent activation and serve as latent leaving groups in selective cleavage reactions. Application of this method to the synthesis of a number of bioactive compounds is reported and will highlight the versatile nature of this tether for small molecule synthesis.

**Cited References:**

(1) Waetzig, J. D.; Hanson, P. R. A Multifaceted Phosphate Tether: Application to the C1–C14 Subunit of Dolabelides A-D. *Org. Lett.* **2008**, *10*, 109–112.

(2) Whitehead, A.; Waetzig, J. D.; Thomas, C. D.; Hanson, P. R. A Multifaceted Phosphate Tether: Application to the C15–C30 Subunit of Dolabelides A-D. *Org. Lett.* **2008**, *10*, 1421–1424.

(3) Thomas, C. D.; McParland, J. P.; Hanson, P. R. Divalent and Multivalent Activation in Phosphate Triesters: A Versatile Method for the Synthesis of Advanced Polyol Syntons. *Eur. J. Org. Chem.* **2009**, 5487–5500.

(4) Thomas, C. D.; Hanson, P. R. Phosphorus and Sulfur Heterocycles via Ring-Closing Metathesis: Application in Natural Product Synthesis. Metathesis in Natural Product Synthesis. (J. Cossy, C. Meyer, Eds), Wiley-VCH: Weinheim, Germany, 2010.

(5) Venukadasula, P. K. M.; Chegondi, R.; Maitra, S.; Hanson, P. R. A Concise, Phosphate-Mediated Approach to the Total Synthesis of (–)-Tetrahydrolipstatin. *Org. Lett.* **2010**, *12*, 1556–1559.

(6) Chegondi, R.; Tan, M. M. L.; Hanson, P. R. Phosphate Tether-Mediated Approach to the Formal Total Synthesis of (-)-Salicylihalamides A & B. *J. Org. Chem.* **2011**, *76*, 3909-3916.

(7) Hanson, P. R.; Chegondi, R.; Nguyen, J.; Thomas, C. D.; Waetzig, J. D.; Whitehead, A. Total Synthesis of Dolabelide C: A Phosphate-Mediated Approach. Featured Article. *J. Org. Chem.* **2011**, *76*, 4358-4370.

**RM_MWGL Regional Meeting 105**

## Progress toward the synthesis of Antascomicin B

*John M. Hutchison, David R. Clay, Juliette Rivero,* ***Matthias C. McIntosh****, mcintosh@uark.edu. Dept. of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, United States*

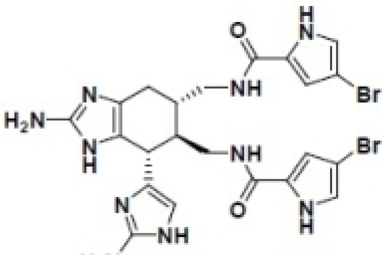
The antascomicins are a small family of macrolides isolated in China from soil bacteria of the genus Micromonospora that exhibits very strong binding to FKBP12. The most potent of these, antascomicin B, binds with an IC50 of 0.7 nM, equivalent to that of FK-506 and rapamycin. The C21-C34 fragment of the potent FKBP12-binding macrolide antascomicin B was prepared using Ireland-Claisen and allylic diazene rearrangements to establish the C26/C27 and the C23 stereocenters, respectively. The fragment possesses 7 of the 11 relevant stereocenters contained in the natural product.

**RM_MWGL Regional Meeting 106**

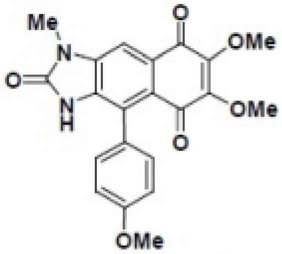
## Total synthesis of marine alkaloids

***Carl J. Lovely****, lovely@uta.edu. Department of Chemistry and Biochemistry, The University of Texas of Arlington, Arlington, Texas 76019, United States*

Our group has been interested in developing strategies and tactics for the total synthesis of secondary metabolites containing either a 2-aminoimidazole or a 2-imidazolone moiety. Broadly speaking our efforts have been directed towards members of the oroidin and *Leucetta* families of marine-derived alkaloids. Among these targets are a collection of molecules which contain a polysubstituted benzimidazole framework which can be assembled through an intramolecular Diels-Alder reaction of vinylimidazole as a diene. Elaboration of these cycloadducts then allows access to the frameworks of several different natural products. This talk will describe the evolution of this strategy and its application to the total synthesis of ageliferin (**1**) and kealiiquinone (**2**).



Ageliferin (1)



Kealiiquinone (2)

## RM_MWGL Regional Meeting 107

## Natural products as leads for anticancer drug discovery.

***Gunda I. Georg***, *georg239@umn.edu. College of Pharmacy, University of Minnesota, Minneapolis, MN 55455, United States*

The US Food and Drug Administration (FDA) has approved over 1000 new small molecule drugs in the last 30 years. Of the approved anticancer agents 74% are natural product-derived. Thus, natural products continue to be an excellent source as drugs or leads for drug discovery efforts (Newman 2008). The preclinical development of a novel phosphonooxymethyl prodrug of the anticancer natural product triptolide will be discussed. The triptolide prodrug, which has been named Minnelide, is highly water-soluble and rapidly reverts back to the parent compound in vitro and in vivo. It has significant activity in vitro and in vivo, is an angiogenesis inhibitor, and acts synergistically with other anticancer agents. Novel results for the synthesis and biological evaluation of phenanthropiperidine alkaloids such as boehmeriasin, tylocrebrine, antofine, tylophorine, and related analogues will be discussed as well.

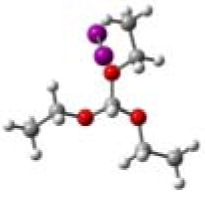
## RM_MWGL Regional Meeting 108

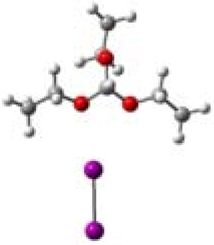
## Iodine Lewis acid catalysis in organic chemistry: Iodine bonding between molecular iodine and triethyl orthoformate

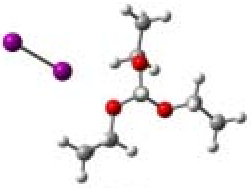
***Stephanie Coyle***, *glaserr@missouri.edu, Rainer Glaser. Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States*

Orthoformates are versatile organic reagents used for selective O, N, and S-alkylation reactions and important applications in quinoline synthesis, in imino Diels-Alder reactions, and in cross-aldol reactions. Orthoformates supply an electrophilic carbon and a nucleophilic oxygen in Lewis acid catalyzed reactions and, recently, it has been discovered that molecular iodine $I_2$ is an effective, mild Lewis acid in many of these reactions. The specific mechanisms of the iodine catalyzed reactions remain unclear and largely unexplored. Here, we report results of NMR spectroscopic and computational studies of aggregates formed between $I_2$ and triethyl orthoformate

(TEOF). The potential energy surfaces of TEOF itself and of its $I_2$ aggregate were explored using density functional theory. We describe five isomers **M1** – **M5** of TEOF that differ with regard to their HC–OEt conformations, report on the complexation of $I_2$ and the three most stable minima of triethyl orthoformate **M1·I$_2$**, **M4·I$_2$**, and **M5·I$_2$**, and discuss the nature of the interaction between $I_2$ and TEOF. The computed structural and thermodynamic results are employed to explain the NMR spectra of TEOF itself and in the presence of iodine. The most stable iodine aggregates of the three most stable TEOF conformers **M1**, **M4** and **M5** are shown.


M1·I$_2$


M4·I$_2$


M5·I$_2$

## RM_MWGL Regional Meeting 109

## Biomass deconstruction using ionic liquids

***Tezcan Guney***, *tguney@iastate.edu, George A Kraus. Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States*

In recent years, the increasing energy demand and diminishing supply of fossil fuels has become a cause of concern on a global scale. As a result, there has been an increasing demand for green technologies in the sustainable energy area. Biomass deconstruction has attracted much interest. Researchers have synthesized 5-hydroxymethylfurfural (HMF) using ionic liquids from biomass, but the field of obtaining 5-alkoxymethylfurfural ethers is largely unexplored. Taking advantage of specifically designed ionic liquids and a biphasic system, a variety of carbohydrates, in particular fructose, have been transformed into a number of 5-alkoxymethylfurfural ethers. Furthermore, 5-hydroxymethylfurfural ethers have significant potential to be used as fuel additives as they are more stable than HMF and have the advantage of increased solubility relative to currently used additives.

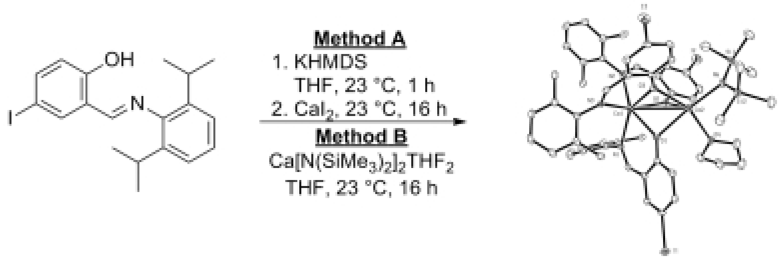
In this presentation, designer ionic liquids in a biphasic reaction media allow for efficient biomass conversion of sugars to 5-alkoxymethylfurfural ethers. These reaction conditions result in good yields under mild conditions and in one step.

## RM_MWGL Regional Meeting 110

## Intramolecular hydroamination of olefins using a novel salicylaldimine calcium complex

***Kamala Kunchithapatham**, kkunchit@chemistry.osu.edu, James P. Stambuli.Chemistry, The Ohio State University, Columbus, OH 43210, United States*

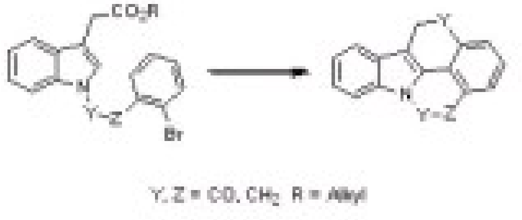
The use of calcium as a Lewis acid catalyst in synthetic transformations has increased dramatically in recent years. The hydroamination of olefins has been one of the synthetic transformations under study. We investigated the catalytic competency of novel salicylaldimine calcium complexes in intramolecular olefin hydroamination reactions. During the course of these reactions, catalyst decomposition to a novel trimeric calcium complex was also observed. Structural determination of these calcium complexes as well as their catalytic activity in intramolecular hydroamination reactions were will be discussed.



## RM_MWGL Regional Meeting 111

## A four step route to a benzannulated benzocarbazole

***Jonathan Beasley**, jsbeasley1s@hotmail.com, George A Kraus. Department of Chemistry, Iowa State University, Ames, IA 50011, United States*



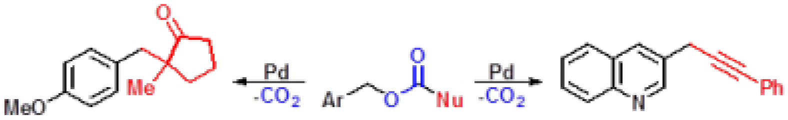
A new class of pentacyclic compounds containing the indole subunit has been synthesized. The key cyclization involves an intramolecular Heck coupling to form a 6-5-6-6 tetracyclic system, which can then be converted into the final pentacyclic system via Friedel-Crafts reaction. The synthesis will also allow for different substitution patterns on both aromatic rings. This class of compounds will be examined for potential anti-viral activity.

## RM_MWGL Regional Meeting 112

### Strategic benzylic cross-coupling via Pd-mediated decarboxylation

***Robert R.P. Torregrosa****, polka21@ku.edu, Jon A. Tunge. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

A strategic benzylic cross-coupling to ketones and alkynes via Pd-catalyzed decarboxylative benzylation is presented. Benzyl esters undergo decarboxylation by using an appropriate Pd catalyst to generate a Pd-π-benzyl electrophile and an enolate or alkyne nucleophile *in situ*. These intermediates rapidly couple to form benzyl ketones or benzyl alkynes. This approach avoids the need of toxic benzyl halide, stoichiometric base and/or preformed organometallics. The methodology is similar to well-developed Pd-catalyzed decarboxylative allylation in which both undergo decarboxylation, generate analogous reactive intermediates (electrophilic Pd-π-benzyl complex and Pd-π-allyl complex, nucleophilic enolate and alkyne), and form products.



---

## RM_MWGL Regional Meeting 113

### Supported patterned lipid bilayers on glycol-terminated monolayers: Formation and characterization

***Matthew K Strulson****, mkstruls@wustl.edu, Joshua A Maurer. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Supported lipid bilayers (SLBs) provide a simple *in vitro* model of cellular membranes. SLBs self-assemble on glass, with a 5-10 Å layer of water between the substrate and the bilayer. These systems offer control over the type of lipid(s) and proteins present, and are highly amenable to characterization by spectroscopy and other surface techniques. However, classic SLBs are known to exhibit a few drawbacks. Most importantly, lipids and transmembrane proteins can interact with the underlying solid substrate creating defects and causing the proteins to denature. Improving these systems would allow for a robust, simplified model to study cell-cell interactions, translocation of pharmaceuticals across membranes, and receptor-small molecule interactions.

In order to minimize lipid/protein interactions with the substrate, we sought to utilize ethylene glycol-terminated self-assembled monolayers (SAMs). These systems are well known to resist non-specific protein adsorption and cell adhesion, as a result SLBs typically do not form on glycol-terminated SAMs. To circumvent this problem, we have used microcontact printing to enable vesicle attachment to the alkane-terminated regions. These attached vesicles rupture to form a lipid monolayer on the alkane-terminated SAM and a lipid bilayer over the glycol-terminated portions of the surface. The resulting patterned SLBs have been characterized by a bevy of surface techniques, and they demonstrated the ability to incorporate the transmembrane protein α-hemolysin. Currently, we are pursuing a number of different applications of this patterend SLB system.

### RM_MWGL Regional Meeting 114

## Improved substituent constant for predicting the strength of cation-π binding

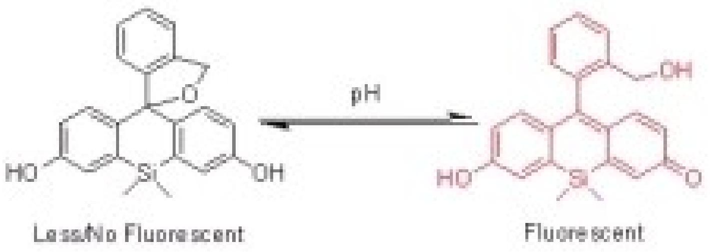
***selina wireduaah***, *swirdua@slu.edu, Trent M Parker, Charles C Kirkpatrick, Miachael Lewis. Department of Chemistry, St Louis University, St Louis, Missouri 63103, United States*

A computational study of the cation binding of a broad array of substituted aromatics will be presented, and a new substituent constant ($\pi^+$) for the accurate prediction of cation-p binding energies ($E_{bind}$) and enthalpies ($\Delta H_{298}$) will be proposed. Symmetry Adapted Perturbation Theory (SAPT) calculations show that the $\pi^+$ parameter primarily describes how electrostatics contribute to cation-π binding; however, it also accounts for the contributions of dispersion, induction and exchange energies to the overall binding. The correlation between $\pi^+$ and either $E_{bind}$ or $\Delta H_{298}$ is significantly better than for any pure electrostatic parameters, like Hammett constants or the aromatic quadrupole moment. Structure optimizations, characterizations, and binding energy/enthalpy determinations were calculated at the MP2(full)/6-311++G** level of theory. SAPT calculations employed the CCSD/6-311++G** level of theory. Results will be discussed in terms of previous work aimed at understanding and predicting the strength of cation-p binding.

### RM_MWGL Regional Meeting 115

## Investigation of silicon analog of fluorescein as pH responsive fluorescent probe

***Narsimha Sattenapally***, *narsi@siu.edu, Quinn A Best, Chuangjun Liu, Cecil Bailey, Daniel Dyer, Lichang Wang, Matt McCarroll, Colleen G Scott. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*



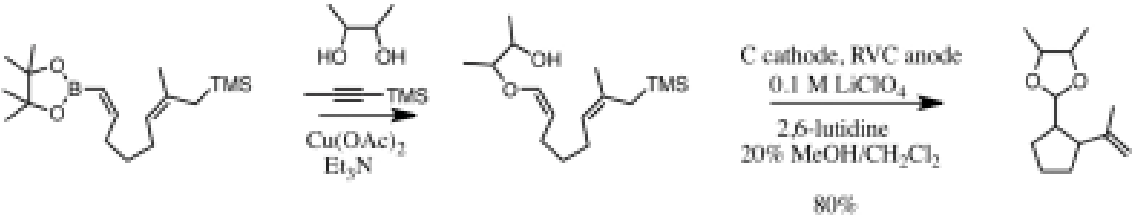
Fluorescent compounds responsive to pH are highly useful in biological applications. A pH responsive probe which has emission in the longer wavelength region, good solubility in biological media, and less or no toxicity is highly necessary. Here in, we are presenting a silicon analog of a fluorescein compound which has longer wavelength emission, good solubility in physiological conditions, and responsiveness to pH. The pH response of the probe, in addition to its synthesis and characterization, will be discussed.

## RM_MWGL Regional Meeting 116

## Anodic electrochemistry: New reaction development and the use of solar power

***Alison M. Redden**, Kevin D. Moeller. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Anodic olefin coupling reactions provide unique opportunites for both synthesizing new ring skeletons and probing the chemistry of reactive radical cation intermediates. In efforts to expand the scope of anodic cyclizations and radical cation chemistry, new substrates have been synthesized by capitalizing on a new method for making enol ethers. Subsequent oxidation of these substrates allows for trapping of both ends of the radical cation, generating bicyclic ring products in good yield.



Additionally, the environmentally benign nature of these types of anodic oxidations will be discussed in the context of solar-powered electrochemistry.

## RM_MWGL Regional Meeting 117

## Effects of antioxidants on atomic oxygen O($^3$P) induced cleavage of DNA

***James Korang**, jkorang@slu.edu, Ryan D. McCulla. Department of Chemistry, Saint Louis University, Saint Louis, Missouri 63103, United States.*

Recently,derivatives of dibenzothiophene *S*-oxides have successfully been used to photochemically generate atomic oxygen O($^3$P) in aqueous medium. Subsequently, we proceed to investigate the effect of atomic oxygen O($^3$P) on DNA in aqueous media. Our findings indicate the structure of the O($^3$P)-precursors have a significant effect on the effectiveness of antioxidants ability to protect the DNA from the observed photoinduced cleavage.

## RM_MWGL Regional Meeting 118

### CREPES, a tool for conformational searching on a potential energy surface

***Michael P Ver Haag**, verhaag@iastate.edu, Tomas A Holme. Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States*

A tool has been created to generate the complete set of rotational configurations of any molecule. The computing power of even modest modern clusters allows for hitherto excluded levels of theory to be used for the investigation of a potential energy surface. The initial search for global minima using more accurate levels of theory allows for greater confidence in the eventually identified minimum. It also helps identify structures that may be important yet excluded or overlooked by chemical intuition.

CREPES automatically generates the iterative combinations of rotations defined by the user. The user can define the number of rotations, rotation step size, and total rotation. CREPES operates on the $DATA group of a GAMESS input deck, therefore any level of theory the user determines appropriate can be used. This amount of flexibly allows CREPES to be useful in many circumstances.

The effectiveness of CREPES for evaluating the potential energy surface will be demonstrated using α and β glucose (glucopyranose) and α and β galacturonic acid.

## RM_MWGL Regional Meeting 119

### Development and testing of torsional potentials for peptides and proteins

***Yuanfang Jiao**[1], yuanfang@ksu.edu, Feng Chen[2], Paul E Smith[1]. (1) Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States (2) Center for Drug Design, university of minnesota twin cities, Minneapolis, MN 55455, United States*

Recently, we have been developing a series of force fields for the eventual simulation of biological systems by attempting to accurately reproduce the experimental Kirkwood-Buff (KB) integrals observed in solution mixtures. The resulting KB derived force fields (KBFF) provide quantitative data concerning solute-solute, solute-solvent and solvent-solvent distributions in solution. Here, we focus on the torsional potentials which complement the KBFF models. Torsional potentials for peptides and proteins are developed from Quantum data on dipeptide analogues using a different approach from other, more traditional, biological force fields. This approach is outlined and the results of MD simulations performed for dipeptides (e.g. glycine, alanine, and proline) in both gas phase and in aqueous solution will be discussed. Furthermore, a series of simulations of a variety of peptides and proteins in aqueous solutions will be presented to demonstrate the reliability of the force field.

## RM_MWGL Regional Meeting 120

## Microwave spectroscopic study of C-H…X (X = π, Cl, F or Br) interactions in a series of weakly bound dimers

***Rebecca A. Peebles***[1], *rpeebles@eiu.edu, Sean A. Peebles*[1]*, Brandon J. Bills*[1]*, Cori L. Christenholz*[1]*, Ashley A. Elliott*[1]*, Lena F. Elmuti*[1]*, Daniel A. Obenchain*[1]*, John M. Sexton*[1]*, Brooks H. Pate*[2]*, Matt T. Muckle*[2]*, Justin L. Neill*[2]*, Amanda L. Steber*[2]*. (1) Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, United States (2) Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States*

The structures of a series of dimers of halomethanes ($CH_2ClF$, $CHClF_2$, $CHBrF_2$, $CH_2F_2$, $CHF_3$) with acetylene, ethylene and fluoroethylene have been studied using chirped-pulse and resonant-cavity Fourier-transform microwave spectroscopy and ab initio calculations. The acetylene- and ethylene-containing species all display C-H…π interactions, along with one or more secondary contacts in which a hydrogen atom from the hydrocarbon interacts with a halogen atom from the halomethane. The fluoroethylene species do not display C-H…π interactions, although both monomers within each fluoroethylene complex serve a dual role as donor and acceptor for weak C-H…X interactions.

Ab initio calculations (MP2/6-311++G(2d,2p)) predict many structures with similar energies for these weakly bound complexes, and the lowest energy ab initio structure is not necessarily the structure observed experimentally. In particular, the preference for chlorine or bromine vs. fluorine as a weak hydrogen bond acceptor clearly involves a delicate balance of forces. The acetylenic hydrogen atom consistently interacts with chlorine or bromine rather than fluorine, while in the ethylene complex with $CH_2ClF$ the halomethane appears to orient itself so that both halogen atoms interact with hydrogen atoms from the ethylene. Finally, in the fluoroethylene species, it appears that an interaction with chlorine is again preferable compared to an interaction with fluorine. This presentation will explore the structural variations of the nine dimers studied in this series so far.

**RM_MWGL Regional Meeting 121**

## Calixarene and pyrogallolarene "suction cups" for the tethering of peptides

***Matthew D Breite****, MDBreite1@sbcglobal.net, John E Adams. Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211-7600, United States*

For the controlled delivery of biologically active materials to desired receptor sites, it would be useful to have a method for encapsulating such a species and tethering it to an agent that preferentially goes to those sites. If the species being transported is large, however, the prospect of devising a method for full encapsulation is poor; a better strategy would make use of a molecular "suction cup" that attaches to the species. We are investigating the attachment of calixarenes and pyrogallolarenes to peptide

sequences in a first attempt to evaluate the practicality of using these cup-shaped molecules to provide the desired binding. Our assessment includes not only a determination of the net binding strength (based on calculations of potentials of mean force) and a characterization of the extent to which the peptide reorients due to interaction with the macrocycle, but also an evaluation of how peptide binding alters the molecular dynamics of the macrocycle itself.

**RM_MWGL Regional Meeting 122**

## Dynamic stability of hydrogen-bonded pyrogallolarene capsules in the gas phase and in solution

***Alicia C Webb**, acwytc@mail.missouri.edu, John E Adams. Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211-7600, United States*

Although the recent syntheses of metal-seamed pyrogallolarene capsules have suggested a strategy for the construction of robust nanomolecular assemblies, the mechanism by which these assembles are formed remains elusive. In an attempt to clarify the first steps in capsule formation, we have undertaken a molecular dynamics study of the stability of a potential precursor, the hydrogen-bonded pyrogallolarene dimer. These simulations indicate that whereas the dimer is stable in the gas phase, it is susceptible to rearrangement in solution, a result suggesting that the metal ions may play a critical role in dimer assembly in solution rather than merely substituting for hydrogens in a preformed capsule. We also are investigating whether guest occupation of the capsule stabilizes the dimer appreciably.

**RM_MWGL Regional Meeting 123**

## Cobaloxime hydrogen catalysts: A comprehensive EPR and computational investigation of the effect of ligand substitution on electronic structure

***Kristy L. Mardis**[1], kmardis@csu.edu, Jens Niklas[2], David M. Tiede[2], Oleg G. Poluektov[2]. (1) Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628, United States (2) Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL 60439, United States*

Solar fuels research aims to mimic photosynthesis and devise integrated systems that can capture, convert, and store solar energy in the form of high-energy molecular bonds such as molecular hydrogen. Difluoroboryl cobaloxime Co(dmgBF$_2$)$_2$ (cobalt complexes with two dimethyl glyoxime ligands) rank among the most promising transition metal complexes for the reduction of protons to molecular hydrogen. However, their catalytic properties are strongly dependent on the surrounding solvent and in particular on the ligand(s) directly bound to the central metal ion. The current work seeks to combine experimental clectron paramagnetic resonance (EPR) results with comprehensive density functional theory calculations to determine the effect of the ligand on the conformation and g-tensor anisotropy. Comparison of experiment and calculation allows

two general types of Co(II) coordination to be distinguished:
five-coordinated $LCo(dmgBF_2)_2$ and six-coordinated $L_2Co(dmgBF_2)_2$, the former having substantially larger g-tensor anisotropy. The largest g-tensor anisotropy is found for bulky organic ligands which probably lead to a deformation of the cobalt macrocycle. The absence of large g-tensor anisotropy for some ligands in the calculations indicates the presence of solvent effects rather than pure conformational causes. Finally, the results when L = $PPh_3$, are consistent with a substantial shift of electron spin density to oxygen indicating the formation of a peroxide radical.

## RM_MWGL Regional Meeting 124

### TDDFT studies of optical properties of silver nanoparticles: Octahedra, truncated octahedra, and icosahedra

***Gyun-Tack Bae**, gbae@k-state.edu, Christine M Aikens.Chemistry, Kansas State University, Manhattan, KS 66502, United States*

The effect of the size, shape, and structure of silver nanoparticles on their optical absorption properties is theoretically investigated in order to understand the plasmonic properties of these systems. Time-dependent density functional theory (TDDFT) calculations are employed to determine optimized geometries and excitation spectra for a series of silver clusters ($Ag_n$, n=6-85) whose structures are octahedral, truncated octahedral and icosahedral in various charge states. Octahedral $Ag_n$ clusters with n=6, 19, 44, 85, truncated octahedral $Ag_n$ clusters with n=13, 38, 55, 79, and icosahedral $Ag_n$ clusters with n=13, 43, 55 are calculated. The charged systems are considered in order to obtain closed shell electronic structures. These calculations are performed with the ADF code with the BP86/DZ level of theory in the optimizations and the SAOP functional and LB94 functional in the excitation calculations. A sharp excitation peak originates from a mixture of orbital transitions and a broad excitation arises from multiple excited states in octahedral, truncated octahedral and icosahedral $Ag_n$ clusters. We predict that the absorption peak maximum red shifts as the cluster becomes larger by theory.

## RM_MWGL Regional Meeting 125

### Structural and single particle and ensemble spectroscopic studies of various core-shell biofunctional quantum dots: Implications for biological imaging

***Colin D Heyes**. Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, ARKANSAS 72701, United States*

A range of core-shell quantum dot systems such as CdSe-ZnS, CdTe-ZnSe, CdSe-CdS-ZnS and $CuInS_2$-ZnS have been synthesized and studied at the ensemble and single particle level. Optical and structural properties are analyzed by a combination of time-resolved ensemble and single molecule fluorescence spectroscopy and high resolution TEM and HAADF-STEM combined with on-particle elemental analysis. I will discuss the influence of the core-shell interface on the radiative and non-radiative exciton recombination rates and the coupling to the external environment, specifically biologically-relevant environments. Single molecule fluorescence properties such as blinking, dark fraction formation and single QD lifetimes are compared to the ensemble fluorescence observations. Applications of the various core-shell systems in single molecule FRET, FLIM and time-gated intracellular imaging are also discussed.

## RM_MWGL Regional Meeting 126

### Attempts to fabricate high efficiency chalcogenide solar cells through patterned growth of nanowires

***Manashi Nath**, nathm@mst.edu, Sukhada Patil.Chemistry, Missouri University of Science & Technology, Rolla, MO 65409, United States*

The efficiency of the solar cells nowadays, relies heavily on the materials chosen to absorb the solar radiation and also on the design of the cells. While the material composition plays a fundamental role in defining the extent of solar light absorption, the reduced dimension and nano-structured morphology plays a decisive role in increasing the efficiency of the solar cell device manifold. The ability to obtain pre-determined periodic arrangement of the nano-structured light absorbers is very crucial for designing efficient solar cells. We have developed a novel technique to grow photovoltaic nanowire arrays on conducting substrates by simple bottom-up technique. The approach has been tested with CdTe, one of the most potential alternatives to Si-based solar cells. The CdTe nanowire arrays with uniform diameter could be grown on large area by electrodeposition on lithographically patterned nanoelectrodes embedded in a polymer matrix. The CdTe nanowires were also grown in a CdS matrix to create a *p-n* junction for the solar cell geometry which generally reduces the recombination. The photocurrent obtained from this nanowire device was comparable to that obtained from a CdTe film of
much higher area.

## RM_MWGL Regional Meeting 127

### Fluorescence intermittency of CdSe nanorods in PMMA/P3HT polymer blend

***Santanu Roy**, santanu@ksu.edu, Daniel A Higgins, Viktor Chikan. Department of Chemistry, Kansas State University, Manhattan, KS 66502, United States*

Hybrid polymer and inorganic quantum confined structures could be potentially very important platforms to produce solar cells cheaply. In this study, we aimed at exploring how charge separation takes place in the P3HT (poly(3-hexylthiophene)) and CdSe nanorods polymer-inorganic hybrid blend by using single particle fluorescence microscopy. The nanorods contain no overcoat from the synthesis other than the solvent ligands to enhance their fluorescence for the single particle fluorescence studies. Similar to others, we show that the fluorescence of the nanorods in the

presence of the P3HT enhanced significantly due to efficient electron transfer to the CdSe nanorods from the P3HT. Analysis reveals that the on times statistics of the fluorescence blinking is significantly affected by the presence of P3HT. This behavior is interpreted as a rapid exchange of charges between the conductive P3HT matrix and the CdSe nanrods. During the course of the experiments, the band edge emission of the CdSe rods is diminished and
their trap emission is enhanced. We show that the trap emission is suppressed in the presence of P3HT as evidence of electrons backfilling of the deep surface traps of CdSe nanorods.

### RM_MWGL Regional Meeting 128

## Carbonyl chemistry-based biorenewable chemicals: Diversifying fatty acid synthesis with polyketide synthesis biocatalysts

***Basil J. Nikolau***, *dimmas@iastate.edu. Center for Biorenewable Chemicals and Department of Biochemistry, Biophysics and Molecular Biology, Iowa State University, Ames, IA 50011, United States*

The chemical industry is reliant on a historically inexpensive, petroleum-based carbon feedstock that generates a small collection of platform-chemicals. These are the precursors from which highly efficient chemical conversions lead to the manufacture of a large collage of chemical products. Given this paradigm, the Center for Biorenewable Chemicals is exploring the potential of exploiting the polyketide/fatty acid biosynthetic pathways as a paradigm that targets the production of a series of platform-biorenewable chemicals. Polyketide and fatty acid biosynthesis share a common series of biocatalytic mechanisms that reiteratively generate a homologous series of alkyl-chains that range from chain lengths of 4-carbon atoms to greater than 30-carbon atoms. These metabolic processes share the common chemistry of having alternating carbonyl and methylene functional groups in their structures, and in the structures of the intermediates of their biosynthetic origins. By amalgamating biocatalysts derived from diverse metabolic and phylogenetic origins within an integrated biological system, we are envisioning a single technological platform that generates a wide variety of biorenewable molecules, which are of variable carbon-chain lengths, and carry defined functional chemical groups at specified sites on the alkyl-chain. Because the envisioned system is based on the reiteration of a series of simple transformations on a homologous series of substrates to generate a collection of chemical products, by analogy to combinatorial chemistry, the envisioned platform can be considered an example of combinatorial metabolism.

### RM_MWGL Regional Meeting 129

## Engineering proteins to improve biological function: Applications to Ag Biotech

***Sonya J. Franklin***, *sonya.j.franklin@monsanto.com. Monsanto Company, Chesterfield, MO 63017, United States*

Advances in the field of molecular biology over the last 30 years have greatly enabled our ability to modify the structure, stability and activity of proteins of interest. The growth of this "protein design" discipline has resulted in the modification of numerous proteins resulting in beneficial therapeutic agents, biochemical reagents, and even enhanced agricultural crops. This talk will highlight advances in protein design as it relates to agricultural applications.

### RM_MWGL Regional Meeting 130

## From climate change to proteins: redox proteomics of ozone-induced responses in soybean

***Joseph M. Jez***[1], *jjez@biology2.wustl.edu, Ashley Galant*[1], *Robert P. Koester*[2], *Elizabeth A. Ainsworth*[2,3], *Leslie M. Hicks*[4]. *(1) Department of Biology, Washington University, St Louis, MO 63130, United States (2) Department of Plant Biology, University of Illinois, Urbana-Champaign, Urbana, IL 61801, United States (3) USDA-ARS Global Change and Photosynthesis Research Unit, Urbana, IL 61801, United States (4) Donald Danforth Plant Science Center, St. Louis, MO 63132, United States*

Ozone ($O_3$) causes significant agricultural losses with soybean being highly sensitive to this oxidant. Here we assess the effect of chronic $O_3$ exposure on the total and redox proteomes of soybean. To understand the molecular responses to chronic $O_3$ exposure in soybean grown at the Soybean Free Air Concentration Enrichment (SoyFACE) facility under ambient (37 ppb), moderate (58 ppb), and high (116 ppb) $O_3$ concentrations were examined by redox-sensitive labeling, mass spectrometry, and targeted enzyme assays. In contrast to changes in leaf and root tissue from plants grown in moderate $O_3$, differences in the total and redox proteomes of soybean leaf tissue exposed to high chronic $O_3$ levels are more widespread and differ from those resulting from short-term acute $O_3$ exposure. In the high $O_3$ leaf, 35 proteins increased up to 5-fold in abundance, 22 proteins showed up to 5-fold higher oxidation, and 22 proteins increased in both abundance and oxidation. These changes occurred in carbon metabolism, photosynthesis, amino acid synthesis, flavonoid and isoprenoid biosynthesis, signaling & homeostasis, and antioxidant pathways. Our data demonstrate that $O_3$ exposure in plants changes the abundance and/or oxidation state of multiple proteins across metabolism and provide a snapshot of biochemical acclimation to chronic $O_3$ stress under field conditions. Understanding how environmental $O_3$ affects redox-sensitive pathways in plants may aid in the development of crops better adapted to this climate change.

### RM_MWGL Regional Meeting 131

## Vacuolar glyphosate-sequestration correlates with glyphosate resistance in ryegrass (*Lolium spp.*): a $^{31}$P-NMR investigation

***Xia Ge***[1], *g_xia@wustl.edu, Dana Andre' d'Avignon*[1], *Joseph J. H. Ackerman*[1], *Alberto Collavo*[2], *Elizabeth L. Ostrand*[3], *Robert Douglas Sammonse*[3]. *(1) Department of*

*Chemistry, Washington University in St Louis, Saint Louis, MO 63130, United States (2) Institute of Agro-environmental and Forest Biology, Italy (3) Monsanto Company, United States*

Species of ryegrass, the worldwide-distributed genus of *Lolium*, are agronomically important. However, ryegrass has a notorious propensity to develop resistance to herbicides. There is growing concern that variants may evolve to pose a serious agricultural challenge. Indeed, glyphosate resistant (GR) ryegrass has now been found on five continents. While reduced translocation of glyphosate and altered target enzyme have been reported as two dominate GR mechanisms in ryegrass, the cellular level mechanism responsible for reduced translocation remains to be elucidated.

Glyphosate resistant and sensitive (GS) ryegrass variants from Australia, Brazil, Chile, and Italy showing differing levels of glyphosate resistance were examined by *in vivo* $^{31}$P-NMR pulse-chase protocols, which enable monitoring of glyphosate uptake into the cell cytosol and migration to the vacuole. All ryegrass variants, GR and GS, showed similar cellular uptake of glyphosate during the pulse phase. However, for GR ryegrass biotypes, glyphosate sequestration occurred within the cell vacuole while GS varieties showed minimal or no vacuole sequestration. Further, the extent of glyphosate vacuole-sequestration correlated qualitatively with the level of resistance.

Previous *in vivo* $^{31}$P-NMR studies of horseweed (*Conyza canadensis*) revealed that glyphosate sequestration imparted glyphosate resistance. (X Ge *et al.*, (2010) *Pest Manag. Sci.* 66, 345-8; X Ge *et al.*, (2011) *Pest Manag. Sci.* in press, doi: 10.1002/ps.2169). New data now suggest that glyphosate vacuolar sequestration is also a strongly contributing, if not the dominant, resistance mechanism in ryegrass as well.

**RM_MWGL Regional Meeting 132**

## Tailoring plant biomass for biofuel production

***Zheng-Hua Ye**, zhye@plantbio.uga.edu. Department of Plant Biology, University of Georgia, Athens, GA 30602, United States*

Secondary walls are the major constituent of wood (secondary xylem), which is the most abundant biomass produced by plants. Secondary walls are composed mainly of cellulose, lignin and hemicelluloses (xylan and glucomannan). To make secondary walls, genes involved in the biosynthetic pathways of cellulose, lignin and hemicellulose need to be coordinately switched on. Understanding the molecular switches controlling secondary wall biosynthesis in wood is of importance in basic plant biology as well as for potential genetic engineering of wood quality and quantity in tree species. We have been using Arabidopsis and poplar as model plants to characterize genes involved in transcriptional regulation of secondary wall biosynthesis and genes involved in xylan biosynthesis. We have uncovered key roles of several transcription factors in regulating secondary wall biosynthesis. One of these transcription factors, SND1, together with its homologs were found to be master switches activating the biosynthetic pathways of the secondary wall components. In addition, we have discovered a number of additional players in the SND1-mediated transcriptional regulation of secondary wall biosynthesis. We hypothesize that a transcriptional network is involved in the activation of secondary wall biosynthetic genes during wood formation. We have also dissected functional roles of a number of glycosyltransferases involved in xylan biosynthesis during wood formation. Further studies of the transcriptional network regulating secondary wall biosynthesis will likely enable us to genetically alter the biosynthetic pathways of individual secondary wall components, and knowledge gained from such studies promises to lead to better strategies for genetic manipulation of biomass composition tailored for biofuel production.

## RM_MWGL Regional Meeting 133

### Improvement of soybean nutritive value by overexpression of a key enzyme involved in the sulfur assimilatory pathway

*Won-Seok Kim[1], Joseph M. Jez[2], **Hari B. Krishnan**[1], Hari.Krishnan@ARS.USDA.GOV. (1) Plant Genetics Research Unit, Agricultural Research Service, United States Department of Agriculture, University of Missouri, Columbia, MO 65211, United States (2) Department of Biology, Washington University, St. Louis, Missouri 63130, United States*

Soybean is an important protein-rich food and feed source. Even though soybeans are excellent protein source their nutritive value can be substantially improved by increasing the concentration of sulfur containing amino acids. Our attempts to increase the concentration of sulfur-containing amino acids through the expression of heterologous sulfur-rich proteins have meet with limited success. Consequently, we have devised a successful strategy to increase the cysteine content of soybean seed through the overexpression of O-acetylserine sulfhydrylase (OASS), a key sulfur assimilatory enzyme. Transgenic soybean plants overexpressing a cytosolic isoform of OASS exhibited a 4 to 10-fold increase in OASS activity when compared to non-transformed wild-type. In contrast to the non-transformed soybean plants, there was no marked decrease in the OASS activity even at later stages of seed development. Importantly, overexpression of cytosolic OASS resulted in a 58 to 74% increase in protein-bound cysteine levels and a 22 to 32% increase in the free cysteine levels compared to non-transformed wild-type soybean seeds. Proteomic analysis revealed that the transgenic soybean plants overexpressing OASS accumulated higher amounts of Bowman-Birk protease inhibitor when compared to that of non-transgenic control plants. Additionally, the accumulation of beta-subunit of beta-conglycinin, a protein devoid of sulfur amino acids, was drastically reduced in transgenic soybean plants overexpressing OASS. The overall increase in soybean total cysteine content satisfies the recommended levels required for the optimal growth of monogastric animals.

## RM_MWGL Regional Meeting 134

## Carbons for lipids or carbohydrate: identifying a potential point of metabolic modulation

***Maoyin Li***[1,2]*, Sung Chul Bahn*[1,2]*, Liang Guo*[1,2]*, William Musgrave*[2]*, Allison Saettele*[1,2]*, Michelle Tang*[1,2]*, Howard Berg*[2]*, Ruth Welti*[3]*, Xuemin Wang*[1,2]*.  (1) Department of Biology, University of Missouri, St. Louis, MO 63121, United States  (2) Donald Danforth Plant Science Center, St. Louis, MO 63132, United States  (3) Kansas Lipidomics Research Center, Division of Biology, Kansas State University, Manhattan, Kansas 66506, United States*

Plants perform photosynthesis to fix carbon and accumulate biomass. Carbohydrates and lipids together account for approximately 60% of plant biomass. Biomass of Arabidopsis leaves is comprised of 60% of carbohydrates and 6% of lipids; while biomass of Arabidopsis seeds is comprised of 20% of carbohydrates and 35% of lipids. To understanding the carbon partition between these compounds, we show that group III patatin-related phospholipase As (pPLAIIIs) play a role in modulating lipids and cellulose levels. Overexpression of pPLAIIIβ in Arabidopsis enhanced the lipid synthesis and decrease cellulose accumulation. pPLAIIIβ hydrolyzes phospholipids and galactolipids, and additionally has acyl-CoA thioesterase activity. These enzymatic activities result in free fatty acid release, and the release of fatty acids from membrane lipids has been implicated in various plant processes. Our preliminary data indicate that free fatty acids modulate the activity of some proteins that are involved in cellulose metabolism. We propose that pPLAIIIs function as an important point modulating lipid and carbohydrate accumulation.

**RM_MWGL Regional Meeting 135**

## Visualizing lipid compositions in plant tissues, cells and subcellular compartments: Could location be a factor in oilseed engineering?

*Patrick J. Horn*[1]*, Purnima B. Neogi*[1]*, Andy R. Korte*[2]*, Kerstin Strupat*[3]*, Tabiwang Arrey*[3]*, Vladimir Shulaev*[1]*, Young Jin Lee*[2]*,* ***Kent D. Chapman***[1]*, chapman@unt.edu.  (1) Department of Biological Sciences, Center for Plant Lipid Research, University of North Texas, Denton, TX 76203, United States  (2) Department of Chemistry, Iowa State University and Ames Laboratory-USDOE, Ames, IA 50011, United States  (3) Thermo Fisher Scientific GmbH, Bremen, Germany*

Advances in mass spectrometry (MS) have made rapid, comprehensive lipidomics analysis of complex tissues relatively commonplace. These compositional analyses, although able to resolve hundred of molecular species of lipids in single extracts, often rely on chemical extraction in organic solvents, and consequently, the original cellular context from which these lipids are derived is lost. Recently, high resolution MS of individual lipid droplets isolated from seed tissues indicated a marked difference in organelle lipid compositions (Horn et al., 2011, J Biol Chem, 286: 3298-306), suggesting that heterogeneity of lipid distributions at the cellular and tissue levels may be prevalent. Here we have employed matrix-assisted laser desorption ionization (MALDI)-MS

approaches to visualize lipid species directly in cottonseed tissues. Standard cottonseed oil is about 55% linoleic acid, 15% oleic acid and 26% palmitic acids, with the remainder being relatively minor fatty acids including small amounts of cyclopropanoid fatty acids. These same relative fatty acid percentages were consistently recovered in MALDI-MS scans averaged over entire seed sections. However, MS imaging of mature cotton embryos also revealed a distinct, heterogeneous distribution of molecular species of triacylglycerols (TAGs) and phosphatidylcholines (PCs), the major storage and membrane lipid classes in cotton embryos. PC serves as a metabolic intermediate in the modification of fatty acids for incorporation into TAGs, and the spatial differences will be discussed in terms of potential metabolic relationships. Overall average mol percentages of major and minor molecular species of TAGs and PCs imaged by MALDI-MS were consistent with quantitative values obtained by lipidomics analyses (electrospray ionization- MS) of cottonseed extracts. We conclude that images generated by MALDI-MS report accurate, relative amounts of lipid species in plant tissues, and can reveal previously unseen differences in spatial distributions. This approach may provide a new tool in the prediction and analysis of metabolic engineering strategies.

### RM_MWGL Regional Meeting 136

## Small business IP – red flags and core concepts

***Harry J Guttman***, *Harry.guttman@stipkalalaw.com. Stipkala LLC, Cincinnati, OH, United States*

Intellectual property provides significant, and sometimes the only, value to a small business. Patents, trademarks, copyrights, and trade secrets each play a role in protecting the assets and in increasing the value of a business. This presentation will provide an overview of important intellectual property concepts and considerations. Focus will be placed on trademarks, copyrights, and trade secrets - how they can be traps for the unwary, but can also add significant value to a small business. Some IP-related, day-to-day business practices will be discussed, including aspects of employee agreements and website design.

### RM_MWGL Regional Meeting 137

## Patent information research and its role in managing intellectual property

***Edlyn S Simmons***, *edlyns@earthlink.net. Simmons Patent Information Service, LLC, Mason, OH 45040, United States*

Companies, both large and small can employ information research in strengthening and defending corporate intellectual property holdings. This paper will describe the uses of patent information research in support of patent application drafting and prosecution and in litigation support.

## RM_MWGL Regional Meeting 138

### So you have an invention, now what? Important considerations when filing a patent application (*develop a patent strategy!*)

***Carlos M Tellez***, *carlos.tellez@finnegan.com. Finnegan, Henderson, Farabow, Garrett & Dunner LLP, Washington, DC 20001, United States*

This presentation will discuss the process that inventors follow to obtain a patent on their invention, starting from: 1) defining the invention, 2) drafting a patent application, 3) carrying out examination at the patent office, and 4) obtaining a patent.

The presentation will identify important factors that patent applicants need to keep in mind at each of those stages, including the importance of developing a patent strategy before filing a patent application. The presentation will discuss the elements of a successful patent strategy and will present ways to implement it throughout the process of obtaining a patent.

As part of the initial steps in developing a patent strategy, the presentation will discuss advantages and disadvantages of filing provisional applications as well as factors to consider when attempting to secure patent protection in foreign countries.

## RM_MWGL Regional Meeting 139

### When is your molecule or method eligible for patent protection? Lessons from recent court cases and practical business guidance

***Scott M K Lee***, *scott.lee@arrigo.us. Law Office of Salvatore Arrigo and Scott Lee, LLP, Washington, DC 20036, United States*

Under the patent law the inventor of a new and useful composition of matter or process may obtain a patent covering his invention. Recent court cases have addressed the amount of human intervention that makes a molecule, such as a gene fragment, “new” and therefore patent eligible. Meanwhile, courts have also identified certain types of diagnostic claims as too abstract for patenting. Understanding the law in this area is critical to developing an intellectual property strategy in diverse fields including personalized medicine and bioprospecting. This talk will summarize the state of the law and offer practical business guidance regarding balancing the tradeoffs between public disclosure to seek patent protection of patent eligible inventions and the confidential pursuit of trade secret protection for proprietary information that is unlikely to be patent eligible.

## RM_MWGL Regional Meeting 140

### Synthesis and Electrochemical Properties of Various Pd(II) Complexes

***Sungho Park**, SPark39@WUSTL.EDU, Fengzhi Tang, Liviu M. Mirica. Department of Chemistry, Washington University, Saint Louis, MO 63130-4899, United States*

While palladium chemistry is an established field that has demonstrated its tremendous potential, research on the catalytic features of Pd(III) complexes has only recently emerged. A cost-efficient pathway for the synthesis of *N,N'*-di-methyl-2,11-diaza[3.3](2,6)pyridinophane, a useful ligand for chelating Pd in various oxidation states, was developed. Using this ligand and tetramethylethylenediamine, several Pd(II) complexes were synthesized. Cyclic voltammetry and controlled potential electrolysis enabled the determination of their electrochemical properties and the formation of Pd(III) complexes.

## RM_MWGL Regional Meeting 141

## Recycling gold from electronics

***Andrew W Hummer**, andrew063090@gmail.com, Heath J Gregg, Timothy L Troyer. Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201, United States*

There has been an increased interest in finding cost effective methods for recycling the gold used in electronic equipment. In general, current methods involve dissolving all the metals in an aqua regia followed by precipitating out the gold and electroplating. It is desirable to develop a technique that is not labor intensive, is low cost, and generate little to no toxic waste. Initial attempts focused on selectively dissolving all metals other than gold. Despite some success, the process was not consistently repeatable. It is surmised that an some amount of oxidant is required in addition to acid. A screen of different acids and different combinations of acids and oxidants were tried. The resulting solutions were then analyzed by flame AAS to determine the concentration of various metals in the resulting solutions. This data will form the basis by which it is determined how effective the step of dissolving, precipitation, and electroplating are in separating the different metals and resulting in a non-toxic solution.

## RM_MWGL Regional Meeting 142

## Pressure-Induced Structural and Optical Changes in $YIn_{1-x}Mn_xO_3$

***Denise Freeman**[1], dfreeman@millikin.edu, Zachary Hayes[1], Karena Chapman[2], Peter Chupas[2], Gregory Halder[2], Clarence Josefson[1], Paris Barnes[1]. (1) Chemistry, Millikin University, Decatur, IL 62522, United States (2) Argonne National Laboratory, Argonne, IL 60439, United States*

A series of blue inorganic compounds with the composition YIn1−xMnxO3 (0 ≤ x ≤ 1) was reported in 2009. The blue color shades are caused by the correlation between the arrangement of atoms with electron distribution; however, the structure can be changed through the application of external pressure. The effects of applied pressure on the crystal structure of several members of this series were examined using synchrotron X-ray diffraction. The compressibilities and changes in the structures of these materials are reported.

## RM_MWGL Regional Meeting 143

### Biomimetic studies of manganese (II) dioxygenase and cobalt-substituted enzymes

***Josh Transmeier***[1,2], *jjtransmeier@mnu.edu, Faith E Jacobsen*[1], *Timothy A Jackson*[2]. *(1) Department of Chemistry, MidAmerica Nazarene University, Olathe, Kansas 66062, United States (2) Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States*

Manganese complexes that activate $O_2$ have been of great interest for their role in biological processes and as catalysts for synthetic oxidation reactions. Manganese dependent enzymes that react with dioxygen catalyze a wide range of reactions such as ring cleavage of catechols and flavonoids. Superoxo- and peroxomanganese species have been postulated as being one of the key reactive intermediates in these manganese-containing enzymes. Due to these biological intermediates being so short-lived, the use of synthetic model complexes aid in understanding their properties. Herein we report the synthesis and characterization of a Mn(II) complex supported by the tris(pyrazolyl(3,5-Ph)borate ligand ($Tp^{3,5\text{-}Ph}$) using mass spectrometry and X-ray crystallography. This Mn(II) complex was then treated with 3-hydroxyflavone and characterized by UV-Vis and electron paramagnetic resonance (EPR) spectroscopies. Attempts at structural characterization using X-ray crystallography are in progress. The synthetic schemes of two starting materials 3,5-phenylmethylpyrazole and $Tp^{Ph,Me}$ ($Tp^{Ph,Me}$ = hydrotris(3,5-phenylmethylpyrazolyl)borate) were discussed. These were then used in the synthesis of [($Tp^{Ph,Me}$)CoCl], which is a good model complex for zinc metalloproteins pertaining to their function in matrix metalloproteinases. The cobalt compound was combined with several ligands to form the resultant [($Tp^{Ph,Me}$)Co(L)] complexes. The UV-absorbance as is relates to the color of each solution was discussed. These cobalt complexes are used because they are spectroscopically active models for the corresponding zinc compounds that are spectroscopically silent.

## RM_MWGL Regional Meeting 144

### Synthesis, electronic structure, and properties of organometallic indium porphyrins

***Jared R. Sabin***, *sabi0034@d.umn.edu, Pavlo V. Solntsev, Samantha J. Dammer, Victor N. Nemykin. Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, United States*

Poly(ferrocenyl)-containing porphryins are a relatively new class of macrocycles that are being studied due to their great stability, mixed-valence properties, and electrochemical reversibility. Although metal-free and several transition-metal poly(ferrocenyl)-containing porphyrins have been characterized, compounds with the central metal located in out-of-plane position have only recently been prepared. In this report, the characterization of new XInTFcP and XInTPP complexes [X = Cl, Fc, or FcCO2; TFcP = 5,10,15,20-tetraferrocenylporphyrin(2-); TPP = 5,10,15,20-tetraphenylporphyrin(2-)] is discussed. All target compounds were characterized using UV-Vis, MCD, NMR spectroscopy, as well as X-Ray crystallography. DFT calculations were performed in order to understand the degree of non-planarity of the porphyrin core in addition to the electronic structure of ferrocene-containing porphyrins. Further analysis of the redox properties of these compounds was conducted in a CH2Cl2/TFAB [TFAB= tetarbutylammonium tetrakis(perfluorophenyl)borate] system using cyclic voltammetry, differential pulse voltammetry, and square wave voltammetry. Redox properties were also examined by chemical oxidation and spectroelectrochemical oxidation methods. In all cases, oxidations of individual ferrocene substituents along with the porphyrin core have been observed Accessible mixed-valence properties of the organometallic porphyrines were analyzed using Hash formalism and suggested class II (in Robin-Day classification) behavior.

**RM_MWGL Regional Meeting 145**

## Preparation and testing of nanoparticle materials and thin films for use as substrates in dye-sensitized solar cells

***Cory A Nicholson**, nicholson_ca@wvwc.edu, Edward A Wovchko. Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201, United States*

Solar cells are important devices that harvest natural light energy and they are key to helping address increasing global energy demands. These photovoltaic devices convert solar radiation to electricity with zero waste products and they can be used practically in many locations. Dye-sensitized solar cells (DSCs) challenge conventional solid-state photovoltaic technologies by functioning at a molecular and nanolevel. The prospect of lower-cost, higher efficiency, greater flexibility in shape, color, and transparency, and the potential for overall improved performance open the way for widespread solar cell application. In this work, several DSC's were constructed using conventional methods from two conductive glass plates, one coated with a nanoscale semiconductor substrate layer, another coated with platinum, a ruthenium-based dye layer, and an iodide electrolyte layer. The current standard nanoparticle semiconductor material, $TiO_2$, was employed in a cell and tested for its ultraviolet-visible light absorption (220-730 nm), voltage and current output performance. These results were then compared to the results of DSCs prepared with synthesized tungsten oxide semiconductor materials and thin films. High surface area $WO_3$ nanomaterial was synthesized using a reverse microemulsion-mediated method utilizing a surfactant, Brij-30. $WO_3$ thin films were prepared in an inert atmosphere by colloid chemistry methods and by combining a non-hydrolytic sol-gel method with a molecular assembly templating strategy.

## RM_MWGL Regional Meeting 146

## Complexation studies of Ru(II) and Re(I) pendant polyamine host complexes

***Allison M Putt****, amp004@lvc.edu, Marc Harris.Lebanon Valley College, Annville, PA 17003, United States*

A series of ruthenium and rhenium pendant polyamine complexes were synthesized and characterized by $^1$H NMR spectroscopy and mass spectrometry. These complexes were investigated as host molecules for alkali and alkaline earth cationic guests such as $K^+$, $Mg^{2+}$, and $Ca^{2+}$ ions. UV-visible and fluorescence spectroscopy titration experiments were used to investigate the binding affinities of the host complexes for the various guest ions. The ruthenium polyamine host complexes were also investigated as ion-transport molecules during liquid-liquid ion extraction studies involving $Li^+$, $Na^+$, $Cs^+$, and $Ba^{2+}$ picrates. The ruthenium polypyridine complexes were also used as molecular probes during neurite outgrowth experiments.

## RM_MWGL Regional Meeting 147

## Preparation and investigation of gallium-based materials for hydrogen storage

***Alan A Fratantuono****, fratantuono_aa@wvwc.edu, Edward A Wovchko. Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201, United States*

Hydrogen has been identified as a promising fuel for meeting future energy needs. However, there are technological difficulties in the efficient storage of hydrogen and the retrieval of it once stored. The design and development of a hydrogen carrying and delivery material is essential to the establishment of a hydrogen based economy. In this work, gallium salts were prepared by dissolving gallium metal in acidic solutions followed by subsequent deposition on high area silica nanoparticle materials. High vacuum techniques and transmission infrared spectroscopy were used to examine the $Ga/SiO_2$ material over a temperature range of 200-550 K. The $Ga/SiO_2$ material underwent hydrogen exposure and was probed by carbon monoxide gas. Further treatment with hydrogen revealed a variety of surface species with infrared absorption bands in the carbonyl and metal hydride regions. Experiments using deuterium were conducted to distinguish carbonyl surface species from hydride species. For comparison, vibrational frequencies were theoretically computed for proposed surface species using *ab initio* methods. The possible formation of gallium hydride moieties will lead to further investigations to determine this material's hydrogen storage capability.

## RM_MWGL Regional Meeting 148

## Novel synthesis and characterization of various pyrazolylsilane compounds

***Nicholas C Boyde****, boydenc@mountunion.edu, Scout Mason. Department of Chemistry, University of Mount Union, Alliance, Ohio 44601, United States*

Novel metal complexes containing a pyrazolylsilane ligand have been prepared. The tetrakis-3,5-dimethylpyrazolylsilane ligand was prepared and was reacted with various metal salts, these included iron (III) chloride, indium (III) chloride, copper (II) chloride, and zinc (II) acetate. The reactions were performed both under inert atmosphere and open air conditions to test for stability. These compounds were then analyzed using melting point and NMR spectroscopy. Computational studies on these complexes are currently underway.

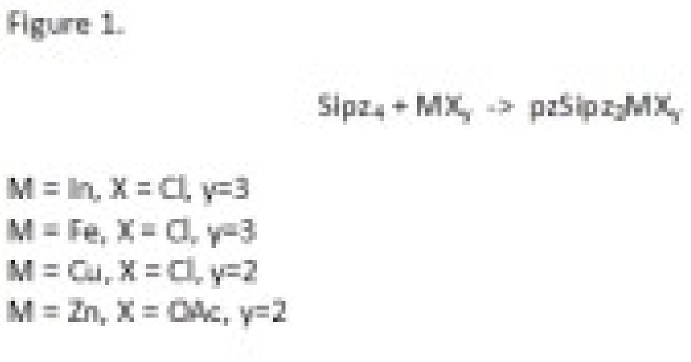


Figure 1.

$Sipz_4 + MX_y$ -> $pzSipz_2MX_y$

M = In, X = Cl, y=3
M = Fe, X = Cl, y=3
M = Cu, X = Cl, y=2
M = Zn, X = OAc, y=2

## RM_MWGL Regional Meeting 149

## Estimating the HOMO-LUMO gaps of siloles by cyclic voltammetry

***Emily A. Weber***, *duane.weisshaar@augie.edu, Barrett E. Eichler, Duane E. Weisshaar. Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

Organic light emitting diodes (OLED's) have become a popular area of research because they are lightweight, mechanically flexible, and energy efficient. Silacyclopentadienes (siloles) have potential for use as emitting materials in OLED's because their low lying LUMO level, especially compared to other cyclic, small molecules, leads to small HOMO-LUMO gaps, and creates light-emission in the visible range. Through the method of cyclic voltammetry the HOMO-LUMO gap was estimated for 6 different 1,1-dimethyl siloles with varying groups on their 2,3,4, and 5 positions. The groups on the 2,3,4,5 positions of the siloles that were studied are phenyl, 1-napthyl, 2-napthyl, 4-biphenyl, 4-trimethylsiylphenyl, and 4-t-butylphenyl. Measured gaps were 2.8 eV – 3.2 eV, corresponding to an excitation wavelength around 400 nm, thus signaling potential for further study for use in OLED's.

## RM_MWGL Regional Meeting 150

## Synthesis and characterization of biomimetic Rieske complexes

***Cory J. Windorff***[1], *cory.windorff@my.uwrf.edu, Caroline T Saouma*[2], *James M Mayer*[2]. *(1) Department of Chemistry, University of Wisconsin-River Falls, River Falls, Wisconsin*

*54022, United States (2) Department of Chemistry, University of Washington, Seattle, Washington 98195, United States*

Rieske clusters are a type of biological [2Fe-2S] cluster that can facilitate both electron transfer, for example in certain oxygenases, and proton-coupled electron transfer, for example, as part of the cty *bc₁* complex electron transfer chains. To gain insight into these processes we are preparing small-molecular models of [2Fe-2S] clusters and exploring their electron transfer kinetics. Using a homoleptic bis-benzimidazolate ligand, both the di-ferric and mixed-valence $[Fe_2S_2(^{Pr}bbim)_2]^{2-/3-}$ congeners have been prepared. These compounds have been characterized by $^1$H NMR spectroscopy, and display temperature dependent shift in the chemical shift, consistent with a paramagnetic center. Mixing solutions of the oxidized and mixed valence species gives a single set of NMR resonances, indicative of rapid electron exchange on the NMR time-scale.

## RM_MWGL Regional Meeting 151

## Predicting the dimensionality of metal halides and oxides

***Stephanie R. Cowin**, srcvg5@umsl.edu, Alicia M. Beatty. Department of Chemistry and Biochemistry, University of Missouri Saint Louis, Saint Louis, Missouri 63121, United States*

Cadmium chloride and other metal halide compounds typically form 2-D networks when reacted with primary amines and anilines. However, it has been established in the Beatty group that it is possible to alter the metal halide assembly by changing the size of the substituent ortho to an aniline amine group. If that ortho group is too large, the assembly will not form layers, and instead will form 0-D and 1-D networks. To determine if this phenomenon occurs generally, we have used variety of metal halides such as $CdX_2$, $PbX_2$, and $CuX_2$ (where X= Cl, Br, I) with a number of ortho-substituted anilines and dianilines. Metal oxides have also been studied and their typical clustered structure and semiconductor behavior have allowed them to be used in a variety of applications such as rechargeable batteries and sensors. We are using ammonium heptamolybdate in combination with ortho-substituted anilines and dianilines, the same approach as with the metal halides, to develop new clusters. We hope to relate the size and shape of the resulting cluster to the nature of the aniline's ortho substituent. If successful, we will be able to create reliable ways to synthesize various metal halide/oxide clusters and/or layers of the desired dimensionality. These clusters and/or layers could then be useful for applications in host-guest chemistry, catalysis, and gas storage, or as superconductors or quantum dots.

## RM_MWGL Regional Meeting 152

## Synthesis and binding studies of anion-responsive terpyridine functionalized calixarenes

Gong Chen[1], **Nicola Y Edwards**[2], nye1@psu.edu. (1) Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, United States (2) Department of Chemistry, The Pennsylvania State University, Dunmore, PA 18512, United States

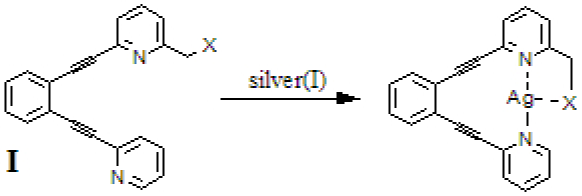
This presentation will describe the synthesis and anion binding studies of terpyridine-functionalized calixarenes. Novel calixarenes with two appended terpyridine moieties at the lower rim have been synthesized in four steps. These calixarenes chelated lanthanide salts which create luminescent centers for sensing applications. The binding ability of these calixarenes for various anions was tested in organic media by monitoring the changes in their UV/Vis and $^1$H NMR and fluorescence spectra as a function of added anions.

## RM_MWGL Regional Meeting 153

## Synthesis of some new tridentate ligands to complex silver

***Lauren R. Verheyen***, *Verheyen989@live.missouristate.edu, Eric Bosch. Department of Chemistry, Missouri State University, Springfield, MO 65897, United States*

This project aims to synthesize a new set of ligands for the specific binding of transition metals like silver(I) and palladium (II). These ligands will have a variety of amino and thio groups in place of moiety X. The synthetic procedure for the preparation of compounds I (X=amines/thiols) will involve palladium catalyzed cross coupling reactions and nucleophilic substitution reactions. Preliminary results and early evaluation of metal complexation binding constants using NMR titration studies will be presented. Previous results will be briefly summarized and the long range goals of these studies will be outlined.



## RM_MWGL Regional Meeting 154

## The (1,1) band of the $b\ ^1\Sigma^+ - X\ ^3\Sigma^-$ transition of $O_2$ by intracavity laser absorption spectroscopy

***Leah C. O'Brien***[2], *lobrien@siue.edu, Emily C. O'Brien*[1,2], *James J. O'Brien*[1]. *(1) Department of Chemistry, University of Missouri, St. Louis, MO 63121, United States (2) Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026, United States*

The (1,1) band of the $b\ {}^1\Sigma^+$ - $X\ {}^3\Sigma^-$ transition of $O_2$ has been recorded by intracavity laser absorption spectroscopy. Improved line positions are presented. Molecular constants for the v=1 of the $b\ {}^1\Sigma^+$ state are given and compared with previous work. A small perturbation is observed at J'=2 in the excited state.

## RM_MWGL Regional Meeting 155

## Reciprocal kinetic curves in electrochemical systems

***Michael Hankins***, *hankinsm@slu.edu, Istvan Kiss, Gregory Yablonsky. Department of Chemistry, Saint Louis University, St. Louis, Missouri 63103, United States*

Experimentally feasible traditional thermodynamic principles operate only in the vicinity of equilibrium. In this contribution we introduce dual kinetic chronoamperometry, in which thermodynamic time invariances are observed at any time. Reciprocal relations between the kinetic curves provide a unique possibility to extract the non-steady state trajectory starting from one initial condition based only on the equilibrium constant and the trajectory which starts from the symmetrical initial condition.

We have performed a numerical and experimental study in which the kinetic curves of the discharge processes from the cathodic and anodic regions limited by mass transfer are analyzed for a reversible first order reaction on a rotating disk electrode. Numerical simulations indicate that the proper ratio of the transient kinetic curves obtained from cathodic and anodic mass transfer limited regions give thermodynamic time invariances related to the reaction quotient of the bulk concentrations. Experimental tests were done with the ferrocyanide/ferricyanide system in which the concentrations of each component could be measured separately using the platinum disk/gold ring dual electrode. Each experiment consisted of setting the ring and disk electrodes to an equivalent far-from-equilibrium potential, such as the anodic or cathodic limit, and allowing each to relax to equilibrium defined by the Nernst potential. After a series of trials it was shown that the concentrations of the oxidized and reduced species followed reciprocal paths as they relaxed toward equilibrium as long as both started from an equivalent state. The results could impact (bio)fuel cell, sensor, and battery technology by predicting the concentrations and currents of the underlying non-steady state processes in a wide domain from thermodynamic principles and limited kinetic information.

## RM_MWGL Regional Meeting 156

## Calibration of model complexes and pyrogallol for metal-coordinated pyrogallol[4]arene capsules

***Collin M Mayhan***, *Andrew V Mossine, Anne E Kroeger, Corey W Dye, Jerry L Atwood, Carol A Deakyne. Department of Chemistry, University of Missouri, Columbia, MO 65211, United States*

For some time now, our groups have been interested in the fundamental properties of metal-seamed pyrogallol[4]arene nanocapsules. Due to the large size of the capsules, an electronic structure calibration study has been performed on the pyrogallol portion of the capsule and on the model system, $Zn(C_2O_2H_3)_2Y$. A variety of Y axial ligands has been investigated for the $Zn(C_2O_2H_3)_2Y$ complexes to determine an appropriate level of theory for future studies of host-guest interactions in the capsule. The effect of including empirical dispersion corrections on the structures and energetics has been examined by comparing the B3LYP and $\omega$B97X-D hybrid DFT methods. Along with pyrogallol, 1,2,4- and 1,2,5-benzenetriol and their sulfur analogs have been investigated to determine the effect of S versus O on proton affinity.

**RM_MWGL Regional Meeting 157**

### Raman scattering of deuterated DNA nucleoside and solid DNA structure

***Chad Hagan****, Hagan605@missouristate.edu, Melissa Hayes, Sarah Nichols, Gary Meints. Department of Chemistry, Missouri State University, Springfield, MO, United States*

DNA-protein interactions are an increasingly important area of study in order to understand the true recognition mechanism in which DNA repair is allowed to take place. The structure and dynamics of the DNA backbone could provide information about the energy barriers that the protein must overcome to facilitate repair. Several deuterated monomers have been synthesized for incorporation into DNA and characterization using Raman spectroscopy and solid state NMR. The monomers include 2'-$^2$H-deoxyadenosine, 2'-$^2$H-ethenodeoxyadenosine, 3'-$^2$H-thymidine, 5'-$^2$H-deoxyadenosine
and 5'-$^2$H-deoxyuridine. The synthesis procedures utilized are standard published protocols that have been applied to deoxynucleoside lesions.
The Raman spectra of the powdered monomers were compared to their respective unlabeled monomers. The spectra were analyzed for changes in peak locations and peak shapes for differences caused by the exchange of a hydrogen atom for a deuterium atom. The DNA sequence ds(CGCGAATTCGCG)$_2$ was also analyzed using Raman scattering. The Raman spectrum of the sequence from a dry powder has been compared to spectra of hydrated samples using various relative humidity chambers to control the amount of water added at each stage. Changes in peak frequencies should correlate with the transition from A to B from DNA upon hydration of the amorphous, hydrated solid.

**RM_MWGL Regional Meeting 158**

### Using Knudsen effusion to measure the vapor pressure of compounds

***Yuan Li****, yuanli@mail.mizzou.edu, C. Michael Greenlief, Gary A. Baker. Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States*

Knudsen effusion has been used to measure the vapor pressure of compounds for a number of years. The method works well for solids with minimal vapor pressures. An all-metal, turbo pumped system is used in these studies. The vapor pressure of the compounds examined in this study, were measured over a temperature range of 325 to 415 K. The measured values are compared to literature values when known. Vapor pressures in the $10^{-4}$ to $10^{-6}$ Pa range can be easily measured, along with the association enthalpies of sublimation. Several nitroamine explosives are studied. In addition, this method has been extended to the study of ionic liquids. Here we also report the vapor pressure of the ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_4mim][NTf_2]$.

## RM_MWGL Regional Meeting 159

## Accurate monitoring of *x*, *y*, and *z* magnetization at any point in an NMR pulse sequence

***EmmaLou T Satterfield****, emma@mst.edu, Klaus Woelk. Department of Chemistry, Missouri S&T, Rolla, MO 65409-0010, United States*

Every year many new pulse sequences are designed for preserving specific NMR coherences while avoiding others. Density matrix calculations and product operator formalism are typically used to predict the magnetization that is finally observed with an NMR spectrometer. Often specific features such as composite or gradient pulses are included to avoid known artifacts. To scrutinize the theoretical outcome of each step in a pulse sequence, we developed a one-dimensional rotating-frame imaging protocol that allows us to record highly accurate $B_1$-field and resonance-offset dependant profiles for all three Cartesian components of magnetization. Experimental results from pulse sequences in which the experimental data deviate substantially from theoretical predictions are used to expose specific spectrometer hardware deficiencies.

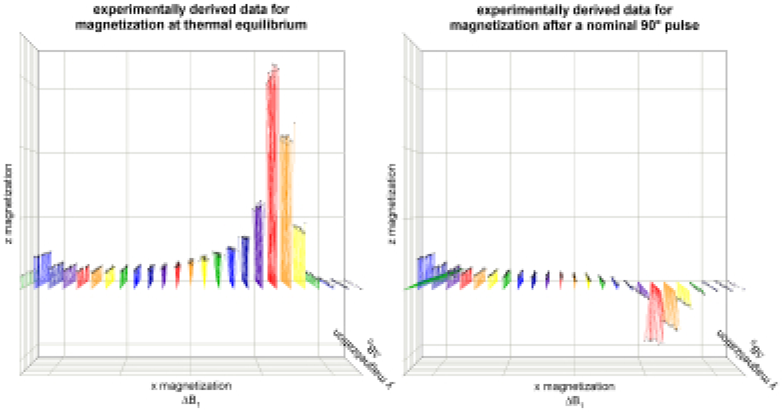


***Figure 1****:* Experimentally derived magnetization vectors obtained from a 5-mm probe as a function of $B_1$ field and resonance offset. Vectors are constructed from three sets of

rotating-frame imaging experiments each recording one of the magnetization's Cartesian components. The experimental procedure provides each component (x, y, and z) with the same accuracy. Vectors shown in the left graph correspond to thermal equilibrium, while the right graph represents magnetization after a nominal 90° pulse. Substantial deviations from an ideal 90° pulse experiment is observed in which only transverse but no longitudinal magnetization should be obtained.

## RM_MWGL Regional Meeting 160

## Low-field NMR spin-lattice relaxation time-constant distributions of shale

***Rex E Gerald II***[1], *geraldr@mst.edu, Lingyu Chi*[1], *Hao Zhang*[2], *Klaus Woelk*[1]. *(1) Department of Chemistry, Missouri S&T, Rolla, MO 65409-0010, United States (2) Department of Geological Sciences and Engineering, Missouri S&T, Rolla, MO 65409-0140, United States*

The hydrogen content and internal pore-size distribution of shale and related sedimentary rock has received a resurgence of interest in the United States and Canada because of the spike in crude oil prices. The petrochemical industry routinely uses NMR relaxation measurements to quantify content and microscopic distribution of oil in shale samples in order to estimate the value of a shale field. We have reconfigured a Varian Inova 400-MHz NMR spectrometer to operate with a Bruker MiniSpec 20-MHz NMR magnet. Monolith and powder samples of shale were placed in 18-mm glass tubes and spin-lattice relaxation measurements with good sensitivity were performed. The inversion-recovery relaxation curves were fitted to a series of weighted exponential terms. Plots of NMR signal intensity versus spin-lattice relaxation time constants typically yield broad bimodal distributions (see figure below). The interpretation of these distributions for different shale samples is under investigation. Control experiments were performed with a series of samples in 5-mm NMR tubes. The tubes contained water-sand mixtures doped with a relaxation agent and were characterized by single spin-lattice relaxation time constants. Different combinations of up to nine control sample tubes were inserted in the low-field NMR probe. Complex inversion-recovery curves were fitted to a discrete sum of exponential terms. By combining different numbers and kinds of control samples, various bimodal distributions could be mimicked.

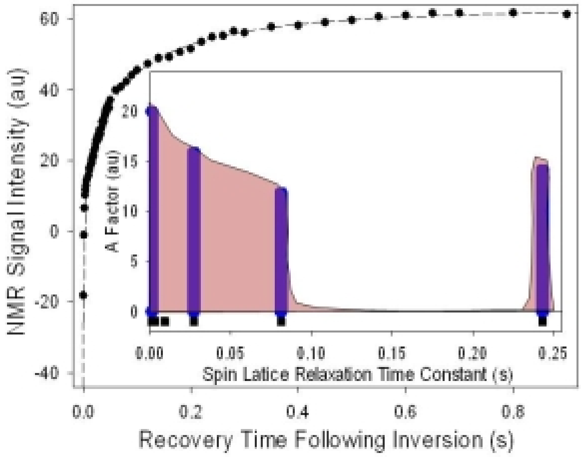


***Figure:*** Bimodal distribution of spin-lattice relaxation time constants for a shale sample.

## RM_MWGL Regional Meeting 161

## Solid-state NMR of inorganic nanomaterials

***Katherine M. Wentz***[1]*, kmwentz@wustl.edu, Brandon Thomas*[2]*, Douglas W. Hammerstroem*[2]*, Steven W. Buckner*[2]*, Paul A. Jelliss*[2]*, Sophia E. Hayes*[1]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Chemistry, Saint Louis University, St. Louis, MO, United States*

Solid-state nuclear magnetic resonance (NMR) is a spectroscopic technique that can give structural information about materials. Solution-state NMR is widely utilized for many organic and inorganic materials but maintaining the solid phase has greater potential in discovering the structural information of semiconductors and nanomaterials. By using techniques such as $\{^{1}H\}^{13}C$ cross-polarization magic angle spinning (CP-MAS), both structural and spatial information can be obtained. NMR can be done both on the surface structure and the nanoparticle center itself. $^{27}Al$ NMR has been performed on several samples of aluminum nanoparticles with different surface ligands as well as $^{13}C$ CP-MAS of the surface ligands. $^{31}P$ MAS NMR of InP nanowires was also evaluated.

## RM_MWGL Regional Meeting 162

## Spontaneously synchronized current oscillations of nickel electrodissolution in an epoxy-based dual electrode microchip flow cell

***Yanxin Jia**, yjia4@slu.edu, István Z. Kiss. Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, United States*

Experiments on oscillatory electrodissolution of two nickel electrodes in sulfuric acid in an epoxy-based microchip flow cell are carried out. The cell was constructed by reversible sealing of a poly-dimethylsiloxane chip with a 0.1mm height and 0.2mm width flow channel over two Ni wires embedded in an epoxy resin. The electrical coupling strength (crosstalk) between the two oscillators can be tuned by adjusting three parameters: distance between the downstream electrode to the reservoir accommodating reference/counter electrodes, total cell resistance, and the surface area of electrodes. In contrast to previous macrocell results, the relatively large ohmic potential drop (due to the constrained current in the narrow flow channel) can induce strong coupling in the microcell. We use a statistical entropy based synchrony index obtained from the phase difference between the oscillators to characterize the effect of the coupling on the dynamical behavior.

Experimental data shows that coupling can be strengthened by increasing the distance of downstream electrode to the reservoir, by increasing of the electrode surface area, and by decreasing the total cell resistance. As the coupling strength is tuned by changing any of these three parameters, we see a transition from phase drift through phase slip to phase locked behavior for weak, intermediate and strong coupling, respectively.

The findings have importance in electroanalytical applications that require collector-generator multi-electrodes wires: the accuracy of the measurement can be improved by proper cell design that diminishes electrical cross talk by weakening the coupling between the electrodes by proper cell design.

**RM_MWGL Regional Meeting 163**

## Using streamlined mutagenesis and screening to increase electron transfer to the B-branch pathway in bacterial photosynthetic reaction centers

***Kaitlyn M Faries**[1], kaitlyn.faries@wustl.edu, Philip D Laible[2], Lucas Kressel[2], Marc Wander[2], Dewey Holten[1], Deborah K Hanson[2], Christine Kirmaier[1]. (1) Department of Chemistry, Washington University, St. Louis, MO 63107, United States (2) Biosciences Division, Argonne National Laboratory, Argonne, IL 60439, United States*

Photosynthetic reaction centers (RCs) convert light energy into chemical energy in a series of extremely efficient electron transfer reactions, accomplishing transmembrane charge separation. The structures of RCs reveal two symmetry-related branches of cofactors that are functionally asymmetric; bacterial RCs use the A pathway exclusively.

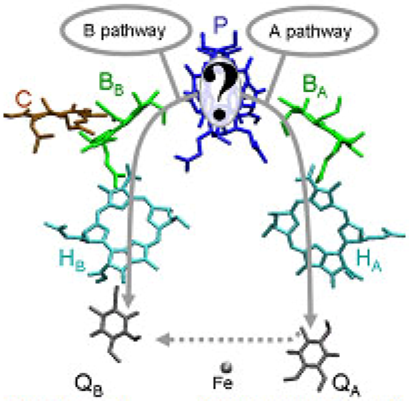


*Figure 1. Arrangement of cofactors in the bacterial RC.*

Using current knowledge of the architectural and energetic factors that underlie the directionality and yields of electron transfer, our goal is to generate a mutant RC that uses the B pathway preferentially and efficiently. Site-specific mutagenesis has produced transmembrane charge separation solely via B-branch activity, but the best overall yield of state $P^+Q_B^-$ is still low, ~15% in the F(L181)Y-Y(M208)F-L(M212)H-W(M250)V (YFHV) mutant. This rational design approach has provided neither the means nor understanding necessary to engineer an efficient B-branch electron-transfer pathway. Therefore, the goal of this project is to produce such an RC via directed molecular evolution, implementing streamlined mutagenesis and high-throughput spectroscopic screening steps to sample a large number of RC variants. The primary experimental vehicle is the RC from the purple photosynthetic bacterium *Rhodobacter capsulatus*. Thus far, using time-resolved millisecond-seconds spectroscopic assays, we have produced and screened 119 mutants, of which 32 exhibit $P^+Q_B^-$ yields comparable to or greater than YFHV. The primary photochemistry in a subset of these RCs has been examined using femtosecond transient absorption spectroscopy.

## RM_MWGL Regional Meeting 164

## Photoreactions in the solid state: An NMR study

***Sarah J Mattler**, sjgresha@wustl.edu, David A Hirsh, Kimberly Harstein, Sophia E Hayes. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

[2+2] photocycloadditions have been the basis of study for many years, due to numerous potential applications, for example: optical switches, polarization filters, and photolithography. Even though these reactions have been widely studied, there are still unanswered questions. These cycloadditions in the solid state become more complicated due to the limited movement allowed by solids. Understanding the effect this limit has on the system is necessary for understanding the photoreaction. A specific example is a single-crystal-to-single-crystal (SC to SC) transformation. Generally, materials undergo a SC to SC reaction when irradiated with light in the tail of the absorption band ("tail" irradiations) or wavelength selective irradiations. The reaction progresses differently with broadband irradiations.

Two materials, cinnamic acid and a supramolecular complex, 2(4,4 bipyridyl ethylene)· 2(resorcinol), have been studied using tail irradiations. The results of $^{13}$C CP (cross polarization) and CPMAS solid state NMR experiments will be discussed. The wavelength selective kinetics curve for the supramolecular complex under tail irradiation has been determined. Domain size experiments using spin diffusion are underway for determining the mechanism of formation of the products under wavelength selective irradiation in cinnamic acid single crystals.

## RM_MWGL Regional Meeting 165

## Ship-in-a-bottle assembly of molecules in porous hollow nanocapsules

***Sergey N. Shmakov***, *sshmakov@memphis.edu, Sergey A. Dergunov, Eugene Pinkhassik. Saint Louis University, United States*

In the present study we demonstrate the entrapment of medium-sized molecules within a hollow polymer nanocapsule. Size-selective pores in the shells of these nanocapsules enable combined assembly and entrapment of large molecules, while permit unhindered transport of small building blocks through the shells. In this way meso-tetratolyl porphyrin was assembled within hollow polymer nanocapsules from p-tolyl aldehyde and pyrrole. Aldehyde and pyrrole molecules are small enough to enter hollow nanocapsule through pores, while the cross section of porphyrin molecule exceeds the diameter of the pores.

Nanometer-thin porous walls provide ultrafast communication of entrapped molecules with the external environment. To illustrate this communication, we carried out the metallation of porphyrin with different metal salts, zinc acetate, manganese dichloride, and iron acetate. Identical behavior of free and entrapped porphyrin and instanteneous spectral change suggest that the walls of nanocapsules do not hinder the transport of metal ions.

## RM_MWGL Regional Meeting 166

## Ytterbium nanocolloids as a potential molecular contrast agent for computed tomographic imaging

***Angana Senpan***, *asenpan@dom.wustl.edu, Dipanjan Pan, Anne H Schmieder, Carsten Schirra, Xiaoxia Yang, Samuel A Wickline, Gregory M Lanza. Internal Medicine, Washington University in St Louis, St Louis, MO 63108, United States*

Colloidal metal nanoparticles offer unique electronic, optical, and magnetic properties and have been intensively investigated for biomedical applications. Recently, various heavy metal (iodine, bismuth, gold) nanoparticles have been introduced as potential

candidates for use as a contrast agent for X-ray based imaging modalities. However, some of them (I, Bi) poses long term safety issues owing to their potential toxicity. Gold provides excellent attenuation in vivo, however in terms of commercial scalability; the use of this metal is dubious due to its extremely high cost.

Herein we report the synthesis, characterization and biological evaluation of metal nanocolloids made from ytterbium (Yb). To the best of our knowledge, the use ytterbium as a CT contrast agent has not been reported earlier. Self-assembled nancolloids were prepared from Ytterbium (III) 2,4-pentanedionate suspended in Polyoxyethylene (80) sorbitan monooleate. The core was encapsulated in a phospholipids monolayer through high pressure homogenization. The synthesis resulted in a colloidal nanoparticles incorporating high payload of ytterbium (>500,000/NP) suitable for use with CT. Average particle sizes were found to be ~280nm using dynamic light scattering and zeta potentials are in the range of -15-20mV with low polydispersities. This agent offers several-fold CT signal enhancement (HU=1200 from microCT) in suspension and in vitro demonstrating high detection sensitivity suitable for in vivo imaging.

As oppose to the conventional iodine-based contrast agents, this new ytterbium based colloidal nanoparticles will simultaneously be cost-effective and will provide high contrast resolution.

**RM_MWGL Regional Meeting 167**

## Nucleic Acid-Directed Self-Assembling Nanoparticles for Imaging and Therapy

***Zifan Li**, zifanli@go.wustl.edu, John-Stephen A Taylor. Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

Dendritic nucleic acids are highly-branched structures with monodispersity that possess numerous branches on the periphery. Herein, we present a bottom-up assembly of nucleic acid dendrimer nanoparticles that are functionalized on their periphery with imaging and delivery agents. A generation one DNA dendrimer consisting of twelve branches was constructed using four-branched DNA building blocks formed by the hybridization of two single-stranded oligodeoxynucleotides. The generation one DNA dendrimer was characterized by gel electrophoresis, size-exclusion chromotography, dynamic light scattering, and atomic force microscopy. The DNA dendrimer was then functionalized by hybridizing with a DNA aptamer, and either a DOTA or fluorescein peptide nucleic acid (PNA) conjugate.

**RM_MWGL Regional Meeting 168**

## Enhancement of commercial antibiotics by synthetic ion channels

***Jason Atkins**[1], jlaqkc@mail.umsl.edu, Mohit Patel[2]. (1) Center for Nanoscience, University of Missouri-St. Louis, St. Louis, MO 63121, United States (2) Department of*

*Chemistry & Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

Hydraphile synthetic ion channels were found to enhance the cytotoxicity to *E. coli* and *B. subtilis* of erythromycin, kanamycin, rifampicin, and tetracycline when co-administered with the antibiotic at sublethal concentrations of channel.

### RM_MWGL Regional Meeting 169

## Coadsorbent effects on DSSC performance and dye loading

***Josh Kofford**, joshua.kofford@sdstate.edu, Brian Logue. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD, United States*

One major loss mechanism in dye-sensitized solar cells (DSSCs) is electron recombination at the photoelectrode/electrolyte interface. Coadsorbents are chemical substances used to treat the photoelectrode surface in order to minimize this loss mechanism. Several coadsorbents (deoxycholic acid (DCA), benzoic acid, hexanoic acid and 3-phenyl propionic acid (PPA)) were tested to determine their effect on DSSC performance. PPA significantly outperformed the other coadsorbents tested. Compared with a DSSC with no coadsorbent, PPA (10 mM) increased the overall efficiency approximately 21% while reducing dye loading by 65%. There was only a slight difference in $V_{OC}$ irrespective of the coadsorbent used, which indicates that the increased efficiency was not due to a shift in the band-edge of the $TiO_2$. Therefore, the increased performance with lower dye loading indicates that limiting dye aggregation and recombination at the photoelectrode/electrolyte interface was the main reason for increased efficiency. Using PPA as a coadsorbent to decrease losses due to dye aggregation and electron recombination at the electrode surface is a step towards maximizing DSSC performance.

### RM_MWGL Regional Meeting 170

## Self-catalyzed growth of semiconducting samarium sesquisulfide nanowires

***Chris M. Marin**, cmarin@huskers.unl.edu, Hsin-Yu Liu, Michael S. Thompson, Chin Li Cheung. Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, United States*

The nanostructuring of thermoelectric materials has been proposed to have a major impact on their thermoelectric figure of merit (ZT). Here, we report the synthesis of highly crystalline α-phase samarium sesquisulfide ($Sm_2S_3$), a material of interest due to its high temperature ZT value, in the form of nanowires. The overall morphology tended to be cables of varying thicknesses composed of bundled wires with average diameters of 20 nm and lengths of up to 15 microns. The identity of these products was verified by x-ray diffraction. Selected area electron diffraction and high resolution transmission electron microscopy indicated the presence of screw dislocations in the crystalline

nanowire structures with a preferred [010] growth direction. Optical absorption and emission measurements confirmed the semiconducting properties of these nanostructured materials and their predicted visible optical band gap. A self-catalyzed growth mechanism is proposed to promote the growth of these nanowires via chemical vapor deposition.

## RM_MWGL Regional Meeting 171

### Impact of "click" functionalization on the toxicity of titanium dioxide nanoparticles in zebrafish embryos

***Sarah P Yang***[1]*, klingbiel@wisc.edu, Kacie M Louis*[2]*, Ofek Bar-Ilan*[3]*, Robert J Hamers*[2]*, Richard E Peterson*[3]*, Warren Heideman*[3]*, Joel A Pedersen*[4]*. (1) Molecular and Environmental Toxicology Center, University of Wisconsin, Madison, WI 53706, United States (2) Department of Chemistry, University of Wisconsin, Madison, WI 53706, United States (3) School of Pharmacy, University of Wisconsin, Madison, WI 53706, United States (4) Department of Soil Science, University of Wisconsin, Madison, WI 53706, United States*

The ability for titanium dioxide ($TiO_2$) to absorb ultraviolet (UV) light has lead to numerous applications for $TiO_2$ nanoparticles (NPs).
Applications now range from cosmetics to environmental remediation to photovolatics. With production volumes expected to surpass 10,000 tons per year by 2014, the potential for release into the environment is inevitable. In aqueous matrices, $TiO_2$ NPs can generate reactive oxygen species (ROS) upon UV absorption. ROS can induce oxidative stress resulting in disease and death in terrestrial and aquatic species. Our group has recently found that employing "click" chemistry to generate water-stable particles with a hydrophobic core and hydrophilic shell significantly reduces the amount of ROS generated in aqueous systems. Thus, we hypothesized that, upon simulated sunlight exposure, "click" functionalization reduces $TiO_2$ NP toxicity in developing zebrafish embryos. To test this hypothesis, we exposed zebrafish embryos to graded concentrations of "click" and polyethylene glycol (PEG) functionalized NPs from 4-6 hours post fertilization (hpf) until 120 hpf in the presence and absence of simulated sunlight. Sunlight was simulated using a metal-halide lamp designed to mimic sunlight to an underwater depth of 1-2 m; the lamp was set to have a 14 h on: 10 h off cycle. At 120 hpf, mortality and body burden were assessed. Dynamic light scattering was utilized to determine $TiO_2$ NP suspension stability. Initially, "click" functionalized NPs have a smaller hydrodynamic diameter ($d_h$) than PEG functionalized NPs. However, after 24 h light exposure, no difference in $d_h$ was observed. Preliminary results indicate that "click" functionalized NPs cause less mortality than PEG functionalized NPs at the same Ti body burden.

## RM_MWGL Regional Meeting 172

## Conjugated polymers as photocatalysts to promote homolytic pinacol coupling of aryl-aldehydes: Effects of Lewis and Brønsted acids

***William D. Rouch**, wrouch@slu.edu, Miao Zhang, Ryan McCulla. Department of Chemistry, St. Louis University, St. Louis, MO 63103, United States*

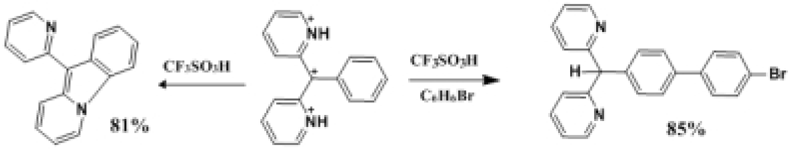
The use of visible light as a “green” catalyst for the promotion of organic functional group transformations has been an expanding area of research. Conjugated polymers are organic semiconductors that absorb visible light, which dramatically increases their reduction potentials. As a result, conjugated polymers are expected to be much stronger reductive photocatalyst than others currently being used, such as $TiO_2$. Driving chemical reactions with visible light is attractive due to its ubiquitous nature; however, the low absorptivity of most organic molecules necessitates the use of a photosensitizer or photocatalyst. The conjugated polymer, poly-(p)-phenylene was synthesized and used to promote homolytic pinacol couplings of aryl-aldehydes with visible light. The reaction requires the use of a sacrificial electron donor ($Et_3N$) and a hydrogen donor. The use of certain Lewis or Brønsted acids in the reaction showed a considerable increase in reaction rates, with carboxylic acids being the most effective.

**RM_MWGL Regional Meeting 173**

## charge delocalization and cnhanced acidity in tricationic superelectrophiles

***Rajasekhar Reddy Naredla**, naredla.raja@gmail.com, Sten O Nilsson Lill, Chong Zheng, Douglas A Klumpp*.Chemistry and Biochemistry, Northern Illinois University, De Kalb, Illinois 60115, United States*

We have studied the charge delocalization in triaryl methanols. The triaryl methanols forms tri cationic intermediates in superacid; these superelctrophiles tend to undergo two different kind of reaction. One set of reaction shows charge migration across aryl group which leads to form remotely functionalized products. And another set of reactions occurs through deprotonation of an unusually acidic site on the tricationic species.

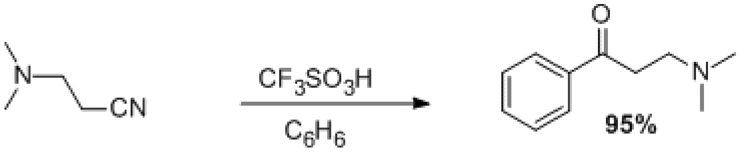


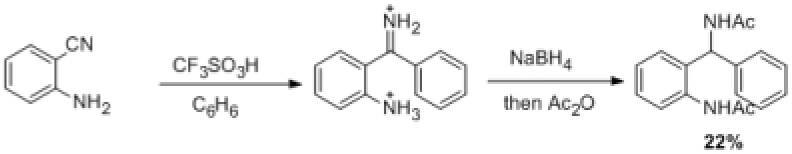
**RM_MWGL Regional Meeting 174**

## Superelectrophilic chemistry of various nitriles

***Erum K Raja**, eraja@niu.edu, Douglas Klumpp*.Chemistry and Biochemistry, Northern Illinois, De Kalb, Illinois 60115, United States*

Superacid promoted Houben-Hoesch reactions of various amino, flouro and related nitriles (figure 1) have been studied resulting in fair to modest yields of products (12-95%). A number of iminium ion intermediates have been reduced successfully representing a direct route to the benzylic amines (figure 2).





## RM_MWGL Regional Meeting 175

## Rapid access to exocyclic allenes by double hydride reduction of 3-trimethylsilylethynyl-2-cycloalkenones

*John M Kum, Andrew K Urick, **Martin Hulce**, mhulce@creighton.edu. Department of Chemistry, Creighton University, Omaha, NE 68178-0323, United States*

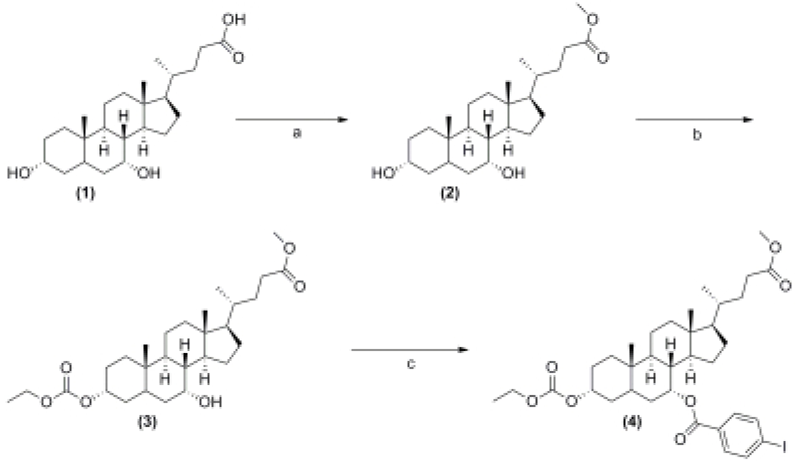
Exocyclic allenes are relatively well-represented among allene-containing natural products. A subunit of the common carotenoid, fucoxanthin, this structural motif has been exploited in syntheses of allene-containing carotenoids, terpenoids such as the grasshopper ketone, and in preparation of analogues of prostacyclins and cephalosporins. Syntheses of this allene class typically rely on either extended conjugate additions to *e.g.* alk-2-en-4-ynones or syn $S_N2'$-like alkylations and reductions of alkynyl oxiranes. We report reaction of trimethylsilylethynyl cycloalkenones with 2 equiv LAH results in reduction of a vinylogously propargylic intermediate alcoholate to provide 3-(2-trimethylsilylethenylidenyl)cycloalkanols in good yields, providing a new, potentially general method for preparation of exocyclic allenes.

## RM_MWGL Regional Meeting 176

## Synthesis and spectra of methyl-3α-carboethoxy-7α-(4-iodobenzoyloxy)-5β-cholanoate

***Himabindu Veeramachaneni**[1], hv2q6@mail.umkc.edu, Murat Turkyilmaz[2], H.R.Ferhat Karabulut[2], Jerry Ray Dias[1]. (1) Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110-2499, United States (2) Chemistry, Trakya University Science Faculty, Edirne, Turkey*

En route to the synthesis of nanostructures built of chenodeoxycholic acid scaffolding units, methyl 3α-carboethoxy-7α-(4-iodobenzoyloxy)-5β-cholanoate **(4)** was synthesized and characterized by $^1$H NMR and $^{13}$C NMR.



**Scheme:** (a) AcCl, $CH_3OH$, at °0C, 2 h; (b) ClCOOEt, py at -15 °C, (c) 4-iodobenzoyl chloride, py, DMAP, THF, reflux, 24 h.

**RM_MWGL Regional Meeting 177**

## Neutral picket fence porphyrins that bind the head group of phosphatidylglycerol, a phospholipid found in bacterial membranes

***Amanda Alliband**, amalliband@wichita.edu, Dennis H. Burns. Department of Chemistry, Wichita State University, United States*

Picket fence porphyrins that bind specifically to a phosphatidylglycerol head group have been postulated as a component of a synthetic antibiotic that would mimic antimicrobial peptides. Therefore, synthetic anion receptors that bind selectively/specifically to a phosphatidylglycerol head group with high affinity is of interest. In this study, we describe the design, synthesis, and structure validation of a series of picket fence porphyrins that recognize the anion portion and the bis-hydroxyls of the phosphatidylglycerol head group. Two receptors were found to bind to the phosphatidylglycerol head group with high affinity ($K_a$ values were 6,000 mol$^{-1}$ and 2,300 mol$^{-1}$). Job plot analysis indicated a 1:1 binding stoichiometry for the phosphatidylglycerol-receptor complex with two of the porphyrin receptors. These receptors contained the most sterically hindered pickets with the most organized binding pockets.

## RM_MWGL Regional Meeting 178

### Synthesis of inosamine derivatives to function as nutritional mediators for nitrogen fixation

***Jennifer L. Meloche****, jenmelo89@live.com, Elke Schoffers. Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008-5413, United States*

Rhizobia bacteria play an important role in fixing atmospheric nitrogen ($N_2$) into ammonia ($NH_3$) during a symbiotic process with legume plants. However, the mechanism of nitrogen fixation is not well understood. Rhizopines are molecules that are found in the root area (rhizosphere) and are thought to act as nutritional mediators. *scyllo*-Inosamine (SIA) is one of two identified rhizopines and has been previously prepared in 7 steps and 34% overall yield in our lab. In this work, a more direct route towards SIA was pursued by oxidizing *myo*-inositol with *Gluconobacter oxydans,* and then attaching a “gallate-derived amine” to increase its solubility in organic solvents. The oxidation with *Gluconobacter oxydans* is very selective and efficient. The ensuing ketone was studied in various reductive amination reactions.

## RM_MWGL Regional Meeting 179

### From NP-HPLC to RP-UPLC: Ultra performance liquid chromatography for in-process analytical support of narcotics in the pharmaceutical industry

***Hengwen Zhong****, hengwenzhong@hotmail.com.Covidien, Webster Groves, MO 63119, United States*

Ultra Performance Liquid Chromatography (UPLC) can be more advantageous than HPLC because of its shorter analysis time, higher sensitivity and separation efficiency. These features of UPLC make it an ideal technique for in-process analytical support in an industry which requires quick turnaround times without compromising on quality and accuracy. This presentation outlines the development and application of a reversed-phase (RP) UPLC method to replace an existing normal-phase (NP) HPLC method for narcotics in-process support in the pharmaceutical industry. The RP-UPLC and NP-HPLC separations of morphine, codeine and their related impurities, including morphine N-oxide, morphinone, 10-hydroxycodeine, pseudomorphine, norcodeine, codeine methyl ether, 10-hydroxythebaine and thebaine, are presented and compared. The results showed that the RP-UPLC method exhibited higher sensitivity, accuracy and significantly reduced analysis time. Separations on different Waters Acquity UPLC reversed-phase columns including BEH phenyl, BEH C18, HSS C18, HSS SB C18 and HSS T3 were compared. The effect of the mobile phase TFA concentration on analyte

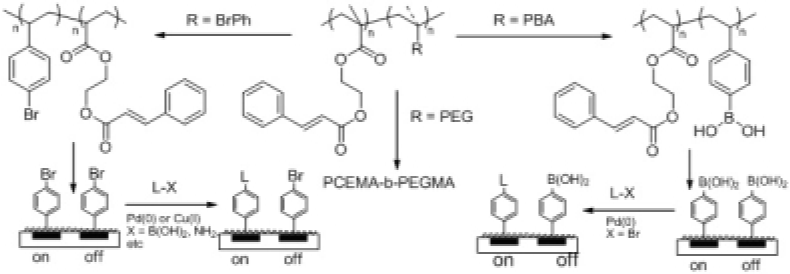
separation was examined. The optimization of flow rate and column temperature to minimize operation issues within a QC environment was discussed.

## RM_MWGL Regional Meeting 180

### Building addressable libraries: UV-Cross-linkable di-block copolymer strategy for functional reaction surfaces on microelectrode arrays

***Libo Hu***, *hulibo_work@hotmail.com, Kevin D. Moeller. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Microelectrode arrays hold great promise as platforms for monitoring ligand-receptor binding events in “real-time” Because each microelectrode in an array is individually addressable, each can be used to monitor a unique member of a molecular library that is associated with its surface. For this reason, we have been developing the synthetic tools necessary for site-selectively building and placing molecules by the microelectrodes in an array. Key to this work is coating the arrays with a porous polymer that allows for the attachment of reaction substrates or completed library members to the surface of the arrays proximal to the microelectrodes. Three types of UV-cross-linkable di-block copolymers have been developed as coating for microelectrode arrays.



All three polymers share the same PCEMA block for cross-linking reaction. The PBrSt-b-CEMA polymer was shown compatible with a series of Pd(0)- and Cu(I)-catalyzed reactions. It was compatible with electrochemical signaling experiments, although it showed non-specific binding to proteins at higher concentrations. In order to study weak binding interactions, PCEMA-b-PPEGMA was developed to reduce non-specific binding. However, it was shown not to be a stable enough surface for array-based reactions. In an effort to make a tunable surface, PCEMA-b-BoSt was made and was shown compatible with Suzuki reactions on the array, however, the inability of achieving a stable current deemed it incompatible with signaling experiments.

## RM_MWGL Regional Meeting 181

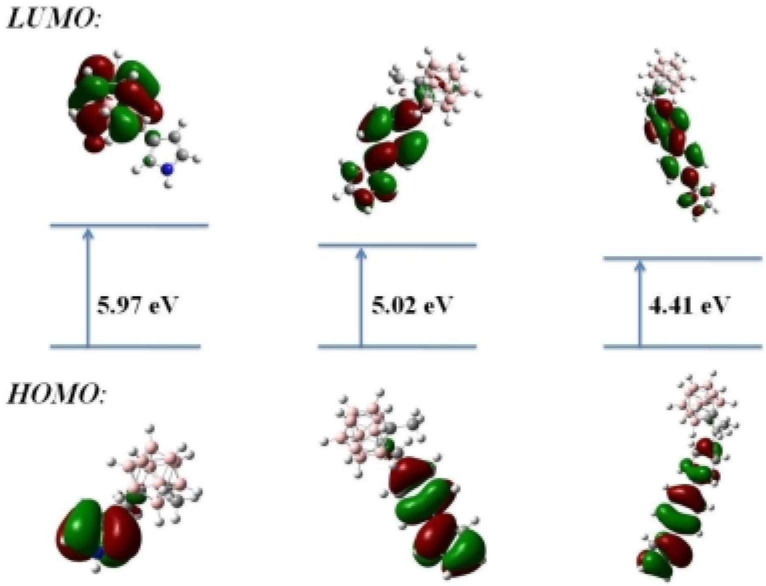
### Band-gap engineering of carborane-containing conducting polymers: A computational study

***Ethan Harak**, petia.bobadova-parvanova@rockhurst.edu, Joseph Varberg, Petia Bobadova-Parvanova. Department of Chemistry, Rockhurst University, Kansas City, MO 64110, United States*

High demand for inexpensive and renewable energy resources has stimulated the design of efficient, low-cost conductive materials, most notably conductive organic polymers. Although they have a lower cost of production than traditional silicon semiconductive materials, conductive polymers are susceptible to photodegredation after prolonged exposure to UV light and heat resulting in a short lifespan.

Fortunately, the most intriguing advantage of conductive polymers is the fact that their properties can be engineered with the use of different substituents on the polymer chain. Recent experiments demonstrated that the addition of substituents containing carboranyl groups significantly increases the stability, therefore extending the lifespan. Further, fine-tuning of the structural units used to attach the carborane cage to the polymer backbone allows for manipulation of the conductivity of the material. Employing computer modeling allows us to determine the HOMO-LUMO gap in a given material without expensive synthesis, and thus, allows us to predict its conductive ability in a more effective, yet reliable manner.

In this study, we modeled computationally the monomers, dimers, and trimers, of a series of carborane substituted polypyrroles. We examined the effect of different combinations of substituents and spacers on the HOMO-LUMO gap. Our results clearly demonstrated how various substituents and spacers affected the band gap energy, allowing us to design and propose the synthesis of new polymers with enhanced conductive ability.



**RM_MWGL Regional Meeting 182**

## Synthesis and characterization of polyionic mixed polymer nanobrushes on gold by ATRP and surface-initiated photopolymerization techniques

***Bojan Mitrovic***, *bojan.mitrovic@gmail.com, Colleen Scott. Department of Chemistry, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

Polymer nanobrushes have been shown to play an important role in a range of applications; for example, in proteomics mixed polymer nanobrushes have been shown to play an important role in the separation of peptides and proteins. We will develop pH responsive polymer nanobrushes on gold substrates, which will be able to swell or collapse by more than an order of magnitude based on the pH of the aqueous solution. In order to take advantage of a range of pH values, we will develop both cationic nanobrushes as well as anionic ones. The brushes will be synthesized by atom transfer radical polymerization (ATRP) and surface initiated photopolymerization techniques giving a range of grafting densities and pH responses.

---

### RM_MWGL Regional Meeting 183

## Soybean-based epoxy-anhydride thermoset coatings

***Adlina Paramarta***, *Adlina.Paramarta@my.ndsu.edu, Thomas Nelson, Xiao Pan, Dean Webster.Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND 58102, United States*

The search for environmentally friendly and greener materials in the polymer field is further explored to decrease dependency toward petroleum-based chemicals. Sucrose soyate, a complex molecule of sucrose and fatty acids of soybean oils, was modified to introduce epoxy functionality and polymerized with anhydride groups through a thermal curing process. They anhydride group chosen was dodecyl succinic anhydride due to its stability at high temperature and its bio-based content. The effect of different amine catalysts and curing conditions were studied by both thermal and mechanical analysis. It was predicted that the amine reactivity had an impact on the coating properties: higher reactivity resulted in more thermal initiation, therefore higher crosslink density and lower molecular weight between the polymer chains. There were no significant differences in properties found between curing of 180 °C for 1 hour and 160°C for 30 minutes followed by 200°C for 30 minutes post-cure. Flow agent was added to the formulation to improve the leveling of coatings during thermal curing; it was shown that the flow agent resulted in more evenly distributed coatings thickness and lower glass transition temperature due to a plasticizing effect.

---

### RM_MWGL Regional Meeting 184

## Thermo- and pH-stimuli responsive water-soluble copolymers and hydrogels based on acrylate monomers

*Maxim A Dergunov*[1,3], ***Sergey A Dergunov***[2,3], *sdrgunov@gmail.com, Eugene Pinkhassik*[2,3], *Grigoriy A Mun*[1]. *(1) Department of Chemistry and Chemical Technology, Kazakh National University, Almaty, Kazakhstan (2) Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, United States (3) Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States*

Water soluble copolymers and hydrogels based on acrylate monomers were synthesized by free-radical polymerization in ethanol, and using light scattering, NMR, IR,UV-spectroscopy, viscometry, scanning and transmittance electron (SEM and TEM) and scanning tunneling (STM) microscopy. The thermal behavior of polymer networks was investigated by Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA). A number of factors has been found to influence the tendency of these hydrophobically modified water-soluble copolymers to associate either inter- or intramolecularly. It was shown that water soluble copolymers form stable complexes with ions of transition metals at acidic pH under room temperature and low concentration of ions in solution. Whereas at neutral pH, complexation took place only at high temperature. For crosslinked hydrogels was shown that they have high water absorption capacity and also have ion exchange groups. The hydrogels have been used to extraction Co2+, Cu2+ and Ni2+ ions from their diluted aqueous solutions. Sorption of these ions has been studied as a function of pH, temperature, nature of backbone polymer and acrylic acid concentration used in the synthesis of hydrogels.

**RM_MWGL Regional Meeting 185**

## Synthesis, extraction and analysis of molecularly imprinted quercetin polymers

***Adam Heck***, *Adam.Heck@usiouxfalls.edu, Brian Schenavar, George Mwangi. Department of Chemistry, University of Sioux Falls, Sioux Falls, SD 57105, United States*

The Objective of this research was to synthesize quercetin polymers, analyze and test the efficacy and properties of rebinding the polymer to the initial template. After a sufficient rebinding, the analogs of quercetin are analyzed in the same polymer to determine the polymers specificity. Polymer microspheres were synthesized via non-covalent polymerization. The functional monomers were itaconic acid and 2-Hydroxyethyl methacrylate (HEMA). The initiator and cross linker were Azobisisobutyronitrile (AIBN) and Trimethylolpropane methacrylate (TRIM), respectively. The quercetin extraction efficiency was evaluated using UV-Vis. Binding studies were conducted by analyzing concentrations of supernatant after the specific concentrations of template were introduced to the extracted polymer; these tests were also done via UV-Vis. It was observed that a 4:1 (methanol: acetic acid) ratio is more efficient at extracting the polymer than a 4:1 (methanol: water) solvent. A suitable extracting solvent was found along with an efficient quercetin polymer. Results from this study established that there was greater re-binding ratio as the when higher concentration of the cross-linker TRIM was present. This optimum amount of TRIM was

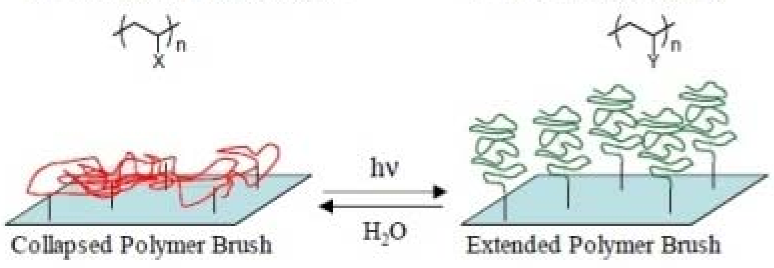
found to be 20 mmol. From the solvents tested, pure methanol provided the best environment for the polymers, to rebind to the quercetin template.

## RM_MWGL Regional Meeting 186

## Synthesis of Photoactive Polymer Brush by RAFT polymerization: Applications in isolation of biological macromolecules

***Milind D Bisen***, *milindb@siu.edu, Matthew J Pabich, Daniel Dyer, Colleen Scott. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

We have been synthesizing pH responsive copolymer polymer brushes of 70% NIPAAM and 30% PMAA for protein separation. Here we report the isolation of protein by combining photoactive polymer brush with Capillary Dynamic Isoelectric Focusing (DIEF). Our polymer brush which can absorb both acidic and basic peptides/proteins is composed of NIPAAM as the major component, and spiropyran as the minor photoactive component. Irradiation with UV light results in a polarity change and the brush goes from a collapse state to an extended state in a polar solvent



.

## RM_MWGL Regional Meeting 187

## Reactivity of cyclic carbonates as substrates for non-isocyanate polyurethanes

***Olivera Bilic***, *obilic@pittstate.edu, Ivan Javni, Doo Pyo Hong, Jian Hong, Zoran S. Petrovic. Kansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas 66762, United States*

Non-isocyanate polyurethanes can be made by reacting cyclic carbonates with amines. This technology has several benefits such as lower environment and health hazard and possible utilization of renewable resources. The additional benefit is the utilization of carbon dioxide, an inexpensive monomer. Using $CO_2$ as a C1 feedstock is a direct route to its recycling and the reduction of carbon dioxide presence in the atmosphere.
The drawback is that the five-member cyclic carbonate ring is relatively stable and the reaction with amines is slow limiting its wider application in polyurethanes. In order to

better understand the effect of structure on reactivity a series of cyclic carbonates of the bio-based (from soybean oil, linseed oil, etc.) and petrochemical origin (ethylene, propylene carbonate, etc.) was tested. The carbonates reacted with 1-aminobuthane at 70 $^{o}$C and the reactivity rate was measured via cyclic carbonate carbonyl concentration with time. The concentration of the carbonyl groups was monitored by FT-IR following the intensity of the absorption band at 1800 cm$^{-1}$. It was found that cyclic carbonates with internal carbonate groups from natural oil based-carbonates, reacted much slower than the carbonates with the terminal carbonate groups.

## RM_MWGL Regional Meeting 188

### High school students' attitude towards chemistry as a science and chemistry studies

***Frackson Mumba***, *frackson@siu.edu, Vivien M Chabalengula, Asiana Banda, Simeon M Mbewe. Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*

This study explored high school students' attitude towards chemistry as a science and chemistry studies in their classrooms. Attitude was defined in terms of three aspects: *Interest, Cognitive, and Affective*. Students were enrolled in four different schools with different demographics. Data was collected through a questionnaire. Overall, high school students valued chemistry as a science despite their perceived difficulties and apathetic interest in chemistry studies. Detailed results and implications on chemistry teaching and learning will be stated and discussed at the meeting.

## RM_MWGL Regional Meeting 189

### *Successes and challenges in the implementation of the laboratory components of a dual credit general chemistry course*

***Janelle L. Torres y Torres***, *jtorresytorres@missouriwestern.edu, Benjamin D. Caldwell, Michael W. Ducey. Department of Chemistry, Missouri Western State University, St. Joseph, MO 64507, United States*

The Missouri Western Dual Credit program in General Chemistry has served more than 1,000 students since it first began in 1999. The program is a cooperative effort between an on-campus faculty member who serves as the instructor of record and high school teachers who facilitate the course at their schools. A primary goal of the program is to maintain the same course content and rigor as the on-campus course. Teachers attend a one-week workshop each year that is divided between the lecture and laboratory portions of the course and are trained to facilitate the laboratory exercises in their school environment with the same philosophy as is used in the on-campus course. Most experiments are performed in high school labs; however, the high school teachers also receive instruction on the instrumentation their students will be using during two on-campus visits. Even with all the on

campus guidance and preparation, challenges to the implementation of the laboratory at the high schools exist, including length of class periods, availability of adequate lab facilities and equipment for the number of students enrolled at each school, assigning consistent grades across schools for the laboratory exercises, safety issues, preparation of students for on-campus lab visits, and coordination of the lecture with on-campus lab visit dates. In this presentation we will share solutions to some of these challenges and discuss our strategies for addressing the challenges facing high school facilitators and students. We will present the results of a teacher survey and contributions by experienced teachers of best practices for translating the on-campus labs to the high school classroom.

### RM_MWGL Regional Meeting 190

## Evaluating the probability of success in general chemistry coursework using placement testing and course prerequisite information

***Yu Kay Law***, *yklaw@fhsu.edu, Edwin G. Olmstead, Jr. Department of Chemistry, Fort Hays State University, Hays, KS 67601, United States*

Three diagnostic instruments were evaluated to determine their ability to predict the success of students in our first-semester general chemistry course: (1) the California Chemistry Diagnostic Test (CCDT, 45 min length) ; (2) the Iowa Chemistry Aptitude Test (ICAT, 55 min length); and (3) a short, four-question math preparation questionnaire on previous high school and college coursework (MPQ, <3 min length). Each of these instruments as well as individual sections of the CCDT and ICAT were investigated to determine which scores (or subscores) contained the greatest predictive power for success in first semester General Chemistry. Surprisingly, within the context of our institution, we show that the short MPQ instrument provides the strongest predictive power for General Chemistry success (defined as the probability of obtaining a C grade or higher). Its efficacy appears to be derived from its ability to predict the success of students with low or high levels of mathematical preparation. In contrast, while the overall course grade obtained is approximately correlated with their placement exam scores, the CCDT and ICAT scores fail to effectively predict general chemistry success for students with low or high levels of mathematical preparation. The CCDT and ICAT are, however, useful for predicting success for students with mathematical preparation between these two extremes. Based upon our results, future chemistry placement work should focus on designing questions that specifically assess mathematical abilities developed in coursework between high school algebra and college calculus.

### RM_MWGL Regional Meeting 191

## Targeting diverse learning needs in general chemistry with a buffet redesign model

***Klaus Woelk**, woelk@mst.edu.Department of Chemistry, Missouri S&T, Rolla, MO 65409-0010, United States*

Missouri S&T's chemistry department participates in a state-wide initiative to redesign large-enrollment courses with technology-supported active learning strategies. Our redesigned general-chemistry course will employ a variety of techniques for learning chemical principles and concepts. This “buffet” will give students the option to participate in lectures face-to-face or synchronously from a remote location. In-class feedback and assessment with clickers will be augmented with online response requests by ResponseWare (Turning Technologies), and videotaped lectures will be available with integrated assessments similar to the clicker questions. Recitations will be replaced with collaborative learning centers of active-learning and problem-solving activities, and online tutorials will be offered based on MasteringChemistry (Pearson Education). MasteringChemistry will also be utilized for common homework assignments, quizzes, and exams, which all students must complete in a timely manner. To ensure engagement in the buffet, students are required to provide and discuss a study plan with TAs or instructors, which may be adjusted in regular intervals. Elective modules will be offered to focus on particularly designed discipline-specific learning activities or as extra credit. The redesigned course will give students the opportunity to select from a wide pool of instructional materials to match their own learning characteristics and needs. This built-in flexibility will allow students to prepare effectively for challenges in subsequent courses. It will encourage active learning over memorization and help individualize study plans even in a large-enrollment course. It will serve the needs of diverse learners and is intended to retain more students of underrepresented minorities, first-generation college students, and students with different science or study-skill backgrounds. The self-paced learning approach will enhance student satisfaction and student success. We will report on the progress and concerns toward implementing the redesigned course as a pilot project in SP 2012 and toward its full implementation in FS 2012

## RM_MWGL Regional Meeting 192

## Teaching chemistry in inclusion classrooms: Implications for chemistry teacher education

***Frackson Mumba**, frackson@siu.edu. Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*

Current science education reforms identify science teachers as key in developing scientific literacy for all students among all students, including those with disabilities. For this study, students with disabilities (SWD) are those identified with non-severe learning or emotional needs who receive special education services in schools. Such students have the cognitive, emotional, and social capacities to construct scientific knowledge, participate in scientific investigations, and apply scientific reasoning for problem solving and decision making inherent in school science curricula. The success of the reforms will be determined in large measure by the practices and beliefs of science teachers

who often teach in inclusion classrooms enrolling both SWD and regular students. Today, several chemistry teachers are teaching inclusive classes. Yet relatively few chemistry teachers have been prepared to teach inclusive classes. Although there have been reported successes in teaching science in lower grades there remains a clear need for research to determine effective chemistry teaching practices for inclusive classrooms. This study will report on the practices and beliefs of four high school chemistry teachers who are teaching inclusive classes in Southern Illinois.

**RM_MWGL Regional Meeting 193**

## Zambian pre-service science teachers' ranking of chemistry education goals

***Asiana Banda***[3], *abanda@siu.edu, Frackson Mumba*[2], *Vivien Mweene Chabalengula*[1], *Simeon Mbewe*[4]. *(1) Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, IL 62901, United States (2) Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, IL 62901, United States (3) Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, IL 62901, United States (4) Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

This study examined Zambian Junior High School pre-service science teachers' ranking of the goals of chemistry education. The sample comprised 62 pre-service science teachers at a University College in Zambia. This sample consisted of 37 males and 25 females. Data were collected using a 30 item Likert scale questionnaire adopted from Gayon (2010). The questionnaire consisted of questions that focused on personal needs, societal issues, career awareness, scientific method, and scientific knowledge as the goals of chemistry education. Results of the study show that the pre-service teachers ranked the goals of chemistry education from highest to lowest as follows; societal issues (M=2.38), personal needs (M=2.03), scientific knowledge (M=2.01), scientific method (M=1.96), and career awareness (M=1.63). Additionally, both males and females ranked societal goal first and career awareness least. Among the males, personal needs goal was ranked second while the females ranked it second last. Both gender ranked scientific knowledge third while males ranked scientific method fourth and the females ranked it second. These results have implications for chemistry teaching and learning and teacher education.

**RM_MWGL Regional Meeting 194**

## Teaching assistants' successes and challenges in Assessment, Review and Instruction System (ARIS) program

*Gary Kinsel,* ***Ven Ney Wong****, venney@siu.edu, Frackson Mumba. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illlinois 62901, United States*

Assessment, Review and Instructional System (ARIS) program has been used as supplemental instruction in freshman chemistry in several chemistry departments. Similarly, in the past five years, the Department of Chemistry and Biochemistry at Southern Illinois Carbondale has used ARIS program in general chemistry courses in a structured Learning Workshop format. Teaching Assistants have been involved in the delivery phase of the ARIS program. This research explored the teaching assistants' pedagogical successes and challenges in the ARIS program. We also identified the factors that led to successes and challenges and how they overcame the challenges. Detailed results and implications will be presented and discussed.

### RM_MWGL Regional Meeting 195

## Impact of computer-based structured learning workshop on graduates teaching assistant's specific chemistry content

*Ven Ney Wong, **Kandalama Kankanama Priyasantha**, kkdp@siu.edu, Gary Kinsel, Frackson Mumba. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*

The incorporation of computer-based Structured Learning Workshops (SLW) in chemistry courses have shown to be an effective tool in improving undergraduate students' achievement and retention of chemistry concepts. While this program successfully demonstrates its positive influence to the undergraduate students, studies have not examined the impact of such programs on graduate Teaching Assistants (TA's) involved in SLW. Therefore, this presentation will focus on the extent to which computer-based SLW has impacted Teaching Assistants in terms of specific chemistry content knowledge. Detailed results and its implications on chemistry teaching and SLW program will be stated and discussed.

### RM_MWGL Regional Meeting 196

## Synthetic organic transporters that function in bilayer membranes

***G.W. Gokel**, gokelg@umsl.edu, Saeedeh Negin, Megan Daschbach, Jason Atkins, Mohit Patel, Priyanka Ogirala, Johnathan Autry, Nicole Curvey. Center for Nanoscience & Departments of Chemistry & Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

The phospholipid bilayer surrounding cells represents a relatively impermeable barrier to the entry of nutrients and the exit of waste products. The transport proteins that regulate the passage of ions or molecules through this barrier are large and complex molecules. In order to model and thus better understand their function, we have prepared families of transmembrane transporter molecules. To date, these include crown ether based hydraphiles that selectively transport sodium cation over potassium or anions. A library of amphiphilic heptapeptides has also been developed that selectively transports chloride anion over potassium cation. These synthetic anion

transporters (SATs) insert in the bilayer and form dimeric (or larger) pores that permit transport through the membrane. More recently, we have prepared a suite of compounds that are designed to be membrane-spanning amphiphiles that embody modularity and structural simplicity. These compounds form functional channels that exhibit modest selectivity. Finally, we have developed a range of molecules based on pyrogallarene chemistry. These compounds self-assemble into bilayers, capsules, and nanotubes. The copper-seamed capsules function as ion transporters and the family of structures exhibit broad and surprising membrane activity. Novel nanotubes formed from pyrogallols give a novel pore formation mechanism in phospholipid bilayers. In addition, we have recently found that several of the membrane-active amphiphiles exhibit synergistic enhancement of antibiotic activity.

**RM_MWGL Regional Meeting 197**

## Transmembrane ion transporters made from various natural products and their analogs

*Soheila Bahmanjah[1], Ning Zhang[2], Soumya Rastogi[3], **Jeffery T. Davis**[4], jdavis@umd.edu. (1) Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States (2) Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States (3) Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States (4) Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States*

Synthetic ion channels and pores not only represent models of natural transmembrane ion channels, but also have potential applications in the areas of drug delivery, biosensors, antimicrobial agents and other molecular devices. In this presentation, synthetic derivatives of natural products that combine both “molecular recognition” and “membrane soluble” features are utilized for the development of synthetic ion channels. Progress in this area of using various natural products, such as nucleosides, bile acids, sphingolipids and prodigiosins as transmembrane transporters of ions and small molecules will be discussed.

**RM_MWGL Regional Meeting 198**

## Protein-binding molecular switches: Designs based on supramolecular and nucleic acid chemistry

***Janarthanan Jayawickramarajah**[1], jananj@tulane.edu, David C. Harris[2], Xiaoye Su[3].*
*(1) Department of Chemistry, Tulane University, New Orleans, LA 70118, United States*
*(2) Department of Chemistry, Tulane University, New Orleans, LA 70118, United States*
*(3) Department of Chemistry, Tulane University, New Orleans, LA 70118, United States*

This presentation will discuss our latest research efforts at the interface of supramolecular and nucleic acid chemistry. In particular, we detail designs and

mechanisms toward structure switching DNA-small molecule chimeras (DCs) that are capable of triggered protein binding in the presence of biologically relevant stimuli. Specifically, we discuss self-assembling DCs with dramatically enhanced matrix metalloproteinase-3 (MMP-3) inhibiting ability in the presence of a small endogenous molecule, adenosine triphosphate (ATP). Here, a single-strand to heterodimer transition is utilized to self-assemble bivalent protein inhibitors. The selectivity of these DCs to inhibit MMP-3 versus other members of the MMP family will also be detailed. In addition, we introduce a novel DC system that binds, in a monodentate fashion to beta-lactoglobulin, in response to specific oligonucleotide inputs. This DC design is based on (a) cyclodextrin derived host-guest interactions and (b) hairpin-to-duplex structural transitions. Within the framework of the abovementioned DC systems, we will present information on DC design and synthesis, stimuli-induced structure switching studies (followed by a combination of fluorescence, UV-vis, and circular dichrosim experiments), and stimuli-responsive protein-binding assays.

## RM_MWGL Regional Meeting 199

## Nor-seco-cucurbit[n]uril molecular containers

***Lyle Isaacs**, LIsaacs@umd.edu. Department of Chemistry & Biochemistry, University of Maryland, College Park, MD 20742, United States*

Interest in the cucurbit[n]uril family of molecular containers has accelerated dramatically in recent years due to the availability of a homologous series of hosts (CB[n], n = 5, 6, 7, 8). In this talk I will discuss our our recent progress in the synthesis of new CB[n] compounds that lack one or more bridging CH2-groups that we refer to as nor-seco-cucurbiturils (*ns*-CB[n]). At a minimum, the following aspects of *ns*-CB[n] chemistry will be discussed: 1) The isolation and structural elucidation of the double cavity bis-nor-seco-CB[10] host and its ability to undergo size dependent homotropic allosterism, 2) The isolation of structural elucidation of the first chiral member of the CB[n] family – namely (±)-bis-nor-seco-CB[6] and its diastereoselective recognition toward amino acids, amino alcohols, and even meso-diamines, 3) The implications of the isolation of nor-seco-CB[n] toward the mechanism of CB[n] formation, 4) The recognition behaviour of acyclic CB[n] congeners toward hydrophobic pharmaceutical agents for use in drug delivery.

## RM_MWGL Regional Meeting 200

## Assembly and binding properties of deep-cavity cavitands in water

***Bruce C. Gibb**, bgibb@uno.edu. Department of Chemistry, University of New Orleans, New Orleans, LA 70148, United States*

Recent studies into the binding and assembly of water-soluble deep-cavity cavitands will be presented. More specifically, the affinity of chaotropic anions for hydrophobic concavity, and how this pertains to the Hofmeister Effect, will be discussed.[1] Also

presented will be the assembly of different cavitands via the Hydrophobic Effect,[2] and how such systems can engender unusual properties such as kinetic resolutions via molecular protection.[3]

**References**

1. Gibb, C. L.; Gibb, B. C., Anion Binding to Hydrophobic Concavity Is Central to the Salting-in Effects of Hofmeister Chaotropes. *J. Am. Chem. Soc.* **2011**.

2. (a) Liu, S.; Gibb, B. C., High-definition self-assemblies driven by the hydrophobic effect: synthesis and properties of a supramolecular nanocapsule. *Chem. Commun.* **2008**, 3709-3716; (b) Gan, H.; Benjamin, C. J.; Gibb, B.C., Nonmonotonic Assembly of a Deep-Cavity Cavitand. *J. Am. Chem. Soc.* **2011,** *133*, 4770-4773.

3. Liu, S.; Gan, H.; Hermann, A. T.; Rick, S. W.; Gibb, B. C., Kinetic Resolution of Constitutional Isomers Controlled by Selective Protection inside a Supramolecular Nanocapsule. *Nature Chemistry* **2010,** *2*, 847-852.

**RM_MWGL Regional Meeting 201**

## New strategy of transforming pharmaceutical crystal forms

***Jerry L. Atwood***, *Atwoodj@missouri.edu, Jian Tian, Scott J. Dalgarno. Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States*

There is difficulty in retaining long-range order in purely molecular organic solids, due to weak intermolecular interactions such as van der Waals forces. Here, we show gas-induced transformations of the well-known pharmaceuticals clarithromycin and lansoprazole. For clarithromycin, the stimulus is capable of converting the kinetic solvate and guest-free crystal forms to the commercial thermodynamically stable polymorph with a huge saving in energy cost relative to industrially employed methods. The synthesis of the marketing form of lansoprazole involves a solvate that readily decomposes and that is stirred in water, filtered, and dried intensively. Our method readily circumvents such synthetic problems and transforms the sensitive solvate to the marketed drug substance with ease.

**RM_MWGL Regional Meeting 202**

## Encapsulation of cantharadin in gold nanoshells for use as a potential cancer therapeutic agent

*Caitlin M Klimavicz,* ***Lindsey Baxter****, lbaxter@millikin.edu, Paris W Barnes, George D Bennett. Department of Chemistry, Millikin University, Decatur, IL 62522, United States*

Cancer therapy has developed significantly but has not come far enough because some tumors still do not respond to conventional treatments. Cantharidin, a toxin secreted by blister beetles (family *Meloidae*), has been shown to cause apoptosis in cells. However, applications are limited because healthy cells are also damaged by the toxin. Encapsulation with nanoshells has the potential to make cantharidin a targeted weapon in the fight against cancer. Attempts were made to synthesize gold nanoshells starting with silver nanoparticles templates coated with cantharidin using a template engaged replacement reaction. Nano-capsule products were characterized using X-ray diffraction, UV-Vis spectroscopy and transmission electron microscopy. This research addresses the potential to encapsulate a powerful but indiscriminate toxin in a nanoshell delivery system.

### RM_MWGL Regional Meeting 203

## Investigating solution-phase architecture of copper-seamed *C*-heptadecylpyrogallol[4]arene nanocapsules

***Nathaniel J Schuster***[1], *Harshita Kumari*[1], *Steven R Kline*[2], *Charles L Barnes*[1], *Jerry L Atwood*[1]. *(1) Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65201, United States (2) NIST Center for Neutron Research, National Institute of Standards andTechnology, Gaithersburg, Maryland 20899, United States*

Small-angle neutron scattering (SANS) has been used to investigate the stability and geometry of copper-seamed *C*-heptadecylpyrogallol[4]arene ($PgC_{17}Cu$) hexamer in *o*-xylene. A novel structural feature is observed at chain length 17 in solution phase. The scattering data curve for the $PgC_{17}Cu$ hexamer at both 1% and 5% mass fractions in *o*-xylene fitted as a uniform ellipsoid rather than a uniform sphere. The geometric dimensions or the size of the $PgC_{17}Cu$ ellipsoid are 24 Å (radius) along the minor axis and 115 Å (radius) along the major axis. Given the long heptadecyl chain length for the hexamer, we expected to have a uniform spherical radius of ~24 Å; however, an approximate ratio of 1:5 between the radii lengths for the minor versus the major axis suggest interpenetration of the heptadecyl chains of adjacent hexamers that form a single ellipsoidal assembly.

### RM_MWGL Regional Meeting 204

## Self-assembled nanoparticles from non-lanthanide metal oleates for magnetic resonance imaging application

*Dipanjan Pan*, ***Ceren Yalaz***, *dipanjan@wustl.edu, Angana Senpan, Anne H Schmieder, Samuel A Wickline, Gregory M Lanza. Internal Medicine, Washington University in St Louis, St Louis, MO 63108, United States*

The recent finding of nephrogenic systemic fibrosis (NSF) has raised concern over the use of currently approved gadolinium based contrast agents and created a high, translational barrier for new agents to address. The goal of this research was to use non lanthanide-based contrast agents for molecular magnetic resonance imaging (MRI). We hypothesize that self-assembled nanoparticle from metal oleates of bivalent manganese

(Mn(II) and copper (Cu(II) can be used as a sensitive paramagnetic MRI contrast agents with high avidity for fibrin. “Soft” type metal oleate nanoparticles were designed and synthesized as vascularly-constrained (130 nm), phospholipids encapsulated nanoparticles and characterized for MR. The multiple copies (~100,000 metals/nanoparticle) of stable form of metals as oleate (thermally decomposed at 325°C) were homogeneously dispersed within a core matrix of polysorbate and encapsulated by phospholipids. This resulted in spherical nanoparticles of size ranges 130-150nm. A negative zeta potential value (-20- -35mV) confirms the successful phospholipids encapsulation. The particles were characterized thoroughly by TEM, AFM, SEM, EDX and uv-vis spectroscopy. Magnetic resonance images (3T) of the colloids in suspension and particles targeting to human fibrin plasma clots were acquired using T1-weighted gradient echo images. MR imaging of nanoparticles targeted to fibrin clot phantoms showed clear contrast enhancement, while control clots (non-targeted and targeted no metal) had no ($p<0.05$) contrast change. Fibrin-specific manganese and copper oleate nanoparticles represent novel, high relaxivity, non-gadolinium, molecular imaging agents that offers sensitive noninvasive MR imaging approach for diagnosis of rupturing atherosclerotic plaque.

## RM_MWGL Regional Meeting 205

## Synthesis and biological evaluation of irregular-shaped micelles prepared from amphiphilic di block co polymer

*Dipanjan Pan, **Benjamin Kim**, dipanjan@wustl.edu, Anne H Schmieder, Samuel A Wickline, Gregory M Lanza. Internal Medicine, Washington University in St Louis, St Louis, MO 63108, United States*

In this work, we report a facile route to synthesize polymeric micelles, which devoid of symmetry. Ultrasonic bath technique was used to synthesize irregular-shaped micelles from a co-self assembly of polystyrene-b-polyacrylic acid (PS-*b*-PAA) and surfactant polyoxyethylene (80) sorbitan monooleate at 50 °C. Dynamic light scattering measurements revealed the particle hydrodynamic diameter as 15-20nm with low electrophoretic values (-10mV). The particles were characterized TEM, AFM and SEM in anhydrous state. We observed the existence of a heterogeneous population of nanoparticles with irregular morpholgies in dilute aqueous solutions. The variance in hydrophobic chain length between the amphiphilic polymer and the polysorbate presumably determined the nature of the micelles. The initial ratio of concentration of block copolymer and polysorbate was 1:6. A water soluble near infrared dye (ADS832WS, $l_{ex}$=824 nm, $1.90 \times 10^5$ L mol$^{-1}$ cm$^{-1}$) was incorporated into the nanoparticles. The fluorescent particles were injected both intradermally and intravenously to mice and fluorescently imaged at time intervals of 0, 0.5h, 2h and 24h. After the whole body imaging, the organs were collected and optically imaged to obtain preliminary bio-distribution profiles of these particles. The details of the synthesis, characterization, dye incorporation and biological evaluation will be presented.

## RM_MWGL Regional Meeting 206

## Infrared studies of photochemistry of adsorbed species over semiconducting nanoparticles

***Joshua Kristalyn***[1], *jkristalyn@gus.pittstate.edu, Jeremy VanAuker*[1], *Sateeshprashad Bandaru*[1], *D. K. Paul*[1], *K. J. Klabunde*[2]. *(1) Department of Chemistry, Pittsburg State University, Pittsburg, Kansas 66762, United States (2) Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

The adsorption and decomposition mechanism of CO over $TiO_2$ and In/Ga-doped $TiO_2$ were investigated at low temperatures by using a specially designed infrared cell which can be used over a wide range of temperatures. Here, the photo-induced chemical reactions were compared with reactions without light. Possible mechanisms for decomposition will be discussed with reference to a detailed IR spectral analysis.

**RM_MWGL Regional Meeting 207**

## Low-temperature photoluminescence spectroscopy of single semiconductor quantum wires

***Robert A Burnett***[1], *raburnett3@gmail.com, Richard A Loomis*[1,2], *Virginia L Wayman*[1], *William E Buhro*[1,2], *John J Glennon*[1,2], *Yi-Hsin Liu*[1], *Benjamin S Hoener*[1]. *(1) Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States (2) Center of Materials Innovation, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

Semiconductor quantum wires (QWs) have important applications in the field of photovoltaic technology and opto-electronics. QWs are nanostructures that are sufficiently small in the radial dimension so that charge carriers in them behave as quantum-mechanical particles in a cylinder. As a result, QWs offer tunability of band-gap energies while still having length dimensions that are useful for efficient charge transport. We are recording the photoluminescence (PL) spectra of CdSe and CdTe QWs as a function of temperature to characterize the subtle variations in the energies along the QWs, and to investigate how more ideal QWs (without potential energy variations) can be synthesized. At room temperature, the PL spectra of single CdSe and CdTe QWs are broad, with Gaussian-shaped distributions. However, at lower temperatures, below 40 and 100 K, respectively, excitons are influenced by the subtle variations in the potential-energy landscapes along the QWs, and the PL often becomes localized at discrete energies and positions along the QWs. Nevertheless, The PL intensity observed at lower temperatures is significantly brighter than observed at room temperature. This would indicate a decrease in the rates for non-radiative recombination pathways. Based on the temperatures at which the localization is observed, the potential minima that localize the excitons are only 3 meV and 10 meV for CdSe and CdTe QWs.

**RM_MWGL Regional Meeting 208**

### Analytical strategies for monitoring and quantifying interactions of gold nanoparticles with thiolated molecules in solution

***Cassandra Burke**, maryuri.roca@lawrence.edu, Maryuri Roca. Department of Chemistry, Lawrence University, Appleton, Wisconsin 54911, United States*

Gold nanoparticles function uniquely at the cellular and molecular level making them attractive platforms for many uses including medical imaging, chemical sensing, and drug delivery. The interaction between gold nanoparticles and ligand molecules occurs at trace concentrations and is characterized by aggregation. Because of these factors, unique methods and technology are required to monitor nanoparticle-ligand interactions. This work shows that conductimetry is a good time-dependent alternative to localized surface plasmon resonance spectroscopy for monitoring nanoparticle-ligand interactions in the absence of aggregation, and that the influence of surface coverage on these interactions can be affected by aggregation.

**RM_MWGL Regional Meeting 209**

### Construction of functional group arrays on SAMs with the guanidium-sulfonate macromolecular synthon

***Gordon Ruan**, ruan.gordon@gmail.com, Matthew Hynes, Amir Munir, Joshua A Maurer. Department of Chemistry & Center for Materials Innovation, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

Self-assembled monolayers (SAMs) have been used to solve a broad spectrum of problems in interfacial chemistry. SAMs formed from alkanethiols on gold are some of the best characterized and most widely studied monolayers. Here, we utilize the guanidium-sulfonate macromolecular synthon to control the spatial location of functional groups within mixed monolayers. These SAMs contain functional group arrays that are formed on gold coated coverslips from ethanolic solution containing tetrabutylammonium 12-mercaptododecane sulfonic acid, 1-decanethiol, and guanidine hydrochloride. Ordered lattices are formed from the 12-mercaptododecane sulfonic acid and guanidine hydrochloride, while 1-decanethiol acts as the filler molecule. Scanning tunneling microscopy and Kelvin Probe Force Microscopy are used to characterize the functional group arrays. The strategy of using macromolecular synthons to produce functional group arrays on SAMs represents a unique approach to controlling surfaces on nanoscale.

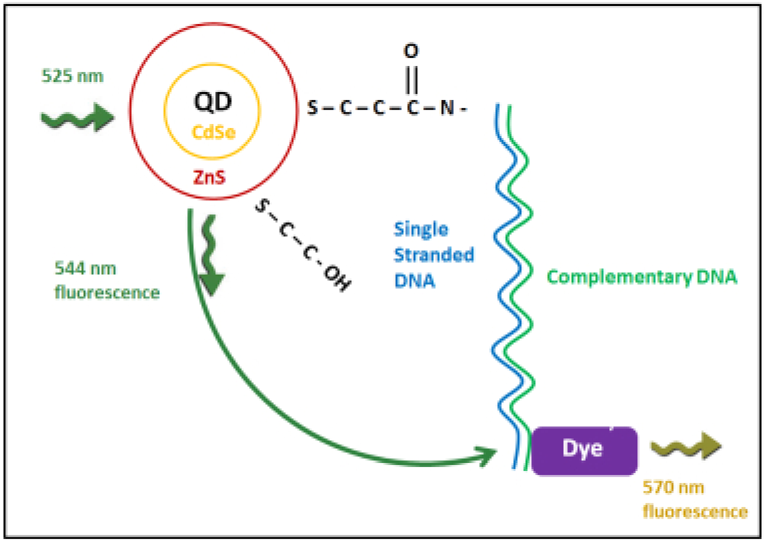
The tetrabutylammonium 12-mercaptododecane sulfonic acid monomer can also be paired with 12-mercaptododecane trimethylamine in a 1:1 ratio. When these two monomers are combined, they resist nonspecific protein binding. We have shown that by microcontact printing hexadecanethiol and backfilling with these two Zwitterionic monomers that we can successfully pattern fibronectin and confine cell growth.

**RM_MWGL Regional Meeting 210**

## Attachment of a Fluorescent Dye to Core-Shell Quantum Dots

***Kristen Luepke***, *kjluepke10@ole.augie.edu, Seth Adrian, Barrett Eichler.Chemistry Department, Augustana College, Sioux Falls, SD 57197-0001, United States*

Core-shell CdSe/ZnS quantum dots (QDs) were synthesized and found to have a fluorescence emission maximum wavelength at 535 nm. The QDs were functionalized with varying lengths of thioacids. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDCI) and N-hydroxysuccinimide (NHS) were used to attach amino-terminated DNA to the thioacids coating the QDs, forming an amide bond. Separate trials using a single strand of amino-terminated DNA with the dye, Cy3, and amino-terminated DNA complexed with its DNA-Cy3 complement were performed. Förster Resonance Energy Transfer (FRET) from the QDs to the Cy3 dye was studied using fluorescence spectroscopy.



## RM_MWGL Regional Meeting 211

## Does the reaction of thiol with surface cluster atoms of Au nanoparticles, prepared by the solvated metal atom dispersion (SMAD) method, yield RS-H or $RS^-$ interactions?

***John E Matthiesen***, *john.matthiesen@wartburg.edu, Kenneth J Klabunde, Deepa Jose, Yen-Ting Kuo. Department of Chemistry, Kansas State University, Manhattan, Kansas 66505, United States*

The solvated metal atom dispersion (SMAD) method was found to be a versatile route towards the synthesis of a variety of nanoparticles like Au, Ag, Pd. The gram scale synthesis of monodisperse 1-dodecanethiol capped Au colloids by the SMAD method and digestive ripening of these colloids to form two- and three-dimensional superlattices was a fascinating discovery. In this current study, we look into the details of interaction between thiols and surface cluster atoms of Au nanoparticles: RS-H or $RS^-$.

The studies lead to the discovery of an $RS^-$ interaction with the gold surface cluster atoms. Two different thiols were used for the synthesis of Au colloids by SMAD method: 1-dodecanethiol and 2-phenylethanethiol. Currently, work is being done on amines to determine if a $RN-H_2$ or RN-H interaction is present. Evidence of a $RS^-$ interaction was indicated by GC proof of $H_2$ evolution during thiol interactions with Au nanoparticles. Further characterization of these thiol-capped Au nanoparticles by FT-IR spectroscopy showed no S-H vibrational mode. This again corroborates the existence of a $RS^-$ species rather than R-SH when the thiol interacts with Au nanoparticles. The interaction between thiol and surface cluster atoms of Au nanoparticles is depicted in Figure 1.

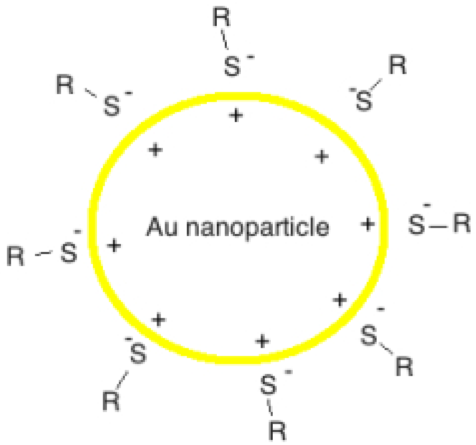


Figure 1. (R=dodecyl or phenylethyl), Additional evidence of the $RS^-$ species was shown by the comparison of the amount of $H_2$ evolved when the thiol comes into contact with Au nanoparticles and a TGA analysis.

**RM_MWGL Regional Meeting 212**

### Degradation of Rhodamine B Using $TiO_2$ Nanofibers Calcined in $O_2$ and $H_2$

***Jennifer Benoy***[1], *jennybenoy@hotmail.com, Emilly Obuya*[2]*.* *(1) Augustana College, United States (2) Binghamton University, United States*

When considering a disposal method for the industrial dyes polluting waterways, absorption and degradation using photocatalysis on the nanoscale level has proven to be a timely and economical choice. At the nanoscale level, the structural properties of the employed catalyst, $TiO_2$, can be manipulated through calcination to create a mixture of phases that will promote crystalline and electronic properties essential in optimizing the performance of the $TiO_2$. These properties, along with the already high surface area to volume ratio characteristic of nanoparticles and the heterogenous nature of the catalyst, are the main reasons $TiO_2$ nanofibers are excellent for photodegradation. Recently, exploration of calcination of the $TiO_2$ in a reductive environment ($H_2$) rather than an oxidative environment ($O_2$) has produced extremely encouraging and improved results for the removal of the industrial dye Rhodamine-B from water. The substantial improvement in removal of the dye stems from the creation of oxygen-ion vacancies during the calcination period that provide inviting sites for absorption and also the doping of the $TiO_2$ with carbon that occurs during calcination in $H_2$. Light conditions ranging from complete darkness to UV light to natural sunlight will be explored in order to study the behavior of the $TiO_2$ catalyst when degrading the Rhodamine-B dye in different environments.

**RM_MWGL Regional Meeting 213**

## Effects of two commercial nanoparticles on two unique environmental bacteria

***Kyle Ruedinger***[1], *crawfork@uwosh.edu, Kevin Crawford*[2]*, Sabrina Mueller-Spitz*[3]*.* *(1) Ripon College, Ripon, WI, United States (2) Department of Chemistry, University of Wisconsin Oshkosh, Oshkosh, WI 54901, United States (3) Department of Biology and Microbiology, University of Wisconsin Oshkosh, Oshkosh, WI 54901, United States*

Zinc oxide and silver metal nanoparticles are used in commercial products for their antimicrobial activity while zinc oxide nanoparticles are also used for UV protection in sunscreen. This study examined the impacts of these particles on two bacterial species, *Cupriavidus necator JMP134* and *Mycobacterium* strain RJGII-135. *C. necator JMP134* is a non-spore forming gram negative strain, which was chosen because it is highly resistant to toxic heavy metals. The *Mycobacterium* RGJII-135 is a gram positive bacteria that has unique abilities to utilize a variety of polycyclic aromatic hydrocarbons as a sole carbon source. The minimum inhibitory concentration (MIC) for each nanoparticle (Ag, and ZnO) in R2B media at full and diluted strength was determined. These bacteria were capable of tolerating up to 100 mg/L ZnO, as compared to tolerating 2 mg/L of Ag nanoparticles. After determining the MIC, the bacterial carbon utilization profiles were determined when exposed to two sub-lethal nanoparticle concentrations. Carbon utilization was reduced by 80% in the presence of Ag (0.25 mg/L) and 16% in the presence of ZnO (2.5 mg/L) for *M.* strain RJG-135. However, carbon utilization was not altered as significantly for *C. necator JMP134* in the presence of ZnO nanoparticles. There was a similar loss of carbon utilization by 42% in the

presence of Ag. Using atomic absorption analysis after centrifuging the cells with nanoparticles, we found that both *C. necator JMP134* and *M.* strain RJGII-135 took up zinc oxide nanoparticles in much higher levels than the silver nanoparticles. Based upon these results, carbon utilization is drastically altered in the presence of Ag nanoparticles, which indicates cell function can be altered significantly at sublethal exposures. The exact mechanism upon cell physiology is unknown, however the size of the Ag nanoparticles (~10nm) may play a role for this metal in gaining entry to the bacteria cell.

## RM_MWGL Regional Meeting 214

## Investigations into Metal-Seamed Dimeric Capsules of Aryl-Pyrogallol[4]arenes

***Sarah M. Hirner****, smhdhd@mail.missouri.edu, Drew A. Fowler, Andrew K. Maerz, Carol A. Deakyne, Jerry L. Atwood.Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, United States*

Pyrogallol[4]arenes, members of the calixarene family of macrocycles, are emerging as useful building blocks in supramolecular chemistry. These molecules demonstrate remarkable self-assembly, particularly the alkyl-subtituted pyrogallol[4]arenes. These molecules preferentially form an all-cis (rccc) “cone conformation” due to intramolecular hydrogen bonding and serve as building blocks for a number of supramolecular architectures, including dimeric and hexameric nanocasules. Examining the trends of functionalized pyrogallol[4]arenes has revealed that the aryl-pyrogallol[4]arenes preferentially form the rctt “chair conformation”, which is thermodynamically favored. Recrystallization of the reaction mixture in a solution of methanol revealed that the rccc conformer was present as a minor product. The formation of metal-seamed nanocapsules through the coordination of cone conformation pyrogallol[4]arenes to metal ions is also an active area of research. The use of aryl-substituted pyrogallol[4]arenes would be seemingly prohibitive due to the unfavorable chair conformation. However, recent results have shown that the formation of a zinc-seamed dimeric capsule has been reported for 4-propoxyphenylpyrogallol[4]arene. The geometry of the macrocycles tail groups in the dimeric capsules provides useful information in determining the conformer used in the synthesis. Recently the formation of dimeric capsules has been achieved for both the rctt and rccc conformers.

## RM_MWGL Regional Meeting 215

## Study of the relation of nanoporous gold structure to optical and electrochemical responses to protein binding

***Jay K. Bhattarai***[1]*, jkbxv3@umsl.edu, Yih Horng Tan*[1]*, Alexei V. Demchenko*[2]*, Keith J. Stine*[1]*.  (1) Department of Chemistry and Biochemistry, Center for Nanoscience, University of Missouri - Saint Louis, Saint Louis, MO 63121, United States  (2) Department of Chemistry and Biochemistry, University of Missouri - Saint Louis, Saint Louis, MO 63121, United States*

Nanoporous gold (NPG) has been widely used as a catalyst and a sensor support because of its high surface-area-to-volume-ratio, conductivity, biocompatibility and inertness. Herein we prove that thin films of NPG can show localized surface plasmon resonance (LSPR) and can be used to study different types of interactions of proteins and receptors. LSPR, a label free technique sensitive to change in local refractive index, can detect small amount of sample down to picomolar concentration and has the ability to determine association and dissociation rates of binding process directly and quickly on real time. For this purpose we prepared thin films of NPG electrochemically on the ultra-flat gold surface and characterized using SEM. Ultra-flat gold was prepared by sputtering gold on freshly cleaved mica and stripping the gold from mica using epoxy glue on a coverslip. We electrochemically prepared alloys of gold and silver on the surface of ultra-flat gold at deposition voltage of -1.0 V in 30%-70% ratio of 0.05M $KAu(CN)_2$ and $KAg(CN)_2$ solution. Then we removed silver from gold using a potential of +1.0 V (vs. Ag/AgCl) in 0.1 M $KNO_3$ solution. We found that under these conditions we can prepare thin films of nanoporous gold. To prove the LSPR property of thus prepared NPG, we used different organic solvents to change the refractive index around NPG surface. We observed red shift in wavelength of reflection minimum with increasing refractive index of solvent proving that NPG can show LSPR responses with changing refractive index of the interface. So, thus prepared LSPR sensitive NPG sensor can be used to study different types of proteins interactions such as the interaction between antigen - antibody and carbohydrate (mannose) - protein (concanavalin A).

**RM_MWGL Regional Meeting 216**

## Electroanalytical studies to determine the surface morphology of nanoporous gold

***Abeera Sharma***[1]*, asfyb@umsl.edu, Yih Horng Tan*[1]*, Jay Bhattarai*[1]*, Alexei V Demchenko*[2]*, Keith J Stine*[1]*, Binod Pandey*[1]*. (1) Department of Chemistry and Biochemistry and Center for Nanoscience, University Of Missouri - Saint Louis, St. Louis, Missouri 63121, United States (2) Department of Chemistry and Biochemistry, University of Missouri - Saint Louis, St. Louis, Missouri 63121, United States*

Nanoporous gold (NPG) has been at the forefront of scientific research in recent years. It is a brittle, random structure of gold with high surface area to volume ratio, resistance to corrosion as well as the ability to tailor the gold surface to be sensitive to various chemical and biological species. NPG is made by selective dissolution of silver from silver/gold alloys. The ability to control surface area is important in enhancing surface reactions and immobilizing molecules. The modification of the pore size of NPG by electrochemical cycling has been studied using scanning electron microscopy (SEM). The effect of varying the identity and concentration of the electrolyte has been investigated, as well as the number of cycles, and the potential limits and scan rates. The effect of changes in the electrolyte solutions on the electrochemically active surface area has been determined, and compared to the surface area of bare gold electrodes and with the surface area determined by gold oxide stripping. The technique of atomic force microscopy (AFM) is being used to examine the immobilization of proteins,

dendrimers, and carbohydrate bearing species within nanoporous gold (NPG) monoliths. AFM has been used for studying polyamidoamine (PAMAM) dendrimers immobilized on the surface of mica and ultra flat gold and NPG at varying concentrations. The PAMAM dendrimers are of known size and serve as a model system for the calibrating the imaging of immobilized proteins, such as the immunoglobulin G (IgG), in the form of a generic polyclonal anti-rabbit antibody. The PAMAM dendrimers may also prove of interest as linkers for the presentation of carbohydrate units on the NPG surfaces for recognition studies with lectins and other carbohydrate binding proteins.

**RM_MWGL Regional Meeting 217**

## Surface area and pore size characteristics of nanoporous gold subjected to thermal, mechanical, or chemical modifications studied using BET isotherm analysis, cyclic voltammetry, and scanning electron microscopy

***Jason A. Davis***[1], *jadpn7@mail.umsl.edu, Yih Horng Tan*[1,2], *Alexei V. Demchenko*[1], *Keith J. Stine*[1,2]. *(1) Department of Chemistry and Biochemistry, University of Missouri - Saint Louis, Saint Louis, MO 63121, United States (2) UM-St. Louis Center for Nanoscience, University of Missouri – Saint Louis, Saint Louis, MO 63121, United States*

Nanoporous gold, made by dealloying low carat gold alloys, is a relatively new nanomaterial finding application in microfabrication, as well as in gas storage, actuation, catalysis (both as a catalyst and a catalyst support), sensing, and nanoplasmonics. The use of nanoporous gold (np-Au) in nanoscience research has been a growing topic, due to its high surface-to-volume ratio, tunable porosity, conductivity, stability and biocompatibility. Here we use nitrogen adsorption/desorption isotherms to investigate the Brunauer, Emmett, and Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size distribution of physically modified, thermally annealed, and octadecanethiol functionalized np-Au monoliths. We present the full adsorption-desorption isotherms for $N_2$ gas on np-Au, and observe type IV isotherms and type H1 hysteresis loops. The evolution of the np-Au under various thermal annealing treatments was examined using scanning electron microscopy (SEM). The images of both the exterior and interior of the thermally annealed np-Au show that the porosity of all free standing np-Au structures decreases as the heat treatment temperature increases. The modification of the np-Au surface with a self-assembled monolayer of $C_{18}$-SH was found to reduce the strength of the interaction of nitrogen gas with the np-Au surface, as reflected by a decrease in the 'C' parameter of the BET equation. The inner surface of the np-Au electrode was electrochemically active and the surface areas of the monoliths could be estimated from the charge under the gold oxide stripping peak using sufficiently low scan rates. From cyclic voltammetry studies, we found that the surface area of the np-Au monoliths annealed at elevated temperatures followed the same trend with annealing temperature as found in the BET surface area study and SEM morphology characterization. The study highlights the ability to control free-standing nanoporous gold material with high surface area, and well-defined, tunable pore morphology.

**RM_MWGL Regional Meeting 218**

## The effect of 1-methyl, 2,3 dimethylimadzolium tetrafluoroborate BDMIMBF$_4$ ionic liquid as a mobile phase additive on the adsorption behavior of tryptophan

***Tarab Ahmad**, tj-ahmad@wiu.edu, Kishore Aluguvelli.Western Illinois University, Macomb, IL 61455, United States*

Room temperature ionic liquids have recently gained recognition as environmentally “green” solvents because of their extremely low volatility as compared to traditional volatile organic compounds (VOCs). RTILs posses other properties like low melting point (<100$^o$C), Chemical and thermal stability, No flammability, high ionic conductivity, high heat capacity, high thermal conductivity and wide electrochemical potential window. Because of their favorable properties they are currently investigated in analytical chemistry application. ILs have been explored as functional stationary phases for gas chromatography (GC), additives for high-pressure liquid chromatography (HPLC), and electrolytes for capillary electrophoresis (CE). In this study the ionic liquid 1-butyl, 2, 3- dimethylimadzolium tetraflouroborate (BDMIMBF$_4$) is investigated as a mobile phase additive for the elution of tryptophan using reversed phase liquid chromatography. The adsorption isotherms were determined by the frontal analysis method and by the inverse method. The adsorption data are fitted to a Langmuir model. An excellent agreement was found between the experimental overloaded band profiles and t the calculated profiles.

**RM_MWGL Regional Meeting 219**

## Investigation of the effect of 1-butyl -3-methyl immidazolium terafluoroborate ionic liquid on the separation of basic drugs

***Tarab Ahmad**, tj-ahmad@wiu.edu, Kishore Aluguvelli, Tariq Ahmad, Sahar Salam. Department of Chemistry, Western Illinois University, Macomb, IL 61455, United States*

Room temperature ionic liquids (RTIL) are good solvents for both inorganic and organic materials, they are non-volatile, nonflammable, thermally stable, and recyclable solvents and they have some particular properties in chemical reactions etc., currently they are being investigated widely as “green chemistry” solvents. Ionic liquids are used in reversed phase high performance liquid chromatography RP-HPLC as blockers for silanol activity [1] and as mobile phase additives [2-5] and as a replacement of organic modifiers[6]. In HPLC the addition of ionic liquids has great effects on the separation of the compounds. They decrease the band tailing, reduce band broadening and improve resolution. The objective of this work is to study the effect of 1-butyl 3-methyl imidazolium tetrafluoroborate BMIMBF$_4$ as a mobile phase additive on the retention and separation of Nortriptyline and Amitriptyline on reversed phase liquid chromatography. Different concentrations of BMIMBF4 and different percentages of acetonitrile were used in the mobile phase. The effect of these experimental conditions on the retention

factors and the asymmetry factors of the individual compounds and the resolution of mixtures of these compounds is investigated in this study.

## RM_MWGL Regional Meeting 220

## Dye-loaded porous polymer nanocapsules as new optical sensor platform

***Mariya D Kim**[1,2], mashakim2003@yahoo.com, Sergey A Dergunov[1,2], Ernö Lindner[2], Eugene Pinkhassik[1,2]. (1) Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, United States (2) Department of Chemistry, The University of Memphis, Memphis, TN 38152, United States*

Liposomes-templated polymer nanocapsules, prepared by directed assembly within bilayers scaffolds, can retain medium-sized molecules such as pH-sensitive indicator dyes, catalysts, imaging agents and provide uninhibited access for small molecules to the capsule interior. Entrapment of small sized molecules in porous nanocapsules can lead to new functional nanocomposite materials, such as nanoreactors, sensors, or imaging systems. Chemical sensors are commonly classified as surface or bulk sensors to emphasize the importance the signal generation process and stress the relevance of the analytical information provided by the different sensors. Here we present on a novel optical sensing platform that utilizes dye loaded, porous nanocapsules embedded in a polymer matrix for pH sensing. It was shown that free and an encapsulated dye changes its color at the same rate upon pH changes in the solution. When low density hydrogels are doped with dye loaded nanocapsules the rate of the color change of the gel is only controlled by the gel thickness and the diffusion coefficients of hydronium ions in the gel. The diffusion coefficient of the 100 nm diameter nanocapsules in the gel is negligible compared to free dye molecules, i.e., no leaching from the gel could be detected. In addition, the encapsulation of the dye into the nanocapsules significantly improved the stability of the dye against photobleaching.

## RM_MWGL Regional Meeting 221

## Surface chemistry studies of $CO_2$ with the MgO(100) surface

***Juan Wang**[1], jwkw6@mail.missouri.edu, C Michael Greenlief[1], Thomas R Marrero[2]. (1) Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States (2) Department of Chemical Engineering, University of Missouri-Columbia, Columbia, MO 65211, United States*

There is significant interest in methods to aid in the removal of metabolic carbon dioxide from confined spaces. The methods range from sequestration to catalytic transformations. In sequestration, $CO_2$ is collected from emission sources, and may be stored in a variety of materials including metal-organic frameworks. Catalytic research often involves the transformation of $CO_2$ to another hydrocarbon such as methane. The majority of these latter studies focus on the use of photocatalysis for the conversion of $CO_2$. An alternative method, discussed in this presentation, is to examine the surface

chemistry for the adsorption and reaction of carbon dioxide with magnesium oxide surfaces. We are also interested in gaining a better understanding of the refractory nature of $CO_2$. X-ray photoelectron and Auger electron spectroscopies are used to probe the MgO after exposure to $CO_2$ at surface temperatures between 475° and 650°C. Results of these studies will be presented along with possible surface reaction mechanisms.

## RM_MWGL Regional Meeting 222

## Analysis of variance components in spectroscopic imaging data

***Jin Tae Kwak***[1,2], *kwak5@illinois.edu, Rohith Reddy*[2,3], *Saurabh Sinha*[1], *Rohit Bhargava*[2,3,4,5,6]. *(1) Department of Computer Science, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (2) University of Illinois at Urbana-Champaign, Beckman Institute for Advanced Science and Technology, Urbana, IL 61801, United States (3) Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (4) Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (5) University of Illinois at Urbana-Champaign, Micro and Nanotechnology Laboratory, Urbana, IL 61801, United States (6) University of Illinois at Urbana-Champaign, University of Illinois Cancer Center, Urbana, IL 61801, United States*

Fourier transform infrared (FT-IR) spectroscopic imaging provides simultaneous chemical and structural information from heterogeneous material of interests and is being used increasingly for biomedical studies. The analysis of cell types and disease using FT-IR spectroscopic imaging is promising but requires an appreciation of the limits of performance for the technology to be developed better by researchers and to be accepted by practitioners. One factor limiting performance is the variance in data arising from biological diversity, measurement noise or some other source of error. In fact, from every aspect of the technology, the variation could arise and have substantial and unexpected effects on the analysis. Here we identify the various sources of variation by first employing a high throughout sampling platform of tissue microarrays (TMAs) to record a sufficiently large and diverse dataset. Next, a comprehensive analysis of variance (ANOVA) model is employed to analyze the data. Estimating the portions of explained variation, we quantify the primary sources of variation, find the most discriminating spectral metrics, and recognize the aspects of the technology to improve. It is also recognized that there exist a considerable biological variation within a tissue and cell as well as variations among different TMAs for several spectral metrics. Therefore, this study provides a framework for the development of protocols for clinical translation and provides guidelines to design statistically valid studies in the spectroscopic analysis of tissue.

## RM_MWGL Regional Meeting 223

## Improving the compatibility of macrocyclic polyamide compounds within ion-selective membranes for fluoride analysis

***Qiyang Zhang***[1]*, Jeremy T. Mitchell-Koch*[1]*, Kristin Bowman-James*[2]*. (1) Department of Physical Sciences, Emporia State University, Emporia, Kansas 66801, United States (2) Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States*

The ability of a compound to function as a selective ionophore within a polymer membrane electrode requires solubility within the matrix. Macrocyclic polyamide compounds have been shown to bind fluoride in both organic solution and the solid state. Our initial studies incorporating these compounds into ion-selective membranes have shown excellent selectivity for fluoride. However, as a result of limited ionophore solubility, these membranes suffer from poor response characteristics (slope, detection limits and electrode lifetime). Reported in this poster are a variety of approaches to address this compatibility/solubility issue. In particular, membrane composition, and ionophore loading and modification are addressed.

### RM_MWGL Regional Meeting 224

## Method for testing antibiotic residues in milk, fish, and distiller grain

***Jessica Baldwin****, jkbaldwin8246@jacks.sdstate.edu. South Dakota State Univeristy, United States*

Finding efficient methods for testing multiple classes of antibiotics residues in food and feeds are on the rise. There is also a continuing demand to test larger number of compounds in shorter times and produce less waste. In this paper, one method is used to test six different types of antibiotics in fish, milk, and distiller grain using LC/MS/MS. It has shown to be an efficient and reliable method for the detection of antibiotic residues in different compounds. The LC/MS/MS successfully detected all of the antibiotics tested in different products.

### RM_MWGL Regional Meeting 225

## Transmission Raman tomography for determining the position and size of targets buried in light scattering media

***Matthew R Kole****, matthew.kole@gmail.com, Matthew V Schulmerich, Matthew K Gelber, Rohit Bhargava. Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, Il 61801, United States*

The use of Raman spectroscopy to provide label-free chemical contrast of analytes buried below light scattering media has a wide variety of biomedical related applications ranging from disease diagnosis to monitoring drug delivery. Developing and validating methods for obtaining the size, shape, and position of buried targets is a first step towards realizing this potential. In this research, we present experimental results and theoretical considerations from a series of transmission Raman tomography

measurements on targets (Teflon spheres) buried inside of Intralipid-based tissue phantoms along with the resulting two-dimensional image reconstructions. Measurements were collected with a fiber-based Raman instrument using varying source-detector collection angles. We compare two forward-modeling methods, radiative transport calculation (Nirfast, an open-source diffuse optical tomography modeling package)[1] and Monte Carlo simulation (written in-house), for the modeling of light fluence throughout the phantom. Reconstruction of the size and position of buried targets can be employed without the use of spatial priors via an iterative modified-Tikhonov minimization algorithm, and these results are validated against computed tomography (CT) images. We present the differences between the two forward algorithms and highlight the important advantages and disadvantages of each approach.

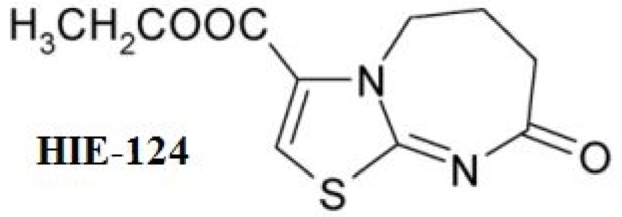
(1) Dehghani, H.; Eames, M.E.; Yalavarthy, P.K.; Davis, S.C.; Srinivasan, S.; Carpenter, C.M.; Pogue, B.W.; Paulsen, K.D. *Commun. Numer. Meth. Engng.* **2008**, *25* (6), 711-732.

**RM_MWGL Regional Meeting 226**

## Application of three chromatographic techniques in the bioanalysis of a new thiazolodiazepin ultra-short-acting hypnotic

***Ehab A Abourashed***[1]*, eabouras@csu.edu, Mohamed Hefnawy*[2]*, Hussein I El-Subbagh*[3]*. (1) Department of Pharmaceutical Sciences, Chicago State University, College of Pharmacy, Chicago, IL 60628, United States (2) Department of Pharmaceutical Chemistry, King Saud University, College of Pharmacy, Riyadh, Saudi Arabia (3) Department of Pharmaceutical Chemistry, Future University, Faculty of Pharmaceutical Sciences & Pharmaceutical Industries, Cairo, Egypt*

Ethyl-8-oxo-5,6,7,8-tetrahydrothiazolo[3,2-a][1,3]diazepin-3-carboxylate (HIE-124, **1**) is a potent member of a new class of synthetic ultra-short-acting hypnotics. As part of the quality control and pharmacokinetic profiling of **1**, three chromatographic methods were developed, validated and applied for its determination in mouse serum and spiked human plasma. The developed methods included high-performance liquid chromatography (HPLC), high-performance thin-layer chromatography (HPTLC) and microemulsion electrokinetic capillary chromatography (MEEKC). All methods utilized an internal standard and UV detection. Validation parameters included accuracy, precision, limits of detection and quantitation, selectivity, and sensitivity. A comparison of the developed methods and their performances is presented. Also presented is the application of the HPLC method to determine 8-oxo-5,6,7,8-tetrahydrothiazolo[3,2-a][1,3]diazepin-3-carboxylic acid (**2**), the major metabolite of **1**, in mouse serum.



**HIE-124**

## RM_MWGL Regional Meeting 227

### Determination of DNA base pairs by surface-enhanced Raman scattering spectroscopy

***Michael W Stutelberg**, michael.stutelberg@sdstate.edu, Brian A Logue. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, United States*

Surface-enhanced Raman scattering (SERS) is a spectroscopic technique with the ability to detect trace concentrations of unlabeled molecules by utilizing roughened gold or silver surfaces (substrates) to enhance the Raman signal of adsorbed molecules. Using this technique, complimentary strands of ssDNA bound to silver surfaces have been used to detect strands of target DNA, and may allow for detection of single mononucleotides as evidence of life. In this study, SERS was used to detect adenine mononucleotides using a 12-base pair ssDNA probe comprised exclusively of thymine bases. The ssDNA was bound covalently to a silver substrate using a thiol linker. The silver foil was then exposed to an adenine solution, and SERS signals were observed for both thymine DNA and adenine after extensive washing. The use of this proposed method to detect mononucleotides, offers the ability to detect single adenine bases and may be applicable for the verification of life in extreme environments.

## RM_MWGL Regional Meeting 228

### Effect of sodium hydroxide and sodium pyrophosphate on the extraction of humic acid and humin from different source materials

***Cyndey Johnson-Edler**, cyndey.johnson-edler@sdstate.edu, Gabriela Chilom, James Rice. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, United States*

Humic acid and humin comprise composites of varying chemical composition; a non-amphiphilic fraction, a lipid fraction, and an amphiphilic fraction. The distribution and chemical characteristics of these composites after extraction with two different solutions is examined. Two aqueous extraction systems, an alkaline solution (0.5M NaOH) and neutral salt solution (0.1M $Na_4P_2O_7$) were used to extract humic acid and humin from the IHSS Leonardite and the Poinsett silt loam mineral soil. The predominant fraction,

humic acid for Leonardite and humin for Poinsett, remained the same regardless of the solvent used for extraction. However, the neutral salt extracted less humic acid in the case of Leonardite and more humic acid in the case of the Poinsett soil. Distribution and nature of humic acid and humin, as well as, their composites, the non-amphiphilic fraction, an amphiphilic fraction and the lipid fraction were characterized by mass balance, $^{13}C$ DPMAS solid state NMR, solution surface tension, and thermal analysis. The total of humic acid extracted from Poinsett soil increased along with its aromatic character when extracted with the neutral salt. Conversely, extraction with the neutral salt increased the amount of humin extracted from Leonardite, as well as, its aliphatic character. The distribution of the composites of humic acid and humin, and surface tension measurements appeared to be unaffected by the type of solution used for extraction for both materials studied. The ramifications of these findings on the understanding of the structure of humic materials are discussed.

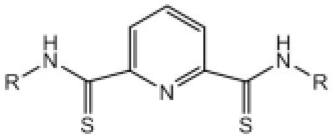
---

**RM_MWGL Regional Meeting 229**

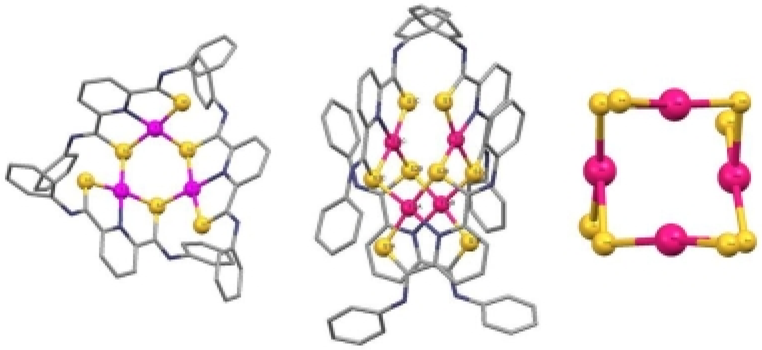
## Solvent dependent cluster formation of thioamide-based Pd and Pt pincer complexes

***Rowshan A. Begum***, *rowshan@ku.edu, Qi-Qiang Wang, Victor W. Day, Kristin Bowman-James. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

Thioamide-based transition metal clusters are not very common. While exploring Pt and Pd-based pincer complexes of thioamide ligands and their catalytic acitivities for past couple of years, we came across simple methods to obtain molecular clusters. A trimeric platinum complex, and a series of tetrameric palladium complexes, were prepared with SNS pincer ligands (**L**) (where R = phenyl, substituted phenyl, and naphthalene groups) and will be presented here. All of these oligomeric complexes were isolated by simple recrystallization of the monomeric complexes from different solvents, either in presence or in absence of a base. For example, the SNS ligand (where R = Ph) forms a trimer when its Pt-complex was re-crystallized from $CHCl_3$ in presence of $Et_3N$. A series of tetrameric Pd-complexes were obtained (R = Ph, Ph-$CH_3$, Ph-$NO_2$, naphthalene) when the orange colored powdered products obtained from the reactions of ligand and $Pd(PhCN)_2Cl_2$ were recrystallized from DMF in contrast to recrystallization from DMSO (that afforded only monomeric products).



L



## RM_MWGL Regional Meeting 230

### Free energy correlations of platinum(II) biphenyl complexes containing 2,2'-bipyridine derivatives

*Wei Huang[1], D. Paul Rillema[1], Khamis Siam[2], **Arvin John Cruz**[2], Derek Base[2], ajfiloteo.cruz@gmail.com.  (1) Department of Chemistry, Wichita State University, Wichita, KS 67260, United States  (2) Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, United States*

Five platinum(II) biphenyl complexes containing 2,2'-bipyridine derivatives were synthesized and their physical and photophysical properties were examined. X-Ray crystal structures were obtained for three of the complexes. Structures obtained by density functional theory were in agreement with the parameters obtained by x-ray diffraction. Electron density of the HOMO was located on the metal center and the biphenyl ligand; for the LUMO it was located primarily on the bipyridine ligand. The results of time dependent density functional theory calculations were in agreement with a MLCT low energy electronic transition assignment. The optical and emission energies correlated with Hammett sigma functions giving rise to excellent free energy correlations for the series of complexes.

## RM_MWGL Regional Meeting 231

### Developing oligourea-based anion ligands inspired by metal coordination

***Chuandong Jia***[1]*, jiacd@ku.edu, Shaoguang Li*[2]*, Biao Wu*[3]*, Kristin Bowman-James*[1]*. (1) Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States (2) State Key Laboratory for Oxo Synthesis & Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu 730000, China (3) College of Chemistry and Materials Science, Northwest University, Xi'an, Shaanxi 710069, China*

By mimicking the scaffolds of well-developed metal ligands, and with urea as the coordination vector, a series of highly selective ligands for sulfate and phosphate have been developed. What is amazing is that the similarity in the backbone is very successful in inducing binding properties similar to those observed for transition-metal complexes, including the host (ligand)/guest (metal or anion) binding mode, reversible binding and release of the guest, and guest templated formation of helices. These results deepen our belief of the fact that the newly emerged anion coordination is actually a mirror world of the extensively studied transition-metal coordination, and the two subjects together should compose a complete subject of *Coordination Chemistry*.

**RM_MWGL Regional Meeting 232**

## Diffusion of tin from TEC-8 conductive glass into mesoporous titanium dioxide in dye sensitized solar cells

***Julienne Cabell****, julienne_kabre@yahoo.fr, Robert J. LeSuer. Department of Chemistry and Physics, Chicago State University, United States*

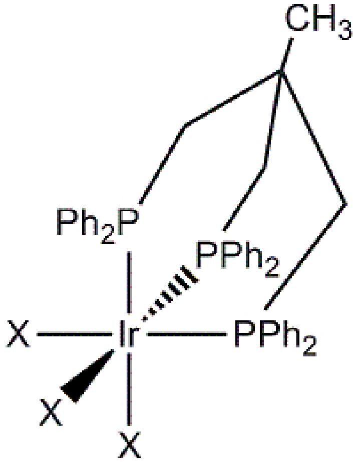
The photoanode of a dye sensitized solar cell is typically a mesoporous titanium dioxide thin film adhered to a conductive glass plate. In the case of TEC-8 glass, an approximately 500 nm film of tin oxide provides the conductivity of this substrate. During the calcining step of photoanode fabrication, tin diffuses into the titanium dioxide layer. Scanning Electron Microscopy and Electron Dispersion Microscopy are used to analyze quantitatively the diffusion of tin through the photoanode. At temperatures (400 to 600 °C) and times (30 to 90 min) typically employed in the calcinations of titanium dioxide layers for dye sensitized solar cells, tin is observed to diffuse through several micrometers of the photoanode. The transport of tin is reasonably described using Fick's Law of Diffusion through a semi-infinite medium with a fixed tin concentration at the interface. Numerical modeling allows for extraction of mass transport parameters that will be important in assessing the degree to which tin diffusion influences the performance of dye sensitized solar cells.

**RM_MWGL Regional Meeting 233**

## (Triphos)Ir(III)-Complexes for photo Chemistry Study

***Andreas Ross****, arf95@mail.missouri.edu, Paul R. Sharp, Charles Barnes. Chemistry Department, University of Missouri, Columbia, MO 65211-7600, United States*

Nowadays, a great challenge is the storage of solar energy, in order to facilitate it in everyday life.[1]The smallest unit in which the solar energy may be stored is in the chemical bond.[2] There are many ways for solar energy storage investigated, from water splitting to lithium ion batteries. One foreseeable approach is the HX (X = halide) splitting (2 electron transfer). For this approach it is required to find the right catalyst to eliminate the halogen. The reductive elimination of the halogen occurs on a late transition metal center, therefore iridium is attractive for our studies. The triphos ligand ($CH_3C(CH_2PPh_2)_3$) was chosen to avoid isomerization of the iridium(III) complexes to *fac* and *mer* configuration.[3] The products evolved by illuminate sun light at the complexes (triphos)$IrCl_3$ and (triphos)$IrBr_3$ are under investigation.



(1) Thomas S. Teets and Daniel G. Nocera* *J. Am. Chem. Soc.*, **2009**, *131* (21), 7411

(2) Daniel G. Nocera, *Inorg. Chem.* **2009**, *48*, 10001

(3)Brookes P.R., Masters C., and Shaw B. L., *J. Chem. Soc. (A)*, **1971**, 3756

**RM_MWGL Regional Meeting 234**

## Elucidating the mechanism of electrocatalytic dioxygen reduction with copper complexes

***Matthew A Thorseth***, *thor0411@gmail.com, Christopher S Letko, Thomas B Rauchfuss, Andrew A Gewirth. Department of Chemistry, University of Illinois at Urbana/Champaign, Urbana, Illinois 61801, United States*

The reduction of dioxygen in fuel cells remains a large hurdle to the widespread implementation of polymer electrolyte membrane fuel cells. Current technologies rely on Pt based catalysts that are expensive and also exhibit an overpotenial of 300 mV for the oxygen reduction reaction (ORR).[1] In nature, the copper based enzyme laccase reduces dioxygen to water with less than 50 mV of overpotential.[2] By using copper complexes to model the reactivity of laccase, we hope to create an electrocatalyst for the ORR with activity comparable to laccase.

Our research has examined a wide variety of Cu complexes. The best activity to date is found in a complex of $CuSO_4$ with 3,5-dimethylamino-1,2,4-triazole supported on carbon exhibiting an overpotential of approximately 400 mV at pH 13.[3] Additionally, we discovered that $[CuTPA](ClO_4)_2$ (TPA=tris-(2-ethylpyridyl)amine) has the lowest overpotential at pH 1 of 700 mV.[4] We examined a large number of derivatives of these complexes in order to understand the underlying mechanism of the electrocatalysis.

The binding mode of dioxygen to the copper center appears to be the most critical consideration. Cu complexes that bind oxygen side-on in both the peroxo and oxo states have larger overpotenials than those complexes that bind end-on. Addition of hydrogen bonding groups near the open coordination site have little effect on the overpotential for complexes that bind $O_2$ end-on but play a large role in side-on binding complexes. Suprisingly, the $Cu^{I/II}$ potential plays little role in the overpotential for the ORR, suggesting that the rate determining step is not reduction of $Cu^{II}$ to $Cu^{I}$.

## References

(1) Gasteiger, H.A. *Appl. Catal., B* **2005**, *56*, 9.
(2) Mano, N.;Soukharev, V.; Heller, A. *J. Phys. Chem.B* **2006**, *110*, 11180.
(3) Thorum, M. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 165.
(4) Thorseth, M. A. *Inorg. Chem.* **2011**, *50*, 6158.

## RM_MWGL Regional Meeting 235

## Rhenium complexes as photocatalysts in the reduction of $CO_2$ to CO

***Eric Oweggi****, eooweggi@wichita.edu, Venugopal Komreddy, D. Paul Rillema.Department of Chemistry, Wichita State University, Wichita, KS 67260, United States*

$Re(bpy)(CO)_3X$ (X = Cl, NCS) and $Re(dcbpy)(CO)_3X$ (X = Cl, NCS) were synthesized, characterized by NMR and IR techniques and investigated for their capacity to reduce $CO_2$ to CO and other reduction derivatives. The complexes were irradiated at $\lambda > 360$ nm in a $CO_2$ saturated DMF: TEOA solution in a Pyrex tube capped with a serum cap. The CO produced in the reaction is tracked using a gas chromatograph fitted with a molecular sieves column. $Re(dcbpy)(CO)_3X$ (X = Cl, NCS) was then attached to $TiO_2$ and its catalytic $CO_2$ reduction was examined as outlined above in solution.

## RM_MWGL Regional Meeting 236

## Preparation, characterization and photocurrent efficiency of Re(I) and Ru(II) bipyrazine complexes

***Venugopal Komreddy**, vxkomreddy@wichita.edu, Navaneetha Subbaiyan, Eric Oweggi, D. Paul Rillema, Cameron Wilkinson. Department of Chemistry, Wichita State University, Wichita, KS 67260, United States*

A series of Re(I) complexes of the form ReL$(CO)_3$Cl, where L = 2,2'-bipyrazine (bpz), 5,5'-dimethyl-2,2'-bipyrazine (dmbpz), 5,5'-dimethoxy-2,2'-bipyrazine (dimethoxybpz) and 5,5'-dicarboxyl-2,2'-bipyrazine (dcbpz), have been synthesized and their physical and photophysical properties examined. The dcbpz derivative was obtained by base hydrolysis at room temperature of directly coordinated dimethoxybpz and the progress of the reaction was followed by $^1$H NMR. The carboxyl groups withdraw electron density from the metal center shifting electronic absorptions to the red. Weak emission from the complexes is also observed. Attachment of the complexes to $TiO_2$ as a dye in photoelectrochemical cells for energy conversion applications leads to the observation of photocurrent.

**RM_MWGL Regional Meeting 237**

## Effect of graphene nanofillers on flexible molded polyurethane foam properties

***Nikola Bilic**, nbilic@pittstate.edu, Ivan Javni, Zoran S. Petrovic. Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS 66762, United States*

One of the unresolved issues during burning of flexible polyurethane foams is fire spreading by dripping. Different nano and macro fibrous fillers are effective in preventing dripping but the most effective are carbon nanotubes. A shortcoming of the carbon nanotubes is their high price. We have attempted to solve this rheological problem by incorporating graphene nanofiler. Incorporating fillers in foams affects all their properties. We studied the effect of concentration of graphene on the foaming process, mechanical, thermal and burning properties of polyurethane foams based on a polypropyleneoxide triol of molecular weight 4800, toluene diisocyanate and water as the blowing agent. Graphene is an expandable graphite obtained by processing natural graphite ore.

Two types of graphenes were tested in the concentration range 0-6%. The differences between used graphenes were in the expansion volume at temperatures higher than 200 $^o$C. The expansion volume affects the flame retardant properties during foam burning.

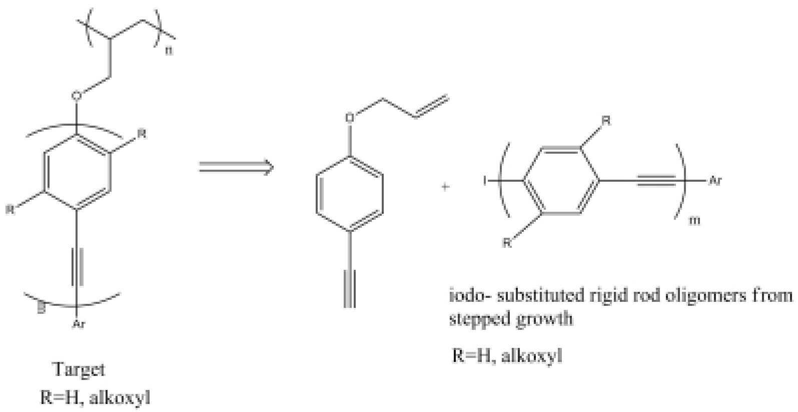
All foam samples had good morphology, open cell content over 98% and density around 30 kg/m$^3$. Graphenes improved compression strength but decreased tensile and tear strength. At concentrations of 2% or higher, dripping during the foam burning was suppressed completely. Both graphenes affected the burning in the same way.

**RM_MWGL Regional Meeting 238**

## Synthesis of comb-like polymers with rigid-rod side chains

***Xinyan Bai***[1]*, xb967@mail.umkc.edu, Xueyi Chen*[2]*, Jerry Dias*[1]*, Tom Sandreczki*[1]*. (1) Chemistry, University of Missouri-Kansas City, Kansas City, MO 64112, United States (2) Biochemistry& Molecular Biology, University of Kansas-Medical Center, Kansas City, KS 66160, United States*

Comb-like fluorescent polymers have been successfully synthesized by polymerization of various 1-(allyloxy)-4-*oligo*-phenylethynylenes. Prior to polymerization, the key monomers, 1-(allyloxy)-4-ethynylbenzenes, were synthesized by reacting 4-iodo-phenol with allyl bromide, followed by palladium-catalyzed coupling with ethynyltrimethylsilane and desilylation by TBAF. The iodo-substituted rigid-rod oligomers were synthesized by step-growth via the Sonogashira coupling reaction. The polymerizations were conducted using anionic and ATRP polymerization methods. The resulting polymers were characterized by UV-Fluorescence, GPC, and NMR.



**RM_MWGL Regional Meeting 239**

## Foam from cashew nut shell liquid

***DooPyo Hong**, dhong@pittstate.eud, Mihail Ionescu, Ivan Javni, Zoran S Petrovic. Pittsburg State University, Kansas Polymer Research Center, Pittsburg, KS 66762, United States*

Cashew nut shell liquid (CNSL) is an excellent renewable raw material having phenyl groups in the structure. It has unsaturated hydrocarbon chains which can be functionalized and applied in various polymers. Since it is not a triglyceride it has no ester bonds, which means it is chemically very resistant especially to hydrolysis. Because it has both aromatic and aliphatic structures in the molecule, polyols from CNLS would be very good for rigid polyurethane foam application. Polyols from CNSL with primary hydroxyl group were synthesized by hydroformylation and ethoxylation, and used for rigid polyurethane foams. Polyurethane foam with density 30 kg/m$^3$ was

prepared with polymeric methylene diphenyl isocyanate. It had excellent mechanical properties: compressive strength of 150 KPa and tangent modulus of 2,644 KPa.

## RM_MWGL Regional Meeting 240

### Dynamic solid phase microextraction sampling for monoterpenes in the present of ozone

***Weiwei Hua***, *WEIWEI@SIU.EDU, Kara E Huff Hartz. Department of Chemistry and Biocchemistry, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

Particulate matter that forms from the reaction of ozone and monoterpenes ($C_{10}H_{16}$) is a source of indoor environmental pollution and exhibits deleterious health effects. A reliable analytical method to determine the concentrations of gas phase monoterpenes in a simulated indoor environment is needed. Sampling via solid phase microextraction (SPME) coupled to determination by gas chromatography/mass spectrometry is a fast, reliable, and environmentally friendly method. This method has been applied in SIUC environmental smog chamber to determine the concentrations of limonene and 3-carene at the ppb level. First, the gas phase monoterpenes enter the smog chamber via two clean air lines which connect to the chamber. Second, the sample of air is pumped through the dynamic sampling port while the SPME fiber is exposed to the sample air. After 2 minutes of sampling time, the SPME fiber is inserted into the injection port of gas chromatography/ mass spectrometry immediately for thermal desorption and analysis. Typically, relative standard deviations lower than 15% were achieved with a 2 min sampling time when the range of ozone concentration present in the chamber is from 0 ppb to 20 ppb. The effect of sampling time, flow rate, and ozone concentration can be the future work for this method.

## RM_MWGL Regional Meeting 241

### Plastic debris: Is Lake Superior invaded by synthetic polymers?

***Lorena M Rios***, *lriosmen@uwsuper.edu. Natural Sciences Department, University of Wisconsin Superior, Superior, Wisconsin 54880, United States*

Plastic materials are ubiquitous pollutants on beaches around the world. The increase of floating plastic in oceanic waters is under study but still not well understood. The production of cheap plastic items is massive. The high resistance to degradation has made these materials one of the most persistent contaminants on the planet. Lake Superior now has visible plastic debris on remote and otherwise pristine beaches and shorelines. The debris creates not just a visual impact but also brings significant risks to the freshwater environment because of the known potential to adsorb persistent organic pollutants that can harm aquatic organisms. This is the first study that provides basic assessment of the pollution by plastic debris on beaches and shorelines around Lake Superior. The objective of this study was to ascertain the presence and types of plastic

materials on beaches around Lake Superior with significant possibility to be a source of plastic fragments in the water of Lake Superior. The results presented are from 22 samples collected from May 26 to July 24, 2011. The plastic debris collected was classified by color, size, and chemical type of synthetic polymer. Minnesota has been running the program of Beach Sweep which in 2010 showed that 81% of the man-man debris collected from beaches was plastic.

**Figure 1. Plastic debris found at Burlington beach on Lake Superior (2011)**

**RM_MWGL Regional Meeting 242**

## Self-assembled polyelectrolyte complex: Sericin/DDAB

*Rungsima Chollakup[1], **Wirasak Smitthipong**[1], aapwss@ku.ac.th, Karine Mougin[2], Michel Nardin[2]. (1) Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI), Kasetsart University, Bangkok, Thailand (2) Institut de Sciences des Matériaux de Mulhouse (IS2M), Mulhouse, France*

The objective of this work is to prepare the polyelectrolyte complex for using as a biomaterial. Electrostatic interaction between oppositely charged polyelectrolytes can lead to self-assembled multilayers made of polyanions with positively charged polycations. Silk, natural fiber, contains a fibrous protein termed fibroin that forms the filament and glue-like proteins termed sericin surrounding the two filaments to cement them together. The sericin is eliminated during degumming process, therefore resulting in large volume of wastewater. The challenge of this project is to extract the sericin from silk's waste water using a spray dry method. Two types of sericin is presented here: (i) reference sericin from waste water and (ii) hydrolyzed sericin with citric acid to obtain shorter sericin chain. Based on the thermo-gravimetric analysis, obtained sericin has a decomposition temperature at 250°C. Main amino acids of sericin are serine, aspartic acid, glutamic acid and glycine. Molar mass of reference and treated sericin is 120 and 1.9 kDa, respectively. Polyelectrolyte complex is prepared by conjugating through electrostatic interaction between sericin as anionic polymer and didodecyldimethylammonium bromide (DDAB) as cationic amphiphiles at 1:1 stoichiometry. With this preparation technique, DNA (protein nucleic acid)/DDAB complex is used as a reference material which its structure has been well-studied from a previous study [1]. The elemental analysis, differential scanning calorimetry and X-ray diffraction are being used to characterize these complexes. One can imagine that the sericin complex could have significant application as a drug delivery material, a functional material and many other kinds of biodegradable material.

Reference:

[1] W. Smitthipong, T. Neumann, S. Gajria, Y. Li, A. Chworos, L. Jaeger and M. Tirrell, *Biomacromolecules* 2009, 10 (2), 221-228.

**RM_MWGL Regional Meeting 243**

### Surface modification of silk fabric using polyelectrolyte technique

***Rungsima Chollakup**[1], aaprmc@ku.ac.th, Wirasak Smitthipong[1], Rattana Tantatherdtam[1], Michel Nardin[2]. (1) Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI), Kasetsart University, Bangkok, Thailand (2) Institut de Sciences des Matériaux de Mulhouse (IS2M), Mulhouse, France*

Color fastness to washing is one of important problem for silk fabric. The present work is focused on the surface modification of silk fabric using layer by layer (LbL) technique of polyelectrolyte between poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH). The silk fabric is chemically grafted to be positive charge on the surface with 50 g/l of 2,3-epoxypropyltrimethylammonium chloride (60%). The parameters of surface modification for the silk fabric using PAA/PAH are investigated: number of polyelectrolyte layer (4-40) and pH of PAA (4 and 7). After surface modification, silk fabric is dyed with acid dye in a regular way. Dyeing properties, color value before and after washing, including color change of fabric after washing (Delta E) are determined. We found that the optimum condition of this LbL technique for the silk fabric is 30 layers of polyelectrolyte deposition at pH 7. This condition gives the better physical properties of the silk fabric compared to the other conditions. Furthermore, anionic polyelectrolyte type between strong acid as polystyrene sulfonic acid (PSS) and weak acid as PAA are also studied. PSS, strong acid, can be dissociated to give a negative charge higher than PAA weak acid. Thus, 20 layers of polyelectrolyte deposition of PSS/PAH provides better results compared to 30 layers of polyelectrolyte deposition of PAA/PAH. Effect of molar mass of PAA between 5,000 and 50,000 kg/mol with PAH of 70,000 kg/mol is investigated. The dyeing properties of the silk fabric give the same tendency which is

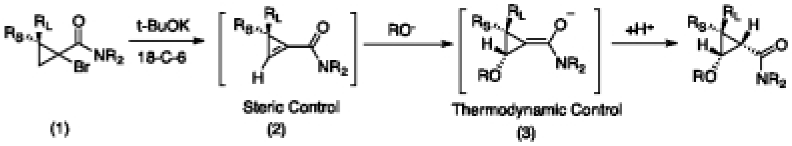
not significantly different between low and high molar mass of PAA. This means that degree of dissociation of weak acid is not affected by molar mass.

## RM_MWGL Regional Meeting 244

## Dual control of selectivity in the synthesis of donor-acceptor cyclopropanes via the addition of alcohols to *in situ* generated cyclopropenes

***Pavel G Ryabchuk**, pasha@ku.edu, Jonathon P Matheny, Ivan A Babkov, Marina Rubina, Michael Rubin.Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States*

A highly diastereoselective protocol for the synthesis of stereodefined densely substituted donor-acceptor cyclopropanes from tetrasubstituted 1-bromocyclopropylcarboxamides (1) will be described.



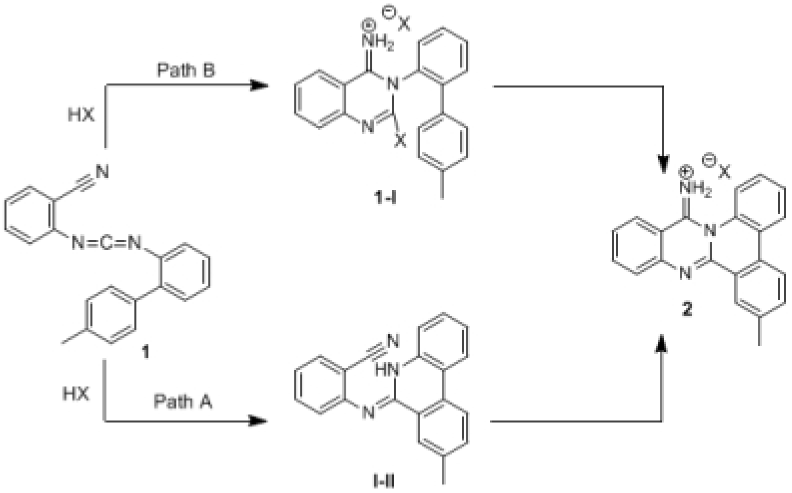
Existing stereogenic center at C-2 of the bromocyclopropane sets two other stereocenters on the cyclopropane ring via the sterically controlled addition of alkoxide across the double bond of *in situ* generated cyclopropene (2), followed by thermodynamically driven epimerization of the resulting enolate intermediate (3). Scope and limitations of this methodology will be discussed in detail and the mechanistic implications will be provided.

## RM_MWGL Regional Meeting 245

## Investigating the mechanism of formation of phenanthridine fused quinazoliniminiums from heteroenyne-allenes.

***Kevin Robb**, sundeep@ksu.edu, Sundeep Rayat. Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Fused quinazolines and their derivatives exhibit a wide variety of biological activities and therefore new methods that provide an easy access to these ring systems are highly desirable. We have found an efficient and versatile synthetic route to obtain phenanthradine-fused quinazoliniminiums **2** from heteroenyne-allenes **1** upon reaction with a hydrogen halide generated *insitu* from the reaction of a Lewis acid with trace water. We proposed two pathways for the formation of these *N*-fused heterocycles. Path A involves an intramolecular electrophilic aromatic substitution in the heteroenyneallene **1** to form **1-I** which is followed by a nucleophilic attack at the nitrile group to form **2**, while Path B involves addition of HX to the carbodiimide moiety followed by a nucleophilic attack on the nitrile group to form **1-II** and a subsequent, electrophilic aromatic substitution to afford **2**. In order to explore these two mechanistic pathways, we synthesized a model compound lacking a cyano group and studied its cyclization in the presence of Lewis acid and trace water. We reasoned that if product like **1-I** (but without the cyano group) is observed from this latter reaction, it would suggest that the cyano group is not necessary for the initial ring formation and thus be evidence in favor of the Path A. However, an absence of such a product would suggest that Path B might be operating in the formation of the *N*-fused heterocycles.



**RM_MWGL Regional Meeting 246**

## Molecular Scaffold in Biocatalysis

*Xi Song, Wei Niu, **Jiantao Guo**, jguo4@unl.edu.Department of Chemistry, University of Nebraska - Lincoln, Lincoln, NE 68588, United States*

Cellulosome is a complex of enzymes used by many anaerobic bacteria and fungi to degrade plant cellulosic material. Assembly of cellulosome occurs by a high-affinity interaction between cohesin domains of scaffoldin protein and dockerin domains of catalytic subunits. As a multi-enzyme machinery, cellulosome promotes synergistic action among different resident enzymes and enables highly efficient hydrolysis of cellulosic and hemicellulosic materials of plant cell wall. Our research is to devise a cellulosome-based molecular scaffold and apply it as a general platform to design a variety of protein complexes with defined molecular assembly for biochemical studies (e.g., to generate artificial signaling pathways) and biotechnological applications (e.g., to evolve designer cellulosomes for the degradation of various types of plant cellulosic materials for bioenergy production). To ensure the precise association of protein subunits at prearranged positions, orthogonal cohesin-dockerin pairs are being generated via directed evolution.

## RM_MWGL Regional Meeting 247

## Studies towards the synthesis of protected derivatives of 4(5)-benzylhistidine suitable for peptide synthesis

*D. David Smith[1], **Vincent M Crowley**[2], dsmith@creighton.edu, Wayne Gergens[2], Peter W Abel[3], Audrey T Gallagher[2], Martin Hulce[2].  (1) Department of Biomedical Sciences, Creighton University, Omaha, Nebraska 68178, United States  (2) Department of Chemistry, Creighton University, Omaha, Nebraska 68178, United States  (3) Department of Pharmacology, Creighton University, Omaha, Nebraska 68178, United States*

The key component of the potent, human selective, CGRP antagonists N-α-Bn-(4(5)-BnHis)$^{10}$-CGRP(8-37) (1) and N-α-Bzl-(4(5)-BnHis)$^{10}$-CGRP(8-37) (2) is the unique 4(5)-benzylhistidyl residue in position 10. Solid phase synthesis of these antagonists employs a global benzylation step of the assembled, resin-bound, protected peptide. Unfortunately, this benzylation step proceeds in a 40% yield reducing the overall isolated yields of (1) and (2) to 6%. Consequently, we sought the synthesis of the amino acid 4(5)-benzylhistidine and recently optimized a two-step published preparation using a Pictet-Spengler condensation of benzaldehyde and L-histidine followed by hydrogenolytic cleavage of a doubly benzylic C-N bond. The yield over two steps was increased from 62% to 85% and the total reaction time for both steps was reduced from 17 hours to one hour and 15 minutes.

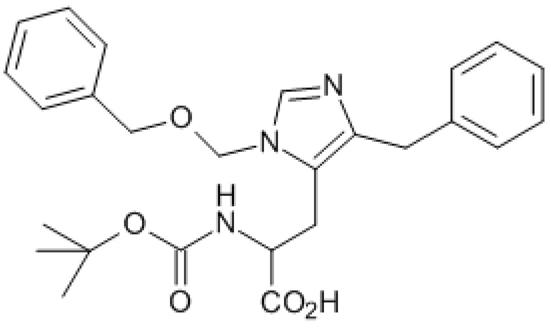


Figure. Na-*tertiary*-butyloxycarbonyl-N*im*-benzyloxy-methyl-4(5)-benzylhistidine

Results of our efforts to protect the α-amino and side chain imidazole groups of 4(5)-benzylhistidine will be presented. Initially, the target compounds will be Nα-*tertiary*-butyloxycarbonyl-N*im*-benzyloxymethyl-4(5)-benzylhistidine (Figure) for use in peptide synthesis using Boc-amino acid derivatives and Nα-fluorenylmethoxycarbonyl-N*im*-trityl-4(5)-benzylhistidine for use in peptide synthesis using Fmoc-amino acid derivatives.

**RM_MWGL Regional Meeting 248**

## Synthetic applications of indole aryne cycloadditions. New strategies for the construction of complex natural products

*Nalin Chandrasoma[1], **Alok Nerurkar**[1], aloknerurkar@mail.umkc.edu, Lincoln Maina[1], Neil Brown[1,2], Diheng Luo[1], Allen Brassfield[1], Joseph DeCapo[1], Susana Suarez[1], Keith R. Buszek[1,2]. (1) Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110, United States (2) Center of Excellence in Chemical Methodologies and Library Development, University of Kansas, Lawrence, KS 66047, United States*

Indole arynes (indolynes) are the newest class of reactive aryne intermediate that we discovered and reported beginning in 2007 (see for example, Buszek, Luo et al., Org. Lett. 2007, 9, 4135; Buszek, Brown et al., Org. Lett. 2009, 11, 201; Brown, Luo et al., Tetrahedron Lett. 2009, 50, 63; Brown, Luo et al., Tetrahedron Lett. 2009, 50, 7113; Garr, Luo et al., Org. Lett. 2010, 12, 96; Thornton, Brown et al., ACS Comb. Sci. 2011, ASAP). As their unusual and fascinating chemistry is revealed, they are becoming attractive and emerging tools for use in organic synthesis. Indeed, indolyne cycloaddition methodologies have already proven their value, as we demonstrated in our recently completed total synthesis of the trikentrins and the herbindoles, and in the construction of annulated indole libraries. Subsequent work on different natural products from the Garg laboratories (Tian, Huters et al., Org. Lett. 2009, 11, 2349; Bronner, Goetz et al., J. Am. Chem. Soc. 2011, 133, 3832), and other recent studies from Lautens on Rh(I)-catalyzed ring opening of indole aryne-furan cycloaddducts (Nguyen, Webster et al., Org. Lett. 2011, 13, 1370) have validated this point of view . In this presentation we describe our ongoing efforts to exploit the advantages of indolyne cycloaddition chemistry in the efficient total synthesis of other complex molecules of biological interest.

**RM_MWGL Regional Meeting 249**

## Parallel Synthesis of Alkyl and Aryl *S-tert*-butylthioethers

***Rebecca Norcross**, rnorcross@sycamores.indstate.edu, Jessica Stanfield, Richard W. Fitch. Department of Chemistry and Physics, Indiana State University, Terre Haute, IN 47809, United States*

This project examined the scope and limitations of acid-promoted *tert*-butylation of thiols using tert-butanol as solvent. By adding a removable *tert*-butyl group to the sulfur on the compound, the sulfur is “capped” and thereby protected from certain reagents in synthesis. Nine thiols were tested including aromatic and aliphatic thiols as well as dithiols. Reactions were performed in parallel at least four times. Into 4 mL reaction vials

were placed 0.5 mmol of thiol, 11.5 equivalents of *tert* -butanol (per thiol group) and 1 equivalent of acid (per thiol group). Vials were sparged with nitrogen or argon to eliminate oxygen from the environment and prevent disulfide formation. Vials were placed into heating blocks at 80°C. Conducting reactions in sealed vials retains the volatile byproduct isobutylene and recycles it into the reaction, thus increasing yields. Pressures developed are modest (~2 atm) and we did not observe any vial failures. The reactions were monitored by TLC and after 24 hours, saturated sodium bicarbonate was added drop wise to the reaction vials to neutrualize the mixture. Anhydrous sodium sulfate was used to dry the reactions and products were extracted with dichloromethane. Crude yields were determined and NMR and GCMS were used to identify and quantify the product, an isobutyl isomer, and disulfide. Of the tested nine tested thiols, eight of them successfully *t*-butylated in high yield and purity and in several cases could be purified by kugelrohr distillation. However, a notable failure was 4-trifluoromethyl-2-nitrobenzenethiol, which gave only recovered starting material. For these reactions, deoxygenation is critical or disulfide formation is predominant. The reaction was scaleable to 30 mmol for thiophenol and 4-tert-butylbenzylmercaptan. We believe this to be a useful and efficient process for preparing tert-butyl sulfides for general synthesis and medicinal chemistry.

**RM_MWGL Regional Meeting 250**

## Enhanced Fourier transform infrared (FT-IR) spectroscopic imaging

***Rohith K Reddy***[1,2]*, rkreddy2@uiuc.edu, Paul Scott Carney*[2]*, Rohit Bhargava*[1,2]*. (1) Department of Bioengineering, University of Illinois at Urbana Champaign, Urbana, IL 61801, United States (2) Beckman Institute for Advanced Science and Technology, Urbana, IL 61801, United States*

Fourier transform infrared (FT-IR) spectroscopic imaging is an emerging technique that provides simultaneous spatially and chemically resolved information. Mid-infrared wavenumbers provide rich chemical information and this may be utilized for computer-aided determinations of structure or pathologic state of biological specimens. The spatial heterogeneity of samples, which makes spectroscopic imaging more useful than point spectroscopy also results in spectral distortions when compared to pure material spectra. In particular, we observe that measured spectra in a mixture of chemical species not only depend on the individual chemical spectra, but also on the geometric distribution of these chemical species. We present models based on rigorous electromagnetic wave theory for quantifying the interaction of infrared light with the sample and characterize the nature of these systematic distortions due to sample geometry. We observe shifts in peak positions and variation in peak heights at the boundary of two materials primarily due to optical effects. We demonstrate the effect of changing the thickness of homogeneous samples on recorded spectra in transmission and reflection (transflection) modes.

We present a simple optical model for propagation of light through an FT-IR spectroscopic imaging system and derive the relation between the spatial frequencies of

incident light, sample and detected light intensity. The effects of the numerical apertures of all the cassegrains in the system are quantified and related to the detector measurements. One of the conclusions from this model is that current FT-IR spectroscopic imaging instruments do not utilize all the information available. We argue that more spatial (morphological) information can be obtained from current instruments by reducing the pixel size from about 5.5μm to 1.39μm. Still further spatial information can be gained by using a 0.65 NA objective cassegrain and reducing the pixel size to 0.96μm. The theoretical bases for these calculations, the assumptions and trade-offs involved are detailed.

**RM_MWGL Regional Meeting 251**

## Towards the design of an enzymatic breath sensor for acetone

***Nina Hausmann***[1], *Shelley D Minteer*[1,2]. *(1) Department of Chemistry, Saint Louis University, St. Louis, MO 63104, United States (2) Department of Chemistry and Materials Sciences an Engineering, University of Utah, Salt Lake City, UT 84108, United States*

After glucose is depleted in diabetic patients, ketone bodies, such as acetone, are produced. Acetone has shown to be one of the most abundant volatile organic compounds (VOC) in human breath and high acetone levels result in ketoacidosis. Many acetone sensors have been developed, however disadvantages such as poor selectivity and specificity, higher operating temperature, long response times, and complex systems are present. Currently, there is a breath acetone amperometric sensor that was designed by Kemeta that utilizes three different enzymes, alcohol dehydrogenase (ADH), lactate dehydrogenase (LDH) and pyruvate oxidase (PO). However, it forms a $H_2O_2$ byproduct, which is detrimental to many biosystems. Therefore, there is a need for a more specific, biologically friendly, and simpler biosensor for breath acetone detection for diabetics. This study has outlined a procedure for the isolation, purification, and characterization of the NADPH-dependant carbonyl reductase in order to be used towards the development of a specific amperometric acetone sensor. Carbonyl reductase is an enzyme that it is not commercially available; therefore it was extracted from cultivated *Saccharomyces pastorianus* yeast cells and purified using column chromatography. Carbonyl reductase activity was evaluated using activity assays and was also studied electrochemically and has shown positive activity in both experimental analyses. Furthermore, this study outlines a procedure for a flow injection method used for the detection of aqueous acetone in the presence of carbonyl reductase. Acetone was detected amperometrically by measuring the current produced at various concentrations. Concentrations of acetone in the 50 mM to 450 mM concentration range were successfully sensed using the purified carbonyl reductase and a linear correlation between concentration and current was obtained.

**RM_MWGL Regional Meeting 252**

## Measuring protease concentrations in dog urine: A new diagnostic method for cancer detection?

***Leonie K. Bossmann***[1], *lkb12@ksu.edu, Dinusha Udukala*[1], *Colette Robinson*[1], *Hongwang Wang*[1], *Mausam Kalita*[2], *Matthew T. Basel*[2], *Marla Pyle*[1], *Dudley McCaw*[3], *Deryl L. Troyer*[2], *Stefan H. Bossmann*[1]. *(1) Chemistry, Kansas State University, Manhattan, Kansas 66506-0401, United States (2) Anatomy&Physiology, Kansas State University, Manhattan, Kansas 66506, United States (3) Clinical Sciences, Kansas State University, Manhattan, Kansas 66506, United States*

Although “cancer” is often referred to as a single condition, it actually consists of more than 100 different diseases. According to the American Cancer Society, “These diseases are characterized by uncontrolled growth and spread of abnormal cells. Cancer can arise in many sites and behave differently depending on its...origin.” It is apparent that early detection of cancer is of great importance with regard to proper treatment. Cancer cells are known to over-express numerous matrix metalloproteinases (MMPs) such as MMP1, MMP2, MMP7, MMP11, MMP13, as well as urokinase-type plasminogen activator (uPA) and cathepsins B, L, and D. We are developing a Fe/$Fe_3O_4$ nanoparticle-based system, which has the potential to identify and quantify the presence of these proteases in urine samples. It is our paradigm that the resulting “protease spectrum” is indicative of the presence of (early) cancer. Furthermore, the protease spectrum may be indicative of the kind of cancer that is developing. Here, we report quantitative protease measurements in dog urine collected from dogs that have been treated for cancer at Kansas State University's veterinary hospital. Urine from apparently healthy dogs has been used as a control. We will correlate our findings with the diagnoses by our veterinarians.

**RM_MWGL Regional Meeting 253**

## Sub-diffraction determination of changes to the actin network by stimulated emission depletion microscopy

***Michael D Lesoine***[1,2], *mlesoine@iastate.edu, Sayantan Bose*[1,2], *Jacob W Petrich*[1,2], *Emily A Smith*[1,2]. *(1) Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States (2) Ames Laboratory, Ames, Iowa 50011, United States*

We are using fluorescence microscopy to measure the organization of proteins and lipids in the cell membrane and the role of cytoplasmic proteins in altering this organization. The spatial resolution that can be achieved in traditional optical microscopy is governed by the diffraction limit of light, and features smaller than ~200nm cannot be resolved. In order to non-invasively measure smaller features a sub-diffraction microscopy is needed. We have developed a stimulated emission depletion (STED) microscope, with 50nm resolution. The basic operating principle of STED microscopy is inhibiting the fluorescence at the periphery of a diffraction limited spot by stimulated emission. A tightly focused scanning excitation laser and a ring shaped STED laser shaped by phase modulation are used. The excitation wavelength

corresponds to the fluorophore's maximum excitation wavelength. The STED wavelength is lower in energy in a region where fluorophore does not have appreciable absorption. The stimulated emission pulse depopulates the excited electronic states of the fluorophores within the doughnut beam profile, leaving only a smaller than diffraction limit spot of excited fluorophores at the center of the doughnut. The net result is the collection of the fluorescence from an excitation volume that is smaller than the dimensions set by diffraction. With this instrument we are measuring the integrin membrane proteins and the actin organization of cultured cells expressing wild type and mutant integrins. The STED images reveal information about the structure or some function of the cell not revealed by traditional optical microscopy methods. This allows an enhanced understanding of the factors controlling cellular organization and how this relates to biological function.

**RM_MWGL Regional Meeting 254**

## Measurements of integrin mobility in the membrane of cultured cells using fluorescence recovery after photobleaching (FRAP) and single molecule imaging

***Dipak Mainali***, *dmainali@iastate.edu, Neha Arora, Emily Smith. Department of Chemistry, Iowa State University, Ames, IA 50011, United States*

The cell membrane is composed of up to 50 to 60% membrane proteins. Many of these proteins are essential for basic cellular activities. Integrins is one class of important transmembrane proteins involved in cell signaling, growth, and adhesion. We aim to measure the role of other membrane proteins in altering integrin dynamics in cultured cells. Specifically, fluorescence recovery after photobleaching (FRAP) is used to quantify the lateral mobility of integrins within the membrane of cultured cells. Combining FRAP and RNA interference, the effect of other membrane proteins on integrin dynamics has been quantified. RNA interference has been used to inhibit the expression of select proteins, including tetraspanins, epidermal growth factor, and notch transmembrane proteins. Integrin lateral mobility increases in cells expressing wild-type integrin after the RNAi treatment against all targeted membrane proteins included in this study. In contrast, for cells expressing ligand-binding domain integrin mutants, the lateral mobility decreases when the expression of ephrin or some tetraspanins are reduced. The interactions between integrins and other membrane proteins may depend on integrin engagement to extracellular ligand, a property that is altered in the mutant integrin. This would explain the differing roles of ephrin and tetraspanins in altering integrin diffusion in the wild-type and mutant integrin. These results are supplemented with single molecule tracking measurements of integrin diffusion, which reveal heterogeneous behaviors that are averaged in the FRAPmeasurements.

**RM_MWGL Regional Meeting 255**

## Scanning Angle Total Internal Reflection Raman Microscopy of Plant Cell Wall Biopolymers

***Emily A. Smith***[1,2], *esmith1@iastate.edu, Kristopher McKee*[1,2], *Matthew Meyer*[1,2], *Jason Lupoi*[1,2]. *(1) Ames Laboratory, Ames, IA 50011, United States (2) Department of Chemistry, Iowa State University, Ames, IA 50011, United States*

A scanning angle total internal reflection (SA-TIR) Raman microscope has been developed for chemical content measurements with control over the depth the signal is collected at an interface. The instrument provides an order of magnitude improved spatial resolution perpendicular to the focal plane compared to confocal Raman microscopy. The instrument is based on a traditional wide-field optical microscope platform with added beam steering optics to vary the angle of the incident light on a prism/sample interface. Varying the angle of incident radiation upon a prism/sample interface tunes the depth of penetration of the evanescent wave, and in turn the depth over which Raman scatter is generated. The incident angle can be scanned to collect signal from depths up to approximately 1500 nm from the substrate. Under TIR, background signals are minimal since the probed volume is confined to the interface. On the other hand, the small sample volumes limits the measurements of weak Raman scattering samples, such as proteins, lipids and polysaccharides. Signal enhancement is required for the analysis of these samples. The use of smooth and rough metal films at the interface enhances the collected Raman scatter and enables TIR Raman measurements of weak Raman scattering samples. The instrument has been used for noninvasive and nondestructive measurements of thin polymer films, plant tissues and cell wall biopolymers. The products and yields of the enzymatic hydrolysis of plant cell wall polymers will be discussed.

**RM_MWGL Regional Meeting 256**

## Design and characterization of a dual-signaling DNA sensor based on target hybridization-induced change in DNA probe flexibility

***Weiwei Yang***, *wyang.chem@gmail.com, Rebecca Y Lai. Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, United States*

We report the design and characterization of a dual-signaling DNA sensor that is based on target hybridization-induced change in the flexibility of surface-immobilized DNA probes. To fabricate this sensor, we co-immobilized two types of thiolated DNA probes onto a gold electrode. Each probe is modified with either a methylene blue (MB-P) or ferrocene (Fc-P) redox label. The seven bases at the 3'end of Fc-P are designed to be complementary to the seven bases at the 5' end of MB-P, thereby forming a 7 base-duplex at the distal end of the two probes. In presence of the 17-base target that is complementary to MB-P, the 7-base duplex will be replaced by the MB-P-target duplex and releases Fc-P. This strategic probe displacement by the target DNA induces a simultaneous enhancement in the rigidity of MB-P and flexibility of Fc-P, giving rise to a large MB signal suppression and Fc signal enhancement when interrogated using alternating current voltammetry (ACV). Of note, we found that sensors fabricated with 8-mercapto-1-octanol as the diluent, when compared to those fabricated using 6-mercapto-1-hexanol, show larger change in the Fc redox signals upon target

hybridization. In addition to the choice of passivating diluents, the applied AC frequency has also been shown to affect the signaling capabilities of the two redox labels. Last, to verify the proposed sensing mechanism, we systematically characterized the electron transfer properties of MB-P and Fc-P, both in absence and presence of the target DNA, using cyclic voltammetry (CV). Results from both ACV and CV allude to a sensing mechanism that is governed by target hybridization-induced change in probe flexibility.

**RM_MWGL Regional Meeting 257**

## Multivariate spectral analysis of phase partitioning in methacrylate-based dentin adhesive

***Qiang Ye***[1], *yeq@ku.edu, Paulette Spencer*[1,2], *Ranganathan Parthasarathy*[1], *Jonggu Park*[1], *Jennifer S. Laurence*[3], *Anil Misra*[1,4]. *(1) Bioengineering Research Center, University of Kansas, Lawrence, K6 66045, United States (2) Department of Mechanical Engineering, University of Kansas, Lawrence, KS 66045, United States (3) Department of Pharmaceutical Chemistry, University of Kansas, Lawrence, KS 66047, United States (4) Department of Civil Engineering, University of Kansas, Lawrence, KS 66045, United States*

Water is ubiquitous in the mouths of healthy individuals and it is a major interfering factor in the development of a durable seal between the tooth and composite restoration. Phase separation in dentin adhesives and water blisters are defects that undermine the tooth/composite bond. Our group has analyzed phase partitioning of dentin adhesives using HPLC, but this analysis is time-consuming and labor-intensive.

**Objective:** To develop a methodology for rapid, reliable and accurate quantitative analysis of near-equilibrium phase partitioning in adhesives exposed to conditions simulating the wet, oral environment.

**Methods:** The model adhesive consisted of hydroxyethylmethacrylate (HEMA) and 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA) with a mass ratio of 45/55. Water was added at 16, 33 and 50 mass% into the neat resins. Shaking, sonication and centrifugation were required to yield well-separated resin/water phases. Each phase was determined by FTIR-ATR spectroscopy (spectral resolution: 4 $cm^{-1}$). Principal component analysis was performed using Perkin-Elmer QUANT+ expert Version 4.6. FTIR spectral data were compared with results from HPLC.

**Results:** Three chemometric approaches, partial least-squares (PLS1 & PLS2) and principle component regression (PCR+), were used. Full cross-validation was used to compare the reference with predicted monomer concentrations of samples not included in the model development. The best results were obtained with the PLS1 method. The application of this method over the full spectral range resulted in a 3-factor (or less) model with high correlation coefficient ($R^2$>0.99) and a cross-validation error of 0.002~0.005. The predicted values

matched very well the HPLC
results.

**Conclusion:** In comparison to HPLC, quantitative analysis of phase partitioning behavior using FTIR spectroscopy offers distinct advantages. These advantages include rapid technique, i.e. multiple components are analyzed simultaneously. As compared to HPLC, the FTIR spectroscopic technique requires limited sample preparation and overall, the technique is less time-consuming and labor-intensive.

NIH/NIDCR R01DE014392 &
1R01DE022054.

### RM_MWGL Regional Meeting 258

## Quantitative investigation of surface functionalization of cylindrical nanopores derived from polystyrene-poly(methylmethacrylate) diblock copolymers

***Feng Li***, *lfeng@ksu.edu, Ruben Diaz, Takashi Ito. Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

This paper reports quantitative measurements of surface modification efficiency on nanoporous films (20-35 nm in thickness; 14, 20 and 30 nm in pore diameter) derived from cylinder-forming polystyrene-poly(methylmethacrylate) diblock copolymers. The density of free -COOH groups on the nanopore surface was determined by measuring their probe counter cations released via cation exchange using spectrofluorometry and inductively coupled plasma mass spectrometry. Two methods were used to immobilize the nanopores surface: amidation in aqueous phase mediated by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and amidation or esterification in organic phase using oxalyl chloride reaction. The yields of aqueous-phase amidation mediated by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide were 20-30%. In contrast, organic-phase amidation and esterification using oxalyl chloride offered much higher yields (87–89%), providing efficient means for functionalizing the nanopore surface. Quantitative information on the surface modification will provide a basis for assessing the influences of the surface functionality on the efficiency of chemical separations with the nanoporous films.

### RM_MWGL Regional Meeting 259

## In vitro simulation studies for the development of a nocturnal hypoglycemic alarm based on near-infrared spectroscopy

***Sanjeewa Rasika Karunathilaka Ranasinge Pathirajage***, *sanjeewara-ranasinghepathirajage@uiowa.edu, Gary W Small. Department of Chemistry, University of Iowa, Iowa City, IA 52242, United States*

Noninvasive glucose monitoring has been the subject of considerable research because of the high number of diabetes patients who must monitor their glucose levels daily by

taking blood samples. Among methods being evaluated for possible use in this application, near-infrared spectroscopy has received significant attention because of available glucose absorption bands that can be observed in the presence of the large aqueous background found in tissue spectra. The objective of the research presented here is to evaluate the potential for implementing a noninvasive nocturnal hypoglycemic alarm with near-infrared spectroscopy. Such an alarm would be used by a diabetic to detect potentially dangerous occurrences of hypoglycemia during sleep. The approach used is to collect spectra continuously from the patient during the sleep period, followed by the application of pattern recognition methods to determine if a spectrum represents a blood glucose level that exceeds a hypoglycemic threshold. A reference spectrum is collected and a conventional finger-stick glucose concentration measurement is made at the start of the sleep period. The ratio is then taken of each subsequent spectrum to the collected reference, forming a differential spectrum corresponding to the signed difference in concentration relative to the reference. The identification of these differential spectra as “alarm” or “non-alarm” is performed with a classification model computed with piecewise linear discriminant analysis (PLDA). This methodology is tested with in vitro laboratory data that simulate the glucose excursions that occur during sleep. In this work, a tissue phantom is constructed to simulate the near-infrared spectral background of human tissue.

## RM_MWGL Regional Meeting 260

## Utilizing enzyme cascades for deep oxidation of a variety of biofuels

***Daria Sokic-Lazic***[1], *Shelley D Minteer*[1,2]. *(1) Department of Chemistry, Saint Louis University, St. Louis, MO 63104, United States (2) Department of Chemistry and Materials Science and Engineering, University of Utah, Salt Lake City, UT 84108, United States*

Maximizing both energy density and power density is of crucial importance when building a biofuel cell. Most biofuels have high energy density and are metabolized by a series of oxidoreductase enzymes that undergo individual two-electron oxidation reactions. In order to get high energy density out of the biofuel, it is necessary for the biofuel to be completely oxidized rather than it undergoing a single step oxidation. To achieve this deep oxidation of biofuels, multiple enzymes must be employed. One of the main metabolic pathways living cells utilize to completely oxidize biofuels to carbon dioxide and water is called the citric acid cycle. Due to the versatility of this complex system, the starting point can vary depending on the fuel/substrate available. In order to mimic this metabolic pathway on a carbon electrode, several enzymes are utilized to add increased selectivity for sensing applications. Dehydrogenase enzymes (known to be the electron producing enzymes) are immobilized in cascades along with non-energy producing enzymes necessary for the cycle to progress. Three different starting points (biofuels) have been investigated: ethanol, pyruvate, and lactate resulting in slightly different enzymatic cascades. For each of the different biofuels employed at 100 mM concentrations, power curves have been generated. Even though, each one these biofuels has high energy density, ethanol can only be employed in concentrations up to

100 mM due to its solvent properties and solubility of pyruvate is only 900 mM which in comparison to lactate whose solubility is 7.6 M is a significant difference. Therefore, complete oxidation of lactate due to its high solubility has the potential of extracting most of the energy density out of lactate (3041 Whr/L).

### RM_MWGL Regional Meeting 261

## Optimizing the growth of *M. smegmatis* with respect to cell mass yield and fermentation cost

***Sebastian O Wendel***[1], *sw87@ksu.edu, Ayomi S Perera*[2], *Peter H Pfromm*[1], *Peter Czermak*[3], *Stefan H Bossmann*[2]. *(1) Department of Chemical Engineering, Kansas State University, Manhattan, Kansas 66506, United States (2) Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States (3) Department of Biotechnology, TH Mittelhessen, Giessen, Hessen, Germany*

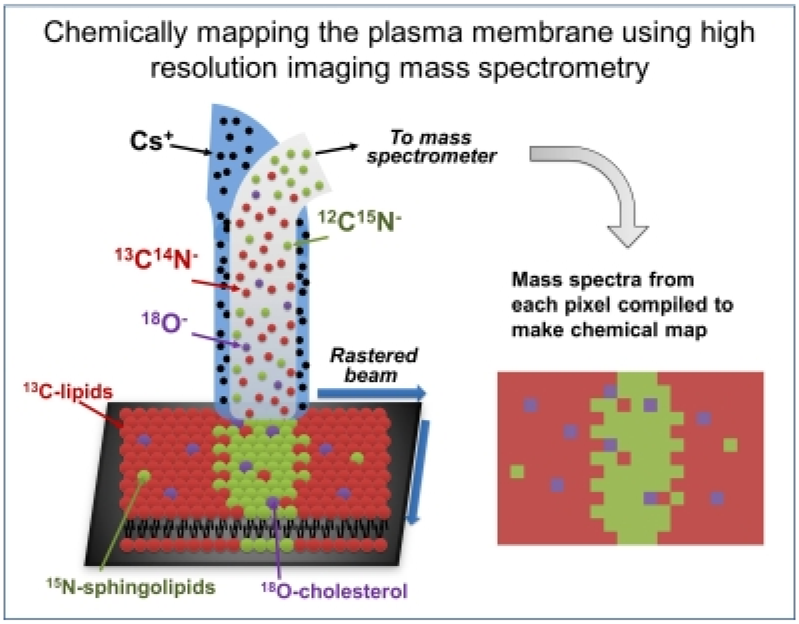
In order to supply collaborating research groups and to investigate the properties of the mycobacterial porin A (MspA), a protein with outstanding qualities regarding its stability and possible applications (understanding and treatment of tuberculosis, protein solar cells, template for gold nano-wires or gold nano-dots) an effective way to grow the host organism *Mycobacterium smegmatis* is a key part. High cell mass yield at a simultaneously cost efficient use of resources is important. Following the successful introduction of an inexpensive minimal medium to M. smegmatis and determining the growth kinetics the tools of experimental design were used to further optimize the obtained cell mass yields and lower costs. Two parameters immanent for mycobacterial growth, Nitrogen and Iron content of the medium, were varied in a Doehlert matrix to achieve maximum cell and product yields. The glucose concentration in the medium was analyzed subsequent to the fermentation to minimize the carbon hydrate wastage. MspA was successfully extracted and purified using gel electrophoresis for identification.

### RM_MWGL Regional Meeting 262

## High resolution imaging mass spectrometry of sphingolipid and cholesterol distributions in intact mammalian plasma membranes

***Jessica F Frisz***[1], *jfrisz2@illinois.edu, Kaiyan Lou*[1], *Haley Klitzing*[1], *Robert Wilson*[1], *William P Hanafin*[1], *Raehyun Kim*[1], *Vladimir Lizunov*[3], *Peter K Weber*[2], *Joshua Zimmerberg*[3], *Mary L Kraft*[1]. *(1) School of Chemical Sciences, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801, United States (2) Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, Livermore, California 94551, United States (3) Program in Physical Biology, Eunice Kennedy Shriver National Institute of Child Health and Human Development, National Institutes of Health, Bethesda, Maryland 20892, United States*

The organization of lipids in mammalian cell membranes has been widely debated, specifically pertaining to the existence and nature of lipid rafts which are thought to be nanoscale sphingolipid- and cholesterol-enriched domains within a phospholipid-dominated matrix in the plasma membrane. The ability to chemically assay the lipid composition at relevant size regimes (tens of nanometers to a few microns) has been unattainable by any single technique until the application of high resolution imaging mass spectrometry. We have developed a method for incorporating non-perturbing heavy isotope labels into lipid molecules of interest by culturing cells in the presence of labeled metabolites and allowing them to synthesize and distribute the molecules of interest in the cell membrane. Using a NanoSIMS 50 (Cameca), we have chemically mapped the distributions of labeled sphingolipids and cholesterol within the plasma membrane of murine fibroblasts with resolution of 87 nm. Here we will discuss the results of these experiments in the context of cell membrane organization.



## RM_MWGL Regional Meeting 263

## Diffusion dynamics of single molecules confined in biomimetic crowded environment

*Robb Welty[1], Jacob Bentley[1], Dhanushka Wickramasinghe[1],* ***Ahmed A Heikal[1,2]****, aaheikal@d.umn.edu. (1) Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, United States (2) Department of Pharmacy Practice & Pharmaceutical Sciences, University of Minnesota Duluth, Duluth, MN 55812, United States*

The crowded environment in living cells plays an important role in regulating intermolecular interaction associated with signal transduction and macromolecular assembly. Using a combination of time-resolved anisotropy and fluorescence correlation

spectroscopy, we investigate the role of chemical structure and non-specific binding of rhodamine green and EGFP multi-scale diffusion as a function of crowding. Ficoll, bovine serum albumin, and ovalbumin were used as biomimetic crowding agents and compared with glycerol as a continuum. The rotational (ps - ns) and translational (μs-s) diffusion of these fluorophores were investigated as a function of cellular-level crowding, which suggest deviation from the Stokes-Einstein model. These biomimetic studies on molecular crowding will guide our cellular studies associated with the allergic response in mast cells as triggered by the cross-linking between IgE and its high affinity receptor.

**RM_MWGL Regional Meeting 264**

## New molecular biomarkers for cancer detection

***Christopher D. Nusbaum**, christopher@nusbaum.us, Sanaa Almowallad, Sarah A. Wolfe, Joshua E. Mayfield, James G. McAfee. Department of Chemistry, Pittsburg State University, Pittsburg, KS 66762, United States*

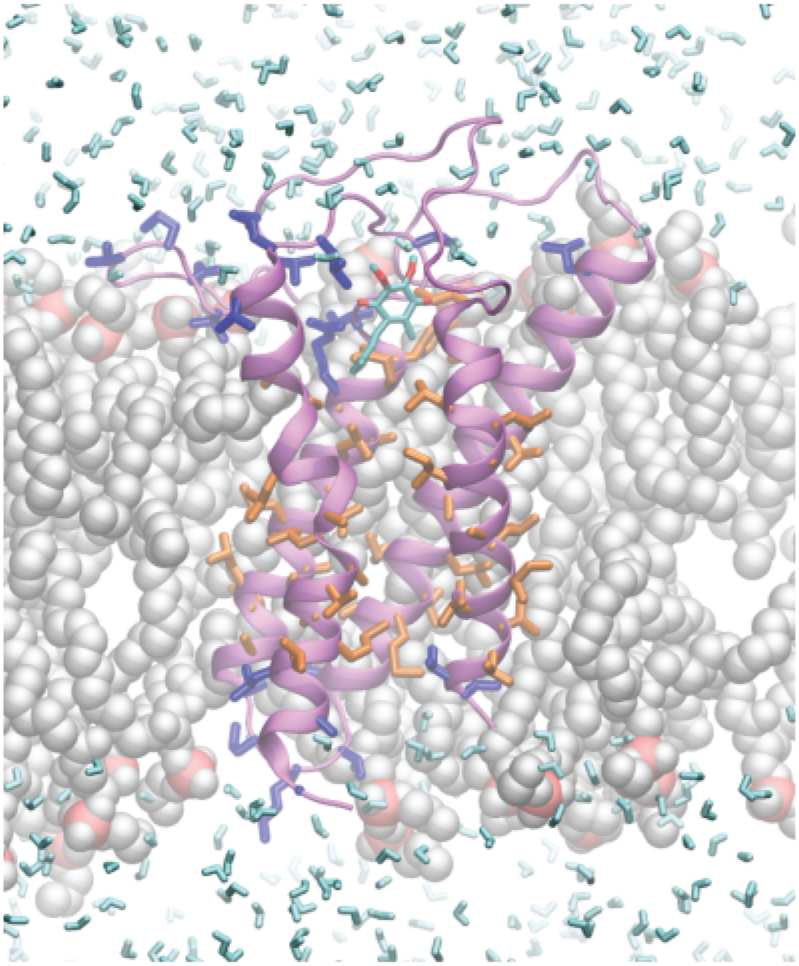
The heterogeneous nuclear ribonucleoprotein C (hnRNP C) family of pre-mRNA binding proteins consists of hnRNP C1, C2, and hRaly. The hnRNP C proteins have been extensively characterized and have been shown to be associated with playing a central role in pre-mRNA biogenesis as well as regulating IRES mediated mRNA translation and mRNA stability. We have shown that the cellular paralog, hRaly, is functionally indistinguishable from the hnRNP C proteins with regard to thermodynamic parameters associated with RNA binding, and with regard to protein interaction partners.
Recent research indicating that the expression levels of some hnRNP proteins are altered in transformed cell lines prompted an investigation to analyze the expression of hRaly and hnRNP C in normal and tumor tissues. Quantitative Northern analysis of three different RNA dot blots containing 24 paired tissue samples (normal and tumor tissues) revealed at least a two-fold difference in expression of hRALY (mRNA) in liver, lymph node, parotid, testis, thymus, and uterine tumor tissues compared to their normal tissue counterparts. Moderately differentiated endometrial adenocarcinoma (uterine cancer) was especially overexpressed, with cancerous tissue expressing hRALY at 5-11 times the level of normal tissue. Preliminary Northern analysis of hnRNP C on a single RNA dot blot containing the same paired tissue samples also showed a 9 fold enhanced expression level in the endometrial adenocarcinoma tissue sample. These data indicate that hRALY and hnRNP C would be useful biomarkers in the detection of uterine tumors. Our preliminary data also suggest that they may serve as molecular biomarkers in the detection of additional cancers.

**RM_MWGL Regional Meeting 265**

## Membrane topology and mechanistic view of a disulfide bond generating membrane protein by a structural model of membrane-embedded DsbB

***Ming Tang**[1], mingtang@illinois.edu, Anna E Nesbitt[1], Lindsay J Sperling[1], Deborah A Berthold[1], Charles D Schwieters[2], Robert B Gennis[1], Chad M Rienstra[1]. (1) Department* *of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States  (2) Division of Computational Bioscience, Center for Information Technology, National Institutes of Health, Bethesda, MD 20892, United States*

The integral membrane protein DsbB in *Escherichia coli* is responsible for oxidizing periplasmic protein DsbA, which forms disulfide bonds in substrate proteins. We obtained a structural model by embedding the high-resolution DsbB structure, from the joint calculation with X-ray reflections and solid-state NMR restraints, into the lipid bilayers through molecular dynamics simulations in order to examine the mechanism of DsbB function in the membranous environment. Membrane topology of DsbB was probed by selective proton spin diffusion experiments, and the correlations from water or lipid acyl chains to DsbB are consistent with the structural model. The flexible periplasmic loop and the interhelical hydrogen-bond link between Glu26 and Tyr153 are found to facilitate the disulfide-bond rearrangements and the binding or release of the cofactor ubiquinone.



**RM_MWGL Regional Meeting 266**

## Microglial activation by Aβ(1-42) protofibrils

***Geeta S. Paranjape***[1], *GeetaParanjape@umsl.edu, Lisa K. Gouwens*[1], *David C. Osborn*[2], *Michael R. Nichols*[1]. *(1) Department of Chemistry and Biochemistry, University of Missouri-St Louis, St Louis, MO 63121, United States (2) Center for Nanoscience, University of Missouri-St Louis, St Louis, MO 63121, United States*

One of the characteristic features of the Alzheimer's disease (AD) brain is the extracellular deposition of amyloid-β protein (Aβ) in both fibrillar (senile plaques) and diffuse forms. Significant proinflammatory markers including activated microglia and cytokines have been detected surrounding the plaques but are absent in diffuse areas suggesting that microglial activation is sensitive to Aβ structure. Since Aβ displays structural polymorphism *in vitro*, we sought to determine the relationship between Aβ aggregation state and cellular proinflammatory response. Soluble oligomers of Aβ(1-42) were able to induce tumor necrosis factor-α (TNFα) production more effectively than Aβ(1-42) fibrils in both BV2 and primary mouse microglia. Size exclusion chromatography (SEC) purification of freshly reconstituted Aβ(1-42) in NaOH/F12 cell culture medium isolated classical 100 nm long curvilinear protofibrils which were very effective at stimulating microglial TNFα. The Aβ(1-42) protofibrils produced a concentration-dependent response in the low micromolar range and were not toxic to the cells. In contrast to Aβ(1-42), Aβ(1-40) required a pre-incubation of 24h at 25$^0$C in order to produce protofibrils. Although both preparations were similar in morphology, Aβ(1-42) protofibrils were a much better stimulator of microglia than Aβ(1-40) protofibrils. As expected, freshly-purified Aβ(1-42) or Aβ(1-40) monomer were not effective in stimulating microglia, but surprisingly, neither were Aβ(1-42) fibrils even though they exhibited extensive Thioflavin-T fluorescence compared to protofibrils. These findings suggest that Aβ(1-42) protofibrils may be the most effective inducers of a proinflammatory response in mouse microglia.

**RM_MWGL Regional Meeting 267**

## Secondary structure comparison of the early onset Parkinson's disease related mutants and wild-type α-synuclein fibrils

***Luisel R Lemkau***[1], *lrodri20@uiuc.edu, Gemma Comellas*[2], *Lars K Rikardson*[1], *Shin W Lee*[1], *Wendy S Woods*[3], *Julia M. George*[3], *Chad M Rienstra*[1,2,3,4]. *(1) Department of Chemistry, University of Illinois, Champaign, IL 61822, United States (2) Center for Biophysics and Computational Biology, University of Illinois, United States (3) Department of Molecular and Integrative Physiology, University of Illinois, United States (4) Department of Biochemistry, University of Illinois, United States*

Inclusions in brain, mainly composed of aggregated protein termed α-synuclein (AS) fibrils, are proposed to cause Parkinson's disease (PD), multiple system atrophy and other neurodegenerative diseases. Although the detailed mechanism of how these fibrils are formed is not well understood, three AS point mutations—A53T(*1*), A30P(2) and E46K(*3*)—have been identified in the familial form of PD. In the current

investigation, the advantages of multidimensional solid-state NMR spectroscopy have been utilized to obtain site-specific chemical shift assignments for the identification of perturbations in secondary structure upon mutation.(*4*) Locating the structural anomalies induced by these mutations will lead to a more complete model of AS fibril formation important to the understanding of the pathogenesis of Parkinson's disease.

References
1. Polymeropoulos, M. H., et al. (1997) *Science 276*, 2045-2047.
2. Kruger, R., et al. (1998) *Nat. Genet. 18*, 106-108.
3. Zarranz, J. J., et al. (2004) *Ann. Neurol. 55*, 164-173.
4. Comellas, G., et al. (2011) *J. Mol. Biol. 411*, 881-895.

**RM_MWGL Regional Meeting 268**

## Rapid and accurate determination of entrapped volume and permeability in liposomal suspensions

***Jeffrey T Buboltz**, buboltzj@uwplatt.edu. Department of Chemistry and Engineering Physics, University of Wisconsin-Platteville, Platteville, WI 53818, United States*

Liposomes have long been used for a wide variety of purposes, ranging from clinical applications (e.g., anticancer drug formulations) to basic research (e.g., simple models for biological membranes). Over the last 45 years, an impressive toolbox of preparative techniques has been developed, allowing liposome scientists to produce suspensions of variable particle size, lamellarity, dispersity, and permeability. Perhaps the most popular parameter used to characterize suspensions is “entrapped volume”— aqueous volume enclosed per unit lipid—with values ranging from a lower limit of 0.3 µl/mg to 15 µl/mg or more. Here we describe a new assay that we have developed for determining both entrapped volume and permeability in liposomes. We compare our results to those obtained using independent methods, and we discuss important issues to be considered when undertaking such measurements.

**RM_MWGL Regional Meeting 269**

## Zinc and Manganese Homeostasis in Streptococcus pneumoniae and Myxococcus xanthus

***Faith E Jacobsen**[1], fejacobsen@mnu.edu, Lauren Brumley[1], Krystyna Kazmierczak[3], Malcolm Winkler[3], David Giedroc[2], Rion Taylor[1]. (1) Department of Math and Science, MidAmerica Nazarene University, Olathe, KS 66062, United States (2) Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States (3) Department of Biology, Indiana University, Bloomington, Indiana 47405, United States*

ICP-MS analysis of Streptococcus pneumoniae reveals a high cell-associated Mn(II) concentration that is comparable to that of Zn(II). Stressing these cells with 100-200 µM Zn(II) leads to a slow-growth phenotype and a total Mn(II) concentration that is reduced, with no decrease of other metal ions. Supplementation of the growth media with as little as 10 μM Mn(II) fully restores the growth defect and cell-associated Mn(II) to normal levels. DNA microarray analysis reveals that zinc stress induces the expected upregulation of czcD (encoding a zinc effluxer), but also a pleiotropic transcriptional response suggestive of mild cell wall stress. We conclude that Zn(II) toxicity results in a cytoplasmic Mn(II) deficiency, likely caused by competition at the uptake transporter protein PsaA. Subsequent studied on the bacteria Myxococcus xanthus may help illuminate the exact mechanism of toxicity.

**RM_MWGL Regional Meeting 270**

## Archaeal Histones: Homo- or Heterodimers?

***Lisa Gray**, lisagray@gus.pittstate.edu, Joshua Kristalyn, Meagan Miller, James G. McAfee, Irene S. Zegar.Chemistry, Pittsburg State University, Pittsburg, KS 66762, United States*

The histone fold is a structural domain that mediates homo and heterodimeric protein-protein interactions. Though the motif is ubiquitous in all three domains of life, it is more prevalent in the Archaea and Eukarya. The structure consists of a short N-terminal alpha helix followed by a loop that is linked to a very long alpha helix followed by a loop and a smaller alpha helix. This domain mediates homodimer and heterodimeric formation in a wide array of proteins associated with virtually every aspect of cellular metabolism. Since multimeric associations play key roles in cellular metabolism, it is essential that we understand the molecular determinants along with the kinetics and thermodynamics governing this association. The Euryarchaeota branch of the Archaea all contain histone orthologs that are designated as A and B types that share a high degree of sequence homology. All these proteins fold into homodimers when expressed in E. coli. We have cloned and over expressed the A and B type genes of the histone from the mesophilic Archaeon *Methanobreviter smithii* (*M. smithii*). Using reconstitution experiments and native gel electrophoresis, we have shown that both the heterodimers as well as homodimers of these two histones form. We have also conducted molecular docking studies and have shown that the heterodimer is as structurally feasible as the homodimer. To assess what structure occurs under physiologically relevant conditions where both proteins are expressed in the same cell, we will generate recombinant constructs that allow both A and B to be expressed from a polycistronic message. By linking each construct to a different affinity tag, we can selectively purify the homodimer and the heterodimer and quantify the resulting species using western analysis. We will investigate the kinetics and thermodynamics of homodimer and heterodimer formation using spectroscopic techniques.

**RM_MWGL Regional Meeting 271**

## New mass spectrometry technology for protein sequence analysis and beyond

***Joshua J Coon**, sbaustin@chem.wisc.edu. Departments of Chemistry and Biomolecular Chemistry, University of Wisconsin-Madison, Madison, WI 53706, United States*

We describe the development and use of new mass spectrometry technology – an electron transfer dissociation (ETD)-enabled Orbitrap – to map and quantify proteins on a global scale. The instrument allows for the implementation of multiple peptide dissociation methods, i.e., ion trap collision-activated dissociation (CAD), beam-type CAD (HCD), infrared-multiphoton dissociation (IRMPD), ETD, and combinations thereof, for the automated selection of each in a real-time based on precursor peptide attributes (i.e., data-dependent decision tree). Protein quantification is readily accomplished through use of isotopic labels – either SILAC or iTRAQ. The instrument will likewise propel top-down proteomics as acquisition of ETD-MS/MS spectra in the high resolving power Orbitrap allows for direct analysis of intact proteins on a sub-second timescale with ~300 ppb mass accuracies. Such mass accuracies are used to directly annotate ETD tandem mass spectral peaks with ion type and chemical composition. We demonstrate these and many other aspects of the instrument on a variety of applications.

**RM_MWGL Regional Meeting 272**

## Characterization of D-amino acid-containing peptides (DAACPs) in the central nervous system

***Lu Bai**[1,3], bailu.uiuc@gmail.com, Elena V Romanova[1,2], Itamar Livnat[1,3], Jonathan V Sweedler[1,2]. (1) Department of Molecular and Integrative Physiology, University of Illinois, Urbana-Champaign, Urbana, IL 61801, United States (2) Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (3) Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Neuropeptides play essential regulatory roles in cell-to-cell signal transmission in many aspects of body functions. Although it has been assumed that peptides in higher animals are made exclusively of L-amino acids, several D-amino acids have been found. Over 30 DAACPs have been described which target mulitple receptors in a variety of organisms spanning several phyla. In almost every case reported the endogenous DAACPs have shown higher bioactivities than the all-L epimers; these peptides form unique structures and also have slower digestion by exo-peptidases than the all-L forms of the peptide.

However, conventional sequencing techniques and mass spectrometry (MS) do not automatically distinguish different configurations. The lack of effective analytical techniques has hindered the identification of novel DAACPs.

A direct and targeted approach was developed using homology search followed by MS confirmation. A novel DAACP, GdFFD, was discovered through homology with a similar

peptide in a related species. In order to identify novel DAACPs, we used an aminopeptidase digestion method which consumes all-L peptides faster than DAACPs. Chiral analysis was then conducted for potential DAACPs. This method combines the classic Marfey's reagent labeling method and the Multiple Reaction Monitoring techniques. Each L- and D-amino acid pair is resolved into separate channels and baseline separation was achieved for each pair at a detection limit of $10^{-15}$ mol. We have identified putative DAACPs which are to be confirmed by further analysis with the use of standards.

We hypothesize the distribution of DAACPs throughout the metazoan is wider than currently known, and with these approaches we will be able to test this hypothesis in the mammalian brains. My research combines a novel suite of tools to provide new physiological understanding of what may be the most enigmatic modification in a peptide.

**RM_MWGL Regional Meeting 273**

## Protein interaction reporter: “News” on protein topologies in cells

***James E Bruce**, jimbruce@u.washington.edu, Juan D Chavez, Chunxiang Zheng, Li Yang, Chad Weisbrod. Center for Genome Sciences, University of Washington, Seattle, WA 98109, United States*

Life on earth has evolved to use proteins nearly exclusively as functional molecules due to the diversity and specificity of topological features that are possible with sequences of amino acids. In cells, proteins interact with other molecules either by directly binding or reaction. In all cases, interactions are resultant from protein topological features that are themselves, the products of selective adaptation. These molecular interactions, protein abundance levels and other factors such as posttranslational modifications serve in complex ways to regulate global functional levels in cells. However, topological features of proteins and their interactions are ultimately at the origin of all fundamental biological processes. Therefore, improved technologies that can help visualize topological features of protein interactions in cells will increase understanding of functional networks and their relationships to disease and normal function. This presentation will highlight our efforts to develop and apply Protein Interaction Reporter (PIR) technology (1) to enable topological measurements of proteins and protein complexes in cells. Because of its unique features, PIR technology enables unambiguous cross-linked peptide identification that has resulted in the largest set of identified in vivo cross-linked peptides produced to date (2). Several examples of in vivo PIR data will be discussed to illustrate the excellent agreement with available protein and complex crystal structures. Finally, examples from our PIR data will also be presented to show how this technology can provide novel in vivo topological information that can impact understanding of biological function, even for cases where high resolution structures are not known.

1. Tang X, Munske GR, Siems WF, Bruce JE. Mass spectrometry identifiable cross-

linking strategy for studying protein-protein interactions. *Anal Chem.* 2005 Jan 1;**77(1)**:311-8.
2. Zheng C, Yang L, Hoopmann MR, Eng JK, Tang X, Weisbrod CR, Bruce JE. Cross-linking measurements of in vivo protein complex topologies. *Mol Cell Proteomics*. 2011, in press.

## RM_MWGL Regional Meeting 274

### Directed mass spectrometry: Molecular dissection of androgen signaling networks in human disease

*Jordy J Hsaio, Harryl D Martinez, **Michael D Wright**, michael-e-wright@uiowa.edu. Department of Molecular Physiology & Biophysics, University of Iowa Carver College of Medicine, Iowa City, IA 52242, United States*

Quantitative proteomic technologies have immense value in the study of human health and disease. They allow us to delineate signal-transduction pathways involved in biological processes, assess their dynamic behaviors in response to inputs, and establish how their dysregulation contributes to the diseased state. I will present a label-free, quantitative proteomic workflow in which directed mass spectrometry (MS) is used to study androgen signaling networks in human prostate cancer. In addition, I will describe proteomic experiments that have taken advantage of this approach to: define the complement of androgen-sensitive glycoproteins present in prostate cancer cells, delineate the androgen-dependent protein expression networks in prostate cancer cells, and profile glycoprotein biomarker expression in clinical tissue samples of human prostate cancer. I will highlight both the simplicity of implementing these label-free, quantitative workflows on the Agilent Accurate-Mass 6520 Q-TOF mass spectrometer, and the advantages that directed MS workflows offer over traditional shotgun proteomic workflows with respect to studying complex protein mixtures.

## RM_MWGL Regional Meeting 275

### Mass spectrometry characterization of a therapeutic antibody conjugate

***Justin B. Sperry**[1], justin.sperry@pfizer.com, Jason C Rouse[2], James A Carroll[1]. (1) BioTherapeutics Mass Spectrometry, Pfizer, Chesterfield, MO 63017, United States (2) BioTherapeutics Mass Spectrometry, Pfizer, Andover, MA 01810, United States*

The diversity of biotherapeutics continues to expand through the use of novel constructs and unique conjugation strategies, which further emphasizes the importance of thorough structural characterization during process and product development. Biotherapeutics, at present, encompass various modalities including peptides, oligonucleotides, carbohydrates, recombinant proteins, monoclonal antibodies, fusion proteins, and protein conjugates with drugs, polypeptides, synthetic polymers, polysaccharides, etc. The in-depth characterization of biotherapeutics relies heavily on a variety of routine and non-routine mass spectrometry-based assays. Our ability to

understand the inherent complexity of biotherapeutics has advanced along with mass spectrometry technology and instrumentation. This presentation will highlight bottom-up, middle-down and top-down mass spectrometry-based assays used to characterize a therapeutic antibody conjugate. The assays encompass several strategies for characterization, including the use of multiple proteolytic enzymes to verify site occupancy and post-translational modifications, the use of an immunoglobulin degrading enzyme (IdeS) from *S. pyogenes* to generate isotopically resolved antibody subunits, and ETD-based fragmentation of intact and antibody subunits.

**RM_MWGL Regional Meeting 276**

## Helical dimanganese-(salen) complexes and application in asymmetric epoxidation of olefin

***Tingting Liu**, tingting@ksu.edu, Christopher Levy, John Desper.Chemistry Department, Kansas State University, Manhattan, KS 66502, United States*

A series of chiral dimanganese(III/III, IV/IV) complexes with helix-directing salen ligands have been prepared, characterized and studied. The ligands have either the (*1R*,*2R*)-cyclohexyl or (*R*)-binaphthyl chiral backbones. In most cases the metal adopts a *β*-cis octahedral geometry and *M*-helicity. The Mn(III)-Mn(III) dimer has one $h^4$-salen ligand coordinated to each metal center as well as a bridging salen ligand, which is $h^2$ to one metal center and $h^1$ to the other in the solid state structure. The Mn(IV)-Mn(IV) species are bis(*m*-oxo) bridged dimers that result from dioxygen oxidation. The Mn(salen) complexes could effectively and enatioselectively catalyze the asymmetric epoxidation of some *trans*, *cis* and terminal olefins using various oxidants and conditions.

**RM_MWGL Regional Meeting 277**

## Anisotropy tensor alignment in {$Fe^{III}{}_nNi^{II}{}_m$} cyanometalate-based single-molecule magnets

***Philip J Janini**[1], pjjm84@mail.umsl.edu, Yuanzhu Zhang[1], Uma P Mallik[1], Nigam Rath[1], Rodolphe Clérac[2], Stephen M Holmes[1,3]. (1) Department of Chemistry and Biochemistry, University of Missouri-Saint Louis, Saint Louis, Missouri 63121, United States (2) Centre de Recherche Paul Pascal, Université de Bordeaux, Pessac, France (3) Center for Nanoscience, University of Missouri-Saint Louis, Saint Louis, Missouri 63121, United States*

Recently reported cyanometalate complexes are compared in terms of their structures, total spin state, and anisotropy tensor alignment. We find that anisotropy tensor alignment, achieved through ligand choice, acts to increase the magnetic isotropy of single molecule magnets (SSMs), and concomitantly affords higher barriers to magnetization reversal.
Examples of this behavior are found in two cyano-bridged single-molecule magnets (SMMs) of {$Fe^{III}{}_4Ni^{II}{}_2$} (**1**) and {$Fe^{III}{}_6Ni^{II}{}_3$} (**2**) stoichiometry. Both **1** and **2** exhibit slow

relaxation dynamics that are related to structural distortions of their molecular cores and the relative orientations of their anisotropy axes. Further support for this hypothesis is found when comparing a new low symmetry and linear octanuclear cyano-based $\{Fe^{III}_4Ni^{II}_4\}$ single-molecule magnet (**3**) to its more symmetrical box-shaped analogue (**4**). We find that compound **3** exhibits the highest energy barrier ($D/k_B$ ~ 33 K) for magnetization reversal seen for any first-row cyanide-based complex demonstrating that the overall molecular structure and projection of single ion anisotropy tensors is often more important than overall spin of these single-molecule magnets.

## RM_MWGL Regional Meeting 278

## Coordination of bqp on Rhenium(I)

***Clayton J. Bosworth****, clayton.bosworth@my.und.edu, Delanie J. Losey, Daniel R. Black, Sean E. Hightower. Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202, United States*

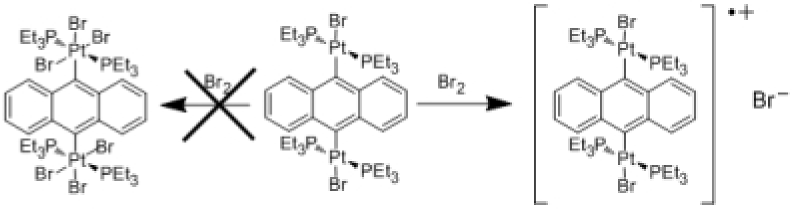
Rhenium(I) diimine complexes have shown similar reactivity as comparable ruthenium(I) and osmium(I) complexes. Compounds with bipyridine (bpy) and terpyridine (tpy) ligands have been studied and show improved visible absorption when moving from the bis- to the tris-chelation. The use of larger aromatic imines has suggested stronger as well as complete visible absorption. The object of this study was to the coordination of 2,6-bis(8'-quinolinyl)-pyridine (bqp) ligand to form complexes of the type *fac*-$[Re(\eta^2\text{-bqp})(CO)_3L]^{n+}$ and *cis*-$[Re(\eta^3\text{-bqp})(CO)_2L]^{n+}$ (where L is $Cl^-$, $NCCH_3$, $NC_5H_5$, or $PPh_3$; n = 0 or 1). The investigation was to determine if earlier methods would coordinate the bqp ligand and assess the reactivity.
These compounds were characterized using IR, NMR, UV-Vis, and fluorescence spectroscopy, as well as, studying the electrochemical properties. The complexes *fac*-$[Re(\eta^2\text{-bqp})(CO)_3(NCCH_3)]^{1+}$ and *fac*-$[Re(\eta^2\text{-bqp})(CO)_3Cl]$ were able to be formed from earlier methods. This is attributed to increased hindrance caused by the free quinolinyl ring on larger entering groups. These compounds have higher molar extinction coefficients and absorb more of the visible region than related rhenium(I) bpy and tpy complexes.

## RM_MWGL Regional Meeting 279

## Electronic communication and reaction chemistry of dinuclear anthracene bridged platinum complexes

***Yang Li****, ylt3c@mail.missouri.edu, Paul R Sharp. Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, United States*

The dinuclear anthracene bridged platinum compound di-trans-$Pt(PEt_3)_2$ (Br) (anthracen-9,10-yl) (**1**) can be easily oxidized to form a stable monocationic radical when treated with $Br_2$, while normal low valent late transition metal complexes will undergo oxidative addition or metal-carbon bond cleavage. The electronic properties of complexes **1** and [**1**]**BF$_4$** were investigated using cyclic voltammetry (CV), variable temperature EPR, IR, near-IR and UV/Visible spectroscopy. Derivatives of **1** are also synthesized and characterized.

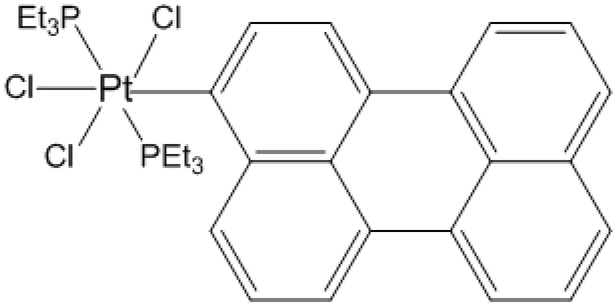


**RM_MWGL Regional Meeting 280**

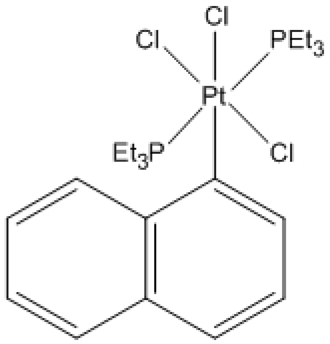
## Reductive Photoelimination of Chlorine from Organoplatinum(IV)Chloro Complexes

***Tharushi A Perera***, *tap53f@mail.missouri.edu, Morgan Moody, Paul R Sharp.Chemistry, University of Missouri, Columbia, Missouri 65201, United States*

Solar energy storage in Chemical bonds is vital in renewable fuel technologies. Halogen photoelimination is a crucial step in possible transition metal catalyzed solar energy storage processes but is uncommon. We have found chlorine photoelimination from the Pt(IV) centers of *trans*-Pt(Cl$_3$)(PEt$_3$)$_2$(C$_7$H$_4$F$_3$) and *trans*-Pt(Cl$_3$)(PEt$_3$)$_2$(C$_{14}$H$_9$) in the presence of chlorine traps. Our studies of these reactions will be reported along with those of analogous Pt(IV)chloro complexes of perylene



and naphthalene



that have yet to be prepared.

## RM_MWGL Regional Meeting 281

## Cloning, Purification and Characterization of Acetate Kinase from Methicillin resistant *Staphylococcus aureus* Mu50 strain

***Tyler McCune**, tyler.mccune@mtmc.edu, Chun Wu. Department of Chemistry, Mount Marty College, Yankton, SD 57078, United States*

Methicillin Resistant *Staphylococcus aureus* (MRSA) refers to the various strains of the gram-positive, coccal bacteria that are resistant to one, or multiple, antibiotics. Our previous study revealed that development of a new class of antibiotics targeting bacterial central metabolism is promising to combat MRSA and its ever-increasing list of resistances. MRSA acetate kinase was one of such targets due to its involvement in central metabolism, its *in silico* essentiality to the survival of MRSA, and its absence in humans. In this study, the gene encoding MRSA acetate kinase (sav1711) was PCR amplified, ligated into pRSET plasmid A and transformed into *E. coli* Dh5α - DNA sequencing confirmed 100 % fidelity. The recombinant plasmid was transformed into *E. coli.* BL21(DE3)pLysS for IPTG induced overexpression. The protein was purified by Ni-NTA system(Qiagen). MALDI-MS analysis and kinetic assay confirmed its acetate kinase nature. Future work includes: validation of essentiality of MRSA acetate kinase, crystal structure development of both apo acetate kinase and acetate kinase-adenosine 5-[γ-thio]triphosphate complex, and rational inhibitor design.

## RM_MWGL Regional Meeting 282

## An Exploration on Purification of putative Fructose 1, 6-Bisphosphate Adolase from Methicillin resistant *Staphylococcus aureus Mu50* strain

***Emily Girad**, emily.girard@mtmc.edu, Chun Wu. Mount Marty College, United States*

Methicillin resistant *Staphylococcus aureus* (MRSA) are antibiotic resistant strains of bacteria which cause life-threatening infections in immunocompromised patients. Through our previously reported *in silico* approach, a class of potential drug targets

essential to the survival of MRSA and absent in the human genome were identified, among which putative fructose 1, 6 bisphosphate aldolase (FBPA) was investigated in this study. The gene encoding FBPA was cloned into plasmid pRSET A. The recombinant plasmid was transformed into competent *E. coli.* DH5α then expressed in *E. coli.* BL21(DE3)pLysS. Western blot confirmed the presence of his-tagged FPBA in IPTG induced whole cells and cell lysate, which is in contradictory to the incompetence of 6×His/Ni-NTA system to purify the protein. The conventional ionic exchange chromatography and size exclusion chromatography were employed consecutively. MS analysis revealed that the purified protein was Glyceraldehyde 3-Phosphate dehydrogenase from *E. coli,* as opposed to *MRSA* FBPA, which may be imputed to the preferential interaction between FBPA and glyceraldehyde-3-phosphate dehydrogenase (G3PD) in a mixture of cytosolic proteins. Future work includes MS detection of *MRSA* FBPA in cell lysates and development of alternative purification system to separate FBPA from FBPA-G3PD mixture.

## RM_MWGL Regional Meeting 283

## Comparative analysis of protein phosphorylation in the Protein Databank: What have we known?

***Mengyi Zha***[1], *mzha@unomaha.edu, Julia Warnke*[2]*, Haizhen Zhong*[1]*. (1) Department of Chemistry, University of Nebraska at Omaha, Omaha, NE 68182, United States (2) College of Information Science & Technology, University of Nebraska at Omaha, Omaha, NE 68182, United States*

Protein phosphorylation is involved in many cellular processes, such as DNA replication, gene transcription, cell growth and metabolism, and intercellular communications. In mammalian cells, signal transduction in many cases is accomplished by protein phosphorylation, a process that adds a phosphate group on the hydroxyl moiety of an amino acid side chain, modifying a Ser, Thr, and Tyr to pSer, pThr, and pTyr, respectively. In this project, we studied the sequential and structural features for the phosphorylation of Ser, Thr, and Tyr by comparing available sequences in the protein databank. We have identified some unique motifs for each family of the above phosphorylated proteins. We have also investigated the structural changes caused by the phosphorylation.

## RM_MWGL Regional Meeting 284

## Synthesis of 3-pyridylmethyl glucosinolate from 3-pyridylacetonitrile

***Joseph W Keppen****, jwkeppen10@ole.augie.edu, Jordan J Clark, Jared R Mays. Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

*Brassica* vegetables exhibit chemopreventive activities as a result of the enzymatic hydrolysis of glucosinolates into isothiocyanates (ITCs) via myrosinase. Non-natural ITCs have been identified as promising lead compounds versus the natural product, L-

sulforaphane. While 3-pyridylmethyl isothiocyanate demonstrated potent antiproliferation activity, its corresponding glucosinolate has yet to be produced, largely due to difficulties in obtaining the intermediate 3-pyridylethanal. Several reductive methods to obtain 3-pyridylethanal from 3-pyridylacetonitrile have been investigated. Preliminary evidence suggests 3-pyridylethanal can be formed through the reduction of 3-pyridylacetonitrile with DIBAL.

### RM_MWGL Regional Meeting 285

## Synthesis and RP-HPLC Monitored Hydrolysis of Non-natural Glucosinolates

***Kayla J. Vastenhout**, kjv_2008@yahoo.com, Jared R. Mays. Augustana College, Sioux Falls, South Dakota 57197, United States*

Studies have shown that diets rich in the Brassica vegetables are associated with reduced risks of cancer. These vegetables contain chemopreventive precursors, called glucosinolates, that undergo a myrosinase-dependent hydrolysis when digested in the body. The goal of this project was to synthesize two non-natural glucosinolates and monitor their hydrolysis to isothiocyanates using RP-HPLC. Both glucosinolates were successfully synthesized in 11% and 19% yields over five steps. An RP-HPLC assay was developed as a method to compare the ability of synthetic glucosinolates to serve as myrosinase substrates and extract the kinetic parameters of the transformation. Using this method, $K_m$ and $k_{cat}$ were determined for both glucosinolates by monitoring multiple wavelengths.

### RM_MWGL Regional Meeting 286

## Exploring the Significance of F427 in Anthrax Protective Antigen using $^{19}$F-NMR

***Letisha J Ferris**, ljmassey@wichita.edu, James G Bann. Department of Chemistry, Wichita State University, Wichita, KS 67208, United States*

The anthrax toxin is secreted by *Bacillus anthracis* and is composed of three components, which are protective antigen (PA), lethal factor, and edema factor. Heptamerized PA enters a host cell by way of receptor-mediated endocytosis. Decreased pH within the endosome is thought to trigger the formation of a pore that spans the endosome membrane. That is to say, the conversion of the prepore heptameric structure to a functional pore is thought to be a pH sensitive process. Lethal factor and edema factor are the enzymatic components of the toxin and are translocated into a host cell by way of the transmembrane heptameric pore formed from protective antigen. The exact mechanism of pore formation and translocation of lethal factor and edema factor is unknown, but research suggests specific residues play essential roles in these processes.

PA is composed of four domains. Domain 2 lies on the luminal aspect of the prepore heptamer structure. During the prepore to pore conversion, the F427 residues are

thought to converge in order to facilitate the unfolding and translocation of the enzymatic components of the anthrax toxin. In order to study the significance of F427, we labeled this residue with fluorophenylalanine by utilizing Furter's site-specific labeling methodology, which requires the use of a nonessential heterologous amber suppressor tRNA/synthetase pair along with an F427Amber mutant of *pa*. Because the fluorine atom is sensitive to molecular environment, placing a single fluorine at the para position of F427 allows monitoring of the conformational changes at F427 using 19F-NMR. Our initial studies indicate that in the heptamer, F427 senses two separate molecular environments, which we propose represent pore competent and pore incompetent states.

## RM_MWGL Regional Meeting 287

### Optical and DNA binding studies of *N*-fused heterocyclic cations based on quinazoline scaffold

***Clayton Galloway****, sundeep@ksu.edu, Christopher A Larson, Olajide Alawode, Vijaya Kumar Naganaboina, Sundeep Rayat. Kansas State University, United States*

Among the various intercalators known to date, the cationic heterocycles show increased propensity to bind to DNA due to the electrostatic interactions between the positively charged guest and negatively charged sugar phosphate backbone of the DNA. These have found applications as light-up probes for the detection of nucleic acids, and photoactivated DNA cleaving agents for intentional DNA damage. In our laboratory, we have achieved the synthesis of a new class of *N*-fused heterocyclic cations based on quinazoliniminium scaffold. In this study, the absorption and fluorescence spectra of these compounds were obtained in a range of solvents. The fluorescence quantum yields of these compounds were calculated in solution and were found to be low. The DNA binding studies were carried out by a combination of UV, fluorescence and circular dichroism spectroscopy. The UV titrations show that the synthesized compounds interact with DNA in more than one binding mode. Upon binding of these cations to DNA, an enhancement in fluorescence was observed.

## RM_MWGL Regional Meeting 288

### A putative mammalian riboswitch in the spermine biosynthetic pathway

***Katie Del Vecchio****, katiedelvecchio@creighton.edu, Jodi Monahan, Molly McDevitt, Garrett Soukup, Juliane Soukup. Creighton University, United States*

Riboswitches are elements within messenger RNAs (mRNAs) that directly bind to cellular metabolites and modulate gene expression. Approximately 20 metabolite-binding riboswitch classes have been characterized, and many provide a mechanism of feedback regulation for gene products within the biosynthetic pathway of the cognate metabolite. Although riboswitches are widespread among bacteria, and one class further resides in fungi and plants, no riboswitches have been identified in animals. We

are investigating a highly conserved frameshift stimulatory pseudoknot (PK) RNA that we hypothesize is a mammalian riboswitch involved in polyamine biosynthesis. Our results indicate that the PK RNA binds with greater specificity to the polyamine spermine than do other PK RNAs and that spermine binding to the PK RNA specifically elicits conformational change, a fundamental property of riboswitches. Moreover, the integrity of the PK RNA facilitates spermine-dependent reporter protein expression and inhibits general polyamine-induced alternative open reading frame usage. Although spermine binding is a universal property of nucleic acids, our results suggest that the PK RNA utilizes the interaction to hone protein translation. Function of the PK RNA as a spermine sensor and putative mammalian riboswitch indicates a substantially broader distribution of riboswitches among eukaryotic organisms and offers a novel target for affecting a key metabolic process relevant to cancer and other disease.

The project described was supported by the NIH grant number P20 RR016469 from the INBRE Program of the National Center for Research Resources. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of NIH.

## RM_MWGL Regional Meeting 289

## *glmS* ribozyme mechanism and development of artificial agonists as candidate antibiotics

***Erin Johnson***[1]*, erinjohnson2@creighton.edu, Molly McDevitt*[1]*, Danielle Renner*[1]*, Xiang Fei*[2]*, David Berkowitz*[2]*, Garrett Soukup*[1]*, Juliane Soukup*[1]*. (1) Creighton University, United States (2) University of Nebraska-Lincoln, United States*

The bacterial *glmS* ribozyme is a mechanistically unique functional RNA among both riboswitches and RNA catalysts. Its self-cleavage activity is the basis of riboswitch regulation of glucosamine-6-phosphate (GlcN6P) production, and catalysis requires GlcN6P as a coenzyme. A substantial body of biochemical and biophysical data relating the structure and function of the *glmS* ribozyme has been amassed in a relatively short period of time since its discovery. However, a precise and comprehensive mechanistic understanding of coenzyme function in *glmS* ribozyme self-cleavage has not been elaborated. Careful consideration of the available biochemical and biophysical data relating the structure and function of the *glmS* ribozyme necessitates that general acid and general base catalysis in a coenzyme-dependent active site mechanism of RNA cleavage are inherently interdependent. We have proposed a comprehensive mechanistic model wherein the coenzyme, GlcN6P, functions both as the initial general base catalyst and consequent general acid catalyst within a proton-relay, thus fulfilling the apparent biochemical requirements for activity. Preliminary results reveal a kinetic isotope effect in the presence of deuterium indicating a role for protons in the mechanism of the ribozyme. We are also developing non-natural GlcN6P analogs that retain coenzyme function and work as artificial riboswitch agonists. Two such compounds are candidate antibiotics that might disrupt normal cell metabolism in a variety of human pathogens that harbor the *glmS* ribozyme.

The project described was supported by the NIH grant number 2R15GM083641-02. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of NIH.

## RM_MWGL Regional Meeting 290

### Thermodynamic contribution of pseudouridine·adenosine base pairs in oligoribonucleotides

***Graham A. Hudson**, ghudson2@slu.edu, Richard Bloomingdale, Wanying Qu, Vikram E. Ponnusamy, Brent M. Znosko. Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

Pseudouridine (Ψ) is the most abundant modified nucleoside present in naturally occurring RNA. Ψ is thought to play a significant role in the formation and stabilization of RNA secondary and tertiary structure. Most non-coding RNAs depend on structure to function correctly, emphasizing the necessity to accurately model and predict secondary and tertiary structures. Secondary structure prediction is most commonly done using the nearest neighbor model which derives thermodynamic parameters for double stranded nucleic acids as a whole by summing the interactions between adjacent base pairs. Currently, nearest neighbor parameters for Ψ·A base pairs have not yet been derived. As such, the thermodynamic contribution of Ψ·A base pairs to duplex stability was investigated via optical melting. Thermodynamic parameters for a series of 16 oligoribonucleotides containing single Ψ·A pairs adjacent to Watson-Crick pairs are reported here. In order to determine the nearest neighbor parameters for Ψ·A pairs, four duplexes containing 3'-terminal Ψ·A pairs and four duplexes containing 5'-terminal Ψ·A pairs have also been thermodynamically characterized. Nearest neighbor parameters for all nearest neighbor combinations of Ψ·A pairs and an additional parameter for terminal Ψ·A pairs have been derived via linear regression. The stabilities of duplexes containing Ψ·A pairs were compared to the stabilities of the same duplexes containing U-A pairs.

## RM_MWGL Regional Meeting 291

### Establishment of photo-activated localization microscopy (PALM) for imaging signaling complexes on the surfaces of cells

***Bradley E Iverson**, beiverson@jacks.sdstate.edu, Adam Hoppe. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57007, United States*

Photo-Activated Localization Microscopy (PALM) allows visualization of fluorescent molecules inside cells at 10 times the resolution of existing optical microscopes. The 10-50 nanometer resolution afforded by PALM should provide new insight into the organization of receptor signal transduction occurring on the surfaces of cells. Our initial

work focused on cells expressing phagocytic Fc receptor (FcR) fused to photo-activateable Green Fluorescent Protein (paGFP). At the start of the experiment the paGFP-FcR were not fluorescent. A small fraction of the paGFP molecules were photo-activated using a 405 nm laser such that single molecules could be imaged using 488 nm laser excitation until they photobleached. Both lasers illuminated the sample by through-the-objective Total Internal Reflection (TIR), which allowed for selective imaging of molecules within about 200 nm of the cell/coverglass interface. By alternating laser excitations, thousands of images of single molecules were obtained. These images were then analyzed using the ImageJ plugin, QuickPALM, which performs a least squares fit of a two dimensional Gaussian to each fluorescent spot captured in the PALM images. This process then recovered the most probable position of each paGFP-FcR molecule to create super resolution images of the distribution of paGFP-FcR in the cell. Ongoing efforts are aimed at establishing two color PALM to determine the distribution of signaling receptors relative to key regulators of signaling.

## RM_MWGL Regional Meeting 292

## Evaluating transgenic *Xenopus* as a model system for the expression of secreted proteins

***Katelyn R Marshall***[1], *krmarshall@coe.edu, Maria A Dean*[1], *Joseph G Laird*[2], *Sheila A Baker*[2]*. (1) Department of Chemistry, Coe College, Cedar Rapids, IA 52402, United States (2) Department of Biochemistry, University of Iowa, Iowa City, IA 52242, United States*

Model systems such as E. coli and yeast are frequently used to express and purify heterologous proteins for subsequent biochemical analyses. However, some proteins, particularly those that are extensively post-translationally modified, can be toxic and difficult to purify from these systems. In this study we used GFP as a reporter to investigate the feasibility of expressing heterologous proteins from secretory tissues of transgenic tadpoles (*Xenopus laevis*). Tadpoles were made transgenic by restriction enzyme mediated integration (REMI). GFP was cloned under the control of the larval keratin promoter to drive expression in the skin. GFP expression in the skin was apparent in early developmental stages, but expression was non-uniform in distribution and brightness. Next, we cloned a signal sequence onto GFP so it would be secreted from the skin into the buffer housing the tadpoles. GFP was secreted from the skin, easily collected and assayed using Western blot and a GFP fluorescence assay. We also cloned GFP under the control of the XAG-1 promoter to drive uniform and robust expression in the cement and hatching glands. GFP expression in these tissues was observed using both promoters. We conclude that secretion from tadpole skin may be a viable method to obtain heterologous proteins for subsequent biochemical analyses.

## RM_MWGL Regional Meeting 293

## Potential for using waste glycerol from biodiesel production as a carbon source for heterotrophic algal feedstock production

***Chloe Wooldridge***, *chloewoo@ku.edu. Department of Civil, Environmental and Architectural Engineering, University of Kansas, Lawrence, Kansas 66045, United States*

The popularity and use of biodiesel has been increasing in recent years as an alternative fuel source. However, there is an issue with biodiesel production in the abundance of crude glycerine produced as the primary by-product, considering there are no feasible markets or disposal options for the product. It is possible that there could be a use for this by-product in algal growth, which is a high-lipid yielding feedstock.

This experiment explores the possibility of using this crude glycerine by-product and three different purified forms of crude glycerine as carbon sources for heterotrophic algal growth. Five flasks inoculated with heterotrophically grown algae and five with autotrophically grown algae were fed one of five types of media: (1) glucose, (2) crude glycerine, (3) distilled glycerine, (4) undistilled and acid washed glycerine, and (5) distilled and acid washed glycerine. Flasks were operated as semi-continuous flow reactors with a 10 day hydraulic residence time. Analyses were conducted to determine the toxicity of each media to algae (propidium iodide staining for dead cell count), growth of algae (total suspended solids, optical density, chlorophyll *a*, and 6-day growth rate), consumption of carbon from each media (chemical oxygen demand), and the production of lipids (total lipids by gas chromatography mass spectroscopy).

Results indicate that heterotrophic algae were able to grow and produce lipids best with acid washed glycerine (both distilled and undistilled). These two glycerine types maintained a healthy population (80-90% of total cells were alive) and a higher lipid content per dry weight (11-13% for the heterotrophic inoculated flasks) than the other glycerine types. Of these two, undistilled, acid washed glycerine will be used in additional experiments as it requires less pretreatment than distilled acid washed glycerine, making it more economical for large-scale use.

**RM_MWGL Regional Meeting 294**

## Thermodyanic Parameters for the Formation of RNA Duplexes with Triple Nucleotide Bulges

***Meghan H Murray***, *mmurra24@slu.edu, Jessicah A Hard, Amber R Davis, Brent M Znosko. Department of Chemistry and Biochemistry, Saint Louis University, Saint Louis, Missouri 63103, United States*

Triple nucleotide bulges in RNA commonly occur in nature, yet, little data exists concerning the thermodynamic parameters of this motif. Algorithms that predict RNA secondary structure from sequence currently attribute a constant free energy value, 3.2kcal/mol, to all triple nucleotide bulges regardless of bulge sequence. To test the accuracy of this model, RNA duplexes containing triple nucleotide bulges were optically melted, and their thermodynamic parameters: enthalpy, entropy, free energy, and melting temperature were determined. The LINEST function in Excel was then used to

derive a new model predicting the free energy of triple nucleotide bulges. This model takes both closing pair and bulge sequence into account and predicts free energy values more accurately than the current model.

### RM_MWGL Regional Meeting 295

## Effects of non-nearest neighbors on the stability of RNA GNRA tetraloops

***Pamela L. Vanegas**, pvanegas@slu.edu, Teresa S. Horwitz, Brent M. Znosko. Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

The structure-function relationship in RNA is well known yet not well understood. The primary cause of the lack of understanding stems from the abundance of RNA sequences for which the three-dimensional structure is still unknown. An essential first step in tertiary structure prediction is accurate secondary structure prediction, as secondary structure forms faster and is stronger than tertiary structure. Currently, several models exist that predict the secondary structure of RNA, one of which is free energy minimization using the Nearest Neighbor Model. This model predicts the lowest free energy secondary structure from a primary sequence by summing the free energy contributions of the Watson-Crick nearest neighbor base pair combinations and any non-canonical secondary structure motif. It also assumes that the secondary structure motif is solely dependent on the identities of the nucleotides within the motif and the motif's nearest neighbors. In order to test the assumption that the non-nearest neighbors do not affect the stability of the motif, different stem-loop sequences were optically melted to experimentally determine their thermodynamic parameters. In each of these sequences, the hairpin loop sequence and the adjacent base pairs were held constant, while the first or second non-nearest neighbors were varied. The experimental results show that the thermodynamic contribution of the hairpin loops was dependent upon the identity of the first non-nearest neighbor, while the second non-nearest neighbor had a less obvious effect. These results were then used to create an updated model to predict the thermodynamic contributions of a hairpin loop to the overall stability of the stem-loop.

### RM_MWGL Regional Meeting 296

## Fluorescence polarization imaging of sub-resolution membrane curvature during endocytic events

***Eric D Swanson**, eric.swanson@jacks.sdstate.edu, Jason G Kerkvliet, Hoppe D Adam. Department of Chemistry & Biochemistry, South Dakota State University, Brookings, South Dakota 57006, United States*

The curvature of lipid bilayers is essential to the formation of vesicles and viruses. Understanding the biochemistry behind these events requires new tools to quantify membrane curvature as well as membrane associated proteins. Axelrod and co-workers have shown that Total Internal Reflection Fluorescence (TIRF) microscopy enables

high-sensitivity visualization of membrane curvature within about 100 nm of the cover glass/cell interface. Here, we devised a novel approach for creating s-pol and p-pol TIRF fields by positioning lasers at distinct azimuthal positions in the back focal plane using a commercial two-dimensional scan head. A system was developed to measure membrane curvature on live mammalian cells utilizing the fluorescent carbocyanine dye DiI-C18-(3) (diI). DiI diffuses laterally through a lipid bilayer orienting such that its transition dipoles are parallel to the surface of the membrane. Thus, p-pol excites DiI perpendicular to the glass/liquid interface and s-pol excites the DiI parallel to the glass liquid interface. By dividing p-pol by s-pol, the curvature of the membrane was obtained. To visualize endocytic sites, Cos7 cells expressing YFP-clathrin and co-labeled with DiI were observed by TIRF microscopy under 514 nm and 561 nm laser illumination. This allowed visualization of clathrin association with the plasma membrane and curvature induced by clathrin. P/s ratios were measured at YFP-clatrhin endocytic sites.

### RM_MWGL Regional Meeting 297

## Determination of adenine nucleotide levels in rat urine by HPLC to elucidate the role of resveratrol in reducing cisplatin toxicity

***Heath J Gregg***[1]*, gregg_hj@wvwc.edu, Andrew W Hummer*[1]*, Timothy L Troyer*[1]*, Monica A Valentovic*[2]*. (1) Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201, United States (2) Department of Pharmacology, Marshall University, Huntington, WV 25704, United States*

Resveratrol has been shown to decrease the toxicity of cisplatin. It is proposed that the toxicity of cisplatin is a result of oxidative stress and that resveratrol attenuates the oxidative stress. Oxidative stress has been observed as function of the ratio of the adenine nucleotides. The ratio of adenine nucleotides has been determined using an HPLC assay. This project has been a collaborative effort between researchers at West Virginia Wesleyan College and Marshall University. Herein, we report the data we have collected on the ratio of the adenine nucleotides as determined in the HPLC assay at West Virginia Wesleyan College.

### RM_MWGL Regional Meeting 298

## Investigation of alcohol-tolerant deoxyribozymes

***Anit K. Behera****, abehera@slu.edu, Kennedy O. Alila, Dana A. Baum. Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

Deoxyribozymes, or DNAzymes, are DNA sequences with catalytic abilities. Utilizing a process known as in vitro selection, we set out to identify DNA sequences that rely on the presence of a pesticide to catalyze the ligation of two RNA substrates. Such pesticide-dependent deoxyribozymes are intended to serve as the basis for small molecule sensors. While characterizing the active deoxyribozymes that were isolated during these selection efforts, we found the sequences did not preferentially ligate the

RNA substrates and therefore were not dependent on the pesticide target as desired. Instead, we found that some of the deoxyribozymes required the inclusion of methanol, which was used in the selection reactions to improve pesticide solubility, for optimum RNA ligation activity. Currently, we are investigating this methanol dependence and are testing the inclusion of other alcohols and solvents. The results of these studies will be discussed.

## RM_MWGL Regional Meeting 299

### Synthesis of 1-butyl-3-methylimidazolium derivatives

***Mathew E Amundson***, *duane.weisshaar@augie.edu, Austin R Letcher, Gary W Earl, Duane E Weisshaar. Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

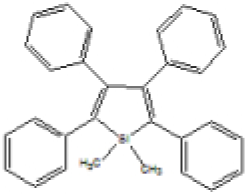
Prompted by a request from a colleague, this work sought to develop a reliable method of quaternizing butylimidazole using dimethyl carbonate (DMC) and converting the resulting methylcarbonate salt to the citrate. Butylimidazole was reacted with DMC at 130$^{o}$C in a pressure reactor for 20 hours (internal pressure ~100 psi). The reaction mixture was slowly added to enough citric acid to produce an equal mixture of the bis and tris product. The new mixture was maintained at 40$^{o}$C for 2 hours with continuous $N_2$ sparging to remove $CO_2$. Product was isolated by roto-evaporation at 100$^{o}$C. NMR and cation HPLC showed quaternization produced a mixture of 1-butyl-3-methylimidazolium methylcarbonate and the 2- or 4-carboxylate zwitterions. The citric acid reaction converted all products to the desired 1-butyl-3-methylimidazolium citrate. Proton integration of NMR spectra indicate the product was essentially the bis-product.

## RM_MWGL Regional Meeting 300

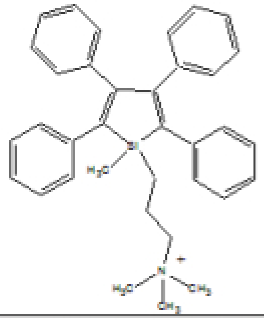
### Synthesis and Characterization of Hydrophobic and Hydrophilic Siloles for Cytotoxicity Studies and Applications in Printable Radio-frequency Antennas

***Evan Gardner***, *emgardner09@ole.augie.edu, Barrett Eichler. Chemistry Department, Augustana College, Sioux Falls, South Dakota 57197-0001, United States*

Siloles are highly pi-conjugated molecules with unique photoluminescent properties that have proven useful as fluorescent sensors in biological systems. Although they are efficient sensors for specific toxins such as chromium (VI) and arsenic (V), there have been few toxicity studies to date to determine if these properties are applicable. The synthesis and characterization of 1,1-dimethyl-2,3,4,5-tetraphenylsilole and 1-methyl-1-(3-amino)propyl-2,3,4,5,-tetraphenylsilole will be discussed. These siloles will be tested with liver cells to determine their cytotoxicity.



1,1-dimethyl-2,3,4,5-tetraphenylsilole



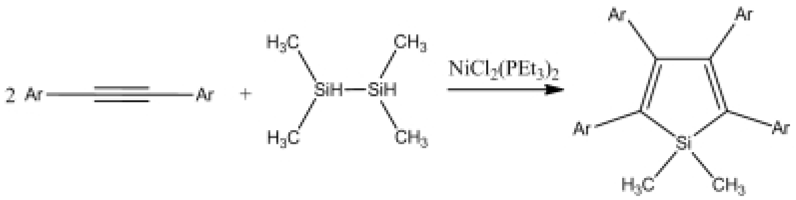
1-methyl-1-(3-trimethylammonium)propyl-2,3,4,5,-tetraphenylsilole

## RM_MWGL Regional Meeting 301

## Synthesis and Characterization of Novel 2,3,4,5-Tetraarylsilacyclopentadienes

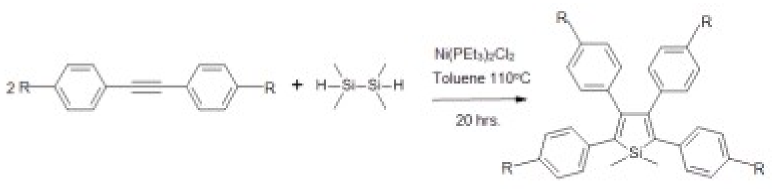
***Jared Drenkow***, *jrdrenkow08@ole.augie.edu, Barrett Eichler. Chemistry Department, Augustana College, Sioux Falls, SD 57197-0001, United States*

1-Silacyclopentadienes (siloles) are useful materials for organic light emitting diode (OLED) technology. Siloles exhibit a relatively low LUMO energy level, and the s*-π* conjugated gap located in the silicon-cyclopentyl ring results in a visibly luminescent material. Bis(3-quinolinyl)acetylene, bis(4-isoquinolinyl)acetylene, and dismesitylacetylene were synthesized for use to make 2,3,4,5-silicyclopentadienes by using a nickel catalyst with 1,1,2,2-tetramethyldisilane. Both quinoline-based acetylenes were synthesized in good yields and the novel dismesitylacetylene was created with a yield of 18.3%. Attempts to synthesize and isolate the desired siloles from these acetylenes will be discussed.



## RM_MWGL Regional Meeting 302

## Soluble Luminescent 2,3,4,5-Tetraarylsiloles Synthesis and Characterization for Use in OLED Devices



***Bailey Jackson**, bjjackson09@ole.augie.edu, Barrett Eichler.Chemistry Department, Augustana College, Sioux Falls, SD 57197-0001, United States*

Siloles are promising luminescent materials for the creation of organic light-emitting diodes (OLEDs). Attempts were made to create siloles with 4-bromophenyl, 4-*t*-butylphenyl, 4-trifluoromethylphenyl, and 4-trimethylsilylphenyl substituents on the 2,3,4,5-positions of the silole by using a nickel-catalyzed synthesis first proposed by Kumada in 1972. These particular substituents were chosen to compare and contrast the effects on the photophysical properties based on electron-donating versus electron-withdrawing groups. All products were characterized using proton, carbon, and silicon NMR, UV-vis absorption, melting point, and fluorescence. Further testing was done on successfully synthesized siloles to create OLED devices to test for quantum efficiencies.

### RM_MWGL Regional Meeting 303

## Synthesis of matrix metalloprotease chemical probes to profile enzyme activity

***Michelle E Boursier**[1], bourmi01@luther.edu, Kajal Nandy[2], Aaron T Wright[2]. (1) Department of Chemistry, Luther College, Decorah, Iowa 52101, United States (2) Department of Biological Separations and Mass Spectroscopy, Pacific Northwest National Laboratory, Richland, WA 99354, United States*

Activity-based protein profiling (ABPP) characterizes the function of enzymes through the use of substrate-mimicking chemical probes. Each of these probe molecules consists of three components: a reactive group that binds with the target enzyme, a binding group that acts like the body of the mimicked substrate, and a latent click-chemistry compatible reporter-tag that allows for the target enzyme to be detected, isolated, and identified in a biological system. ABPP was used in this study to specifically analyze the activity of matrix metalloproteases with the creation of four chemical probes. Matrix metalloproteases are important research targets as they are known to be upregulated during cancer pathogenesis and also contribute to bacterial and fungal pathogenesis. Two different amino acid scaffolds using phenylalanine and asparagine were created to determine the preferred substituent. Additionally, two different photoreactive groups of benzophenone and diazirine were added to the probes. Such groups are required for matrix metalloprotease probes to target only active enzymes, and the smaller diaziridine group could be a less-inhibiting probe component than the bulkier benzophenone. Although the four final probes have yet to be produced, the precursors were successfully synthesized using standard liquid-phase and solid-phase organic chemistry techniques. They were characterized though thin layer chromatography and $^1$H NMR analysis, showing that the projected synthetic route has thus far been successful. Overall yields for many of the synthetic steps were fairly low, but the projected amount of each probe produced will be enough to perform biological analyses using SDS-PAGE and LC-MS in the future. The complete synthesis of these probes and future syntheses using other amino acid groups will contribute to creating a library of probes for profiling the matrix metalloprotease enzyme family.

## RM_MWGL Regional Meeting 304

### Synthesis of isothiocyanates with electron-deficient aromatic rings

***Zachary Erickson***[1], *ericksoz@stolaf.edu, Jared R. Mays*[2]. *(1) Department of Chemistry, St. Olaf College, Northfield, MN 55057, United States (2) Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

Isothiocyanates (ITCs) with electron-deficient aromatic rings have potential uses as anti-cancer drugs. We set out to prepare four electron-deficient ITCs using a general synthetic scheme which utilized bromination, formylation, amination, and reduction reactions as the key steps. Significant progress has been made toward our target molecules and we envision these ITCs will be obtained and evaluated in the near future. More generally, we believe this work has established a valid approach to generate diverse synthetic ITCs.

## RM_MWGL Regional Meeting 305

### Selective COX-2 inhibition and anticancer activity of diarylalkynylsulfonamides complexed with hexacarbonyl dicobalt

***Peter Mancina***, *mancinap@lawrence.edu, Stefan Debbert.Department of Chemistry, Lawrence University, Appleton, Wisconsin 54911, United States*

Non-steroidal anti-inflammatory drugs (NSAIDs) such as aspirin and ibuprofen work by inhibiting the enzyme cyclooxygenase (COX), which plays an important role in inflammation. However, the COX enzyme is known to have multiple isoenzymes; if the isoenzyme COX-2 is selectively inhibited, the side effects associated with general NSAIDs are reduced. NSAIDs complexed with cobalt have shown both increased COX inhibition and notable anticancer activity.
Linear diarylalkynylsulfonamides have been shown to inhibit COX-2 selectively; by adding a cobalt complex to these drugs, we can modify the shape of these compounds to resemble known selective COX-2 inhibitors (i.e. Celebrex) more closely. Novel compounds of this kind were synthesized in three to five steps, and characterized by nuclear magnetic resonance (NMR) spectroscopy. The compounds are currently being assayed for both COX inhibition and activity against certain cancer cell lines. The results of these assays will be discussed.

## RM_MWGL Regional Meeting 306

### Synthesis of novel alkyne hexacarbonyldicobalt complexes and their effect on human breast and prostate cancer cells

**Catie Vornholt**, *childofshdws@gmail.com, Stefan Debbert. Department of Chemistry, Lawrence University, Appleton, Wisconsin 54911, United States*

Medicinal chemists have been able to increase asprin's anti-inflammatory properties and impart to it remarkable anticancer activity by attaching a cobalt-alkyne complex. The mode of action of that cobalt-alkyne-aspirin conjugate (Co-Asp) is thought to involve inhibition of a cyclooxygenase (COX) enzyme via transfer of an acetyl group; however, several other cobalt-alkyne compounds that lack an acetyl group still show good anticancer activity. To gain broader insight into the mode(s) of action of this novel class of anticancer compounds, we synthesized an array of [1-aryl-1-ethynylmethanol]hexacarbonyldicobalt compounds in three linear steps and characterized them by nuclear magnetic resonance (NMR) spectroscopy. These compounds share much in common with the lead compound, having similar polarities, molecular weights, and potential leaving groups adjacent to the cobalt-alkyne moiety. Compounds containing either electron-donating or electron-withdrawing groups on the aromatic ring were made; our hypothesis was that the former groups should stabilize cleavage of the propargyl C-O bonds, resulting in greater anticancer activity. These compounds are being assayed for activity against breast and prostate cancer cell lines (MDA-MB-231 and LNCap lines, respectively). Preliminary results suggest an $IC_{50}$ of 3-11 μM against the MDA-MB-231 line for all four cobalt-alkyne compounds tested. Further tests comparing the anticancer activities of these compounds before and after cobalt complexation are planned, along with other assays, including COX inhibition and caspase-3 activity.

---

**RM_MWGL Regional Meeting 307**

### Synthesis of a new monomer for a fluorescent conjugated polymer to act as a chemosensor

**Anne Pfeifle**[1], *ampfeifle09@ole.augie.edu, Jetty Duffy-Matzner[1], Sherryllene Pinnock[2], Megan Fegley[2], Abigail Oakes[2]. (1) Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States (2) Department of Chemistry, Binghamton University, Binghamton, NY 13902, United States*

The presence of metal cations in water has become an increasing environmental concern since 1970. There are a number of ways to test for the presence of these pollutants in the laboratory, but there is demand for a sensitive chemosensor which detects chemical analytes and is easy to synthesize, green, and portable for field use. One type of chemosensor, fitting these requirements, is a conjugated fluorescent polymer. Because of the electronic communication along the polymer backbone, conjugated fluorescent polymers are sensitive to the concentrations of metal cations. Jones, et al. have reported the synthesis and characterization of a polymer backbone, poly [*p*-(phenyleneethynylene)-*alt*-(thienyleneethynyl)] containing 1,4-diethynyl-2,5-didodecyloxybenzene. In order to increase conjugation of the polymer backbone, 2,6-diethynyl-1,5-didodecyloxynaphthalene was synthesized via a five step process and introduced into the polymer backbone. This monomer was characterized via $^1H$ and $^{13}C$

NMR. Photophysical studies of the new polymer, poly[2,5-(3-[N-methyl-N-(N',N'-dimethyl-2-ethanamino)methylamino]thiophenediyl)-1,2-ethynediyl-2,6-(1,5-didodecoxynaphthalenediyl)-1,2-ethynediyl], were done using UV-vis.

## RM_MWGL Regional Meeting 308

## Synthetic efforts towards a selective photodynamic therapy agent

***Frances A Venable***[2], *frances.venable@park.edu, Quinn A Best*[1], *Colleen N Scott*[1]. *(1) Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901, United States (2) Department of Natural Sciences, Park University, Parkville, Missouri 64152, United States*

We report on the synthesis and characterization of a series of fluorophores, which potentially could be used as photodynamic therapy agents. These fluorophores were designed to have a pH responsive action that may better target cancer cells that are known to be more acidic. The fluorophores consist of brominated analogs of rhodamine regulated by a spiro-cyclic structure that is responsive to environmental pH. It is our long term goal that this PDT agent could simultaneously be used for medical imaging and cancer treatment.

## RM_MWGL Regional Meeting 309

## Preparation of sulfones utilizing a new green ruthenium/aluminum oxide heterogeneous catalyst

***Garrett Meyer***[1], *mhali@semo.edu, Jacqueline Heath*[1], *Tawanika Willliams*[1], *Luke Clippard*[1], *Mohammed Ali*[1], *Bjorn Olesen*[1], *Brindaban Ranu*[2]. *(1) Department of Chemistry, Southeast Missouri State University, Cape Girardeau, MO 63701, United States (2) Organic Chemistry, Indian Association for the Cultivation of Science, Kolkata, West Bengal, India*

This paper reports on the result obtained by a group of Southeast Missouri State University undergraduate students participating in an International Research Experience for Undergraduate Students funded by the National Science Foundation. The work was done at the Indian Association for the Cultivation of Science in Kolkata, India. A number of different sulfides were oxidized to the corresponding sulfones using a new green ruthenium/aluminum oxide heterogeneous catalyst. The reactions were done in dimethyl carbonate at room temperature. Reaction yields ranged from 53 to 100% with reactions times of 1-3 hours. Sterically hindered sulfides gave lower yields and required longer reaction times.

## RM_MWGL Regional Meeting 310

## Preparation of sulfones utilizing a new green ionic liquid oxidizing reagent

*Tawanika Williams*[1]*,* ***Luke Clippard***[1]*, bolesen@semo.edu, Jacqueline Heath*[1]*, Garrett Meyer*[1]*, Mohammed Ali*[1]*, Bjorn Olesen*[1]*, Brindaban Ranu*[2]*. (1) Chemistry, Southeast Missouri State University, Cape Girardeau, MO 63701, United States (2) Organic Chemistry, Indian Association for the Cultivation of Science, Kolkata, West Bengal, India*

This paper reports on the result obtained by a group of Southeast Missouri State University undergraduate students participating in an International Research Experience for Undergraduate Students funded by the National Science Foundation. The work was done at the Indian Association for the Cultivation of Science in Kolkata, India. A number of different sulfides were oxidized to the corresponding sulfones using a new green periodate/ionic liquid reagent. The reactions were done at 60-70°. Reaction yields ranged from 23 to 92% with reactions times of 5-7 hours.

## RM_MWGL Regional Meeting 311

## Synthesis and DNA or RNA intercalation of 4-substituted naphthalimides

***Yi Ren****, yren2@slu.edu,* ***Tyler Zahrli****, Laura K. E. Hardebeck, Michael Lewis. Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, United States*

Intercalating agents are an important class of molecules because they can bind reversibly to DNA. These planar and aromatic compounds bind to DNA or RNA via insertion parallel to the hydrogen bonds and between two sets of base pairs. Naphthalimide, and its derivatives, bind to DNA and stabilize the double helix, eventually leading to apoptosis. The synthesis of four-substituted naphthalimide derivatives containing nitro, bromo, chloro, and amino groups, via condensation and hydrogenation reactions, will be presented. The characterization of all products and intermediates was performed by means of LCMS and NMR. The synthesized 4-substituted naphthalimides were intercalated into DNA and RNA and the resulting naphthalimide-DNA/RNA duplex was melted to obtain a $\Delta T_m$ value, which indicates the strength of the binding between the DNA/RNA and the naphthalimide. The synthesis, DNA/RNA-melting experiments, and analysis of the results will be presented.

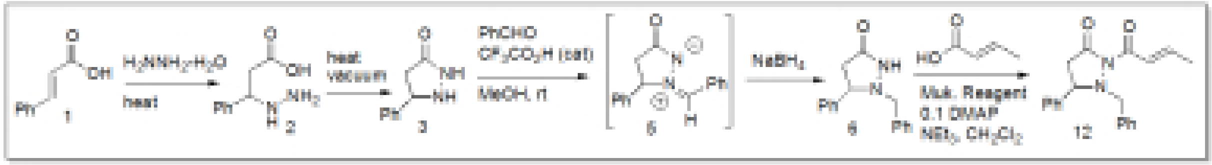
## RM_MWGL Regional Meeting 312

## Optimization of a Multistep Synthesis of Acyl Pyrazolidinones

***Pedro E Flores Gallardo****, Craig P Jasperse. Department of Chemistry, Minnesota State University, Moorhead, Moorhead, Minnesota 56563, United States*

The modular multistep synthesis of acyl pyrazolidinones such as **12** has been evaluated and partially optimized. The process begins with unsaturated acids (**1**) or esters. Reductive amination using aldehydes was used for introducing the N-1 alkyl substituent (**3**→**6**). A novel N-2-acylation using carboxylic acids can be effected by Mukaiyama's reagent (**6**→**12**). NMR (often with solvent suppression) and GC/MS have been used to

monitor the progress and purities of reaction. The vacuum requirements for effective ring closure (**2**→**3**) were screened, as well as conditions for rapid chromatographic purification of **6**. The modular synthesis is being developed for usage in undergraduate organic chemistry laboratory.



## RM_MWGL Regional Meeting 313

## Toward $^{18}$F-naproxen radiotracer synthesis via reductive elimination of a diaryliodonium salt

***Katey S Glaspy***[1], *easdon@cofo.edu, Jerry C Easdon*[1], *Linlin Qin*[2], *Kiel Neumann*[2], *Stephen DiMagno*[2]. *(1) Department of Chemistry, College of the Ozarks, Pt. Lookout, MO 65726, United States (2) Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68516, United States*

Positron Emission Topography (PET) is a non-invasive nuclear medical imaging technique that relies upon radioactive isotopes, such as F-18, to create images of functional processes in the body. PET uses various drug-like molecules, such as 2-deoxy-2-fluoroglucose or 6-fluoro-L-DOPA, that have been radiofluorinated. Previous methods of F-18 arene incorporation into electron rich aromatic compounds relied principally on electrophilic fluorination. This method produces tracers of low specific activity. The pharmacological profile of certain tracer candidates, such as $^{18}$F-fluorodopamine ($^{18}$FDA), renders the use of low specific activity radiotracers impractical.

This presentation discusses progress toward the goal of using “no-carrier-added” (n.c.a.) F-18 fluoride for the functionalization of electron-rich arenes. Specifically, diaryliodonium salt precursors are fluorinated by thermolysis of the fluoride salts in nonpolar solvents. To demonstrate the scope of this method we discuss preparation and attempted fluorination of a diaryliodonium salt derivative of naproxen. The overall synthetic methodology is: 1) protection of the carboxylic acid moiety of naproxen as a methyl ester, 2) electrophilic aromatic substitution with iodine, 3) oxidation of the iodine to I (III) (making the molecule into an iodonium salt), and 4) conversion to a diaryliodonium salt.

We describe herein our progress including nmr analysis of the intermediate compounds. Future research including optimization of fluorination with F-19, followed by radiofluorination at St. Jude Children's Research Hospital will also be described.

## RM_MWGL Regional Meeting 314

### Interference by matrix esters during headspace-gas chromatography analysis of volatile alcohols

***Grant M. Fischer***, *Martin.Power@Rockhurst.edu, Martin D. Power. Department of Chemistry, Rockhurst University, Kansas City, Missouri 64110, United States*

Phase II of an ongoing, multiphase study of the matrix interference phenomenon in headspace-gas chromatography (HS-GC) is being conducted. Phase I Data showed that the presence of primary amines in the sample matrix suppressed the GC peaks of the volatile aldehydes during the analysis HS-GC in comparison to the analyses of the sample matrix containing no amine. The current study explores the analysis of volatile alcohols in the presence and absence of esters in the sample matrix. Preliminary HS-GC data for methanol, ethanol, and 1-butanol supports our hypothesis that the alcohol signals are affected by the presence of added esters in the matrix. Specifically, the target analyte GC peak was suppressed and a new alcohol peak was observed. While the exact mechanism is beyond the scope of this work, the results are consistent with a transesterification mechanism in the interaction of the volatile alcohols with the matrix esters.

## RM_MWGL Regional Meeting 315

### Mechanistic Investigation of the γ-C-alkylation of β-Ketoesters using Equilibrating Conditions

***Joshua G Hinman***, *jghinman@mail.bradley.edu, Wayne B Bosma, Brad Andersh.Department of Chemistry and Biochemistry, Bradley University, Peoria, IL 61625, United States*

A green method for performing γ-C-alkylation of β-ketoesters using equilibrating bases (carbonate and alkoxide salts) has been developed. This reaction is unusual because: 1) it was previously believed that two equivalents of much stronger bases were necessary for this transformation, and 2) similar reaction conditions have been used for α-C-alkylation to generate enones via a Knoevenagel condensation reaction. Previous research on the mechanism for this unusual reaction has shown that the reaction proceeds by deprotonation at γ-carbon of the β-ketoester, addition of the resulting enolate ion of the β-ketoester to an aldehyde, followed by an intramolecular transesterification of the resulting hydroxyketoester intermediate. In an effort to understand how the γ-anion of the β-ketoester forms, computational and synthetic experiments were performed. Based upon this work, it appears that an intramolecular proton transfer is occurring to generate the γ-anion from the α-anion of the β-ketoester. The resulting γ-anion then adds to a non-enolizable aldehyde to either yield a hydroxyketoester or a 3-oxo-δ-lactone depending upon what solvent is used for the reaction.

## RM_MWGL Regional Meeting 316

## Utilization of β-Ketoester Monoanions for Amide Formation

***Jacob J Remsza**, jremsza@mail.bradley.edu, Brad Andersh. Department of Chemistry and Biochemistry, Bradley University, Peoria, Il 61625, United States*

A new method for the synthesis of amides from β-ketoesters has been developed. By treating the monoanion of a β-ketoester with two equivalents of an amine in ethanol, amide formation occurs in high yield with almost no detectible side products. In addition, both carbonyls of the β-ketoester undergo amidation and therefore, the only byproducts from the reaction are ethanol and sodium chloride after an acidic workup. Previously published methods for conducting similar chemistry involved placing an electron-withdrawing group on the α-carbon of the β-ketoester to improve the leaving group ability of the acetate ester anion. We have found that additional stabilization of the ester enolate is not necessary. Results from work on the identification of general reaction conditions that are compatible with a variety of amines and β-ketoesters will be presented.

## RM_MWGL Regional Meeting 317

## γ-C-alkylation of β-Ketoesters using Equilibrating Conditions: The Identity of the β-Ketoester

***Mollie E Roark**, mroark@mail.bradley.edu, Brad Andersh. Department of Chemistry and Biochemistry, Bradley University, Peoria, IL 61625, United States*

It has been found that β-ketoesters undergo γ-C-alkylation with non-enolizable aldehydes when one equivalent of an equilibrating base such as a carbonate or alkoxide salt is used. This discovery is surprising because it was previously believed that two equivalents of stronger bases were necessary for this transformation, and because similar reaction conditions have been used for α-C-alkylation to generate enones via a Knoevenagel condensation reaction. In an effort to understand how the structure of the β-ketoester influences the outcome of this reaction, the reactivity of a series of acetoacetate esters was investigated. In addition, the conformationally constrained β-keto ester, ethyl-2-oxocyclopentanecarboxylate, was used for this reaction to provide additional information about the mechanism by which this unique reaction is occurring.

## RM_MWGL Regional Meeting 318

## Synthesis and characterization of novel high-nitrogen energetic materials

*Dian E Romonosky, **Chelsea M Hadsall**, chadsall@millikin.edu, George D. Bennett, Paris W. Barnes. Department of Chemistry, Millikin University, Decatur, IL 62522, United States*

Fireworks displays are a year round attraction, but most people do not realize the harmful and toxic chemical species that are released into the environment during the explosion. Our goal is to synthesize new energetic materials that would be used as a pyrotechnic fuel to make them more environmentally friendly compared to what is currently being used. 3,6-dihydrazino-1,2,4,6-tetrazine and the 1,1-dimethylhydrazine derivative were synthesized and analyzed using $^{1}$H NMR, $^{13}$C NMR, and bomb calorimetry. If a compound is discovered that can be easily synthesized and releases the appropriate amount of energy, further research will be done to see if it can be incorporated into fireworks that produce minimal environmental waste.

## RM_MWGL Regional Meeting 319

### Synthesis of 3-oxo-δ-lactones via γ-C-alkylation of β-Ketoesters using Equilibrating Conditions

***Felicia S Couri***, *fcouri@mail.bradley.edu, Brad Andersh. Department of Chemistry and Biochemistry, Bradley University, Peoria, IL 61625, United States*

The synthesis of 3-oxo-δ-lactones is of interest because compounds containing this functionality exhibit antioxidant, antifungal, antiviral, and pain relieving properties. We have discovered a simple method for synthesizing these compounds, which involves treating a non-enolizable aldehyde and an acetoacetate ester with one equivalent of an equilibrating base in an anhydrous alcohol solvent. This reaction is unusual because it was previously believed that two equivalents of a strong base were necessary for the γ-C-alkylation of a β-ketoester, and because similar reaction conditions have been used for the Knoevenagel condensations (α-C-alkylation of β-ketoesters). Previous research on the mechanism for this unusual reaction has shown that the reaction proceeds by deprotonation at γ-carbon of the β-ketoester, addition of the resulting enolate ion of the β-ketoester to an aldehyde, followed by an intramolecular transesterification of the resulting hydroxyketoester intermediate. Results from our work with non-enolizable aldehydes including benzaldehyde derivatives, heteroaromatic aldehydes, and alkyl aldehydes will be presented.

## RM_MWGL Regional Meeting 320

### Towards the synthetic development of an anion binding molecule

***Elizabeth Sullivan***, *cbagwill@slu.edu, Samuel Garvey, Andrew Dawson, Christina Bagwill, Michael Lewis. Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

Intermolecular interactions of aromatics play a significant role in chemistry and biology, and the Π-electron density of aromatics has been shown to interact with cations, anions, and other aromatics. Anion-Π interactions of aromatics have received increasing attention, and computational work in our group has suggested ion-substituent interactions are important in anion-Π interactions.

In support of the computational predictions, this work focuses on the synthetic development of an anion binding molecule. The starting material, diethanolamine, provides two reactive functional groups, two primary alcohols and a secondary amine. Protection of the primary alcohols was accomplished with *tert*-butyldiphenylsilyl (TBDPS) groups, allowing for the addition of a phenyl acetyl group to the secondary amine. Deprotection of the primary alcohol produced *N*,*N*-bis(2-hydroxyethyl)-2-phenylacetamide. Reactions were monitored and purified using standard chromatographic techniques. LCMS confirmed each intermediate step. Future work will involve the formation of a macrocyclic cryptand with para substituted phenylacetyl side arms.

**RM_MWGL Regional Meeting 321**

### Synthesis and Characterization of Peptide-capped ZnS Nanoparticles

***Kimberly L. Holt***[1], *patton@lvc.edu, Walter A. Patton*[1,2]. *(1) Department of Chemistry, Lebanon Valley College, Annville, PA 17003-1400, United States (2) Program in Biochemistry & Molecular Biology, Lebanon Valley College, Annville, PA 17003-1400, United States*

Our group has investigated the synthesis and characterization of peptide-capped zinc sulfide nanoparticles. Zinc sulfide nanoparticles were synthesized using fresh aqueous solutions of sodium sulfide, zinc acetate, and acidified solutions of capping agents, including polyphosphate, cysteine, tryptone (a tryptic digest of casein), and peptone (an animal protein hydrosylate). The resulting nanoparticles were washed three times with di-water and were prepared as an aqueous suspension for characterization UV absorption and fluorescence emission spectroscopies, as well as MALDI-TOF mass spectrometry. Using the UV spectrum, calculations based on the Brus equation yielding average nanoparticle sizes from 3.0 nm for polyphosphate to 4.3 for peptone and tryptone. MALDI-TOF mass spectra demonstrated that peptides from both tryptone and peptone were immobilized to the washed nanoparticles, suggesting they effectively served as capping agents for the nanoparticles. Synthesis performed with capping agent that had not been acidified, yielded nanoparticles that displayed differing mass spectra and UV analysis demonstrated that such nanoparticles tended to be smaller.

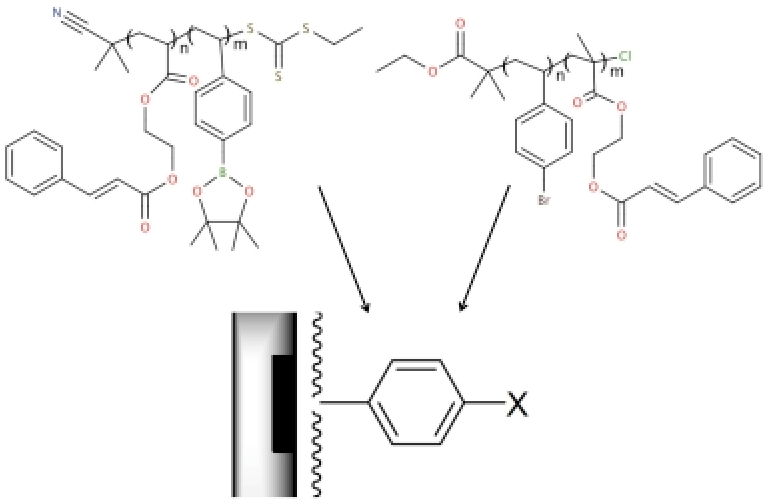
**RM_MWGL Regional Meeting 322**

### Optimization of polymer coatings for building addressable libraries on microelectrode arrays

*Libo Hu,* ***Matthew Graaf****, mgraaf@wustl.edu, Kevin Moeller.Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

We have shown the successful development of di-block copolymers as coatings for microelectrode arrays[1]. However, non-specific binding of biological targets with the

polymer has led to a limit of the device's detection of binding interactions. Here we propose polymer modifications as a solution to decrease these undesired interactions and improve the signal to noise ratio of these devices.

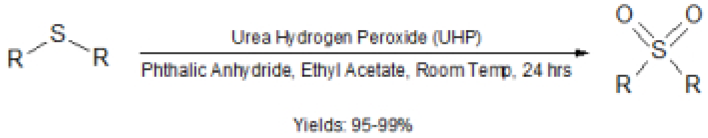


[1] Hu, Libo; et al. *J. Am. Chem. Soc.* **2009**, 131, 16638-16639

**RM_MWGL Regional Meeting 323**

## Efficient and general approach for safe oxidation of alkyl and aromatic sulfides to sulfones

***Marlon R Lutz Jr***[1]*, mlutz@registech.com, Kevin Boyer*[2]*, Dave Baehr*[2]*, Eric Blumenthal*[3]*, Igor Likhotvorik*[1]*. (1) Process Research and Development, Regis Technologies Inc, Morton Grove, Illinois 60053, United States (2) Department of Production, Regis Technologies Inc, Morton Grove, Illinois 60053, United States (3) Regis Technologies Inc, Morton Grove, Illinois 60053, United States*



A safe, efficient, and scalable method for oxidation of alkyl and aromatic sulfides to sulfones has been demonstrated on gram to kilogram scale using urea hydrogen peroxide (UHP) and phthalic anhydride in green solvents at room temperature for 24 hours. Typical yields ranged from 95-99% with >99% purity.

## RM_MWGL Regional Meeting 324

### “Click, Click, Click, Cyclize” strategy to novel tricyclic sultams

***Kyu Ok Jeon***[1,2], *jeon0816@ku.edu, Paul R. Hanson**[1,2]. *(1) Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States (2) The Center of chemical Methodologies and Library Development (KU-CMLD), University of Kansas, Lawrence, KS 66047, United States*

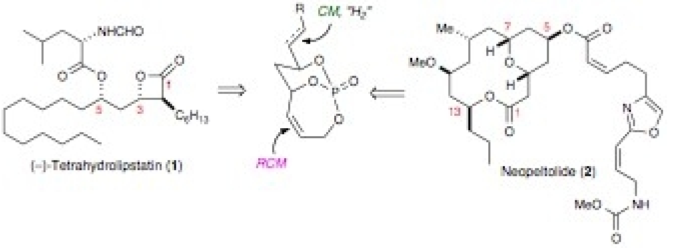
The development of new methods to access diverse sultams based on central α-halo benzenesulfonamide and vinyl sulfonamide building blocks is reported. These molecules are inspired by a number of biologically active sulfonamides and sultams reported in the literature. A strategy termed “Click, Click, Click, Cyclize” is reported for the generation of an array of benzofused tricyclic sultams. Screening of these libraries within the MLPCN will provide insight into their potential bioactivity and allow for second-generation evolution of synthetic methodologies leading to more refined libraries.

## RM_MWGL Regional Meeting 325

### Tether-mediated, one-pot metathesis processes: Application in small molecule and total synthesis

***Phanindra K. M. Venukadasula***, *phani@ku.edu, Gregory M Suryn, Rambabu Chegondi, Soma Maitra, Paul R Hanson*. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

A phosphate-mediated, one-pot, sequential RCM/CM/hydrogenation reaction for the desymmetrization of $C_2$-symmetric 1,3-*anti*-diol substrate is reported. The application of this method for small molecule synthesis as well as in the total synthesis of (–)-tetrahydrolipstatin and in the synthetic studies of the marine macrolide neopeltolide is reported. In addition, the method also provides advanced polyol fragments of several other bioactive natural products



## RM_MWGL Regional Meeting 326

## Resveratrol: Efficient synthetic method and selective delivery method to target cancer cells

***Harshi C Manawadu***[1], *harshi@ksu.edu, Tej B Shrestha*[2], *Deryl L Troyer*[2], *Stefan H Bossmann*[1]. *(1) Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States (2) Department of Anatomy and Physiology, College of Veterinary Medicine, Kansas State University, Manhattan, Kansas 66506, United States*

Resveratrol (3,5,4'-trihydroxy-trans-stilbene) is a naturally occurring polyphenol found mainly in grapes and red wines. It has become significant in the scientific field during past decades due to its therapeutic potential against cancers, inflammation and cardiovascular diseases. It is noteworthy that resveratrol has shown much promise as a potent drug in the chemoprevention and chemotherapy of pancreatic cancers. Selective introduction of resveratrol makes the target cancer cells more susceptible to chemotherapy and radiation. Moreover, apoptosis (programmed cell death) in the targeted tumor tissue was remarkably increased due to the presence of resveratrol.

Numerous approaches have been used to synthesize resveratrol and related trans-stilbene structures through Wittig, Diels-Alder/Wittig, Heck and Horner-type reactions. But most of these synthetic procedures were rather long and lead to low overall yields of the desired products. Therefore, the development of simple and reliable methods for the synthesis of resveratrol is highly advantageous. This goal can be achieved best if a convergent synthesis is developed requiring a minimum number of synthetic steps. Furthermore, to attain the production of resveratrol in a large-scale synthesis, well known and relatively simple/inexpensive synthetic methods will be employed.

Selective introduction of chemotherapeutic drugs to the target tumor sites is very problematic due to the defense system in the body. To maximize the selective delivery of the drugs and diagnostics, Dextran is used as drug carriers. Targeting oligonucleotide sequences (eg: iRGD) are used as linkers to bind drug and other diagnostics to the dextran carrier.

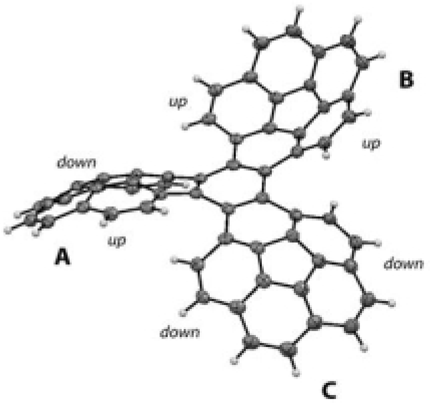
## RM_MWGL Regional Meeting 327

## Buckytriplet: Cyclotrimerization of Corannulyne

***Michael Yanney***[1], *my84@msstate.edu, Andrzej Sygula*[1], *Frank Fronczek*[2], *William P. Henry*[1], *Debbie Beard*[1]. *(1) Department of Chemistry, Mississippi State University, Starkville, Mississippi 39762, United States (2) Department of Chemistry, Louisiana State University, United States*

Palladium catalyzed cyclotrimerization of 1,2-didehydrocorannulene, generated from 2-trimethylsilylcorannulenyl triflate produces $C_{60}H_{24}$ hydrocarbon
with 40-45% yield. This highly non-planar trimer exhibits interesting dynamics which

was studied by variable temperature NMR. The X-ray crystal structure determination shows a $C_1$ symmetry of the trimer with full agreement with the B97-D/TZVP calculations. Steric congestion experienced by the three corannulene subunits leads to different inversion barrier for each bowl.



**RM_MWGL Regional Meeting 328**

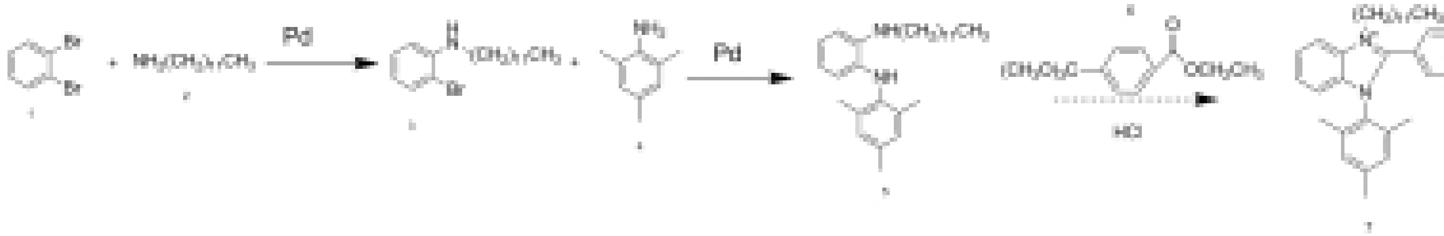
## Synthesis of benzimidazolium ions for dye-sensitized solar cells

***Rachel Clinestine Hawkins***, *rhawki21@gmail.com. Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628, United States*

Abstract:

Solar energy is an attractive option for power generation because of the limited environmental impact. Dye-sensitized solar cells (DSSC) are one of those potential alternatives that utilize energy from sun light. One of the components in DSSC's, the dye, is an organic molecule capable of undergoing electron excitation which can be used to generate electricity. The most efficient dye used in DSSC's allow for about 11% efficiency. A number of researchers are trying to figure out how the structure of the dye affects the overall efficiency of the DSSC. This presentation will discuss our effects on synthesis and performance of dyes based on benzimidazolium ions. The dye used in DSSC, uses solar energy which excites an electron in the dye and converts it into electrical energy, similar to the photosynthesis in plants. The synthesis is a three step process, which includes two amination reactions and a condensation step. Step

one includes an amination reaction of 1,2-dibromobenzene with dodecylamine producing **3**. Reacting 3 with 2,4,6-trimethylamiline produces **5**. The last step requires a condensation reaction with **5** and methyl 4-chlorocarbonylbenzoate to form the benzimidazolium dye, **7**.

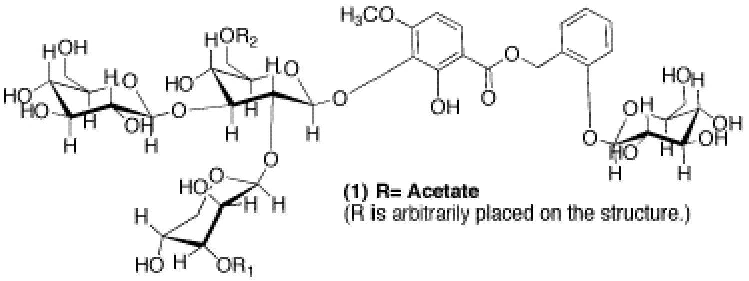


## RM_MWGL Regional Meeting 329

## Comparing Reductive Cleavage Methods in the Structure Determination Of Natural Products

***Kirk P. Manfredi****, manfredi@uni.edu. Department of Chemistry and Biochemistry, University of Northern Iowa, Cedar Falls, Iowa 50614, United States*

North American prairie plants produce a wide array of glycosylated natural products. The identity and quantity of the glycone portion of these glycosides can vary greatly. If sufficient quantities of the natural product are available, high field NMR spectroscopy can be used to determine both monosaccharide composition and locations of ester and glycosidic linkages. When sample quantity is limited, a common procedure is to use GC/MS after reductive cleavage of the glycoside. We recently identified the glycoside (1)



**(1) R= Acetate**
(R is arbitrarily placed on the structure.)

from the extract of the prairie plant Oligoneuron rigidum. The plant produces nearly equal quantities of the mono and diacetate. The mono acetate can be easily separated from the diacetate, but NMR analysis of the two compounds indicates that they are mixtures of regioisomers. Determining the structures of these regiosomers via NMR spectroscopy is difficult because of overlapping signals (at 400 MHz). To determine the structures of these glycosides they were subjected to two different reductive cleavage methods, followed by acetylation and analysis via GGC/MS. This presentation will discuss the results of the GC/MS analysis of the products and the structural determination of the regioisomers of (1).

## RM_MWGL Regional Meeting 330

### Isolation and characterization of novel natural products isolated from plants utilized in traditional folk medicine

***Kindra N Whitlatch**, whitlatch_kn@wvwc.edu, Jacob D Wagoner, Jeannie Sparks, Luke G Huggins, Timothy L Troyer. Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201, United States*

Plants have afforded several medically important and potent compounds. Many plants have been utilized in traditional folk medicine. Medicinal properties of the red mangrove (*Rhizophora mangle*) have been realized by indigenous populations in Central and South America. Our study was initiated by the discovery of antibacterial activity in the ethanolic extract of red mangrove propagules by our collaborators at the University of Belize. We have since identified cytotoxic activity in the aqueous extract of the red mangrove propagules.

The isolation of biologically active compounds from plants can be performed in a variety of ways. Often a highly polar organic solvent capable of forming hydrogen bonds is utilized for the initial extraction followed by extensive chromatography. Our bioassay directed isolation of antibacterial and cytotoxic natural products from the propagules of the red mangrove (*Rhizophora mangle*) have led us to a fairly unique process. We utilize both an aqueous extraction in addition to extraction with ethanol. These two separate extracts are then partitioned between water and ethyl acetate. The cytotoxic activity is found primarily in the aqueous partition and the antibacterial activity is found primarily in the organic partition. These two partitions have been further fractionated by a combination of column chromatography and preparatory HPLC. We have found that the biological activity can be traced to particular fractions of these purification steps. Biologically active fractions were preliminarily characterized by LC-MS and LC-NMR.

Our bioassay directed isolation procedure was then applied to three species of the *Centaurea* genus. Biologically active compounds have been isolated from a variety of *Centaurea* species endemic to Greece. There are no reports of isolating biologically active compounds from *Centaurea cyanus* (bachelor buttons), *Centaurea nigra* (black Knapweed), or *Centaurea maculosa* (spotted knapweed). We have been able to demonstrate antibacterial activity in certain fractions from the ethanolic extract from *Centaurea nigra*.

## RM_MWGL Regional Meeting 331

## Phosphate tether-mediated synthetic studies towards the total synthesis of fostriecin and analogs

***Susanthi Jayasinghe Mudiyanselage****, susanthi@ku.edu, James P McParland, Paul R Hanson. Department of Chemistry, University of Kansas, Lawerence, KS 66045, United States*

Recent synthetic efforts toward the total synthesis of fostriecin and analogs, employing both ring-closing metathesis (RCM) and cross metathesis (CM) are presented. Fostriecin, an antitumor antibiotic isolated from *Streptomyces pulveraceus*, is the most potent inhibitor of protein phosphatases 2A and 4, known to-date ($IC_{50}$s 3.2 *n*M and 3 *n*M, respectively). It has been shown to be active against L1210 and P388 leukemia cells in vivo and in vitro against leukemia, lung, breast, and ovarian cancer cells. Diastereoselective ring-closing metathesis reaction, regioselective oxidation and cross metathesis, all mediated by a temporary phosphate tether, have established a scaleable route toward the goal of total and analog synthesis of fostriecin.

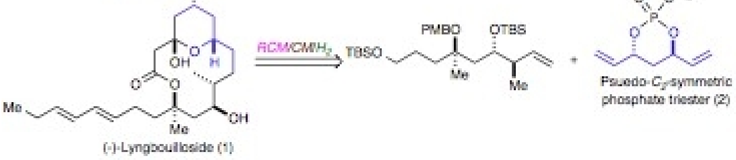
---

### RM_MWGL Regional Meeting 332

## Synthetic studies towards (–)-lyngbouilloside and phosphate tether-mediated ring-closing metathesis studies

***Rambabu Chegondi****, ramchegondi@ku.edu, Soma Maitra, Jana Markley, Paul R Hanson. Department of Chemistry, University of Kansas, Lawrence, Kansas 66045-7582, United States*

Synthetic efforts towards the total synthesis of the 14-membered cytotoxic marine macrolide (–)-lyngbouilloside (**1**) are reported. Temporary phosphate tether-mediated diastereoselective ring-closing metathesis studies will be discussed probing other parameters such as ring size, stereochemistry and conformation. Overall, an integrated platform employing phosphate-mediated processes will be detailed and which have led to the synthesis of dolebelide C, (–)-tetrahydrolipstatin, (–)-salicylihalamide A as well as the construction of the advanced intermediates enroute to (–)-bitungolide F, fostriecin, and neopeltolide.



---

### RM_MWGL Regional Meeting 333

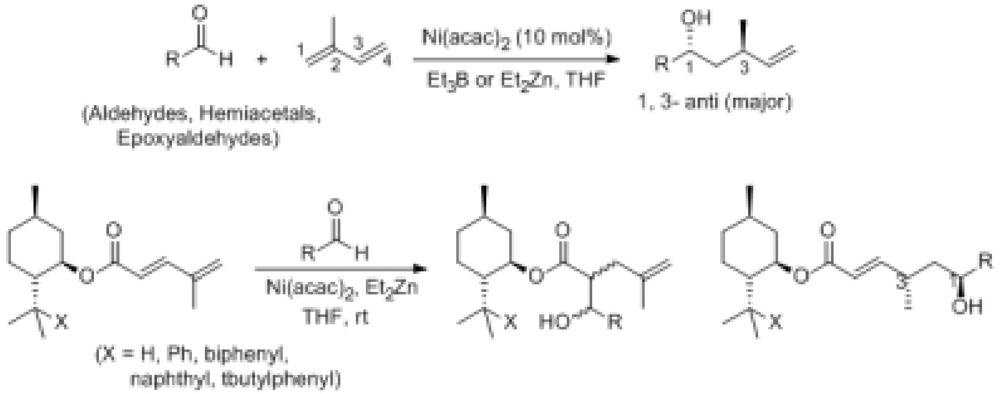
## Recent developments on the homoallylation reaction and its application in the synthesis of the tetrahydrofuran ring

***Mahesh P Paudyal***, *mpp2nf@mail.umsl.edu, Christopher D Spilling. Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

Homoallylation of aldehydes with 1,3-dienes in the presence of a catalytic amount of Ni(acac)$_2$ and triethylborane (or diethylzinc) provides hydroxyalkene with good yield and excellent regio- and stereoslectivities. Triethylborane serves as both a promoting and reducing agent. In this reaction, reductive coupling occurs between the aldehyde and the diene delivering a hydride from the reducing agent to the allylic position of 1,3-dienes.

We studied the homoallylation reaction of hemiacetals and epoxyaldehydes with dienes. These reactions proceeded with good diastereoselectivity. We have applied this protocol to synthesize the trisubstituted *trans*-tetrahydrofuran ring of the densely functionalized C1-C9 fragment of the cytotoxic natural product amphidinolide C, C2 and F.

Also, the homoallylation reactions of dienes having different chiral auxiliaries were investigated with a variety of aldehydes. The dienes having 8-arylmenthol derived esters underwent a very smooth reaction with the aldehydes in the presence of diethylzinc giving the anti 1,3- *anti*-hydroxylalkene as the major product. Various combination of these chiral diene esters and aldehydes were reacted which gave diastereoselectivity ranging from 2.2:1 to about 5:1.



---

**RM_MWGL Regional Meeting 334**

## Crystal engineering cocrystals: Application in the structure determination of a chiral ladderane

***Leonard R. MacGillivray***, *len-macgillivray@uiowa.edu. Department of Chemistry, University of Iowa, Iowa City, IA 52245, United States*

We have demonstrated how multi-component solids in the form of co-crystals can be developed to control the organization of molecules in the solid state with implications in organic synthesis, pharmaceutics, and organic electronics. In this presentation, we will demonstrate an application of the co-crystal approach to the structure determination of a molecule that resists crystallization as a pure form (*Proc. Nat. Acad. Sci. (USA).* **2011**, *108*, 10974-10979). The idea of crystallizing a target compound with an auxiliary species (*i.e.* co-crystal former) is well established in the structure determination of proteins. Here, the application allows us to conduct a structure determination of an unusual molecule in the form of a [5]-ladderane. Ladderanes are rod-shaped molecules that contain a core set of fused cyclobutane rings. The molecules are promising building blocks in optoelectronics and recently have been discovered as a structural motif in lipid natural products. In our work, we have managed to synthesize two *cis-trans* isomers of a [5]-ladderane. Although we were able to obtain the X-ray crystal structure of one isomer, which is achiral, a second, which is chiral, refused to crystallize under a variety of conditions. We show that the co-crystal approach enables us to confirm the structure of the chiral isomer, particularly where standard approaches to spectroscopy (*e.g.* multidimensional NMR) are not successful.

**RM_MWGL Regional Meeting 335**

## Structural variations, dynamics, and molecular intercalation and transport in layered ammonium carboxylates

***Alicia M. Beatty**, beattya@umsl.edu.Center for Nanoscience & Department of Chemistry & Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

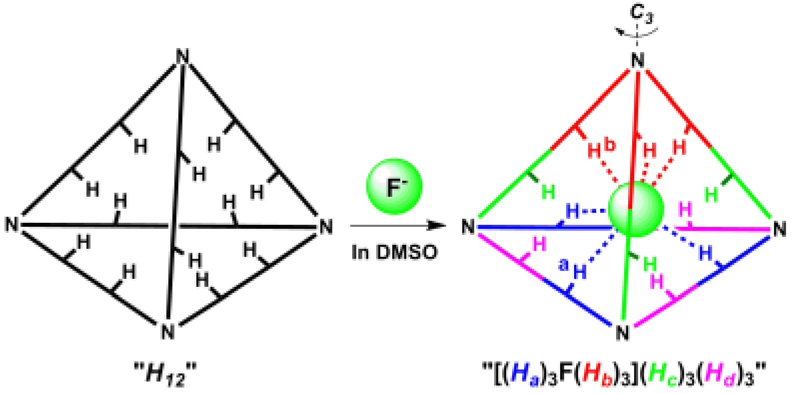
Small organic or coordination complexes containing ammonium and carboxylate moieties have been useful building blocks for layered materials. A combination of 3,5-pyrazole dicarboxylic acid with a variety of amines has yielded a predominance of bilayered structures, but ways in which amine substituents can be altered to force the overall assembly into single layer and other motifs. In addition, metal-containing dicarboxylic acids, again combined with amines, have a greater potential for useful properties. Strong hydrogen bonds are robust enough to sustain guest loss and reuptake in both close-packed and porous frameworks. Further, water ligands may be (at times reversibly) replaced by small, organic Lewis bases. Examples of the synthesis and dynamics of each of these types of materials will be discussed.

**RM_MWGL Regional Meeting 336**

## Molecular pipes and boxes: Containers for anions

*Qi-Qiang Wang, Victor W. Day, **Kristin Bowman-James**, kbjames@ku.edu. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

Supramolecular hosts come in a variety of shapes and sizes. In recent forays into expanded molecular hosts for anions, our group has synthesized and characterized two new classes of hosts that can be conveniently described as a pipe and a box in terms of overall shape. The pipe is a tricyclic host made by connecting two macrocycles with two linker chains. It binds organic dicarboxylates of various lengths by contracting to fit the anionic guest. The box is also a cyclic host, but in the shape of a tetrahedron. It consistently encapsulates a tetrahedral cluster of water molecules. The water cluster then centrally binds either another water molecule, resulting in a cluster of five water molecules known as Walrafen's pentamer, or a single fluoride ion. The structure and binding properties of multicyclic anion hosts will be described.

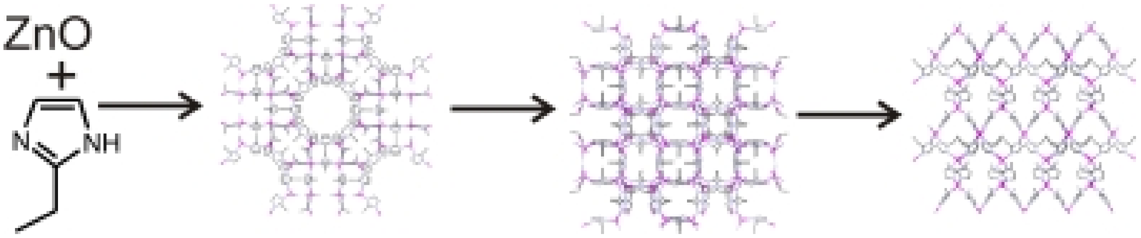


## RM_MWGL Regional Meeting 337

## Supramolecular concepts in mechanochemical synthesis

***Tomislav Friscic***, *tomislav.friscic@mcgill.ca. Department of Chemistry, McGill University, Montreal, Quebec H3A 2K6, Canada*

Solid-state mechanosynthesis,[1] i.e. reactivity induced by mechanical force, is emerging as a viable alternative to conventional solution-based synthesis. This renaissance can be attributed to the application of concepts traditionally associated with solution-phase supramolecular chemistry, such as molecular recognition,[2] structure templating[3] and dynamic combinatorial chemistry, to highly concentrated solid-state reaction systems. Conversely, mechanochemical methods allow the otherwise inert metal oxides to become involved in mild room-temperature processes resembling molecular self-assembly (Figure 1). This presentation will illustrate how supramolecular chemistry is transforming mechanosynthesis into a versatile tool for the inexpensive, solvent- and energy-economical synthesis of a variety of products, including technologically relevant metal-organic frameworks,[3] pharmaceuticals[4] and small molecules.



References:
[1] T. Friščić *J. Mat. Chem.* 2010, *20*, 7599.
[2] T. Friščić, R. W. Lancaster, L. Fábián, P. Karamertzanis *Proc. Natl. Acad. Sci. USA* 2010**,** *107*, 13216.
[3] T. Friščić, D. G. Reid, I. Halasz, R. S. Stein, R. E. Dinnebier, M. J. Duer *Angew. Chem. Int. Ed.* 2010, *49*, 712.
[4] V. M. André, A. Hardeman, I. Halasz, R. S. Stein, G. J. Jackson, D. G. Reid, M. J. Duer, C. Curfs, M. T. Duarte, T. Friščić *Angew. Chem. Int. Ed.* 2011, *50*, 7858.

**RM_MWGL Regional Meeting 338**

## Exploring the surface modifications of macrocycles via copper catalyzed azide-alkyne cycloaddition “click” coupling

***Scott M. Grayson****, sgrayson@tulane.edu, Yejia Li, Bruce Gibb. Department of Chemistry, Tulane University, New Orleans, LA 70118, United States*

Cyclic molecules, both polymeric and “small molecule”macrocycles, exhibit an inherent ability to interact in a non-covalent fashion with guest molecules. While the interactions between crown ethers, cyclodextrins and cucurbiturils have been the subject of extended investigation, the ability to construct either deeper cavities, (e.g. deep cavity cavitands) or wider cavities (e.g. cyclic polymers) offers promise to extend these interactions into a larger length scale. For both structures, the ability to modify the surface in a modular fashion is critical for investigation their applications. A “click” approach to modifying both cavitands and cyclic polymers has been explored. This route shows broad versatility, enabling the coupling of a broad range of polymer side chains, both polar and non-polar, both branched and liner.

**RM_MWGL Regional Meeting 339**

## Responsive nanoassemblies

***S. Thayumanavan****, thai@chem.umass.edu. Department of Chemistry, University of Massachusetts-Amherst, Amherst, MA 01003, United States*

Non-covalent encapsulation of guest molecules and their triggered release is of paramount importance in the field of drug delivery. Achieving such release characteristics using proteins as trigger would have significant implications in both drug

delivery and bio-sensing, since protein imbalances are primary bases for the most of human diseases. Custom-designed facially amphiphilic dendrimers have been utilized for this purpose due to their unique ability of sequestering guest molecules through of aggregation of several dendritic molecules. Micellar assemblies, such as the ones above, are promising scaffolds to overcome many of the problems faced with traditional chemotherapies, because of their capacity for non-covalent, hydrophobic guest molecule binding. However, the stability of encapsulation with such self-assembled systems is limited during blood circulation because of a requisite concentration for assembly formation. Thus, deliberate molecular design for stable encapsulation, targeting and triggered release is required. For this purpose, we have developed a facile synthetic method for highly stable, polymeric nanogels using a simple intra/inter-chain crosslinking reaction. We show a simple, emulsion free method for the preparation of biocompatible nanogels that provides the ability to encapsulate hydrophobic guest molecules. The resulting nanogels show sizes of several hundred nanometers with well-defined shapes. The nanogel surfaces can be functionalized with specific groups, allowing for potential functionalization for targeted delivery. We show that the non-covalently encapsulated guest molecules can be released in response to a biologically relevant stimulus. The release of the guest molecules can be tuned by crosslinking density and in situ release was observed through in vitro fluorescence resonance energy transfer (FRET) experiments. Hence, the reversible nanogel formation using self crosslinking polymers and the corresponding method of surface modification are a promising platform for creating polymer nanogels for a range of biomedical applications, from drug delivery to bionsensing.

**RM_MWGL Regional Meeting 340**

## Glowing rotaxanes: a new paradigm for optical imaging

***Bradley D. Smith**, smith.115@nd.edu. Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, IN 46556, United States*

The lecture will describe efforts over the last six years to develop new families of fluorescent and chemiluminescent molecular probes. Cell microscopists have a need for fluorophores with high photostability, extreme brightness, low phototoxicity, and user friendly bioconjugation. Whereas, in vivo imaging researchers strongly prefer fluorescent probes that emit low energy near-IR light since it can penetrate through skin and tissue. Having produced improved fluorophores, we have come to realize the limitations of fluorescence imaging. Instead of incremental improvements with better fluorophores a more transformational effect is gained by replacing fluorophores with new technology - self-illuminating molecules. We have discovered a new set of near-infrared dyes that are both chemiluminescent and fluorescent and we have used them to fabricate dye-doped nanoparticles for dual modality optical imaging. The chemiluminescence is thermally-activated (that is, no chemical or electrical stimulus is needed) which means that the probes can be stored at low temperature and they only become chemiluminescent when warmed to body temperature. Self-illuminating,

chemiluminescent systems are especially attractive since they have inherently high signal contrast due to the lack of background emission.

## RM_MWGL Regional Meeting 341

### Metal-organic calixarene assemblies

***Scott J. Dalgarno****, S.J.Dalgarno@hw.ac.uk. Department of Chemistry, Heriot-Watt University, Edinburgh, Scotland EH14 4AS, United Kingdom*

In the cone conformation calix[4]arenes possess lower-rim polyphenolic pockets that are ideal for the complexation of various transition-metal centres. Reaction of these molecules with manganese salts in the presence of an appropriate base (and in some cases co-ligand) results in the formation of a family of calixarene-supported [Mn(2)(III)Mn(2)(II) clusters that behave as single-molecule magnets (SMMs). Other clusters such as Fe(2)(III)Ln(2)(III) clusters have been synthesised under facile bench top conditions. Ramifications of these initial studies will be discussed.

## RM_MWGL Regional Meeting 342

### Evolution of herbicide resistance

***Doug Sammons****, rdsamm@monsanto.com. Monsanto Company, Saint Louis, MO 63167, United States*

One of the oldest tools, that by itself identifies an ancient society as agrarian, is the hoe. The ability to cultivate the land to grow a crop simultaneously created the need to control weeds, unwanted plants in the crop. For many millennia the tool used was the hoe right up to the invention of chemical agriculture in the 1950's. By the 1960's farmers relied more on chemical sprays then the cold steel of cultivators and today it is rare indeed to see the old cultivator. The broad acre adoption of herbicides was shortly accompanied with the development of herbicide resistant weeds. Weeds used their own gene pool to successfully enhance the specific trait through herbicide selection to overcome the lethal assault of the herbicide. The management of weeds then took on a variety of sophisticated management systems requiring specific timings and multiple applications to use the post emergent and pre-emergent herbicides available. The invention of herbicide tolerant crops dramatically simplified the management of weeds and the adoption of the glyphosate resistant row crops as Roundup Ready® replaced conventional systems in the major crops in the last decade. The selection of glyphosate resistant weeds substantiates the *Jurassic Park* adage “life finds a way to break through” (Michael Crichton, 1990). The understanding of the mechanisms of herbicide resistance is fundamentally the same as understanding the process of evolution in plant growth and development. The principal mechanism of herbicide resistance will be discussed and the new more rare mechanism for glyphosate resistance will be put into perspective.

## RM_MWGL Regional Meeting 343

### Plant natural products in a modern drug discovery program

***Russell B. Williams**, rwilliams@sequoiasciences.com. Lead Discovery and Rapid Structure Elucidation Group, Sequoia Sciences, Inc., Saint Louis, MO 63114, United States*

At one time most major pharmaceutical companies pursued some form of natural products research for compound leads in their drug discovery programs. Today most have abandoned this line of research. Does this mean that natural products are no longer relevant? Are major pharmaceutical companies producing a plethora of biologically active compounds based on synthetic methodologies? At Sequoia Sciences we have continued to pursue natural products as a source of pharmaceutical lead compounds based on plant biomass. To facilitate this research path we have developed 'high-throughput natural product techniques' in order to address the obstacles found in natural product research. We have accelerated the research path by using extensive fractionation and fraction normalization prior to biological screening. This prescreening sample preparation allows us to rapidly identify active components that are found at low concentrations in the crude plant extracts. Further combination of this prescreening fractionation with extremely sensitive NMR techniques allows us to rapidly perform structure elucidation without the need to perform prohibitive large scale isolations. All of this has culminated in the development of three separate medicinal chemistry projects to develop leads identified from plant natural products.

## RM_MWGL Regional Meeting 344

### Post-genomic elucidation of plant natural product pathways

***Toni M. Kutchan**, tmkutchan@danforthcenter.org, Dan Ruzicka, Megan Rolf. Donald Danforth Plant Science Center, Saint Louis, MO 63132, United States*

The study of the biosynthesis of plant alkaloids at the enzyme and gene level has greatly advanced in recent years. We now have a number of genes available from the monoterpenoid indole-, tetrahydrobenzylisoquinoline-, and structurally related to both of the previous classes, the terpenoid-isoquinoline alkaloid biosynthetic pathways. To date, however, only partial understanding of the formation of medicinal natural products at the enzyme and gene levels has been attained. The explosive increase in understanding of biology over the past two decades has been enabled by work on model genetic organisms, including the plant *Arabidopsis thaliana*. The study of selected species-specific medicinal natural products, however, requires investigation of those plant species that harbor all or most components of the focal biosynthetic pathway. Detailed genetic and biochemical information on these highly specialized species is often missing. This knowledge gap slows research advances in the field of plant-derived pharmaceuticals. Having comprehensive medicinal plant transcriptomes would advance research on medicinal plant species from an orphan-like status closer to

that of model organisms. We now seek to generate and use transcriptome data to understand the complete formation, storage and regulation of plant-derived medicinal compounds at the enzyme and gene level. Improved understanding will enable the development of both alternate sources of medicinal alkaloids that lie along the biosynthetic pathways and of novel drugs. Results will be presented from efforts to date to produce deep transcriptome datasets from members of the Papaveraceae and to interrogate the datasets for candidate alkaloid biosynthetic genes.

## RM_MWGL Regional Meeting 345

### High sensitivity absorption spectra using broadband intracavity laser spectroscopy

***James J. O'Brien***[1]*, obrienjja@umsl.edu, Leah C. O'Brien*[2]*. (1) Department of Chemistry and Biochemistry and the Center for Nanoscience, University of Missouri – St. Louis, St. Louis, MO 63121, United States (2) Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026-1652, United States*

Intracavity Laser Spectroscopy (ILS) provides a very sensitive method for performing absorption measurements on gas phase species at high resolution. Enhancement factors up to $10^6$ have been reported compared with traditional absorption methods. In this presentation, the principles of ILS will be briefly outlined. We will provide examples of its use in studying formally forbidden transitions, such as the spin-forbidden and electric-dipole-moment-forbidden transitions of the (0,0) and (1,1) bands of the $b\ ^1\Sigma^+_g$ - $X\ ^3\Sigma^-_g$ transition of oxygen, and high overtone spectra of methane and HCl. Additional examples of the use of ILS with transient metal-containing diatomic species, such as PtF, AuO and $Pt_2$ created in an intracavity plasma also will be given.

## RM_MWGL Regional Meeting 346

### Fiber laser-induced fluorescence and laser-induced phosphorescence spectroscopy for atmospheric measurements

***Frank Keutsch****, keutsch@chem.wisc.edu. Department of Chemistry, University of Wisconsin Madison, Madison, WI 53706-1322, United States*

The continued growth in the versatility of diode and fiber laser technology combined with high-sensitivity spectroscopic methods permits the design of instrumentation, for areas such as atmospheric measurement, which is more inexpensive, rugged, power-efficient, and compact than was previously possible. Two emerging techniques, FIber Laser-Induced Fluorescence (FILIF) and Laser-Induced Phosphorescence (methyl)GLyOxal Spectrometry (LIPGLOS), utilize these novel laser technologies in combination with highly sensitive spectroscopic methods to achieve atmospherically relevant limits of detection and time resolution.

By using a novel class of narrow-bandwidth UV fiber lasers, FILIF combines the

sensitivity of LIF with the selectivity of rotational spectroscopy to create a reliable and very precise measurement. LIPGLOS exploits the characteristic phosphorescence lifetimes of glyoxal and methylglyoxal to differentiate these species at a single wavelength, which results in a highly sensitive technique without the need for rotational resolution. Field and laboratory measurements using these techniques will be presented in the context of ambient concentrations of formaldehyde, glyoxal, and methylglyoxal.

**RM_MWGL Regional Meeting 347**

## New approaches to high-resolution, high-sensitivity spectroscopy of molecular ions

***Benjamin J. McCall***, *bjmccall@illinois.edu. Departments of Chemistry, Astronomy, and Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

The development of velocity modulation spectroscopy in 1983 initiated an era of enormous improvements in the spectroscopy of small molecular ions. However, the application of this technique to larger and more complex molecular ions has been problematic because the high plasma temperatures lead to large partition functions, which reduce the intensity of the Doppler-limited transitions below the noise floor. Alternative approaches using cooled hollow cathode discharges and supersonically expanding plasmas have enabled the study of lower-temperature ions, but at the (considerable) expense of the loss of ion-neutral selectivity. In our laboratory, we have been developing two new approaches for molecular ion spectroscopy to overcome these challenges.

The first technique is a twist on conventional velocity modulation spectroscopy in a positive column discharge, which involves placing a moderate-finesse cavity around the plasma. A cw laser is then locked to this cavity, and heterodyne spectroscopy can be performed using a sideband frequency equal to the cavity's free spectral range – a technique known as Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy, or NICE-OHMS. The high intracavity power produces sub-Doppler Lamb dips, enabling line center measurements to ~1 MHz precision. We have demonstrated this technique using $N_2^+$ in the near-infrared, and plan to extend it to more complex ions in the mid-infrared. The high resolution and sensitivity of this technique can be expected to breathe new life into velocity modulation spectroscopy.

The second technique is based on direct absorption/dispersion spectroscopy of a fast molecular ion beam to enable mass-identified, high-resolution spectroscopy of rotationally cold molecular ions. We call this approach Sensitive, Cooled, Resolved, Ion BEam Spectroscopy (SCRIBES). Using NICE-OHMS, we have recently observed the first ion spectrum in this instrument, using a cold cathode source. In the near future we aim to extend this work to the mid-infrared, and to rotationally cold ions.

**RM_MWGL Regional Meeting 348**

## Single-conformation spectroscopy of synthetic foldamers, peptides, and model lignin compounds

*Evan G. Buchanan, Jacob C. Dean,* ***Timothy S. Zwier****, zwier@purdue.edu. Department of Chemistry, Purdue University, West Lafayette, IN 47907-2084, United States*

The infrared or ultraviolet spectroscopy of large molecules with biological relevance is challenging in that the spectra contain contributions from many conformational isomers each of which has many low frequency vibrations populated. At the same time, sample sizes are often limited. This talk will describe the experimental methods used to study such molecules under isolated molecule conditions, combining laser desorption with mass-resolved, resonant two-photon ionization spectroscopy. Single-conformation spectra in the infrared and ultraviolet are recorded using double-resonance methods. Results from recent studies of synthetic foldamers, peptides, and model lignin compounds will be used to illustrate the kinds of information to be derived from such spectroscopy.

**RM_MWGL Regional Meeting 349**

## Transient absorption microscopy studies single metal and semiconductor nanostructures

***Gregory V. Hartland****, ghartlan@nd.edu. Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States*

Single particle spectroscopy is a powerful tool for studying the optical properties of nanomaterials. It is capable of revealing information about how differences in size, shape and environment affect properties. Usually these experiments are implemented by detecting emission – which makes it difficult to study fast processes, or materials with low quantum yields (such as metals or semiconductor nanowires). In this talk I will present results from transient absorption experiments performed with diffraction limited spatial resolution. These measurements allow the study single nanostructures, and provide information about their dynamics that is washed out in ensemble experiments. The systems investigated include plasmonic metal nanowires, II-VI semiconductor nanowires and carbon nanostructures. The time scales range from a few hundred femtoseconds, to several hundred picoseconds. The results provide detailed information about how these materials interact with their environment, about trapping and recombination of electrons and holes in semiconductor nanowires, and energy transport and dissipation in metal nanowires.

**RM_MWGL Regional Meeting 350**

## Who owns patented technology? A review of the U.S. Supreme Court's recent decision in Stanford v Roche and how it applies to federally-funded research

***Stephen C Hall**, steve.hall@skofirm.com. Stoll Keenon Ogden PLLC, Louisville, KY 40202, United States*

The technology world often resembles an elaborate ecosystem. Innovators frequently deal with other entities and organizations as they develop and market an invention. Research partnerships, licenses, non-disclosure/non-competition agreements, and consulting agreements are just some of the kinds of contracts involved. However, these private contracts may have important consequences in terms of the ownership of intellectual property.

Stanford University v. Roche Molecular Systems, Inc. was a recent U.S. Supreme Court case decided under the Bayh-Dole Act. Bayh-Dole is federal legislation enacted thirty years ago, to provide incentive to commercialize federally funded research in order that the public would benefit from research funded by taxpayers. To accomplish this objective, the Act makes it possible for a University or others – as opposed to the federal government – to own federally-funded inventions, if certain conditions met.

In this case, researchers at Stanford made important discoveries and advances in the treatment of HIV. However, after patents issued on the technology, a dispute arose over whether Stanford was the sole owner, or whether the small biotechnology company where some of the research occurred was also part owner. (The biotech company, Cetus, later assigned its rights in the patents to Roche.) On June 6, 2011, the Supreme Court ruled in favor of Roche (7-2), and its decision hinged on a contract that the biotech company and one of the researchers formed well before the patents issued. Accordingly, this presentation is intended to accomplish the following objectives: (i) briefly touch upon and highlight the essential requirements for obtaining patents; (ii) demonstrate that patent law and contract law both must be considered when determining which entity or entities owns the rights to technology; and (iii) discuss the various kinds of agreements that are typically entered into in the context of technology development, and how those can affect important rights.

## RM_MWGL Regional Meeting 351

## Patent law reform legislation: Survival tips for academic and entrepreneurial scientists

***Jeremy Stipkala**, Jeremy.Stipkala@StipkalaLaw.com. Stipkala LLC, Charleston, SC, United States*

Congress is on the verge of passing the America Invents Act, a piece of legislation that will transform American patent law. From first-inventor-to-file to post-grant review, the provisions of this pending legislation will challenge both academic and small business scientists. Indeed, some fear that this legislation unfairly favors Big Business. Nonetheless, forewarned and fore-armed savvy scientists can prosper, using patent law to carve out market niches and protect valuable intellectual property. This talk explores the major provisions of this new law, and identifies opportunities for the small-enterprise scientist.

## RM_MWGL Regional Meeting 352

### Small businesses and their assets: Building an intellectual property wall

***Teresa J Welch**, tjwelch@michaelbest.com. Michael Best & Friedrich LLP, Madison, WI 53701, United States*

The slow, sometimes non-existent, recovery from the recent economic downturn in the United States has called great attention to the importance of small businesses and their growth to provide new jobs. Intellectual property (IP) assets can be a key factor in business growth and development.

Many small business owners believe that it is not worth the time, effort and/or money to secure intellectual property rights. With the rise of competition through the internet and the global market, understanding intellectual property is more critical than ever for small businesses. Entrepreneurs and small businesses need to use IP as a business strategy and to make their IP a competitive advantage. Entire business models can be built on leveraging of the business' IP. The secret to making the most from IP is to identify value, protect, manage and effectively use IP in a business strategy. IP must be identified – for example, business name, trade secrets, research and development outcomes, unique products, services, unique designs of products/packaging. IP must be managed and protected. Protection comes from confidentiality, patents, trademarks, registered designs and copyright. Some of these rights require formal protection, others do not.

Many small businesses are begun with technology licensed from a university or research institute, and often their intellectual property is their only asset. This presentation explores how intellectual property can be grown from a platform technology to a portfolio of patents and other intellectual property rights, *i.e.*, an intellectual property wall, how these intellectual property assets can improve a business' competitiveness and strategic advantage, and how such intellectual property can be leveraged to grow the company or to provide a desired exit strategy (*e.g.*, getting acquired, IPO) for founders and investors.

## RM_MWGL Regional Meeting 353

### Development and Practice of “Air Pollution” Educational Material Unit Aiming at Education for Sustainable Development (ESD) in Korea

***Young Tae Kong**, ytkong@cue.ac.kr. Science Education, Chinju National University of Education, Jinju, Gyeongnam 660756, Republic of Korea*

We have developed an educational material unit “Air Pollution”, focusing on air pollution control measures and changes of production processes in chemical industries in light of Green and Sustainable Chemistry (GSC). This study mainly dealt on ascertaining the change on concepts on air pollution among upper secondary students and freshman students in selected universities in the Korea.

The educational material unit “Air Pollution” includes worksheets, references and a “Study History sheet” (SH sheet) based on one page portfolio assessment. The original version of air pollution unit was developed by Teratani et al., (2007)

During the past three years (2008-2010), the revised version (Korean) of the “Air pollution” unit was practiced as four upper secondary schools and two universities to the extent possible in each school (total approximately 300 students in Korea).

The “Air Pollution” educational material unit is effective for upper secondary and freshman students to conduct enthusiastic investigation activity and develop favorable attitude towards science and technology. Enabling students to obtain information about historical facts including the efforts of scientists and engineers and the GSC approach gave them confidence in science and technology and stimulated to develop scientific perspectives and attitudes.

References

Teratani, S. et. al., (2007). “Some Issues in Practice Abroad.” Developing Educational Materials on Sustainable Development, Report of Grant-in-Aid for Scientific Research (B) in Japan.

**RM_MWGL Regional Meeting 354**

## Comparison on Elementary Science Achievement between Korea and Japan in TIMSS 2007

***Young Tae Kong**, ytkong@cue.ac.kr. Science Education, Chinju National University of Education, Jinju, Gyeongnam 660756, Republic of Korea*

Elementary science questions released by TIMSS 2007 had been translated according to Korea curriculum. In addition, we implemented the survey to find out the science accomplishment level of the 4th graders in 23 elementary schools in Gyeongnam and Ulsan city.

Based on the results from this survey, we compared the science achievement level of the 4th graders in elementary schools between Korea and Japan. Average correct answer rate, answer rate per areas, and international benchmarks have been examined and considered. Moreover, we also looked into the current situation through the scientific notions and misconceptions which both countries' students have.

Average correct answer rate on the 71 questions of elementary science released by TIMSS 2007 was 69.8 % in Korea, 61.7 % in Japan, and both countries' score is higher than international average correct answer rate, 49.2%. We confirm that both countries are in the top level internationally. Average answer rate was about the same in most questions between two countries, but answer rate or question type was different according to the completion period or completion contents. And we were able to analyze the current concepts that students have, and this outcome will lead us to have the better teaching tips. Followed by TIMSS 2003 survey, we considered the level of Korea students' international science accomplishment by the quantitative and qualitative analysis through TIMSS 2007.

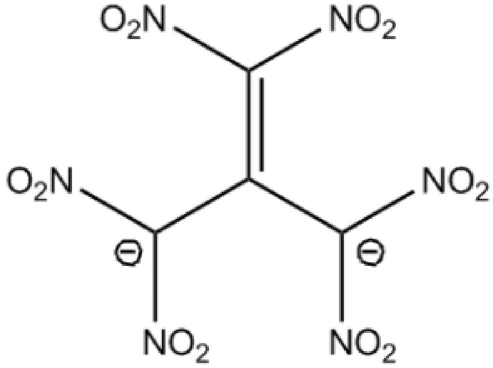
References
Martin, M. O., Mullis, I. V. S. and Foy, P. (2008). TIMSS 2007 International Science Report, IEA: Boston.

**RM_MWGL Regional Meeting 355**

## Tutorial on the facile determination of the number of Kekulé and Dewar resonance structures in conjugated systems

***Jerry R Dias***, *diasj@umkc.edu. Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110-2499, United States*

We show fluoranthene has six Kekulé (***K***= 6) and ninetyone Dewar resonance structures (*DS* = 91) and that the potentially explosive hexanitroisobutene dianion has 768 resonance structures (*SC*= 768).



hexanitroisobutene dianion, *SC* = 768

**RM_MWGL Regional Meeting 356**

## Impact of participation in the Indiana Science Initiative on teachers' beliefs about student learning in science

***Nicole Cook***[1], *cook45@purdue.edu, Gabriela C. Weaver*[1], *Bill Walker*[2]. *(1) Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States (2) I-STEM Resource Network, Purdue University, West Lafayette, IN 47907, United States*

The Indiana Science Initiative (ISI) is an effort to reform K-8 science instruction through the use of research-based curricula and scaffolded guided inquiry (SGI) enhanced with literacy strategies through the use of science notebooks. In the pilot year, teachers received a week of professional development through ISI. As part of the pilot year evaluation data were collected in the form of classroom observations and interviews. To investigate their beliefs about student learning, teachers were asked about their views of desired outcomes for student learning in science and the best ways to promote student learning in science. This poster presents teachers views' on these topics at the beginning and end of the pilot year.

### RM_MWGL Regional Meeting 357

## Discovering $^{13}$C-NMR, $^{1}$H-NMR and IR spectroscopy in the General Chemistry laboratory through a sequence of guided-inquiry exercises

***David C Justice***, *200806194@panthers.greenville.edu, H. Darrell Iler. Department of Chemistry, Greenville College, Greenville, Illinois 62246, United States*

This work describes a sequence of labs designed to introduce C13-NMR, H1-NMR and IR spectroscopy into a first year chemistry course through a guided-inquiry approach. Student survey data along with in-lab observations of student interactions lead us to conclude that these labs enhanced student interest, increased communication between students, and improved students' ability to explain concepts and correct their own misconceptions. As a result of these lab experiences students discovered theoretical principles associated with magnetic resonance and vibrational spectroscopy and learned to run and interpret C13-NMR, H1-NMR and IR spectra to correctly identify functional groups and chemical structures for a variety of organic compounds. These experiences benefit our chemistry students as they move onto Organic Chemistry by providing them a strong foundation upon which to build a more advanced theoretical and practical knowledge of NMR and IR spectroscopy. These labs are also of great value to those students who are in programs that only require one year of chemistry, such as physics, engineering, environmental science, etc., but may find themselves at some point in their future careers acting as practicing spectroscopists.

### RM_MWGL Regional Meeting 358

## Kinetic study of the reaction $H_2O_2 + 3\ I^- + 2\ H^+ \rightarrow I_3^- + 2\ H_2O$ employing spectroscopic methods

***Herman R Krueger**, hkrueger@webster.edu. Department of Biological Sciences, Webster University, St Louis, MO 63119, United States*

A student laboratory experiment is presented that employs spectroscopic methods to elucidate the kinetics of the oxidation of iodide ion by hydrogen peroxide in acidic solution. In contrast to some previous studies of this reaction, the integrated rate law is used to obtain the kinetic information. Visible absorption spectroscopy at 468 nm is utilized to follow the temporal evolution of the triiodide product. The resulting data are used to compute the concentration of hydrogen peroxide reactant as a function of time. By analyzing reactions carried out with a large excess of $H^+$ and $I^-$, the plots of hydrogen peroxide concentration vs. time can be used to determine the integrated rate law and thus the order of the reaction with respect to $H_2O_2$. In addition, for each solution studied, a pseudo rate constant is also obtained from the analysis. By examining the dependence of these pseudo rate constants on $H^+$ and $I^-$ concentration, the order of the reaction with respect to these two reactants can also be determined, along with the actual rate constants for the reaction itself. Further extensions of the experimental procedure are considered. This experiment is suitable for undergraduate general and physical chemistry laboratories and might also be used in an AP high school chemistry course.

---

**RM_MWGL Regional Meeting 359**

## Teaching Precipitation Titration without the Buret: A Coulometric Method for the Determination of Chloride

***Dale W Harak**, dale.harak@rockhurst.edu, Madeleine Kimbrough. Department of Chemistry, Rockhurst University, Kansas City, Missouri 64110, United States*

Precipitation titrations are often relegated to the back of analytical chemistry or quantitative analysis textbooks. That this type of titration has fallen out of favor is probably due in part to the facts that these titrations can be time-consuming and that volumetric analysis is not as appealing to students (and instructors) who tend to gravitate toward instrumental methods. We have developed a simple coulometric method of determining soluble chloride via silver ion precipitation utilizing data acquisition probes and software. This method affords the student the benefits of learning about precipitation titrations while using simple instrumentation—without the buret or the need to standardize a titrant solution.

Students learn about electrolytic cells and how to quantify an analyte based on the amount of electricity that flows in the cell. Students can easily make the connection that they are, in essence, “titrating with electrons”. Because of the simple experimental setup, numerous trials of the experiment can be run in a short period of time, allowing students to take more measurements than is possible with a standard volumetric titration. It will be shown that good precision and reasonable accuracy of those trials can be easily achieved.

## RM_MWGL Regional Meeting 360

### Project SEED in Kansas City

***Eckhard W Hellmuth**, HellmuthE@umkc.edu.Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110, United States*

During the last decades the Kansa City Section coordinated summer research of underpriviledged High School Students.We will discuss our success in the Project SEED 1 and SEES 2 for a number of students and will report on our posters at the SCIMIX at the Denver National meeting.

## RM_MWGL Regional Meeting 361

### Buffer standards for the zwitterionic buffer (ACES) at $I = 0.16$ mol·kg$^{-1}$ from 5 to 55 °C

***Isaac B Henson**, ihenson@drury.edu, Jessica M Stegner, John J Dinga, Lauren Dieterman, Lakshmi N Roy, Rabindra N Roy.Hoffman Department of Chemistry, Drury University, Springfield, MO 65802, United States*

The buffer compound *N*-(2-acetamido)-2-aminoethanesulfonic acid has been studied in the temperature range 5 to 55 °C using potentiometric technique using the cell: Pt, $H_2$ (g, 1 atm)|ACES ($m_1$) + NaACES ($m_2$) + NaCl ($m_3$)|AgCl, Ag. The extended form of the Debye-Hückel equation of the Bates-Guggenheim convention was used for the calculation of pH. The value of pH at 37 °C is 7.387 for $m_1 = 0.02$ *m* ACES, 0.1 *m* NaACES, and *m*3 = 0.06 m NaCl. This value is very close to the pH of blood serum. It is recommended as a secondary standard for physiological study.

## RM_MWGL Regional Meeting 362

### Buffer standards for the physiological pH of *N*-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]glycine (TRICINE) from $T$ = (278.15 to 328.15) K

***Jaime A Veliz**, jveliz@drury.edu, Jessica M Stegner, Clark E Summers, Gregory L Suhrheinrich, Lakshmi N Roy, Rabindra N Roy.Hoffman Department of Chemistry, Drury University, Springfield, MO 65802, United States*

The zwitterionic buffer compound TRICINE has been extensively studied in the temperature range (278.15 to 328.15) K using electromotive force method technique of the cell type: Pt, $H_2$ (g, 1 atm)|TRICINE ($m_1$) + NaTRICINE ($m_2$) + NaCl ($m_3$)|AgCl, Ag. Four buffer solutions at an isotonic saline solution $I = 0.16$ mol·kg$^{-1}$ were studied. For buffer solutions with molality $m_1 = 0.06$ mol·kg$^{-1}$, $m_2 = 0.02$ mol·kg$^{-1}$, and $m_3 = 0.11$ mol·kg$^{-1}$, the pH value at 310.15 K is 7.342 which is in very close agreement with that of blood. It is recommended as a secondary pH standard for clinical study.

## RM_MWGL Regional Meeting 363

## New microboiling point technique for the undergraduate laboratory

***William J King**, king_wj@wvwc.edu, Jessica A Lehman, Melissa Hood, Kindra N Whitlatch, Jacob D Wagoner, Timothy L Troyer.Department of Chemistry, West Virginia Wesleyan College, Buckhannon, WV 26201, United States*

Determination of the boiling point of a liquid can be a useful analysis for the characterization of products made in the organic chemistry laboratory as well as in other chemistry laboratories. Measuring the boiling point using a distillation apparatus typically requires larger amounts of liquid than is created in most microscale experiments. A microboiling technique utilizing an inverted closed end capillary tube is also used, but can be cumbersome to operate because it typically uses mineral oil heated in a Thiele tube. This technique also tends to use greater than 0.3 mL of sample. Other techniques for smaller amounts of liquid require special glassware and techniques not always available at some institutions. We have developed a unique microboiling point technique that is accurate with only 0.2 mL to 0.3 mL of liquid. A simple hotplate can be used to heat the sample and the temperature can be measured using a digital thermometer. This techniques allows us to maximize safety in the undergraduate laboratory while decreasing waste.

## RM_MWGL Regional Meeting 364

## Using Non-Silver photography as a discovery based lab for non-science majors

*Jennifer Yukna, **Megan Sparks**, msparks2@live.maryville.edu. Department of Arts and Sciences, Maryville University, St. Louis, MO 63141, United States*

Student interest in STEM subjects like chemistry has dropped alarmingly. Although the incidence varies among schools and districts, it has become a national epidemic. The average student finds their experience in chemistry irrelevant to their everyday lives. In addition, traditional labs do not model the way science is conducted. Students miss opportunities to (a) appreciate the process of science (b) improve their critical thinking skills by executing their own investigations and (c) learn to effectively communicate science. We have decided to create new laboratory experiences to provide an inquiry format coupled with interesting and relevant materials.

Photography is an excellent platform to discuss chemistry because it is exciting and everyone has taken a picture. This idea is not unique – in fact several journal articles have published laboratory experiences using cyanotype photography. Our experiment differs in teaching methodology. We have developed an inquiry based lab that allows students to be responsible; students have the ability to alter the procedure, make observations, and form their own unique conclusion. A detailed explanation of the new

lab will be included as well as a comparison of the traditional to the inquiry-based laboratory experience.

## RM_MWGL Regional Meeting 365

## Theoretical studies of a cyclic peroxide reactive intermediate

***Shedrick Christian****, schristian@missouriwestern.edu, Wesley W. Winn, Jeffrey N Woodford. Department of Chemistry, Missouri Western State University, Saint Joseph, MO 64507, United States*

Cyclic-peroxides form spontaneously at room temperature from the reaction of an aldehyde or ketone with hydrogen peroxide under acidic conditions. In this study we have explored protonated hydroxymethyl-hydroperoxymethyl-peroxide (HMHPMP), $[H_2O\text{-}CH_2\text{-}OO\text{-}CH_2\text{-}OOH]^+$, a hypothesized reactive intermediate leading to the formation of diformaldehyde diperoxide (DFDP). Due to the conformational flexibility of HMHPMP, we have performed computational studies on several low energy conformers of this molecule and the transitions between them.
Preliminary calculations were performed with the RHF/6-31G(d) method, and higher level calculations were performed using the MP2/cc-pVTZ method. We have located 20 low energy conformers and more than 80 transition states. Kinetic and thermodynamic analysis of the lowest energy paths will be presented. Results can be used in understanding the formation and detection of cyclic-peroxide explosives such as diacetone diperoxide (DADP) and triacetone triperoxide (TATP).

## RM_MWGL Regional Meeting 366

## Kinetics of Pore Formation and Receptor (CMG2) Dissociation from the Anthrax Protective Antigen

***Kiran K. Andra****, kkandra@wichita.edu.Departement of chemistry, Wichita State University, Wichita, KS 67208, United States*

The anthrax toxin secreted by *Bacillus anthracis* is the major virulence factor of anthrax disease. The toxin is comprised of three proteins: protective antigen (PA), edema factor (EF) and lethal factor (LF). PA may initiate toxicity by binding to the von-Willebrand factor A (VWA) domain of capillary morphogenesis protein 2 (CMG2), followed by proteolytic cleavage into two fragments of 20 and 63 kD. The 63 kD fragment oligomerizes into heptameric or octameric structures collectively termed “prepore”, which binds EF and LF, forming the anthrax toxin. The toxin is then endocytosed, and within an acidified endosome undergoes a large conformational change to form a membrane spanning pore. Along with pore formation, it is known that the receptor is released, but through mechanisms that are unclear. We have used stopped-flow fluorescence to monitor the dissociation of an Alexa-fluor 488 labeled CMG2 from heptameric Alexa-fluor 350 labeled PA, and our results shows that conformational

change and receptor release occurs at the same pH which support the mechanism that, domain 4 must initially move away from domain 2. This allows conformational change followed by receptor dissociation which is concomitant process with pore formation.

## RM_MWGL Regional Meeting 367

## Structure and function of the Alternative Complex Three from the photosynthetic bacteria *Chloroflexus aurantiacus* and *Roseiflexus castenholzii*

***Erica L. Wunderlich Majumder***, *ewunderlich@wustl.edu, Robert E. Blankenship. Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

The structure and function of the energy-conserving Alternative Complex Three (ACIII) from the electron transport chains of two related photosynthetic bacteria, *Roseiflexus castenholzii* and *Chloroflexus aurantiacus* is under investigation. *Roseiflexus* is a Filamentous Anoxygenic Phototroph, FAP, with ACIII like *Chloroflexus*, but lacks a chlorosome for light harvesting. ACIII is theorized to be a functional replacement for complex III, cytochrome $bc_1$or cytochrome $b_6f$ complex, in mitochondria and chloroplasts respectively, which is absent in these bacteria. ACIII in *Chloroflexus* has previously been purified, identified and characterized. However, it has not been shown if the protein pumps protons across the membrane. Experiments described here probe the proton pumping function of this protein by reconstituting ACIII in liposomes with entrapped pH sensitive fluorescent dye pyranine. Additionally, the complex in *Roseiflexus* is being purified and characterized. Comparisons between the two complexes reveal evolutionary and functional relationships.

## RM_MWGL Regional Meeting 368

## Probing the effect of the electron density distribution in the primary electron on the directionality of charge separation in photosynthetic reaction centers

***Michelle A Harris***[1], *michelleaharris@go.wustl.edu, Philip D Laible*[2], *Lucas Kressel*[2], *Craig Luehr*[2,3], *Marc Wander*[2], *Dewey Holten*[1], *Deborah K Hanson*[2], *Christine Kirmaier*[1]. *(1) Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States (2) Biosciences Division, Argonne National Laboratory, Argonne, Illinois 60439, United States (3) Department of Chemistry, Trinity Christian College, Palos Heights, Illinois 60463, United States*

The reaction center (RC) in photosynthetic bacteria converts light energy to chemical energy through a series of charge transfer steps across the membrane. The process has approximately 100% quantum yield of transfer down the L-side of the RC. The M-side, seemingly symmetrical with identical pigments, is inactive. The reasoning for the M-side inactivity has been the goal of numerous studies since its discovery. In order to probe the influence of contributing factors, Leu to His-L173 or His-M200 mutations were introduced that result in replacement of one bacteriochlorophyll of the dimeric electron

primary donor (P) with a bacteriopheophytin on the L- or M-side of the dimer, respectively, to produce bacteriochlorophyll-bacteriopheophytin heterodimers (D). The excited heterodimer (D*) has greater electronic asymmetry and a lower free energy than the native P*. These changes in the properties of the primary electron donor alter the mechanisms, rates and yields of electron transfer down the L- and M-sides of the RC. These factors were further manipulated by altering the hydrogen bonding interactions of the two macrocycles of D, or swapping the tyrosine and phenylalanine residues near the primary donor on the two sides of the RC. Studies were performed on the various mutants using subpicosecond transient absorption. By observing changes that occur in the yield of L- vs. M-side charge separation, the contributions of the electronic and energetic factors to directionality of electron transfer in photosynthetic s RCs were assessed.

**RM_MWGL Regional Meeting 369**

## Identification of DNA aptamers for a redox cofactor

***Ismaila Emahi***, *iemahi@slu.edu, Allen J. Mason, Kelsey J. Schlund, Dana A. Baum. Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

Nicotinamide adenosine dinucleotide ($NAD^+$) and flavin adenosine dinucleotide (FAD) are essential cofactors for enzyme-catalyzed redox reactions. RNA aptamers for both $NAD^+$ and FAD have been identified and $NAD^+$ is known to bind to ATP aptamers because of the adenosine moiety. However, there are no reported aptamers that can bind to pyrroloquinoline quinone (PQQ), a third redox cofactor used in quinoproteins. We are interested in identifying aptamers that specifically recognize and bind to PQQ. Such aptamers could find use in biofuel cells and could facilitate the development of oxidoreductase deoxyribozymes. Using in vitro selection, or SELEX (Systematic Evolution of Ligands by Exponential Enrichment), we set out to identify PQQ aptamers from a random $N_{70}$ DNA pool. After fifteen rounds of selection, our pool was enriched with binding sequences, which were then cloned. We are currently investigating the specific binding properties of these sequences and the results of these studies will be discussed.

**RM_MWGL Regional Meeting 370**

## *Staphylococcus aureus* and *Enterococcus faecalis* peptidoglycan tertiary structure by rotational-echo double resonance NMR spectroscopy

***Hao Yang***[1], *hyang@go.wustl.edu, Sung Joon Kim*[2], *Manmilan Singh*[1], *Maria Preobrezenskya*[3], *Jacob Schaefer*[1]. *(1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Chemistry and Biochemistry, Baylor University, Waco, TX 76798, United States (3) Gausse Institute of New Antibiotics, Russian Academy of Medical Sciences, Moscow, Russian Federation*

The peptidoglycan of Gram-positive bacteria, such as *Staphylococcus aureus* and *Enterococcus faecalis*, is a heterogeneous and insoluble macromolecular network of unknown tertiary structure. Knowledge about the peptidoglycan tertiary structure would provide crucial insight into the mode of action of glycopeptides, such as vancomycin, which inhibit peptidoglycan biosynthesis. D-[1-$^{13}$C]alanine and L-[$^{15}$N]alanine were incorporated into the peptidoglycan of *S. aureus* by growing the inoculum on a chemically-defined medium in the presence of an alanine-racemase inhibitor. Analysis by rotational-echo double-resonance NMR indicates the $^{13}$C-$^{15}$N average distance in the *S. aureus* peptidoglycan is 4.1 to 4.4 Å between nearest-neighbor stems, which is consistent with a local parallel-stem architecture for a repeating structural motif within the peptidoglycan. *E. faecalis* was labeled with L-[ε-$^{15}$N]lysine, or with L-[1-$^{13}$C]lysine and D-[$^{15}$N]alanine, or with L-[$^{15}$N]alanine and D-[1-$^{13}$C]alanine, respectively. Analysis by rotational-echo double-resonance NMR will provide insight into peptidoglycan structural features, such as relative concentrations of bridge-links, stem-links, and cross-links. This is the first step in determining the architecture of the *E. faecalis* peptidoglycan.

---

### RM_MWGL Regional Meeting 371

## Length requirements of the Hoogsteen bound third strand for the formation of RNA triple helices

***Jason A. Holland**, holland@ucmo.edu, Antonio Cardozo. School of Environmental, Physical and Applied Sciences, University of Central Missouri, Warrensburg, Missouri 64093, United States*

RNA triple helices form when a single stranded region of an RNA molecule binds to the major groove of a preformed Watson-Crick base-paired duplex, through Hoogsteen interactions. RNA triple helices can be intermolecular or intramolecular. An intermolecular triple helix is formed from two or three different RNA strands, while an intramolecular triple helix is formed from a single RNA strand. This study utilizes UV thermal denaturation to investigate the length of the Hoogsteen bound third strand required to form an intramolecular RNA triple helix at acidic pH.

---

### RM_MWGL Regional Meeting 372

## Immobilization of thylakoids with polyethylenimine-based hydrogel for solar energy conversion

***Ganesan Vellaichamy**[1,3], Kyle H Sjöholm[1,2], Matthew T Meredith[1,2], Shelley D Minteer[1,2]. (1) Department of Chemistry, Saint Louis University, St Louis, MO 63108, United States (2) Department of Chemistry, University of Utah, Salt Lake City, UT 84112, United States (3) Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, UP 221005, India*

Thylakoid membranes are subcellular energy conversion devices. They produce energy from photons via protein biocatalysis. They can be used in photobioelectrochemical cells provided that the isolated thylakoids are active for sufficiently long time. Generally, once thylakoid membranes are separated from the tissues, they lose their activity within a very short time, which limits their effective use in photobioelectrochemical cells. In order to overcome this problem, several immobilization techniques are used. In this work, we opted to use an organic hydrogel based on cross-linked branched poly(ethylenimine) (BPEI) to immobilize thylakoids. Thylakoids were isolated from commercially available organic baby spinach leaves and immobilized on Toray carbon paper with cross-linked BPEI.

Physical and chemical methods are most commonly used for thylakoid immobilization. Immobilization using covalent techniques is not suitable, because the thylakoids can be denatured. Normal physical methods of immobilization by adsorption are simple, economic and do not damage the activity, but the interaction of the thylakoids with the electrode forces is weak and desorption of thylakoids is highly possible. This present method provided a solution for these problems and the activity is also maintained as BPEI forms a hydrophilic three dimensional network, around the thylakoids without affecting their activity. A detailed comparison is made with other physical and chemical methods of immobilization of thylakoids on the electrode surface. The immobilization technique, electrochemical properties, and the electron transfer mechanism will be discussed in the paper.

**RM_MWGL Regional Meeting 373**

## Topology and dynamics of conformational exchange of a small multidrug transporter, EmrE

***Supratik Dutta***[1], *Reza Vafabakhsh*[2], *Emma A Morrison*[1], *Greg T DeKoster*[1], *Taekjip Ha*[2], *Katherine A Henzler-Wildman*[1]. *(1) Biochemistry and Molecular Biophysics, Washington University in St. Louis, St. Louis, MO 63121, United States (2) Department of Physics and Howard Hughes Medical Institute, University of Illinois at Urbana-Champaign, Urbana, Urbana, IL 61801, United States*

Multidrug resistance (MDR) efflux proteins export drug molecules from the bacterial cytoplasm and confer resistance towards different classes of drugs. EmrE is a member of small multidrug resistance (SMR) family, found in the inner membrane of *Escherichia coli*. EmrE extrudes polyaromatic cations from the bacterial cytoplasm by coupling it to proton import.

EmrE is one of the smallest transporters of *E. coli* containing 110 amino acids and four transmembrane helices. The minimal functional unit of EmrE is believed to be a dimer, but controversies exist about its structure, topology and oligomeric state. It is proposed that EmrE shows dual topology when it inserts into the membrane but the relative topology of monomers within a dimer has not yet been established. To resolve the

topology of EmrE, three single cysteine mutants (N2C, T56C, and Q81C) of the protein labeled with donor (Cy3) and acceptor (Cy5), were reconstituted into liposomes in presence of TPP$^+$ substrate. Single molecule FRET (SM-FRET) between Cy3 and Cy5 revealed an anti-parallel topology between the two monomers in EmrE dimer.

In order to perform active transport, the protein must interconvert between open and close conformation. To probe this conformational exchange we have labeled the EmrE with donor (Cy3) and acceptor (Cy7). The preliminary SM-FRET results show that the time scale of the conformational exchange is 300-400 msec at 25°C, which is 3 times slower than the time scale obtain by solution NMR $^1$H-$^{15}$N ZZ-TROSY experiments at 45°C.

To further explore the transport mechanism of EmrE we have performed a series of solution NMR experiments to measure the longitudinal relaxation rate (R1), spin-spin relaxation rate (R2) and hetero-nuclear NOE for individual amides in EmrE. Analysis of this data will provide insight into the dynamics of EmrE on nanosec-picosec timescales to complement the slow-timescale dynamics data.

## RM_MWGL Regional Meeting 374

## Exploring lipid interactions in the *E. coli* mechanosensitive channel of small conductance (MscS)

***Hannah R. Malcolm**[1], Yoon-Young Heo[2], Donald E. Elmore[2], Joshua A. Maurer[1].  (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States  (2) Department of Chemistry, Wellesly College, Wellesley, MA 02481, United States*

We have previously used a combination of random mutagenesis and molecular dynamics simulations to identify and understand critical residues for tension sensation in MscL (mechanosensitive channel of large conductance). In MscL, we were able to demonstrate a strong correlation between lipid-protein interaction energy, determined using a molecular dynamics simulation of the closed state structure, and mutant channel function. Mutation of amino acid residues in transmembrane domains that exhibited significant lipid interaction typically displayed either a loss of function or a gain of function phenotype in bacterial assays. Here, we have employed a similar computational analysis to identify potentially critical lipid-binding residues for tension sensation in MscS. Molecular dynamics simulations of a closed state model of MscS and the open state crystal structure were carried out in the presence of an explicit lipid membrane. Energetic analysis of lipid-protein interactions in the first transmembrane domain (TM1) and the second transmembrane domain (TM2) indicated ten residues with increased lipid interactions in the closed state. Using site directed mutagenesis, these residues were mutated to alanine and their ability to rescue MscL/MscS/MscK null *E. coli* from osmotic downshock was determined. Generally, mutating closed-state lipid-interacting residues to alanine resulted in MscS channels that exhibited decreased

ability to rescue bacteria from osmotic downshock, following a similar trend to our previous
studies of MscL.

## RM_MWGL Regional Meeting 375

## Development of specific inhibitors of JmjC-domain histone demethylases

***Barbara Gordon***, *Liviu M Mirica. Department of Chemistry, Washington University in St. Louis, Saint Louis, Missouri 63130, United States*

Histone demethylases are a newly discovered class of non-heme iron enzymes that play an important role in regulating transcription and epigenetic inheritance. We are interested in the design of specific inhibitors for these enzymes using an enzyme-templated approach that takes advantage of the enzyme's substrate specificity. The developed specific inhibitors could be used as tools for studying the role of histone demethylases in cell function and development. We have successfully expressed and purified three histone demethylases, including the cancer-relevant JMJD2C. A detailed enzyme kinetics analysis is achieved through the use of MALDI-TOF mass spectrometry, oxygen electrode measurements and fluorescence coupled assays. To our knowledge this is the first study of oxygen kinetics of JmjC-domain containing histone demethylases. An interesting case of co-substrate inhibition is seen with each enzyme. In the near future we will test the inhibition of JMJD2C in MCF7 cancer cells.

## RM_MWGL Regional Meeting 376

## Design, synthesis, and evaluation of inhibitors of norwalk virus 3c protease

***Sivakoteswara rao mandadapu***[1], *srmandadapu@wichita.edu, Kok-Chuan Tiew*[1], *Guijia He*[1], *Sridhar Aravapalli*[1], *Mallikarjuna Reddy Gunnam*[1], *Kevin R Alliston*[1], *Gerald H Lushington*[2], *Yunjeong Kim*[3], *Kyeong-Ok Chang*[3], *William C. Groutas*[1]. *(1) Department of Chemistry, Wichita State University, Wichita, Kansas 67260, United States (2) Department of Molecular Graphics and Modeling Laboratory, University of Kansas, Lawrence, Kansas 66045, United States (3) Deapartment of Diagnostic Medicine/Pathobiology, Kansas State University, manhattan, Kansas 66506, United States*

Noroviruses are a leading cause of food-borne and water-borne non-bacterial acute gastroenteritis. Norovirus infections constitute an important health problem with an estimated 23 million cases of gastroenteritis occurring annually in the US, causing 50,000 hospitalizations and 300 deaths.

Noroviruses are small enveloped viruses of the Caliciviridae family. The genome of the Norwalk virus, a prototype of noroviruses, is comprised of a single-stranded, positive sense RNA molecule of ~ 7.7 Kilo bases that consists of three open reading frames (ORFs) that encode a 200 kDa polyprotein (ORF1), a major capsid protein VP1 (ORF2),

and a small basic protein VP2 (ORF3). The mature polyprotein is co- and post-translationally processed by a virus-encoded protease to generate mature non-structural proteins. Processing of the mature polyprotein is mediated by this 3C protease, a (chymo) trypsin-like cysteine protease having a Cys-His-Glu catalytic triad and an extended binding site. The substrate specificity of norovirus 3C protease has been determined using in vitro transcription/translation studies, and peptidyl chromogenic and fluorogenic substrates.The protease shows a strong preference for a –D/E–F/Y–X–L–Q–G–P– sequence (where X is H, E or Q) corresponding to the subsites S5–S4–S3–S2–S1–S1$'$–S2$'$–.
Cleavage is at the P1–P1$'$ (Q–G) scissile bond.

We describe herein the first series of peptidyl inhibitors of Norwalk virus 3C protease (represented by structure (**I**) below). The rationale, synthesis and biochemical evaluation of inhibitor (**I**) will be presented.

## RM_MWGL Regional Meeting 377

## Cloning and expression of L-fucose metabolizing genes

***Thomas J Wiese****, twiese@fhsu.edu, Sara C Rogers[1], Liping Yang[1], Thomas J Wiese[1]. (1) Chemistry, Fort Hays State University, Hays, KS 67601, United States*

L-Fucose is a monosaccharide normally present in the serum of mammals in the low micromolar concentration range and represents an important constituent of glycoproteins and glycolipids. There is intense interest in understanding at a deeper level the metabolism of this sugar as L-fucose has been shown, among other things, to influence antibody dependent cellular cytotoxicity (ADCC) of antibodies. As part of a program to understand the metabolism of L-fucose we have PCR cloned several of the genes of both the *de novo* and salvage synthetic pathways of fucose synthesis. The generated clones are being placed into tetracycline responsive plasmids to allow for selective activation or inactivation of the proteins. L-Fucokinase has thus far been refractory to cloning; probably due to the much larger size of this gene relative to the other L-fucose metabolizing genes. The long-term goal of this project is to use RT-PCR to quantify messenger RNA expression of both synthetic and salvage pathways to determine the relative importance of the alternate pathways. This is intriguing as we have recently shown during mouse brain development the activity of the *de novo* pathway decreases and the salvage pathway increases during the last trimester of embryonic development in the first two weeks of postnatal development.

## RM_MWGL Regional Meeting 378

## Use of chromatography to characterize a substrate binding constant for a His-tag immobilized ascorbate peroxidase

***Frank A Kovacs****, Benjamin White, Annette Moser.Chemistry, University of Nebraska at Kearney, Kearney, NE 68849, United States*

The analytical
chromatographic method of frontal analysis has been used successfully to measure binding constant for ligands to proteins. The typical method of protein immobilization for these studies is via a covalent linkage of the protein to a silica resin. In this work we have demonstrated that an enzyme-substrate binding constant can be measured using a Histidine tag to immobilize the protein which can be done in much less time. We have expressed the enzyme ascorbate peroxidase (APX) from switch grass with a His-tag and immobilized it on a Ni-NTA linked agarose resin. We then measured the binding of the enzyme with the substrate, ascorbate. Although no binding constants have been measured previously for switch grass APX, our measured value ($K_d$ = 11.4 ± 2.41) for switch grass APX corresponds well to those for APX from the literature ($K_d$ = 11.6 ± 0.4).

**RM_MWGL Regional Meeting 379**

## Covalent immobilization of C-terminal hydrazide labeled proteins to ketone-presenting self-assembled monolayers (SAMs)

***Ashleigh T. Castner***[1,2]*, acastner@go.wustl.edu, Joshua A. Maurer*[1]*. (1) Department of Chemistry and Center for Materials Innovation, Washington University in St. Louis, St. Louis, Missouri 63130, United States (2) Department of Biomedical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

Protein immobilization and patterning is critical for a variety of applications including patterned cell culture, biosensors, immunoassays,
and protein arrays. Two methods for protein immobilization on a surface are generally employed: physical immobilization via adsorption and specific
immobilization via covalent attachment. Physical protein immobilization occurs through partial protein unfolding on a substrate, resulting in reduced protein activity and variations in surface protein absorptions. Thus, we are working to develop methodologies for specific immobilization of proteins in their native conformations. This work utilizes an intein fusion protein for the site-specific labeling of a protein at its C-terminus through an expressed protein ligation (EPL) reaction with hydrazine. The resulting hydrazide labeled protein is then covalently attached to a self-assembled monolayer (SAM) surface presenting a ketone moiety through a hydrazone linkage. This bioorthogonal attachment strategy allows for the immobilization of a target protein onto an otherwise protein-resistant surface from a crude cell lysate, eliminating the need for a laborious protein purification process. Furthermore, by using SAMs consisting predominantly of ethylene-glycol terminated monomers, this technique results in immobilization of protein in a uniform and more native conformation than could be achieved by physical adsorption. We are using the 10th fibronectin type III domain ($^{10}$FN3) to develop these techniques since it is a small cell adhesion-promoting protein that can be used to create patterned cell culture substrates. Specific reaction of the hydrazide labeled $^{10}$FN3 is demonstrated using surface plasmon resonance imaging (SPRi), MALDI-MS, and fluorescence microscopy. Patterned substrates are also being

created using mixed monolayers to present a surface-exposed photoprotected ketone functionality.

## RM_MWGL Regional Meeting 380

## Inactivation of PTP-SHP2 by peroxymonocarbonate

**Sarah M Lewis**[1], smlcm7@mail.missouri.edu, Derrick Seinner[1], Harkewal Singh[1], Kent Gates[1,2]. (1) Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States (2) Department of Biochemistry, University of Missouri, Columbia, Missouri 65211, United States

Protein tyrosine phosphatases (PTPs) are important in the regulation of cell signal transduction and are able to operate as positive and negative regulators of signal transduction. The protein tyrosine phosphatase Src homology-2 (SHP2) is a positive regulator of the Ras signalling pathway and aids in the progression of the cell cycle. This non-receptor PTP is involved in cell signaling via growth factors and cytokines. Inhibition of SHP2 would allow for down regulation of cancerous cell growth. This study focuses on the redox regulation of SHP2, utilizing bicarbonate ($HCO_3^-$) and hydrogen peroxide ($H_2O_2$) to form peroxymonocarbonte ($HCO_4^-$), which forms in buffered solutions at neutral pH. It was determined that peroxymonocarbonate inactivates SHP2 in a time- and concentration-dependent manner at micromolar concentrations of $H_2O_2$, which is consistent with the cellular concentrations of $H_2O_2$.

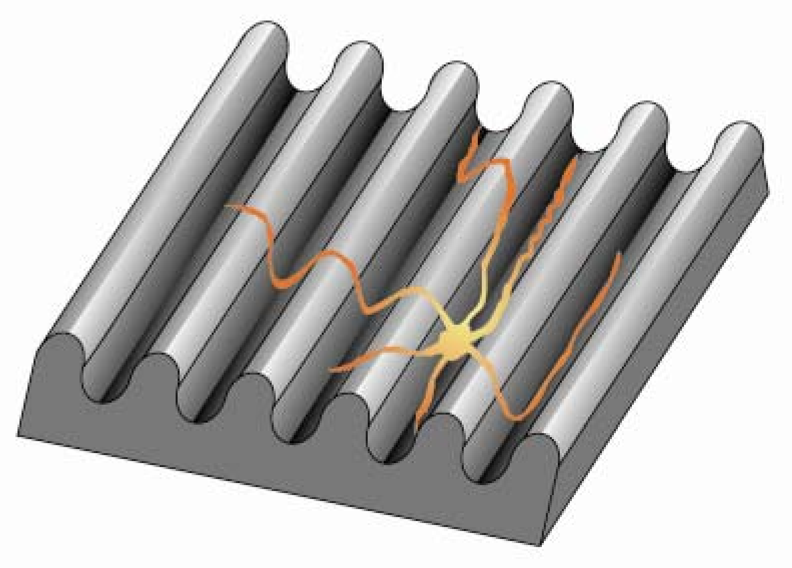
## RM_MWGL Regional Meeting 381

## Studying neuronal behavior in response to changes in microenvironment: An *in vitro* approach

**Dawn M Johnson**, dmyanker@wustl.edu, Skylar M Spangler, Jad P Abi-Mansour, Joshua A Maurer. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States

The development of two and three-dimensional patterned substrates provides new ways to study neuronal behavior. The creation of two-dimensional (2D) patterned surfaces through the use of photolithography, microcontact printing, and self-assembled monolayer (SAM) chemistry allows for the study of axonal differentiation. Through the use of these methods, we have created starburst patterns to which E18 mouse hippocampal neurons are confined. Utilizing immunohistochemistry to specifically stain for the tau protein, predominantly localized along microtubules in the axon, we have found that neurite differentiation is not a predetermined process; rather, it is environmentally determined. The compilation of statistical data has shown that a mere 20μm difference in the distance a neurite is allowed to grow will determine polarization. Utilizing grayscale photolithography, we intend to learn more about how microtopography influences neuronal growth. The fabrication of a continuous three-dimensional (3D) wave pattern, varying height as well as the peak-to-peak distance,

allows for the study of neuronal behavior in response to variations in microenvironment. Neurons experience these types of changes in microtopography *in vivo*; here we aim to determine the threshold at which a neuron is no longer able to extend its processes up and down the wave pattern. This will provide insights into the limitations a neuron may experience during pathfinding *in vivo*.



**RM_MWGL Regional Meeting 382**

## Adenine-4-aminobiphenyl formation by acid hydrolysis of *TP53 exon7* cDNA in the presence of 4-aminobiphenyl as evidenced by LC-ESI-MS/MS

***Paul R. Knoll***[1,3]*, paulrknoll@gmail.com, Jay C Means*[2]*. (1) Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, United States (2) College of Science, Southern Illinois University - Carbondale, Carbondale, IL 62901-4403, United States (3) Chemistry, Lake Michigan College, Benton Harbor, MI 49022, United States*

An authentic adenine-4-aminobiphenyl (Ade-4ABP) standard was synthesized by a Buchwald-Hartwig coupling procedure published in this lab. The Ade-4ABP was characterized by $^1$H-NMR, by IES-MS and by UV. The synthetic 45-*mer TP53 exon7* complementary DNA, 4ABP and Ade-4ABP were solvated in pH 7.4 100 mM KPhos. The 71 ± 2 pmol Ade-4ABP, or 0.2 pmol 4ABP, with 125 pmol cDNA were hydrolyzed for 2 hrs. at 75 °C in equal volumes of 1.0 N HCl, resulting in 0.5 M HCl, 3 mM $MgCl_2$, and 1 mM EDTA clear injection solutions. Reactant concentrations were 'on column' amounts. A 30% to 100 % $MeOH:H_2O$ gradient on a phenyl column produced B, C, D peaks for the 4ABP/cDNA and A, B, C, D peaks for the Ade-4ABP/cDNA hydrolysates at the 303 *m/z* --> 152 amu MRM transition characteristic of Ade-4ABP. The acquisition span was 100 to 600 *m/z*. The LC-MS scans of each peak were selected. All peaks, but check standard (which had only 303 *m/z* of peak A), had 237 *m/z*, 195, 196, 197 *m/z* and 136 *m/z* fragment ions. Peak A: 303, 304 *m/z* 4ABP. Peak B: 303, 304 *m/z* eluted

first with greater RIC, then the 289, 290 *m/z* eluted with greater RIC. ID was the 6-amino conjoined $N^6$-bis-(*N*-(adenine-8-*yl*)-4-aminobiphenyl). Peak C: 303, 304 *m/z* and minor ion 423 *m/z* was given the ID *8,N*-(adenine-$N^6$-8-*yl*)-6-dihydropurine,4ABP. Peak D: 303, 304 *m/z* and a minor ion pair 485 / 493 *m/z*. The chromatographic peaks were similar heights for 4ABP/cDNA and Ade-4ABP/cDNA hydrolysates. Hydrolyzed monomeric dAdenosine/4ABP had no peak and dAdenosine/Ade-4ABP eluted only at peak A. The limiting reagent appeared to be the cDNA. The reactivity of the amine at purine $C^8$ may be a reversible covalent bond. The single-stranded DNA was necessary for reactivity.

## RM_MWGL Regional Meeting 383

## Cyclipostins as Inhibitors of Rat Hormone Sensitive Lipase.

***Elena Vasilieva****, evz7c@mail.umsl.edu, Raj Kumar Malla, Supratik Dutta, Ben Martin, Cynthia M. Dupureur, Christopher D. Spilling.Department of Chemistry & Biochemistry, University of Missouri Saint Louis, Saint Louis, MO 63121-4400, United States*

Hormone sensitive lipase (HSL) is a protein involved in hydrolysis of triglycerides to glycerol and free fatty acids (FFA) in cells. HSL is down regulated by insulin; in the case of type II diabetics HSL is always activated. This leads to FFA accumulation in the bloodstream, which promotes cardiovascular disease. This problem makes HSL a drug target for type II diabetes. Rat HSL was cloned into a baculovirus expression system and purified using affinity chromatography. Cyclipostins were found to be active low nM inhibitors of rat HSL using triolein as substrate (Laszlo Vertesy, et al., J. Antibiotics 2002, 55, 480-494). Cyclipostins consist of the bicyclic Cyclophostin (**1**) ring and an acyl tail off the phosphate (Fig.1). Cyclipostin R (**2**) and P (**3**) were synthesized and tested using a spectroscopic esterase assay with p-nitrophenyl butyrate (PNPB) as a substrate. Both isomers of cyclophostin (**1**) were found to have high uM $IC_{50}$s. Cyclipostin P (**3**) shows a low nM range inhibition against rat HSL. Preliminary, cyclipostin R (**2**) shows high nM inhibition against rat HSL with PNPB as a substrate. Inhibition studies using tritiated triolein (lipase assay) are still in progress (Hans Tornqvist et al., J. Lip. Res. 1972, 13, 424-426).

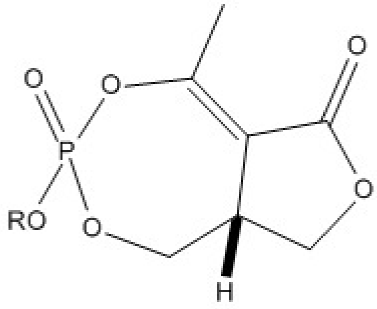


Fig. 1 R=$CH_3$- Cyclophostin (**1**), R=$C_{15}H_{31}$- Cyclipostin R (**2**), R=$C_{16}H_{33}$- Cyclipostin P (**3**)

## RM_MWGL Regional Meeting 384

### Fluorescent sphingolipid precursors and click chemistry cholesterol analogs for imaging of sphingolipid and cholesterol distribution in the plasma membranes of living cells

***Kaiyan Lou****, kylou@illinois.edu, Raehyun Kim, Mary L Kraft.Department of Chemical and Biomolecular Engineering, University of Illinois, Urbana, IL 61801, United States*

Sphingolipids and cholesterol are important components in cell plasma membrane, which plays crucial role in cell signal transduction, cell-cell adhesion, and disease progression such as virus budding. We are developing a new two-step sequence for fluorescence imaging of sphingolipid and cholesterol distribution in cell membranes . We have synthesized a fluorescent sphingosine analog , which is employed to metabolically incorporate fluorescently labeled sphingolipids into living cells. To visualize the cholesterol, we have developed a cholesterol analog that contains a strained alkyne group that enables subsequent introduction of a fluorescent label by copper-free click chemistry. This two-step method may enable assessment of co-localization between sphingolipids and cholesterol within the plasma membrane of living cells.

## RM_MWGL Regional Meeting 385

### Zinc homeostasis and swarm expansion in *Myxococcus xanthus*

***Lauren N Brumley****, brumley.ln@gmail.com, Faith E Jacobsen, Rion G Taylor.Department of Science and Mathematics, MidAmerica Nazarene Univeristy, Olathe, Kansas 66062, United States*

The objective of this study was to evaluate the effects of various concentrations of zinc on the growth and development of *Myxococcus xanthus.* This was accomplished by growing *M. xanthus* cells on nutrient media with exogenous zinc metal added and evaluating growth via measurements and photographs at various time points. We also varied the concentration of zinc. As concentrations of zinc increased, overall colony growth diminished almost completely. In conclusion, high concentrations of zinc disrupt normal cell behavior. Because it is a model organism, the discoveries made with *M. xanthus* can reveal more information about other prokaryotes.

## RM_MWGL Regional Meeting 386

### Study of heparin oligosaccharides binding to proteins using affinity capillary electrophoresis

***Meredith Dinges**, mdinges@gmail.com, Benjamin Rogers, Albert Korir. Department of Chemistry, Drury University, Springfield, MO 65802, United States*

Glycosaminoglycans (GAGs) are linear, highly sulfated, and heterogenous polysaccharides found on cell membranes or in the extracellular matrix. GAGs are known to influence in vivo activities of several proteins including chemokines. Chemokines are critically involved in many biological processes such as inflammation and cell development. For example, GAG binding can facilitate the recruitment of chemokines to certain cells thus aiding in cell migration independently of the receptor. There is considerable interest in determining the sequence and structure of the GAGs that bind to specific chemokines. In this initial study we will develop a method that involves affinity capillary electrophoresis (ACE) to study interaction of heparin-derived disaccharides with a model peptide. ACE is known to be an efficient and accurate technique capable of probing non-covalent interactions and determining binding constants between receptors and ligands. The principle of ACE is based on the change in electrophoretic mobility due to the change in charge-to-mass ratio of the receptor-ligand complex. ACE is well suited for highly anionic analytes such as heparin-derived oligosaccharides, for which large differences in electrophoretic mobility can be observed between the complex and the free target protein. The binding parameters can be obtained reproducibly and with minimal sample consumption. An added advantage of ACE is that the amount of free and bound receptor/ligand need not be known since only changes in migration time are used in estimation of the binding parameters. The analytical strategy developed in this study will
facilitate the identification of sequence and structure of GAGs that bind to specific chemokines.

## RM_MWGL Regional Meeting 387

## Study of carbon assimilation in plants labeled with stable and radioactive isotopes by solid state NMR and direct positron imaging

***Manmilan Singh**, Greg Potter, Rebecca Dirks, Lee Sobotka, Jacob Schaefer. Department of Chemistry, Washington University in St Louis, St Louis, MO 63130, United States*

We have used a frequency-selective rotational-echo double-resonance (REDOR) $^{13}C\{^{15}N\}$ solid-state NMR experiment to measure the concentrations of glycine-glycine pairs in proteins (and protein precursors) of intact leaves of plants exposed to both high- and low-$CO_2$ atmospheres. We illustrate the differences of cell-wall biosynthesis in cheatgrass and soybean leaves by comparing the assimilation of labels from $^{15}N$-fertilizer and different $^{13}CO_2$ atmospheres. Cheatgrass and soybean are both $C_3$ plants but differ in their response to a high-$CO_2$ environment. Direct imaging of positrons from radiolabeled $^{11}CO_2$ (half life of 20 min) administered together with $^{13}CO_2$ to soybean plants provided spatial and temporal distribution of photosynthate *in vivo*. This combination of complementary analytical techniques has led to an unexpected conclusion for photosynthetically heterogeneous soybean leaves: transient starch

deposition is not the temporary storage of sucrose excluded from a saturated sugar transport system.

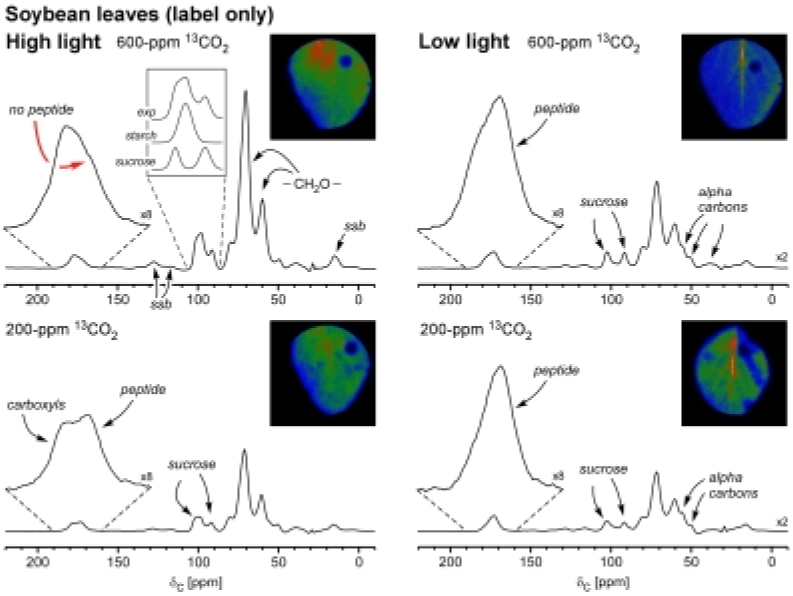


**Figure 1.** 125-Mhz $^{13}C$ CPMAS difference spectra of intact lyophilized soybean leaves labeled in vivo by a combination of $^{11}CO_2$ and $^{13}CO_2$ at a concentration of 600 ppm (top row) and 200 ppm (bottom row) using high-intensity light (about one-half full sunlight, left column) and low-intensity light (about one-sixth full sunlight, right column). Exposure of the leaf to $^{11}CO_2$ was for 2 min, and to $^{13}CO_2$ for 60 min. Natural-abundance $^{13}C$ peaks have been removed by subtraction so NMR signals are due only to label. Images obtained from direct detection of positrons resulting from $^{11}C$ decay are shown in the insets. The images were made 60 min after the $^{11}CO_2$ exposure just prior to freezing and lyophilization of the leaf. Low light causes partitioning of a large fraction of photosynthate into sucrose (insets, right column). Under high $CO_2$ and high-light conditions, the direct incorporation of glycine into proteins from the Rubisco oxygenase pathway is suppressed (upper left, red arrow) and starch is a major product instead.

## RM_MWGL Regional Meeting 388

## Effect of a mutant with altered dynamics on hydride transfers catalyzed by thymidylate synthase

***Thelma Abeysinghe***, *donthelma-abeysinghe@uiowa.edu, Zhen Wang, Amnon Kohen.Chemistry, University of Iowa, Iowa City, Iowa 52246, United States*

Thymidylate synthase (TSase EC 2.1.1.45) catalyzes the final step in the de novo biosynthesis of 2'–deoxythymidine 5'–monophosphate (dTMP), where the cofactor (6 R)-$N^5$, $N^{10}$-methylene-5,6,7,8-tetrahydrofolate ($CH_2H_4F$) serves both as the methylene donor and as the hydride ($H^-$) donor (from its C6 position). Recent focuses on the mutants of highly conserved residue Tyr-209 (in *ec*TSase) have shown a key role of stabilizing the closed enzyme conformation.[1]

According to the crystal structures of of wt *ec* TSase and its Y209W mutant at a 1.3 Å resolution, the structures are nearly identical. The distinct feature of Y209W is the anisotropic B factors of the phosphate-binding loop, which are not uniformly oriented as in the wt.[1] To assess whether this dynamic effect altered on the hydride transfer step (the rate determining step at the physiological temperatures) of the Y209W TSase mutant, KIEs (kinetic Isotope effects) and other kinetic features were examined.

Competitive KIEs on the second- order rate constant (*V/K*) were measured over a temperature range of 5-35°C. The observed H/T ($^{T}V/K_{H}$) and D/T ($^{T}V/K_{D}$) KIEs were used to calculate the intrinsic KIEs throughout the temperature range. The outcome indicated that the hydride transfer was not altered significantly, but that other kinetic and dynamic steps were dramatically affected. While the Tyr-209 is involved mostly with binding of dUMP, Y209W has little effect on dUMP but allows for greater mobility of 5,6,7,8-tetrahydrofolate (THF) prior to the hydride transfer step. This finding emphasizes the importance of long range protein effects in catalysis.

**Acknowledgements:** This work was supported by funding from the NIH GM65368-01

**Reference:**

1. Newby, Z., Lee, T. T., Morse, R. J., Lie, Y., Liu, L., Venkataraman, P., Santi, D. V., Finer-Moore, J. S., Stroud, R. M. (2006) The Role of Protein Dynamics in Thymidylate Synthase Catalysis: Variants of Conserved 2'-Deoxyuridine 5'-Monophosphate (dUMP)-Binding Tyr-261. *Biochem*istry, ***45,*** 7415-7428.

**RM_MWGL Regional Meeting 389**

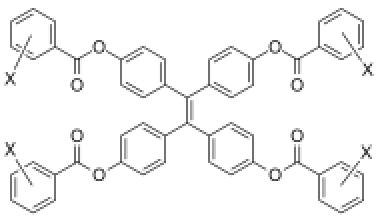
## Halogen bonding interactions in substituted tetraphenylethylenes

***Pradeep P Kapadia***, *pradeepparesh-kapadia@uiowa.edu, Dale C Swenson, F. Christopher Pigge. Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242, United States*

Solid state halogen bonding interactions have been examined in two different classes of compounds derived from a tetraphenylethylene core.

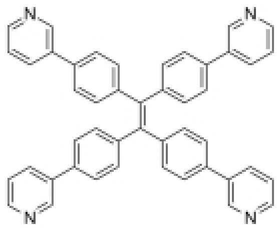
Structurally similar tetratopic haloarenes **1** bearing a common tetraphenylethylene core were synthesized with the aim of providing insight into fundamental solid state halogen bonding interactions. The substrates used in this study all featured four halobenzoate substituents (halogen = Br or I) attached to the four *para* positions of tetraphenylethylene with conformationally flexible ester linkages. A total of nine crystal structures from five different tetraarylethylene substrates were obtained, and the relative importance of various halogen bonding interactions and arene-arene interactions in these structures was determined.

Another class of compound involves tetrapyridyl substituted tetraphenylethylene **2** synthesized via four fold Suzuki coupling. Co-crystalline assemblies of this compound have been obtained with diiodoperfluorobenzenes mediated by C-I···$N_{pyridine}$ halogen bonding interactions .The I···N distance was found to be between 2.7 to 3.1 Å which is one of the shortest known halogen bonds. These interactions result in molecules **2** arranged in two perpendicular planes with iodoarenes connecting the two planes. A layered arrangement and the absence of interpenetration produces channels with sides of ~10 Å are formed in perfluoroiodoarenes are located.



1

X = Br, I



2

### RM_MWGL Regional Meeting 390

## Biosynthetic considerations and progress toward a total synthesis of phomopsichalasin/diaporthichalasin

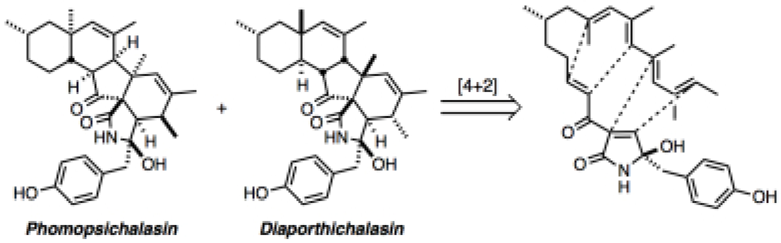
***Julian C Lo***, *loxxx108@umn.edu, Susan G Brown, Elena P Sizova, Thomas R Hoye.Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States*

Phomopsichalasin and diaporthichalasin are hexaepimeric, cytochalasin-type metabolites isolated from different endophytic fungi. Both compounds harbor a high degree of structural complexity, which includes a pentacyclic core and 10 stereocenters, of which 9 are contiguous and 4 are fully substituted.

We believe the biosynthesis of these two compounds can be traced to a polyene precursor that undergoes a pair of consecutive, spontaneous (i.e., non-enzymatic) intramolecular Diels-Alder (IMDA) reactions. The precursor contains a methyl-bearing stereocenter, which we believe exhibits diastereoselective control in the formation of 8 new stereocenters. However, the transition state required for the formation of phomopsichalasin would contain a developing syn-pentane interaction that would lead to an appreciable amount of destabilization. We can draw one of two possible conclusions from this observation, namely 1) the IMDA cascade is actually enzyme-mediated, thus overcoming the developing syn-pentane interaction or 2) the assigned structure of phomopsichalasin is incorrect.

Interestingly, the transition state required for the formation of diaporthichalasin lacks any developing syn-pentane interactions. This observation, coupled with other evidence gathered in our lab, leads us to believe that the true structure of phomopsichalasin is that of diaporthichalasin.

We have taken a convergent approach to synthesizing the polyene precursor, where three fragments will ultimately be joined using a Suzuki cross-coupling and a carbanion coupling reaction. Progress to date on our synthetic studies will be presented.



## RM_MWGL Regional Meeting 391

## Studies of the Bodroux reaction in tetrahydrofuran

***David C. Hawkinson***, *dhawkins@usd.edu, Amanda Furness. Department of Chemistry, University of South Dakota, Vermillion, SD 57069, United States*

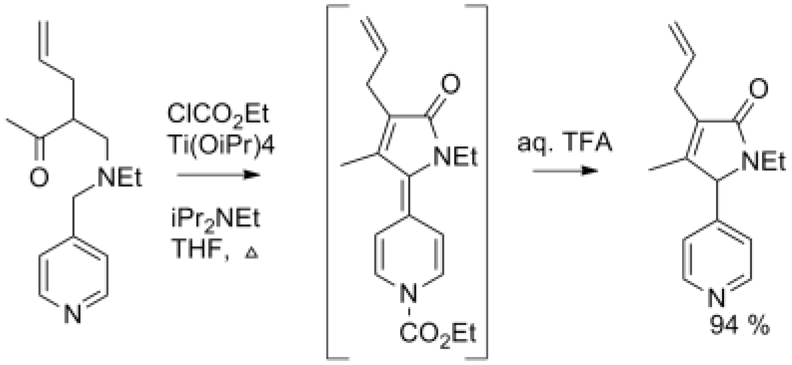
The Bodroux reaction involves the conversion of esters of carboxylic acids to amides using aminomagnesium halides, which are conveniently prepared by reaction of an amine with a Grgnard reagent. Bassett and Thomas (*J. Chem. Soc.* **1954**, 1188) demonstrated that a mixing methyl benzoate and anilinomagnesium iodide (PhNHMgI) in a 1:1 molar ratio in diethyl ether yields a solid with composition (%N and %I) consistent with the addition compound. Treatment of this solid with a second equivalent of PhNHMgI provided much greater yields of amide than decomposition of the intermediate with aqueous acid (87% vs. 32%), and cross-over experiments with PhNHMgI and $Ph_2NMgI$ yielded only the amide of the aminomagnesium halide in the first addition. We find quite different results when the reaction is of methyl benzoate with anilinomagnesium bromide is conducted in tetrahydrofuran: (1) the putative addition compound has sufficient solubility in THF such that no solid intermediate is formed, (2) while reaction of methyl benzoate with anilinomagnesium bromide in a 1:2 ratio forms the amide in good yield (83%), a 1:1 ratio of reactants gives very poor yields (< 5%), and (3) when PhNHMgBr and $Ph_2NMgBr$ are added sequentially to methyl benzoate, N-phenylbenzamide is formed exclusively regardless of which aminomagnesium bromide is added first. In addition, the presence of bromoethane in the reaction mixture results in formation of ethyl benzoate at the expense of decreased yield of amide, transesterification presumably occurring via O-alkylation of the tetrahedral intermediate. These results are discussed in context of the reaction mechanism.

## RM_MWGL Regional Meeting 392

## Anhydrobase mediated annulation reactions of substituted pyridines

***Ashabha I Lansakara***, *ashabha-lansakara@uiowa.edu, Sharavathi G Parameswarappa, F. Christopher Pigge.Chemistry, University of Iowa, Iowa City, Iowa 52242, United States*

Substituted pyridines are well established as synthetic building blocks in heterocyclic and natural product chemistry. Nonetheless, many reaction manifolds available to pyridine derivatives remain significantly underexplored. In this context, we have recently found that certain 4-alkylpyridines participate in intramolecular aldol like condensations with attached carbonyl electrophiles when first converted to acylated anhydrobase intermediates. While the initial products of this reaction show limited stability, they can be immediately subjected to further manipulation (such as rearomatization or hydrogenation) to arrive at tractable products. Transformations of this type appear particularly well suited for construction of bis(piperidine) ring systems encountered in several bioactive marine alkaloids.

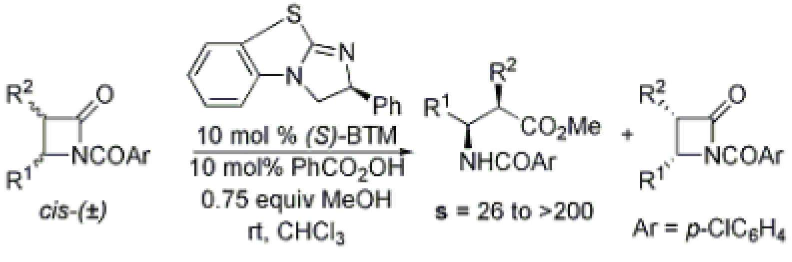


## RM_MWGL Regional Meeting 393

## Kinetic resolution of N-acyl-β-lactams via non-enzymatic enantioselective alcoholysis

***Valentina D. Bumbu***, *vbumbu@wustl.edu, Vladimir B. Birman.Department of Chemistry, Washington University, Saint Louis, MO 63130, United States*

Until recently, kinetic resolution of racemic β-lactams could be accomplished only enzymatically. We have found that benzotetramisole (BTM), an amidine-based acyl transfer catalyst previously developed in our group, promotes highly enantioselective methanolysis of N-aroyl-β-lactams, thus providing an attractive non-enymatic alternative to the traditional enzymatic procedures.

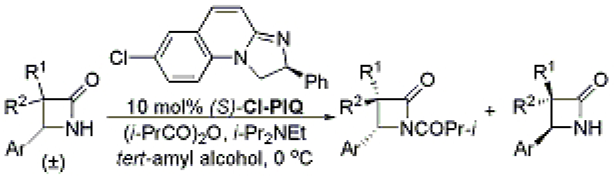


## RM_MWGL Regional Meeting 394

## Kinetic resolution of *β*-lactams via catalytic, enantioselective N-acylation

***Valentina D. Bumbu**, vbumbu@wustl.edu, Xing Yang, Vladimir B. Birman.Department of Chemistry, Washington University, Saint Louis, MO 63130, United States*

We have developed the first catalytic, enantioselective N-acylation of 4-aryl-β-lactams. This reaction, promoted by Cl-PIQ, an amidine-based acyl transfer catalyst developed several years ago by our group, permits effective kinetic resolution of *N-unsubstituted* β-lactams and thus may be viewed as complementary to both the classical enzymatic protocols and our recently developed enantioselective alcoholysis of N-aroyl-β-lactams (see previous poster).



**RM_MWGL Regional Meeting 395**

## Nucleosome Phase Greatly Affects Deamination rate of a 5-Methylcytosine Containing DNA Photoproduct

***Qian Song**, qsong@go.wustl.edu, Vincent Cannistraro, John Stephen A Taylor.Department of Chemistry, Washington University in St Louis, St Louis, MO 63130, United States*

Spontaneous deamination of cytosine to uracil within sunlight induced cyclobutane dipyrimidine dimers (CPD's) occurs within hours to days.[1] Methylation of C increases the frequency of CPD formation at PyCG sites which correlates with C to T mutation hotspots in skin cancers. Studies with nucleosome core particles have shown that the frequency of CPD formation and repair is modulated by its phase with respect to the nucleosome, but the effect of nucleosome phase on the rate of $^{m}$C deamination in a CPD is unknown. We have recently determined that a T=$^{m}$CG photodimer in a reconstituted nucleosome core particle whose backbone faces away from the histone surface deaminates about 9-times faster than in unbound DNA, while one that faces towards the surface deaminates about 5-times slower.[2] We will also report on recent results that indicate nucleosome phase affects the deamination rate of CPDs in the p53 gene of human primary skin cells in a similar way.

1 Cannistraro, VJ.; Taylor, J. S. *J. Mol. Biol.* **2009,** *392:1145-1157.*

2 Song, Q.; Cannistraro, VJ; Taylor, J. S. *J. Biol. Chem.* **2011**, 286, 6329-35

**RM_MWGL Regional Meeting 396**

## Exploring site-selective oxidative cyclizations on microelectrode arrays

*David Kesselring, **Bichlien H. Nguyen**, bichlien.h.nguyen@wustl.edu, Kevin D. Moeller. Department of Chemistry, Washington University in St Louis, St Louis, Missouri 63130, United States*

Site-selective oxidative methods have been developed with a variety of reagents such as palladium and ceric ammonium nitrate. Our recent focus has been to adapt 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) solution-phase oxidations that generate privileged structures for use on 1K and 12K microelectrode arrays. Our goal is to demonstrate the generality of site-selective oxidation reactions and the utility of array-based libraries for probing a variety of biological targets. Progress along these lines will be discussed.

## RM_MWGL Regional Meeting 397

## Development of fluorescent chemosensors for divalent and trivalent cations based on carboxylated ethynylarenes

***Audrey T Gallagher**, audreygallagher@creighton.edu, James T Fletcher. Department of Chemistry, Creighton University, Omaha, NE 68178, United States*

A series of carboxylated ethynylarene derivatives were prepared and screened as chemosensors for the selective detection of divalent and trivalent metal analytes in an aqueous environment. Sonogashira coupling of 1,3,5-tribromobenzene with two equivalents of *meta*-ethynylaniline and two equivalents of phenylacetylene produced a mixture of 1,3,5-tris(phenylethynyl)benzene, 1 (*meta*-aminophenylethynyl)-3,5-bis(phenylethynyl)benzene, 1,3-bis(*meta*-aminophenylethynyl)-5-(phenylethynyl)benzene and 1,3,5-tris(*meta*-aminophenylethynyl)benzene. The monoamino, diamino and triamino derivatives were condensed with each of three cyclic anhydrides (succinic anhydride, glutaric anhydride and diglycolic anhydride) in dichloromethane solvent to produce three different monocarboxylated, dicarboxyalated and tricarboxylated sensor analogs. Condensation reaction progress was monitored by HPLC analysis, and each product was characterized by $^{1}$H NMR, MALDI-TOF mass spectrometry, UV-Visible absorbance spectroscopy and fluorescence spectroscopy. The di- and tricarboxylated arene analogs were soluble in the buffered aqueous environment of the standard assay (pH 7.5 TRIS-HCl) and therefore used in high-throughput fluorescence binding assays to measure fluorescence changes upon mixing with both divalent and trivalent metal cations. Tricarboxylated sensor derivatives displayed sharp fluorescence quenching profiles within 20 minutes, while the dicarboxylated sensor derivatives displayed only gradual quenching within 20 minutes that continued to decrease in intensity over 24 h. The tricarboxylated sensor derivatives are proposed to more rapidly precipitate and signal analyte binding due to the ability to intermolecularly bind metal ions, leading to highly insoluble arene dimer complexes. The dicarboxylated sensor derivatives are proposed to operate only via intramolecular binding of analyte ions, therefore precipitating more slowly as marginally insoluble arene monomer complexes. Although individually these carboxylated arenes do not exhibit a high specificity of analyte binding, when all six analogs are used in tandem they can be used to distinguish various metal cations including Al(III), Ba(II), Ca(II), Cd(II), Co(II), Cu(II), Mg(II), Ni(II), Pb(II), Ru(III), Sr(II), Zn(II) in an aqueous environment. Details of the synthesis, characterization and fluorescence binding assays will be presented.

**RM_MWGL Regional Meeting 398**

## Unusual secondary kinetic isotope efect behaviors in a hydride transfer reaction in solution

***Blake A Hammann***, *bhamman@siue.edu, Qi Liu, Yun Lu. Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026, United States*

The contribution of physical phenomena such as hydrogen-tunneling and coupled motion to enzyme catalysis was examined by comparing an uncatalyzed hydride transfer reaction to a relevant reaction catalyzed by enzymes. The reaction studied is the hydride transfer from 2-propanol to 9-phenylxanthylium ion ($PhXn^+$) in acetonitrile (AN). The magnitude of the β-$2^o$ KIE on 2-propanol was observed to be close to unity, which is contradictory to the prediction by the Hammond postulate. The observed slightly larger $2^o$ KIE in the hydride transfer than in the deuteride transfer appears to violate the Rule of the Geometrical Mean (RGM). These non-classical behaviors are explained as results of the unsynchronized hybridization of donor and acceptor carbons in the transition state, the coupled motions of $1^o/2^o$ hydrogens and the H-tunneling. The findings indicate that the non-classical behaviors reported hitherto for enzymatic reactions are also observed in the solution reaction.

**RM_MWGL Regional Meeting 399**

## Carboxymethylated 1,2,3-triazole-based bidentate and tridentate chelators: Preparation and amide bond conjugation under solution-phase and solid-phase conditions

***James T Fletcher***, *jamesfletcher@creighton.edu, Brent S Bruck, Hee-Jun Ahn, Michael G Keeney. Department of Chemistry, Creighton University, Omaha, NE 68178, United States*

The development of new synthetic approaches to conjugate bioorganic and organometallic units is important in promoting the discovery of novel biomaterials and biomimetic small molcules. The goal of this investigation was to efficiently prepare 1,2,3-triazole-based bidentate and tridentate chelators possessing carboxymethylated units, and confirm the ability of such molecules to undergo conjugation with organic and peptide synthons via amide bond formation. The bidentate chelator 1,1'-bis(carboxymethyl)-4,4'-bi-1*H*-1,2,3-triazolyl was prepared from a multi-step one-pot click transformation by reacting 1,4-bis-trimethylsilylbutadiyne with two equivalents each of alpha-bromoacetic acid and sodium azide under an argon environment using CuI/2,6-lutadine catalyst and an acetonitrile/methanol solvent mixture at room temperature for 24 h. Similarly, the tridentate chelator 2,6-bis(1-carboxymethyl-1*H*-1,2,3-triazol-4-yl)pyridine was prepared from 2,6-bis-(trimethylsilylethynyl)pyridine under analogous reaction conditions. Products were isolated via precipitation from an aqueous acidic environment and simple filtration or centrifugation. Each compound was screened for compatibility with common solution phase condensation conditions reacting with organic amide co-reactants, including carbonyldiimidazole, diisopropylcarbodiimide/HOBt, HBTU/HOBt and PyBOP activating agents. Reaction products were characterized by 1H NMR and MALDI-TOF MS analysis. The ability of each compound to undergo solid-phase peptide coupling with resin-bound small peptides was also investigated, with reaction products characterized by HPLC and MALDI-TOF MS analysis. Identification of optimal coupling conditions to form conjugated products for both solution phase and solid phase reactions, as well as characterization of the compounds studied, will be presented.

**RM_MWGL Regional Meeting 400**

## New functionalized resin for solid extraction of heavy metal ions in water samples

*Sadegh Khazaeli[1], Mohammad Rabbani[2], **Nadia Nezamabadi**[1], nnezama@siue.edu.*
*(1) Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, Illinois 62026-1652, United States (2) Chemistry, Azad University-Tehran, Tehran, Tehran 143568335, Iran (Islamic Republic of)*

A new chelating resin was synthesized by functionalization of a polymer support, Amberlite XAD-4, with salicylic acid through an azo linkage (─N=N─). The products were characterized by scanning electron microscopy, elemental analysis, Fourier transform infrared spectroscopy and thermogravimetric analysis. The optimum conditions for the extraction of Pb(II), Cu(II), Ni(II), Co(II) and Zn(II) ions in aqueous samples were studied by batch and column methods. The determination of the metal ions was carried out by flame atomic absorption spectrophotometry. Sorption equilibrium was reached within 30min. The sorbed metal ions were eluted by 0.5M $HNO_3$(10mL) within 10min with the desorption recovery of ≥90% and R. S. D. less than 1.36% (n=5) .

**RM_MWGL Regional Meeting 401**

## Transition metal nanoparticles as catalysts in fuel cell applications

***Lichang Wang**, lwang@chem.siu.edu. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

One of the goals of our computational studies, largely based on density functional theory calculations, is to understand transition metal nanoparticles as catalysts on various reactions relevant to fuel cell applications. In this presentation, I will focus on the results of PtVFe trimetallic nanoparticles in oxygen reduction reaction and of Cu nanoparticles in hydrogen production as a byproduct from ethanol dimerization.

## RM_MWGL Regional Meeting 402

## DFT optical properties and growth mechanisms of gold nanoparticles

***Christine M. Aikens**, cmaikens@ksu.edu, Brian M. Barngrover, Emilie B. Guidez. Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Density functional theory and the superatom model can be used to explain optical absorption properties of nanoparticles such as $Au_{25}(SR)_{18}^{-1}$ and $Au_{38}(SR)_{24}$. Low-energy metal-metal transitions observed in absorption and circular dichroism spectra arise from excitations between superatom orbitals. The unique surface structure of gold nanoparticles impacts their electronic structure and properties.

The growth mechanisms of gold-phosphine and gold-thiolate nanoparticles are found to be quite different. For gold-phosphine nanoparticles, addition of electrons leads to Au-Au bond formation and to spontaneous dissociation of ligands. Chloride dissociation is preferred over phosphine dissociation, although both are observed. Most reactions involved in gold-phosphine cluster growth are exothermic. A wide variety of products are observed in agreement with experiment.

In contrast, addition of electrons to gold-thiolate oligomers leads to the formation of isolated $Au^-$ ions and $Au_{n-1}(SR)_n^-$ chains. On the other hand, addition of a hydride ion to gold-thiolate oligomers leads to products such as free thiols and compounds that contain both Au(0) and chain-like oligomers $Au_n(SR)_{n+1}^-$ ($n$=1-6), which are plausible intermediates for gold nanoparticle growth. The initial formation of the chain-like oligomers is also discussed.

## RM_MWGL Regional Meeting 403

## Nanoporous organic structures: Creation and novel properties

***Bing Gong**, bgong@chem.buffalo.edu. Department of Chemistry, The State University of New York, Buffalo, Buffalo, NY 14260, United States*

A backbone-rigidification strategy based on the specification of intramolecular noncovalent interactions has resulted in the enforced folding of unnatural molecular strands into well-defined crescent or helical conformations containing internal nanocavities of tunable sizes. Tuning the size of the nanocavities has been achieved without changing the underlying helical topology. The same folding strategy has led to the discovery of a series of shape-persistent macrocycles containing internal lumens of sub-nm to over 30 nm across. By equipping nanocavity-containing, rigid macrocycles with directional non-covalent forces, organic nanotubes with non-collapsible internal pores have been obtained. These nanotubes mimic pore-forming proteins and at the same time, offer more structural and functional tunability. The created porous structures have exhibited novel features including the recognition of molecules and large ions, and highly selective ion and molecular transport. The synergistic interaction of synthesis and self-assembly is expected to lead to nanoporous structures with protein-like functions.

## RM_MWGL Regional Meeting 404

### Computer-aided nanoscience research: Nanoice, nanoclusters, and superhydrophobicity

***Xiao Cheng Zeng****, xzeng1@unl.edu.Department of Chemistry, University of Nebraska - Lincoln, Lincoln, NE 68588, United States*

In this talk I shall report several research findings from my group over the past ten year or so, including: (1) New phases of low-dimensional nano-ice and ice clathrate, and helical ice. (2) Superhydrophobic phenomena at the nanoscale, e.g. Lotus effect at nanoscale. (3) Growth pattern of small-sized gold clusters, and design of new boron nanostructures.

In these studies, tools of computational chemistry, including classical molecular dynamics simulation, density functional theory, and ab initio molecular dynamics simulation are employed.

## RM_MWGL Regional Meeting 405

### Application of twin-chain dithiol amphiphiles in electrochemical DNA sensor fabrication

***Socrates Jose P Canete****, sjpcanete@huskers.unl.edu, Thomas J Fisher, Patrick H Dussault, Rebecca Y Lai. Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska, United States*

Thiolated self-assembled monolayers (SAMs) are often used in the fabrication of electrochemical biosensors that utilize gold as the substrate electrode. In most cases, alkanethiols of various lengths and/or terminal groups are normally employed cognizant of the fact that electron transfer through these monolayers plays an important role in the over-all performance of the sensor. In some cases, specially designed molecules,

including “tripodal” alkanethiols and molecular wires, are used in the formation of the monolayer, with the objective of bestowing enhancement in the over-all sensor performance. Here we report the use of a custom-synthesized twin-chain dithiol amphiphile (dS2) as the passivating diluent in the fabrication of a folding-based electrochemical E-DNA sensor. The results are directly compared to sensors fabricated with 11-mercapto-1-undecanol (C11-OH), the commonly employed passivating diluent. Electrochemical impedance spectroscopic (EIS) characterization of these monolayers using soluble methylene blue (MB) as the redox probe shows interestingly marked differences in the phase angle profiles (Bode plot) between the two SAM systems. When MB-labeled DNA probes are incorporated into the monolayer either via direct insertion of thiolated DNA or “click”-based conjugation of alkyne-modified DNA, changes in the Bode profile suggest that the dS2-passivated sensor can detect hybridization while the C11-OH passivated sensor cannot. Albeit the % signal suppression observed upon target hybridization, as monitored by alternating current voltametry, is essentially the same for the two SAM systems, other sensor performance parameters are slightly different between the two systems and these differences will be discussed in the presentation.

**RM_MWGL Regional Meeting 406**

## Development of a Mitochondria-based Electrochemical Water Quality Sensor for Pesticides

***Stephanie Maltzman***[1]*, Shelley D Minteer*[1,2]*. (1) Department of Chemistry, Saint Louis University, St. Louis, MO 63104, United States (2) Department of Chemistry and Materials Science and Engineering, University of Utah, Salt Lake City, UT 84108, United States*

The contamination of ground and drinking water by pesticides is a very serious problem that must be monitored, as many pesticides are toxic to both humans and the environment. Many pesticide sensors have been developed, but are often expensive or complicated to manufacture. In an effort to develop an inexpensive, easily manufactured, and reliable biosensor for pesticides in water, this study outlines a procedure for harvesting intact mitochondria from cultivated *Saccharomyces cerevisiae* yeast cells and immobilizing the intact mitochondria on a high surface area electrode for detection of pesticides. Most pesticides' mode of action is through the mitochondria, inhibiting one or more complexes in the electron transport chain (ETC). In this study, measurable current response can be obtained from the immobilized functioning mitochondria's metabolism of pyruvate in solution. The pesticide can be detected, when introduced, by a decrease in this measured response due to inhibition. When introduced to each of five pesticides (2,4-D, parathion, paraquat, permethrin, and atrazine), a statistically significant drop in current was seen as the ETC was interrupted. So far, inhibition has been seen with pesticide concentrations of 0.7mg/L (2,4-D), 10mg/L (Parathion), 12.2mg/L (paraquat), saturated (permethrin), and 5mg/L (atrazine).

**RM_MWGL Regional Meeting 407**

## Microdialysis-Microchip Electrophoresis with Electrochemical and Fluorescence Detection

***David E. Scott**, scottde@ku.edu, David R. McKenzie, Ryan Grigsby, Susan M Lunte. Ralph N. Adams Institute for Bioanalytical Chemistry, University of Kansas, Lawrence, Kansas 66049, United States*

A microdialysis-microchip electrophoresis system was developed for the *in vivo* monitoring of excitatory amino acids and reactive oxygen species. The direct coupling of microdialysis with microchip electrophoresis leads to a separation-based sensor that is capable of monitoring the *in vivo* concentrations of several analytes simultaneously. This paper describes progress towards an on-line system that can be employed for the continuous monitoring of fluorescent and electrochemically active analytes simultaneously. Recent developments concerning the coupling of microdialysis to microchip electrophoresis for the determination the continuous monitoring of excitatory amino acids and reactive oxygen species will be discussed. The ultimate goal is to miniaturize the entire system for the purpose of on-animal analysis using telemetry for instrument control and data acquisition.

---

**RM_MWGL Regional Meeting 408**

## Demonstration of rapid single cell analysis on simple microfuidic devices: A study nitric oxide production in Jurkat cells

***Eve C Metto**[1], lessos@ksu.edu, Amita Sharma[1], Anne H Culbertson[1], Karsten Evans[1], Dulan B Gunakesera[2], Christopher T Culbertson[1], Susan M Lunte[2]. (1) Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States (2) Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States*

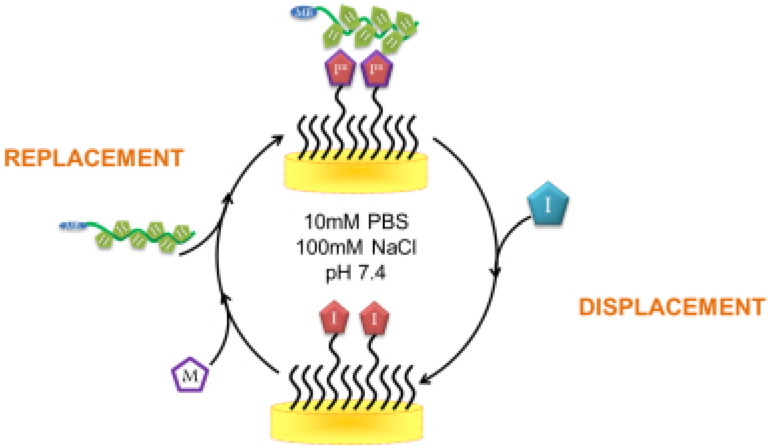
Microfluidic devices are playing an increasingly important role in chemical and cellular analysis thanks to their small channel manifolds that are capable of precise and accurate manipulation of analytes. More attention is being focused on single cell analysis to better understand diseases like cancer which begin with mutations in single cells. Microfluidics can therefore be employed in the development of early detection systems of these diseases. In our group we have used an improved microfluidic device to study the expression of nitric oxide (NO) in over 200 Jurkat cells within a few minutes. Our experiments compared the production of NO in native and induced cells. The cells were labeled with fluorogenic dyes including 4-amino-5-methylamino-2',7'-difluorofluorescein diacetate (DAF-FM DA) which, when hydrolyzed, reacts with NO within the cell. On the microfluidic device, the labeled cells were transported to an intersection where they encountered high voltage that caused cell lysis and electrophoretic separation, prior to laser induced fluorescence (LIF) detection. Analysis of the resulting electropherograms indicated a twofold increase in NO expression in the induced cells. This results compare nicely to recently published bulk cell studies performed for the analysis of NO.

## RM_MWGL Regional Meeting 409

### Design and characterization of an imidazole-metal ion self-assembled monolayer amenable to electrochemical biosensing applications

***Anita J. Zaitouna**, zaitouna.a@huskers.unl.edu, Rebecca Y. Lai. Department of Chemistry, University of Nebraska - Lincoln, Lincoln, NE 68588-0304, United States*

Here we report an alternate peptide immobilization strategy for the electrochemical peptide-based biosensing platform. Unlike the previously established sensor fabrication strategy that requires direct alkanethiol modification of the methylene blue (MB)-labeled peptide probe, this platform utilizes thiolated molecules terminated with organic chelating molecules such as nitrilotriacetic acid (NTA) and imidazole, which in presence of divalent cations such as $Zn^{2+}$, $Ni^{2+}$, and $Co^{2+}$, which can efficiently capture His-tagged modified peptide probes. Our results suggest that we have successfully immobilized His-tagged MB on an electrode and that nickel (II) ions give the most favorable sensor performance. Sensors fabricated using cobalt and zinc (II) ions show similar sensor performance. This probe immobilization strategy has an added facet in which the His-tagged peptide can be readily displaced by a competing ligand, such as imidazole and even the divalent cation, and the electrode can then be reused by chelating a different peptide to be used as a new sensor. The displacement step is highly effective and can remove essentially all the peptide probes immobilized on the electrode. This versatile sensor fabrication strategy will ultimately be implemented in the fabrication of an anti-peanut allergen antibodies sensor using a His-tagged peptide epitope from a major peanut allergen (Arah2).



## RM_MWGL Regional Meeting 410

### Graphene oxide based micro-electronic device for detecting norovirus

***Allan M. Prior**[1], allanp@ksu.edu, Duy D. Le[1], Thi D. T. Nguyen[1], Yunjeong Kim[2], Kyeong-Ok Chang[2], Wenjing Li[3], Nathan A. Oyler[3], Duy H. Hua[1]. (1) Chemistry,* *Kansas State University, Manhattan, KS 66502, United States (2) Department of Diagnostic Medicine and Pathobiology, Kansas State University, Manhattan, KS 66502, United States (3) Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499, United States*

Noroviruses are responsible for more than 60% of all food-water-borne gastroenteritis outbreaks with an estimated 23 million cases annually in the US causing 50,000 hospitalizations, and 300 deaths. The problem is further compounded by the absence of a cell culture system or small animal model for human noroviruses which hampers severely the development of effective therapeutic interventions, such as vaccines and antivirals. Current diagnostic methods for noroviruses include antigen capture enzyme-linked immunosorbent assay (ELISA), latex agglutination assay and reverse transcription-polymerase chain reaction (RT-PCR). Our laboratories recently have been investigating a modified graphene oxide based micro-electronic device for the detection of norovirus genome. Graphene oxides were modified by a covalent attachment of acetic acid function onto the surface, and characterized by solid-state $^{13}$C NMR, IR, and Raman spectroscopy. The device includes a n-type doped silicon chip (a dimension of 1 x 1 cm) silanated with 3-aminopropyltriethoxysilane, microgold electrodes, and modified graphene oxides. The modified graphene oxides have dimensions of ~10 x 60 mm and are single graphene oxide sheets (having a 1 – 2 nm thickness determined from atomic force microscopic images). Various oligonucleotides (short DNAs) were immobilized to the modified graphene oxides and electrical currents were measured using a source meter. Hybridization (or formation of double-helix DNAs) of the immobilized oligonucleotides with complimentary DNA oligonucleotides including fluorescence labeled materials induced a change of electrical currents. Fluorescence microscopic images showed the presence of hybridization. Dehybridization with an aqueous urea solution regenerated the initial single-strand DNA-graphene oxide chip. Hybridization of norovirus RNA was similarly investigated and an increase of current was found, and dehybridization resulted in a decrease of current to the original value. The microelectronic platform may provide an optical-free portable detection device for viruses.

**RM_MWGL Regional Meeting 411**

## Electrochemical study of the diffusion of cytochrome c within nanoscale pores derived from cylinder-forming polystyrene-poly(methylmethacrylate) diblock copolymers

***Bipin Pandey**, Khanh Hoa Tran Ba, Takashi Ito. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

This study reports cyclic voltammograms of cytochrome c on recessed nanodisk-array electrodes (RNEs) based on nanoporous films (11, 14 or 24 nm in average pore diameter; 30 nm thick) derived from polystyrene-poly(methylmethacrylate) diblock copolymers. The faradic current of cytochrome c was observed on RNEs, indicating the

penetration of cytochrome c (hydrodynamic diameter ∼4 nm) through the nanopores to the underlying electrodes. The faradic current on RNEs with 11- and 14-nm nanopores mainly originated from cytochrome c adsorbed on the underlying electrodes, whereas the current on RNEs with 24-nm pores was diffusion-controlled. Interestingly, the diffusion-controlled current of cytochrome c was significantly smaller than that estimated from the faradic current of 1,1'-ferrocenedimethanol on the RNEs. The smaller faradic current suggested more effective decrease of the diffusion coefficient of cytochrome c as compared to that of 1,1'-ferrocenedimethanol, which probably reflected enhanced steric and chemical interactions within the nanopores.

Comparison between experimental data and results of finite-element computer simulations made it possible to assess the structure of the nanoporous films and the diffusion coefficients of redox species within the nanopores. The reported results will provide a means for designing recessed-nanodisk array electrodes for size-based chemical sensing and also for controlled immobilization of biomolecules within nanoporous media for biosensors and bioreactors.

## RM_MWGL Regional Meeting 412

## Finite-element computer simulations on cyclic voltammograms measured at recessed nanodisk-array electrodes derived from Polystyrene-Poly(methylmethacrylate) diblock copolymers

***Khanh Hoa Tran Ba****, sv7508@ksu.edu, Bipin Pandey, Takashi Ito. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

We investigated the characteristics of cyclic voltammograms (CVs) on recessed nanodisk-array electrodes (RNEs) using finite-element computer simulations with COMSOL Multiphysics®. The simulations were performed to understand experimental CVs obtained for 1,1'-ferrocenedimethanol and cytochrome c at RNEs derived from a cylinder-forming polystyrene-poly(methylmethacrylate) diblock copolymer (24 nm in pore diameter, 30 nm in pore depth). Simulated CVs were obtained based on Fick's law, electrode reaction kinetics and mass balance equations by varying the spacing between adjacent nanopores and the diffusion coefficient of a redox species within the nanopore. Comparison between experimental data and simulation results made it possible to address the following two issues regarding experimental CVs at the nanoscale electrodes: First, the RNEs exhibited quasi-reversible, peak-shaped CVs with significantly smaller faradic currents of 1,1'-ferrocenedimethanol as compared with ones predicted by a theory for arrayed microelectrodes. This observation could result from large pore spacing in the RNEs and/or the small diffusion coefficient of the redox species within the nanopore. Second, the diffusion-controlled current of cytochrome c was significantly smaller than that estimated from the faradic current of 1,1'-ferrocenedimethanol on the RNE. This reflected the more effective decrease in the diffusion coefficient of cytochrome c due to the steric and chemical interactions with nanopores.

## RM_MWGL Regional Meeting 413

### Characterization of Lignin from Prairie Cordgrass and Switchgrass by GC-MS analysis of Cupric Oxide and Nitrobenzene Oxidation products, Pyrolysis-GC-MS and MALDI-TOF-MS

***Naga Vinod Kumar Bathula***, *nagavinod.bathula@sdstate.edu. Dept. of Chem and Biochem, South Dakota State University, Brookings, SOUTH DAKOTA 57007, United States*

The relative *p*-hydroxyphenyl/syringyl/guaiacyl (H/G/S) composition of lignin from prairie cordgrass and switchgrass were investigated by GC-MS of cupric oxide and nitrobenzene oxidation products.PCG and SG lignin gave apparent differences in their H/G/S ratios. Phenolic aldehyde structures obtained by oxidative degradation show p-hydroxy phenyl propane units and their ethers, in particular 4-0-alkylated, 4-0-α, and 4-0-β structures are present. Py-GC-MS analysis of both lignin samples also showed similar degradation products with differences in the ratio of their H/G/S moieties. A correlation was noted for the distribution of H/G/S ratios in the GC-MS analysis of oxidation products and pyrolysis-GC-MS analysis products. MALDI-TOF-MS analysis showed lignin oligomers from grass mainly conists H-moieties.

---

## RM_MWGL Regional Meeting 414

### Real-time AC voltammetry-based detection of cancerous protease (legumain) using nanoelectrode arrays

***Lateef Uddin Syed***, *lateefs@ksu.edu, Luxi Zhang, Allan M Prior, Duy H Hua, Jun Li.Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States*

Legumain (also known as asparaginyl endopeptidase) is a lysosomal cysteine protease whose activity is found in several tissues and is highly expressed in a majority of tumors. However, overexpression is not found in normal cells, making it a potential cancer biomarker. In the present study, we employed embedded vertically aligned carbon nanofiber (VACNF) nanoelectrode array (NEA), where only the ends of carbon nanofibers (CNFs) are exposed at the surface of the insulating $SiO_2$ matrix. The exposed CNF tips were functionalized with a tetrapeptide ($NH_2$-$(CH_2)_5$-Ala-Ala-Asn-Leu-Fc) which contains a C5 linker at proximal end and a ferrocene (Fc) at the distal end. Legumain is known to specifically cleave the asparagine site (C-terminus) of the tetrapeptide, which results in the release of Fc moieties from the electrode to the bulk solution. This leads to a drastic decrease in the alternating current voltammetry (ACV) signal. To optimize the ACV conditions for legumain detection, as an initial step towards understanding the electron transfer phenomenon at the CNFs, the exposed CNF tips were functionalized with Fc moieties and a careful investigation of electron transfer rates (ETRs) was carried out using ACV and direct current voltammetry (DCV). We found an anomalous phenomenon, which leads to 100 times higher ETR by ACV

compared to DCV.
Unique conical graphitic stacking of the CNFs was found to be very critical, which facilitates a new capacitive pathway in high-frequency ACV measurements. This indicates that selecting an appropriate electrochemical technique can cope with the intrinsic limit of nanoelectrode materials. Particularly, high-frequency ACV can provide high-performance nano-biosensors and nanoelectronics with CNF NEAs. These findings are being utilized to build an ultrasensitive legumain biosensor for electrochemical monitoring of legumain activity in various cancerous cell lines. Current progress of real-time ACV based legumain detection will also be presented.

**RM_MWGL Regional Meeting 415**

## Identification of peptides from Liver Tissues of 2-Aminoanthracene exposed Fisher-344 Rats

***Henok D Abshiro***, *henok@siu.edu, Worlanyo E Gato, Emilia O Zargham, Jay C Means. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

The toxicity associated with 2-aminoanthracene (2-AA) exposure in Fisher-344 (F-344) rats was investigated using proteomics approach. Twenty four post-weaning 3-4 week old F-344 male rats were fed diets of 0 mg/kg-diet (control), 50 mg/kg-diet (low dose), 75 mg/kg-diet (medium dose) and 100 mg/kg-diet (high dose) 2-AA for 14 and 28 days. This was followed by total protein extraction from liver tissues. Protein samples were separated using one dimensional gel electrophoresis. The gel digests were analyzed by nano LC/MS/MS with a Waters NanoAcquity HPLC system. Generated data were searched using Mascot and quantified via spectral counting. There seem to be more proteins expressed in the short-term study than the long term study. Using a variety of artifactual examination, oxidation and deamidation modifications were greater than acetyl and pyro-Glu protein modifications in both treatment groups. Although the 14 day exposure group showed, greater level of proteins expressed than the 28 day treatment animals, these were not analyzed from the similar size bands. Hemopexin, Adenosylhomocysteinase, Calreticulin, Gc vitamin D-binding protein and Fetub protein may be important in mediating the toxicity of 2-AA. Using relationships analytical tool, SLC2A4 and MAPK3 were found to interact with several proteins identified from the current study. The nature of this interaction is unknown at this point. Understanding the role of SLC2A4 in regulating other proteins as observed in the study will be pursued in future investigations. Combining the current data with other toxicogenomic data from the liver and pancreas will be useful in developing biomarkers due to arylamine toxicity.

Key Words: Protein Identification, 2-Aminoanthracene (2-AA), Liver, Rats, SLC2A4 (glucose transporter type 4), Spectral counting

**RM_MWGL Regional Meeting 416**

## B ring methylated flavonols: Effects on hydrogen bonding, $Al^{3+}$ chelation and the structures and redox chemistry of ruthenium complexes

***Kumudu V Peiris**, pkp42@msstate.edu, Emma Hughes, Benjamin Spears, Joshua Browning, Steven R Gwaltney, William P Henry.Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, United States*

Flavonols are naturally-occurring polyphenols which can chelate metal ions at the 3-hydroxy-4-keto site. In light of the variability of the intramolecular hydrogen bond at this position with methyl substitution on the B ring, we were interested in studying the change in $Al^{3+}$ chelation with the different methyl derivatives. While the 3' and 4' methyl substituted derivatives should show a strictly electronic effect, in the 2'-methylflavonol, steric demands mean that the B and AC rings cannot be coplanar. Using spectroscopic techniques, the formation constants for the binding of flavonols and 3-hydroxychromone with $Al^{3+}$ were determined in methanol. The importance of B ring conjugation on the chelation is demonstrated by the fact that the lowest formation constants were found for 3-hydroxychromone and 2'-methylflavonol. New ruthenium(II) arene complexes of these flavonols were synthesized and characterized by $^1H$ NMR, IR, electrochemistry and X-ray crystallography. Surprisingly, no significant structural differences were found between these complexes and the related hydroxypyranones. However, the oxidation potential of these complexes varies significantly with the methyl substitution. In addition to the above results, the structure of 4'-methylflavonol will be described with emphasis on the hydrogen bonding in the crystal. This structure completes the series for the monomethylated derivatives and the hydrogen bonding parameters will be compared with those for 3-hydroxychromone, flavonol and the 2'- and 3'-methylated derivatives. Besides reporting the experimental work, the results of theoretical calculations on the flavonols themselves and the ruthenium complexes will be described.

**RM_MWGL Regional Meeting 417**

## Synthesis and properties of ferrocenyl-containing porphyrins, tetraazaporphrins, and subphthalocyanines

***Victor N. Nemykin**, vnemykin@d.umn.edu, Pavlo V. Solntsev, Gregory T. Rohde, Jared R. Sabin, Samantha J. Dammer, Katelynn Spurgin.Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, United States*

A large number of symmetric and asymmetric metal-free, main group, and transition-metal metallocenyl-substituted porphyrins,[1] tetraazaporphyrins,[2] and subphthalocyanines have been prepared and characterized by UV-Vis-NIR, MCD, NMR, APCI MS/MS, and Mössbauer spectroscopy. The redox properties of the target compounds were investigated by chemical oxidation method using broad combination of solvents and oxidants as well as by electrochemical and spectroelectrochemical methods using large variety of electrolytes and solvents. An influence of the metallocenyl substituents coordination mode (*i.e.* peripheral *vs.* axial connectivity; direct *vs.* via spacer connectivity) on formation of the mixed-valence states will be discussed.

The electronic, spectroscopic, and geometric parameters of the mixed-valence states in the metallocenyl-containing aromatic macrocycles were determined experimentally and theoretically at Density Functional Theory level. It has been shown that the absorption and fluorescence of the porphyrins, tetraazaporphyrins, and subphthalocyanines with organometallic substituents in NIR region can be switched “ON” and “OFF” under the influence of selected oxidants or specific applied potentials.

References:
1. Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Bizzarri, C.; Galloni, P.; Floris, B.; Nowik, I.; Herber, R. H.; Marrani, A. G.; Zanoni, R.; Loim, N. *J. Am. Chem. Soc.* **2009**, *131*, 14969-14978. Nemykin V. N., Barrett, C. D., Hadt R. G., Subbotin R. I., Maximov A. Y., Polshin E. V., Koposov A. Y. *Dalton Trans.,* **2007**, 3378-3389. Nemykin, V. N.; Hadt, R. G. *J. Phys. Chem. A* **2010**, *114*, 12062-12066. Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Sabin, J. R.; Reina, G.; Galloni, P.; Floris, B. *Inorg. Chem.* **2010**, *49*, 7497-7509. Solntsev, P. V.; Sabin, J. R.; Dammer, S. J.; Gerasimchuk, N. N.; Nemykin, V. N. *Chem. Commun.* **2010**, 6581-6583.
2. Nemykin V. N. and Kobayashi N. *Chem. Commun.* **2001**; 165-166.

### RM_MWGL Regional Meeting 418

## Phosph(on/in)ate-bridging dimers of vanadium (IV) complexes as potential oxidation catalysts

***Craig C. McLauchlan***, *ccmclau@ilstu.edu, Alex E. Anderson, Xavier Riart-Ferrer, Michael P. Weberski. Department of Chemistry, Illinois State University, Normal, IL 61790-4160, United States*

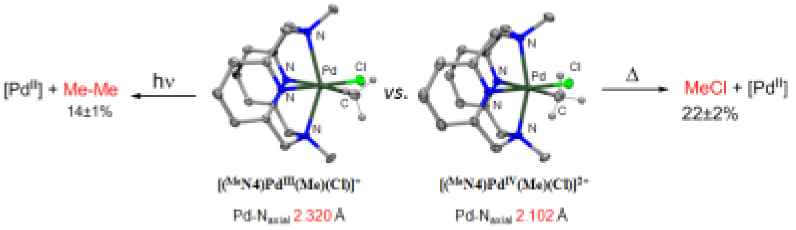
A series of ligand-bridged dinuclear vanadium(IV) complexes have been synthesized. The series can be obtained via aerobic reactions of a tripodal-ligand-bound vanadium(III) species, $CpP^{OEt,OEt}CoVCl_2(DMF)$, with various phosphate, phosphonate, phosphinate, or oxalate salts in solution under ambient conditions. These molecules have been characterized using spectral analyses and X-ray structure determination. The cyclic cores of these complexes exhibit conformational differences based upon the steric and electronic properties of the bridging ligand used. The structural, spectral, and electronic data for these compounds will be discussed. DMF=*N,N*-dimethylformamide.

### RM_MWGL Regional Meeting 419

## Stable mononuclear Pd(III) and Pd(IV) complexes in identical ligand environment: Characterization and direct reactivity comparison

***Fengzhi Tang***[1], *tfz1984@gmail.com, Julia R Khusnutdinova*[1], *Nigam P Rath*[2], *Liviu M Mirica*[1]. *(1) Department of Chemistry, Washington University in St. Louis, Saint Louis, MO 63130, United States (2) Department of chemistry and Biochemistry, University of Missouri-St. Louis, Saint Louis, MO 63121, United States*

Several mononuclear Pd(III) and Pd(IV) complexes were stabilized by the N,N'-dimethyl-2,11-diaza[3,3](2,6) pyridinophane ligand ($^{Me}$N4). The presence of a small N-methyl allows for a stronger interaction between the Pd$^{III}$ center and the axial nitrogen donors compared to the reported Pd$^{III}$ complexes supported by the $^{tBu}$N4 ligand with a bulky N-tert-Butyl substituent. This structural difference leads to notable changes in cyclic voltammetry, UV-Vis, and EPR spectra, as well as the stabilization of the Pd$^{IV}$ oxidation state. This study allowed a direct reactivity comparison between Pd complexes in the +3 and +4 oxidation states with an identical ligand environment. The mono-methyl chloride Pd$^{III}$ complex produces ethane upon photolysis, while the corresponding Pd$^{IV}$ complex leads to C-Cl bond formation upon thermolysis.

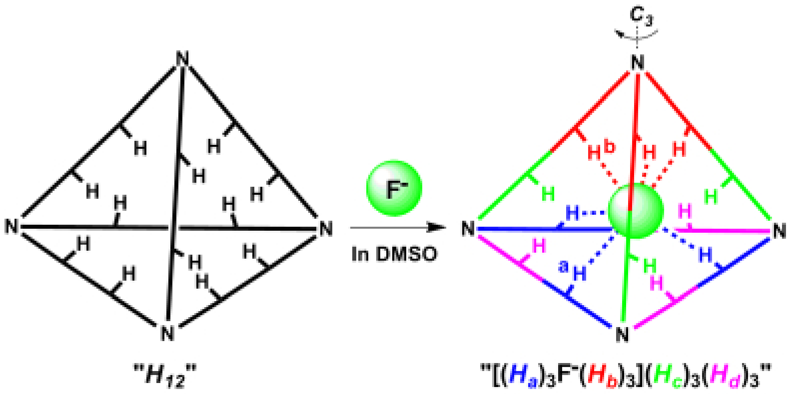


## RM_MWGL Regional Meeting 420

### Pinpointing the position of an encapsulated fluoride in solution: The utility of multidimensional $^1$H and $^{19}$F NMR

***Qi-Qiang Wang**, qiqiangw@ku.edu, Victor W. Day, Kristin Bowman-James. Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States*

An in-depth understanding of the fluoride anion binding inside a specific microenvironment/cavity can contribute not only to the exploration of anion coordination chemistry but also can provide insights for the design and development of novel fluoride receptors and sensors. The new amide-based organic tetrahedral cage “$H_{12}$” was synthesized and possesses a cavity that possesses a tetrahedral organization of bridgehead nitrogen binding sites, with spacers lined with 2,6-diamidopyridine groups. This relatively large host can encapsulate fluoride ion in solution. By collectively using a number of one-dimensional $^1$H, $^{13}$C, and $^{19}$F with two dimensional COSY and HSQC NMR techniques, the position of the encapsulated fluoride ion can be pinpointed within the cavity in solution. Upon encapsulation, the symmetry of the tetrahedral host reduces from $T_d$ to $C_3$ and gives a binding complex $[(H_a)_3F^-(H_b)_3](H_c)_3(H_d)_3$. Six of the hydrogen atoms are closely associated with the fluoride, $H_a$ and $H_b$, while the other six are not, $H_c$ and $H_d$. In the solid state, however a tetrahedral solvated anion cluster $F^-\cdot 4H_2O$ was found to be very symmetrically encapsulated inside the cavity.



## RM_MWGL Regional Meeting 421

# Evaluation of platonic solids as atoms in covalent bonds

***Dayu Wang****, dwk89@mail.umkc.edu, J. David Van Horn. Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2446, United States*

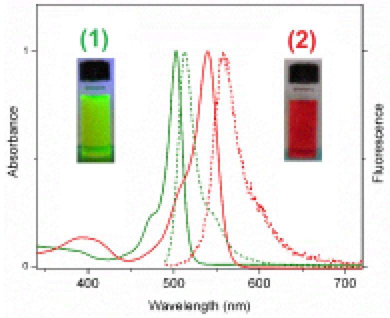
Geometric models provide a fairly simple and intuitive way to understand chemical bonding and structure. While conceptually and visually appealing, a tetrahedral model of a carbon nucleus fails to scale with double and triple covalent bond lengths. A cube gives better results, as demonstrated by the work of Lewis and Langmuir in developing early bonding theory. Here, we report the analysis of all five platonic solids evaluated as atom kernels in covalent carbon and nitrogen bonds. Calculated bond lengths using solid geometry are compared with experimental data. Deviation curves indicate that dodecahedral and icosahedral kernels give the best overall fitting among the platonic solids. The results also depend on the bond order selected as a reference point. In considering single, double and triple bonds, an icosahedron fits the single-to-double bond scaling best, while the dodecahedron best fits the triple-to-double bond scaling. Further analysis suggests that the spacing between static electron pairs decreases when bond order increases. One explanation for this is that the electrons must balance the extra forces created by the approaching nuclei as bond order increases. Finally, any geometric solid having regular circumscribed, edge, and inscribed radii may be used for bond fitting and comparison. “Bonded” platonic solids are illustrated in the figure.

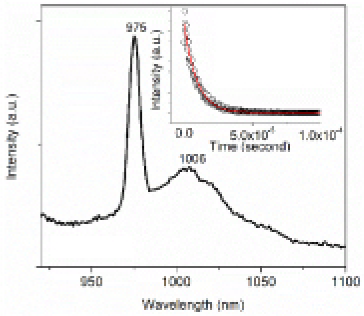
## RM_MWGL Regional Meeting 422

## Novel green light sensitiers for the near-infrared emission of lanthanide ions

***Hongshan He***[1], *hongshan.he@sdstate.edu, Yihan Zhong*[2], *Andrew G Sykes*[3]. *(1) Center for Advanced Photovoltaics, South Dakota State University, Brookings, SD 57007, United States (2) Department of Electrical Engineering, South Dakota State University, Brookings, SD 57007, United States (3) Department of Chemistry, University of South Dakota, Vermillion, SD 56069, United States*

Lanthanide (Ln)-based probes that emit in the near-infrared (NIR) region are proposed as potential sensitive probes for the fluoroimmunoassay (FIA) tests due to the transparency of the biofluid in the near-infrared (NIR) region. To be suitable for FIA applications, the probes should exhibit (1) high emission efficiency to compromise the fluorescence quenching from sample solution and (2) long wavelength sensitization capability to reduce the photobleaching of biosubstrates. To meet these basic requirements, a series of novel boron dipyrromethene (BODIPY)-based sensitizer were designed and synthesized. The structures of sensitizers are characterized by single-crystal X-ray diffraction analysis, indicating unique alignment of BODIPY core to the lanthanide-binding groups (LBGs). The sensitizers form stable lanthanide complexes with molar ratio of Ln:BODIPY 1:1 to 1:3 depending on the starting materials. The complexes exhibit strong absorption in the visible region (>500 nm) due to the presence of BODIPY unit. Under green light (> 500 nm) excitation, the fluorescence of sensitizers was quenched significantly, meanwhile the characteristic emission at 980, 1060 and 1540 nm was observed for ytterbium (III), neodymium (III) and erbium (III) complexes, respectively. The measured lifetimes in the NIR region are much larger than other reported complexes. The results demonstrate the potential of BODIPY dyes as efficient and robust visible light sensitizers for lanthanide-based NIR emitters in medical diagnosis.



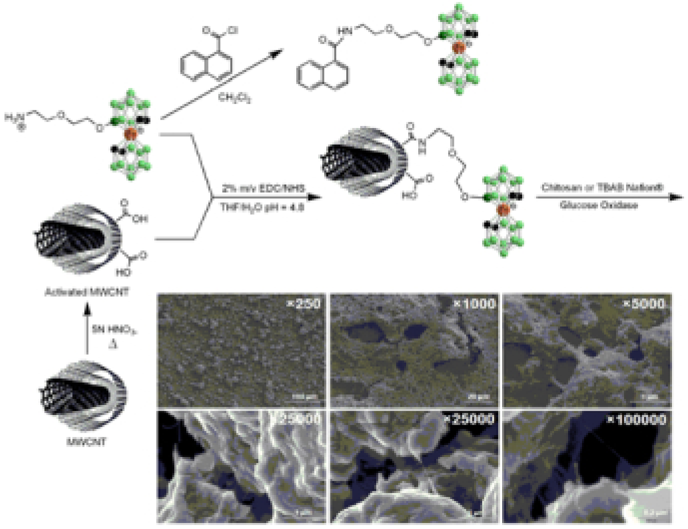


## RM_MWGL Regional Meeting 423

## Use of Ferracarboranes as Electron Transfer Mediators for Glucose Oxidase

***Scott S Graham***[1], *Paul A Jelliss*[1], *Shelley Minteer*[1], *Vojtech Svoboda*[2]. *(1) Department of Chemistry, Saint Louis University, St. Louis, MO 63018, United States (2) CFD Research Corporation, Huntsville, AL, United States*

We present the synthesis and application of various ferracarborane derivatives for use as electron transfer mediators for glucose oxidase immobilized polymer films cast upon a glassy carbon electrode as a bioanode for a fuel cell. The primary objective is to retain the ferracarborane electron transfer mediator at the electrode interface with glucose oxidase in the polymer film, exploiting the reversible $Fe^{III/II}$ redox chemistry of ferracarborane sandwich complexes. Different methods of anchoring the ferracarborane in the enzyme-polymer matrix have been established. The first involves covalently tethering the mediator to the polymer backbone while other methods entail the tethering of the mediator to activated multi-walled carbon nanotubes. The mediator modified carbon nanotubes are then suspended in the polymer matrix with the enzyme. Recent attempts to alter the ferracarboranes reduction potential for improved mediation through bromination have proved successful. In all cases the thin film electrodes were examined using cyclic voltammetry. SEM images of the films were also taken to evaluate the porosity of the films.



### RM_MWGL Regional Meeting 424

## Increasing survival in a murine metastatic pancreatic cancer model, using cell-delivered nanoparticles to cause local hyperthermia

***Gayani S Abayaweera***[1], *gayani@ksu.edu, Matthew Basel*[2], *Tej B Shrestha*[2], *Hongwang Wang*[1], *Olga B Koper*[3], *Sivasai Balivada*[2], *Stefan H Bossman*[1], *Deryl L Troyer*[2]. *(1) Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States (2) Department of Anatomy and Physiology, College of veterinary*

*Medicine, Kansas State University, Manhattan, Kansas 66502, United States (3) Nano Scale Corporation, Manhattan, Kansas 66502, United States*

Pancreatic cancer is known to be one of the most lethal forms of cancer with five year survival rates of less than 5%. Patients diagnosed with pancreatic cancer typically have a poor prognosis, partly because the cancer usually causes no symptoms early on, leading to locally advanced or metastatic disease at time of diagnosis. Discovering new methods for successfully treating metastatic pancreatic cancer is a virtual necessity for combating this disease. It was our interest to use magnetic nanoparticles to absorb alternating magnetic field (AMF) energy as a method for generating localized hyperthermia which has been shown to be a potential cancer treatment. We designed a system that uses tumor homing cells to actively carry iron/iron oxide nanoparticles into tumor tissue for AMF treatment. We have previously demonstrated that Raw264.7 cells (monocyte/macrophage like cells, Mo/Ma) specifically infiltrate pancreatic tumors when injected intraperitoneally (i.p.) without infiltrating other organs. Paramagnetic iron/iron oxide nanoparticles were synthesized and loaded into Raw264.7 cells. To test the system, a murine pancreatic cancer model was generated by injection of Pan02 cells intraperitoneally (i.p.). After tumor development, Mo/Ma loaded with iron/iron oxide nanoparticles were injected i.p. and allowed to enter into the tumor. Three days after injection, mice were exposed to an alternative magnetic field for twenty minutes to cause the cell-delivered nanoparticles to generate heat. This treatment regimen was repeated three times. A survival study demonstrated that this system can significantly increase survival in a murine pancreatic cancer model, with an average post-diagnosis life expectancy increase of 33%. Thus, for the first time, a cell-delivered nanoparticle system for generating localized hyperthermia has been demonstrated that can significantly prolong the life of i.p. pancreatic tumor bearing mice. This system has the potential to become a useful method for specifically and actively delivering nanoparticles for local hyperthermia treatment of cancer.

**RM_MWGL Regional Meeting 425**

## Scanning electrochemical microscopy investigation of tribolayer surface corrosion on CoCrMo alloys used in metal-on-metal (MoM) hip joint bearings

***Robert J LeSuer***, *rlesuer@csu.edu. Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628, United States*

Metal-on-Metal (MoM) hip joint bearings have recently received increased scrutiny due to the large number of device failures and reports of pain from patients. The surface of the CoCrMo alloy used in MoM devices is covered with a passivating metal-organic layer created through tribochemical reactions. A better understanding of this surface layer is needed in order to identify potential mechanisms for device failure. Scanning Electrochemical Microscopy (SECM) is an electrochemical technique that utilizes an ultramicroelectrode, with diameter typically less than 25 μm, to probe chemical processes occurring at a solid/liquid interface. Three dimensional positioning of the ultramicroelectrode allows one to study the heterogeneity of a surface with micrometer

resolution. SECM approach curves and imaging of mechanically polished and tribolayer-coated CoCrMo alloys were performed. Heterogeneous electron-transfer rate constants for the reduction of ferroceniummethanol at the tribolayer-coated alloy are lower than those observed on the mechanically polished surface, demonstrating the passivating properties of the tribolayer. SECM imaging experiments indicate that the tribolayer surface is not continuous, and regions of high surface activity with dimensions on the order of 10 micrometers are observed. The inhomogeneity of the tribolayer surface possibly contributes to the corrosion processes that ultimately result in device failure.

### RM_MWGL Regional Meeting 426

## Germylenes $R_2Ge$: with triplet electronic ground states

***Peter P Gaspar****, gaspar@wustl.edu, Atlee Solomon, Hyejin Yeon.Department of Chemistry, Washington University, Saint Louis, MO 63130-4899, United StatesDepartment of Chemistry, Washington University, Saint Louis, MO 63130-4899, United StatesDepartment of Chemistry, Washington University, Saint Louis, MO, United States*

For the study of the *chemistry* of triplet silylenes, the strategy of employing bulky electropositive substituents to promote triplet ground electronic states (Grev, Schaefer, Gaspar, JACS 1991, 113, 5638) was self-limiting, since the resulting steric shielding discouraged intermolecular reactions (Jiang, Gaspar, JACS 2001, 123, 8622; Sekiguchi *et al*, JACS 2003, 125, 4962). An alkali metal substituent reduced steric hindrance at the expense of experimental difficulties (Sekiguchi, Gaspar *et al*, JACS 2008, 130, 426).

Given the larger bond lengths to germanium and an electronegativity for Ge believed to be greater than that for Si, it is surprising that the computational results reported here suggest that $(tBu_3Si)_2Ge$: and $(tBu_3Si)LiGe$: both possess triplet electronic ground states with modest singlet-triplet energy gaps. A new class of triplet ground state germylenes $Z_2E{=}Ge$: [Z=N,F E=C,Si,Ge,Sn] is predicted to possess larger $\Delta E(S\text{-}T)$, less steric shielding, and greater ease of synthesis. The experimental implementation of these predictions is expected to lead to the first verifiable triplet germylenes and the exploration of their chemistry.

This work has received partial support from the NCSA as Teragrid project CHE070050N.

### RM_MWGL Regional Meeting 427

## Sensing drug mimics using size-tunable solution-phase SERS substrates

***Jenny K. Hedlund****, jenny-hedlund@uiowa.edu, Binaya Shrestha, Marie Pierre, Amanda J. Haes Department of Chemistry, University of Iowa, Iowa City, IA 52242, United States*

The tunable optical properties of noble metal nanostructures are currently being exploited for improved biological and chemical detection. These optical properties (i.e. localized surface plasmon resonance (LSPR)) (1) arise when metal nanoparticles selectively absorb and scatter light in a shape, size, and surface chemistry-dependent manner and (2) can be used to enhance the normal Raman signal of a molecule via surface-enhanced Raman scattering (SERS). In this study, various sizes of solution-phase gold nanoparticles will be used as SERS substrates for the direct detection of 2-naphthalenethiol, a drug mimic. Correlated LSPR and SERS measurements will reveal nanoparticle concentration, nanoparticle size, 2-naphthalenethiol concentration, and incubation time dependent trends. Importantly, systematic trends in nanoparticle aggregation are observed. As a result, this method could be used to develop an inexpensive and rapid sensor for biological and/or chemical sample analysis.

**RM_MWGL Regional Meeting 428**

## Correlating Molecular Surface Coverage and Solution-Phase Nanoparticle Concentration to SERS Intensities

***Marie Carmelle S Pierre****, mariecarmelle-pierre@uiowa.edu, Amanda J. Haes, Prescott M Mackie, Maryuri Roca. Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States*

Control over the composition, shape, size, stability, and local dielectric environment of solution-phase metallic substrates is vital for quantitative and reproducible surface-enhanced Raman scattering (SERS) signals. Because of their inherent instability, solution-phase nanoparticles can undergo uncontrolled aggregation when target molecules are added. Here, we demonstrate that both molecular surface coverage of the Raman active-molecule, 2-naphthalenethiol (2-NT), and nanoparticle concentration are critical parameters for obtaining reproducible SERS signals using solution-phase gold nanoparticles. Both gold nanoparticle and 2-naphthalenethiol concentrations are varied, and the extinction of the nanoparticle substrate and the SERS intensity of the target molecule are monitored as a function of time. These results indicate that extinction and SERS spectral intensities increase predictably below full monolayer surface coverage. When excess molecules are added, uncontrolled and irreproducible nanoparticle aggregation leads to optimal overlap between the plasmonic properties of the nanoparticles and the SERS excitation wavelength. As a result of these systematic studies, predictable molecular detection using solution-phase SERS substrates is likely achievable.

**RM_MWGL Regional Meeting 429**

## Comparison of stability and particle size distribution of gold colloids prepared by the solvated metal atom dispersion method and inverse micelle method

***Deepa Jose****, djose@ksu.edu, Kenneth J Klabunde. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

Thiol capped small Au nanoclusters were prepared by the solvated metal atom dispersion (SMAD) method and inverse micelle method in combination with a process called digestive ripening. Two different kinds of thiols were used in our studies: an alkane thiol (dodecanethiol) and an aryl thiol (phenylethanethiol). In the SAMD method, metal atom vapour was allowed to co-condense with a volatile solvent vapour (butanone or THF or toluene) on the walls of a reactor kept at liquid nitrogen temperature. Irrespective of the solvents used, stable Au colloids with a particle size varying from 1-5 nm were formed when we used thiol (dodecanethiol or phenylethanethiol) as a surfactant in our SMAD method. All these SMAD Au colloids were digestively ripened under Ar atmosphere for 24 h and the course of the reaction was followed by UV-visible spectroscopy and TEM bright field imaging. The more or less featureless nature of UV-visible spectrum of these colloids indicates that most of the particles are less than 2 nm. The thiol capped SMAD Au colloids prepared in butanone was showing different properties compared to those prepared in toluene and THF. The SMAD Au-butanone-phenylethanethiol colloid was precipitating within a few weeks to give yellow colored precipitate of Au(1)-thiolate polymer. Thiol capped Au colloids were also prepared by the inverse micelle method. Digestive ripening of these colloids were also monitored. The details of above studies would be discussed in the presentation.

**RM_MWGL Regional Meeting 430**

## Investigating the proton affinities of pyrogallol versus zinc-seamed *C*-alkylpyrogallol[4]arene dimeric nanocapsules

***Harshita Kumari****, hkyq2@mail.missouri.edu, Collin M Mayhan, Anne E Kroeger, Corey W Dye, Jerry L Atwood, Carol A Deakyne.Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65201, United States*

Metal-seamed organic nanocapsules have attracted much attention in recent years. The protonation of these metal-seamed pyrogall[4]arene dimeric and hexameric nanocapsules is an important aspect that can unravel factors controlling the formation of these architectures. The current study employs quantum chemical calculations of pyrogallol and zinc-seamed pyrogallol[4]arene dimeric nanocapsules to investigate the preferred site of protonation as a function of calculational level. The results for the two systems will be compared and contrasted and tied to experimental observations.

**RM_MWGL Regional Meeting 431**

## Capillary electrophoresis promoted personalized chemotherapy

***Brennan S Ayres****, brennan-ayres@uiowa.edu, Amanda M Jones, Marie Carmelle S Pierre, Amanda J Haes. Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States*

Leukemia treatment typically includes chemotherapy to force the disease into remission and additional anti-cancer therapy using anti-cancer drugs to prevent subsequent

relapses. The go-to drug for the anti-cancer treatment for acute lymphoblastic leukemia is 6-mercaptopurine (6-MP). For most patients, this drug must be used in combination with other medications to promote its anti-cancer properties. Personalized treatment is important because as with most drugs, 6-MP is metabolized into active, inactive, and toxic metabolites by multiple enzymes. Because everyone exhibits different enzyme levels, personalized treatment is warranted. Herein, the metabolism of 6-MP drug cocktails is monitored using capillary electrophoresis. First, a calibration curve is constructed for the anti-cancer drug 6-MP. Next, the drug is metabolized by the enzyme xanthine oxidase (XO) in the presence and absence of the commonly prescribed inhibitor drug, allopurinol (AP) (i.e. promotes the anti-cancer effects of 6-MP). Importantly, capillary electrophoresis is used to successfully detect both drug metabolism and inhibition. The efficacy of 6-MP was increased by nearly 85% when various dosages of AP are included. AP was observed to effectively prevent 6-MP metabolism and preserve 6-MP to be metabolized into its active metabolites, thereby providing a plausible alternative for personalizing anti-cancer treatments.

**RM_MWGL Regional Meeting 432**

## Using Dielectrophoresis for Reversible Capture and Release of *E. coli* cells at Micropatterned Nanoelectrode Arrays

***Lateef Uddin Syed**, lateefs@ksu.edu, Foram R Madiyar, Jianwei Liu, Alex K Price, Yi-fen Li, Christopher T Culbertson, Jun Li. Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States*

There have been frequent instances of pathogen contamination outbreaks in food, water and other resources, which led to considerable financial losses, and also disruption of normal human life. Early detection is the key to prevent or reduce the damage. Successful detection requires manipulation and capture of pathogenic particles for further analysis. In the present study we employ alternating current (AC) based dielectrophoresis (DEP) and electrochemical impedance spectroscopy (EIS) techniques using a nanoelectrode array (NEA) in a microfluidic chip for bacteria capture. DEP is a non-destructive and non-invasive technique, hence a natural choice for manipulating bioparticles. A microfluidic device was constructed using photolithography, which employed a NEA made of vertically aligned carbon nanofiber (VACNF) vs. a macroelectrode of indium tin oxide coated glass in a “points-and-lid” configuration. The optimum frequency of the AC field to generate positive DEP to efficiently capture bacteria was found to be 100 kHz. Due to the high aspect ratio (length to diameter ratio of 50) offered by the VACNFs, electric field gradient at the CNF tips can be enhanced, which helps to overcome large hydrodynamic drag force on *E. coli* cells at high flow velocities. A significant number of *E. coli* cells were captured at flow velocity of 1.6 mm/sec. A noticeable change in absolute impedance (|Z|) value at the NEA was observed in EIS experiments. These methodologies are currently being extended for the manipulation of different strains of viruses. Protocols for culturing, enumeration, and labeling of viruses have been established. DEP manipulation of individual viruses, and

sorting of heterogeneous mixture of virus and bacteria are currently performed, and the progress in this regards will also be presented.

## RM_MWGL Regional Meeting 433

### Development of electrochemical immunoassay for prostate specific antigen (PSA) and carcinoembryonic antigen (CEA) on nanoporous gold

***Binod Prasad Pandey***[1], *bppfg8@mail.umsl.edu, Alexei V Demchenko*[2], *Keith J. Stine*[1]*. (1) Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri - Saint Louis, St.Louis, MO 63121, United States (2) Department of Chemistry and Biochemistry, University of Missouri - Saint Louis, Saint Louis, MO 63121, United States*

Nanoporous gold (NPG) has attracted tremendous research interest in recent years. NPG, a porous nanomaterial, is interesting for several reasons including a high surface to volume ratio, inertness, ease of preparation, and ease of functionalization through self assembled monolayer formation. We have utilized nanoporous gold as a solid support to immobilize antibodies conjugated with a label enzyme, alkaline phosphatase, to develop an ELISA type immunoassay. Square wave voltammetry was used as an analytical tool for the detection of two cancer biomarkers, prostate specific antigen (PSA), a biomarker for prostate cancer and carcinoembryonic antigen (CEA), a biomarker for colon cancer. The immobilized enzyme antibody conjugate has $K_m$ value of 290 mM for its substrate p-aminophenyl phosphate, almost three times higher than the reported $K_m$ value (86 mM) for alkaline phosphatase in solution. The amount of enzyme immobilized on the surface was measured by BCA assay taking the difference in initial concentration and the supernatant concentration after immobilization on the surface. The value suggested submonolayer coverage on the surface. These immunoassays gave a linear range of 0.5 - 35 ng/ml for PSA and 0.1 - 10 ng /ml for CEA. The effect of a model interfering protein was also evaluated taking bovine serum albumin (BSA) as an alternative to the human serum albumin. There was no effect of 5 mg/ml BSA in the linear range of determination.

The immunoassay was studied in a competitive format as well, both by square wave voltammetric technique using p-aminophenylphosphate and by a UV visible technique using p- nitrophenylphosphate as a substrate for alkaline phosphatase. These immunoassays showed competitive behavior of the antigens in solution and on the NPG surface for labeled antibody in solution; however, even though the range was narrow, it was sensitive to very low concentrations of the antigens.

## RM_MWGL Regional Meeting 434

### Abstract withdrawn

## RM_MWGL Regional Meeting 435

## Toxic material forensic container (TMFC)

*Jessica J Cremer[1],* ***Angela M Iseli**[1], aiseli@NanoScaleCorp.com, Shyamala Rajagopalan[1], Jessica Domino[2], Deborah Lickfield[2], Christine W Cole[2]. (1) NanoScale Corporation, Manhattan, Kansas 66502, United States (2) Clemson Apparel Research, Pendleton, South Carolina 29670, United States*

Forensic evidence is collected for use in investigating a variety of crimes. However, not all evidence bags or containers are capable of preserving forensic evidence properly or protecting future handlers from further exposure. Today, many incident scenes arise from deliberate spills or releases of either chemical (toxic industrial chemicals, TICs, and chemical warfare agents, CWAs) or biological materials (infectious or biological warfare agents, BWAs). Evidence containers capable of protecting handlers from contaminated or potentially contaminated materials and providing safe transport and storage of those materials prior to decontamination efforts are urgently needed. NanoActive® materials from NanoScale Corporation have been demonstrated to be highly effective chemical agent decontaminants. In this project, novel materials were prepared from those parent materials and ß-cyclodextrin or silver producing dually active samples capable of chemical and biological decontamination. A variety of common material swatches contaminated with three TICs and two CWA simulants were evaluated by monitoring contamination levels through headspace and solvent extraction. Similarly, biological assays using *Bacillus subtilis* spores and the non-enveloped bacteriophage Phi X174 were carried out. Both tests identified several promising materials which were then incorporated by Clemson Apparel Research (CAR) team into a proprietary composite nonwoven fabric consisting of a thermally bonded web of nonwoven grooved fibers and a sub-micron melt blown fabric. This reactive liner was further tested using a variation of ASTM F 739-07 with FTIR monitoring and biological assays. Preliminary results indicate that an increase in reactive particle loading will produce a highly functional TMFC for storage and transport of contaminated articles. Further refinement of the container design is necessary for optimum performance.

**RM_MWGL Regional Meeting 436**

## Development of antisense agents to detect and suppress iNOS mRNA expression in injured lung

***Yuefei Shen**[1], yshen22@wustl.edu, Huafeng Fang[1], Ritu Shrestha[2], Karen Wooley[2], John-Stephen Taylor[1]. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Chemistry, Texas A&M University, College Station, TX 77843, United States*

Acute lung injury (ALI) is a condition characterized by hypoxemia and pulmonary edema and upregulation of inducible nitric oxide synthase (iNOS). The goal of our research is to develop antisense agents based on PNAs (peptide nucleic acids) and siRNAs to detect and suppress iNOS expression. We first mapped antisense binding sites on

native iNOS mRNA by a reverse transcriptase random oligodeoxynucleotide library (RT-ROL) method. We then prepared siRNAs and PNAs complementary to these sites and investigated the ability of cationic SCK nanoparticles (cSCKs) to bind and deliver these agents into cells. The cSCKs formed strong electrostatic complexes with the siRNA and PNA/ODN duplexes, and inhibited the degradation of the siRNA by human serum. The cSCK-siRNA complexes also showed a significant ability to knock down iNOS mRNA in RAW cells. We will also report on the ability of fusogenic peptides to improve cytoplasmic delivery of siRNA and PNA/ODN by cSCKs by enhancing endosomal escape of these agents.

## RM_MWGL Regional Meeting 437

### High aspect ratio hydroxyapatite nanofibers filled dental restorative nanocomposites

***Liang Chen***[1], *chenlia@missouri.edu, Kathryn Giddens*[1], *Yong Wang*[2], *Qingsong Yu*[1], *Hao Li*[1]*. (1) Mechanical and Aerospace Engineering, University of Missouri Columbia, Columbia, Missouri 65211, United States (2) School of Dentistry, University of Missouri Kansas City, Kansas City, Missouri 64108, United States*

Dental composite resins, now used in over 95% of all anterior direct restoration and about 50% of all posterior direct restoration, are becoming more popular in clinical restoration due to the advantage of less environmental concern and better aesthetic effect. However, the inadequate mechanical properties and shrinkage have lead to composite restoration suffer a prohibitive high failure rate. In this study, X-ray diffraction (XRD) and Scanning electron microscopy (SEM) results indicated that the hydroxyapatite (HAP) nanofibers with aspect ratio of 600 to 800 can be successfully fabricated with a simple wet-chemical method in aqueous solution. Biaxial flexural tests revealed impregnation of small mass fractions of the HAP nanofibers into the BisGMA/TEGDMA dental resins (5 wt%, 10 wt%) / composites (2 wt%, 3 wt%) could substantially improve the biaxial flexural strength of the resulting nanocomposites. A percolation threshold, beyond which more nanofibers will no longer further increase or even reduce the mechanical properties of nanocomposites containing HAP nanofibers, was observed for the nanocomposites with or without silica particles. In addition, our mechanical testing and fractography analysis indicated that the relatively good dispersion of HAP nanofibers at low mass fraction are the key reason for the significantly improved biaxial flexural strength, while higher mass fraction of HAP nanofibers tends to lead to bundles that cannot effectively reinforce the dental resin or composites and may even serve as defects and degrade the mechanical strength of resulting nanocomposites. In summary, the use of HAP nanofibers with good dispersion can improve the mechanical property significantly compared to the conventional restorative composites and the resulting dental composite is a promising candidate for clinical restoration.

## RM_MWGL Regional Meeting 438

## Synthesis and structural analysis of a novel iodinated cyclopentadienone *via* ring-contraction iodination and its application as a substrate for oxygen-free Sonogashira reactions

***Xueyi Chen***[1], *xchen@kumc.edu, Xinyan Bai*[2], *Thomas C. Sandreczki*[2], *Jerry R. Dias*[2]. *(1) Department of Biochemistry and Molecular Biology, University of Kansas-Medical Center, Kansas City, Kansas 66160, United States (2) Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, United States*

The first iodinated cyclopentadienone was synthesized via a novel ring contraction iodination reaction. The product was isolated and its structure was confirmed by single crystal X-ray analysis. Based on this intermediate, the first direct C–C bond formation on cyclopentadienone ring was achieved by oxygen free Sonogashira reaction. More than ten novel ethynylated cyclopentadieone derivatives were obtainded in good yields and characterized by $^{1}$H-NMR, $^{13}$C-NMR and HRMS. Furthermore, the photo induced intramolecular charge transfer of alkynylated cyclopentadienones was evaluated by solvent polarity effect on their electronic absorption spectra.

### RM_MWGL Regional Meeting 439

## Monomer-on-Monomer (MoM) Mitsunobu Reactions and ROMP-Derived Oligomeric Phosphates for the Application in Parallel Synthesis

***Pradip K Maity***[1,2], *pmaity@ku.edu, Alan Rolfe*[1,2], *Quirin M Kainz*[4], *Saqib Faisal*[1,2,3], *Thiwanka B Samarakoon*[1,2], *Toby R Long*[1,2], *Ryan D Kurtz*[1,2], *Oliver Reiser*[4], *Paul R Hanson*[1,2]. *(1) Chemistry, University of Kansas, Lawrence, Kansas 66045, United States (2) NIH Center for Chemical Methodologies and Library Development at the University of Kansas (KU-CMLD), Lawrence, Kansas 66047, United States (3) H.E.J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi 75270, Pakistan (4) Organic Chemistry, University of Regensburg, Regensburg, Germany*

The development of facilitated, chromatography-free Mitsunobu protocols and new ROMP-derived oligomeric phosphate reagents for application in purification-free parallel synthesis are reported. A Monomer-on-Monomer (MoM) Mitsunobu protocol utilizing norbornenyl-tagged benzylethyl azodicarboxylate (Nb-BEAD) and Nb-tagged triphenylphosphine (Nb-TPP) is presented whereby purification/ sequestration of Nb-tagged reagents is rapidly achieved using ring-opening metathesis (ROM) polymerization. Additional efforts utilizing surface-initiated polymerization from Nb-tagged silica (Nb-Si) and Nb-tagged Cobalt-graphite (Nb-Co/C) magnetic nanoparticles is also discussed. An array of oligomeric benzyl phosphates (OBP) and their corresponding oligomeric triazole phosphate (OTP) derivatives were successfully synthesized for the efficient benzylation and triazolation of nucleophilic species. These oligomeric reagents are readily synthesized from commercially available materials and are conveniently polymerized and purified in a one-pot process, affording pure white,

free-flowing solids on multi-gram scale and in excellent yield. Utilization in benzylation and triazolation reactions with a variety of nucleophiles is also reported.

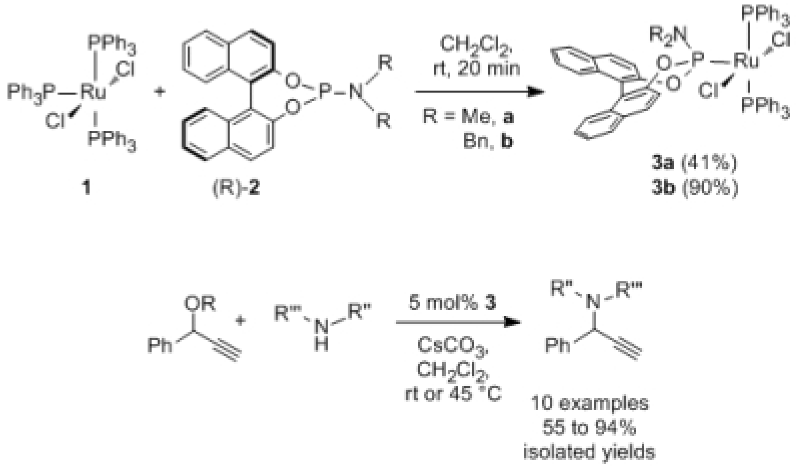
## RM_MWGL Regional Meeting 440

### Novel five-coordinate Ru(II) phosphoramidite complexes and their catalytic activity in the amination of propargylic acetates

*Andria K. Widaman, **Eike B. Bauer**, bauere@umsl.edu. Department of Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, MO 63121, United States*

The first five-coordinate ruthenium complexes of the general formula [$RuCl_2(PPh_3)_2L$] will be presented, where L is a phosphoramidite ligand. The complexes are accessible by ligand exchange of [$RuCl_2(PPh_3)_3$] with phosphoramidite ligands L (Scheme 1, top). As shown by X-Ray, the new complexes take a square-pyramidal coordination geometry and the phosphoramidite ligand L occupies the position trans to the open coordination site. As opposed to [$RuCl_2(PPh_3)_3$], the new complexes are configurationally stable in solution; they exhibit sharp signals in their $^{31}P$ NMR spectra, as opposed to the starting material [$RuCl_2(PPh_3)_3$], whose $^{31}P$ NMR spectrum shows a broad peak, indicating dynamic processes in solution.

The new complexes were employed as catalysts for the amination reactions of propargylic esters (18 h, at room temperature or 45 °C, $Cs_2CO_3$) to give propargylic amines in isolated yields up to 94% (Scheme 1, bottom). The complexes [$RuCl_2(PPh_3)_2L$] is the first ruthenium-based catalytic system for this reaction. Evidence will be presented for the allenylidene species Ru=C=C=$CR_2$ to be an intermediate in the catalytic cycle rather than a metal-stabilized propargylic cation.



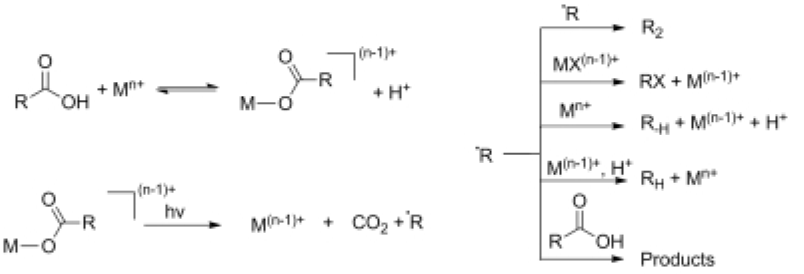
**Scheme 1**. Synthesis of ruthenium complexes of the general formula [$RuCl_2(PPh_3)_2L$] and their application in propargylic amination reactions.

## RM_MWGL Regional Meeting 441

### Metal-assisted photochemical conversion of carboxylic acids to alkanes, alkenes, and halocarbons

***Jack M Carraher***, *carraher@iastate.edu, Andreja Bakac.Department of Chemistry, Iowa State University, Ames, IA 50312, United States*

From fermentation of sugars in beer to increasing the performance of biofuels; decarboxylation is a vital part of many processes. More specifically photochemical decarboxylation has been studied for a variety of conversions including decarboxylation of protected amino acids, regiospecific addition to electron deficient alkenes, deuteration, and several others. This presentation will briefly discuss iron and copper mediated photochemical conversions of carboxylic acids of varying chain length to alkanes, alkenes, haloalkanes, and alpha-olefins. The effects of chemical environment like pH, solvent composition, solublizing agents, concentration, wavelength of irradiation, and coordinating versus non-coordinating anions will also be described. Rate constants for reactions of ethyl and methyl radicals with iron halide species were determined by competition reactions.



**RM_MWGL Regional Meeting 442**

### Preparation of Benzoxazoles and Benzothiazoles Utilizing a Green Procedure

***Mohammed Ali***, *mhali@semo.edu, Shravani Madabhusi. Department of Chemistry, Southeast Missouri State University, Cape Girardeau, MO 63701, United States*

Oxidative condensation of 2-aminophenol and 2-aminothiophenol with various aromatic aldehydes utilizing a green procedure were carried out to produce 2-aryl benzoxazole and 2-arylbezothiazoles in good to excellent yields. The reaction procedure utilized Magtrieve®, a heterogeneous oxidizing reagent, and benzotrifluoride as the reaction media. Benzoxazoles synthesized using this procedure produced high yields. However, benzothiazole yields were moderate to good. A side reaction was responsible for the lower yields in benzothiazole syntheses. A detail account of this green procedure will be presented at the meeting.

**RM_MWGL Regional Meeting 443**

## Deciphering intermolecular communication between 2-aminopyrimidines and carboxylic acids

***Angela B. Grommet***, *dahl1545@k-state.edu, Christer B Aakeroy, John Desper.Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States*

Over the years, organic chemists have worked to build a library of reactions that systematically make and break covalent bonds. Meanwhile, supramolecular synthesis – the assembly of molecules into a supramolecular lattice using intermolecular interactions like hydrogen bonding – has remained much less explored. With the advent of the Cambridge Structural Database (CSD), however, chemists have begun adding to the knowledge base of non-covalent intermolecular bonding – a process which may eventually enable us to approach supramolecular synthesis with the same confidence with which we use covalent synthesis today. We are specifically studying the hydrogen bonding patterns of various 2-aminopyrimidines and their co-crystals with the aim of using our observations to successfully predict future co-crystals of these compounds. Co-crystal structures from our own lab have been supplemented with structures from the CSD, yielding a total of some fifty structures for comparison. In our analysis of these structures, the identity of the co-crystallizing agent, the identity of the 2-aminopyrimidine, and the symmetry of both components were taken into consideration. Spartan (semi-empirical AM1) was used to calculate the charges on all hydrogen bond donors and acceptors to determine the role charge plays in the observed binding patterns of these co-crystals of 2-aminopyrimidines.

**RM_MWGL Regional Meeting 444**

## Thiophilicity of atomic oxygen in solution.

***Miao Zhang***, *mzhang3@slu.edu, Ryan McCulla.Department of Chemistry, Saint Louis University, United States*

Competition experiments were used to gauge the reactivity of atomic oxygen (O($^3$P)) towards a variety of different organic compounds. It was found that thiols were significantly more reactive than expected based on previous findings in the gas phase. To investigate if O($^3$P) could be used to oxidize critical cysteine residues, adenosine-5'-phosphosulfate kinase (APS kinase) was exposed to decreasing amounts of O($^3$P). APS kinase is a homodimer that upon oxidation of cysteine residue 14 or 41 forms a disulfide bond connecting the two subunits. Irradiation of low levels of photoactivated O($^3$P)-precursors was able to dimerize APS kinase.

**RM_MWGL Regional Meeting 445**

## *cis*-5,6-Dihydro-1,10-phenanthrolines as a new class of ligands: Enzymatic resolution of *cis* and *trans* phenoxy alcohol isomers and assignment of absolute stereochemistry

***Elke Schoffers***[1], *Elke.Schoffers@wmich.edu, Lars Kohler*[1]*, Erin Driscoll*[1]*, Matthias Zeller*[2]*, Schmiesing Carla*[1]*. (1) Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008-5413, United States (2) Department of Chemistry, Youngstown State University, Youngstown, OH 44555, United States*

5,6-Dihydro-1,10-phenanthrolines can display axial and central chirality and are of great interest to supramolecular chemistry. We herewith report the use of triphenyl borate to functionalize the B-ring of 1,10-phenanthroline. The formation of the ensuing *cis* and *trans* phenoxy alcohol isomers was influenced by the choice of solvent employed during the opening of the corresponding epoxide. Each racemate was subjected to enzymatic kinetic resolution and separated with high E values (>200). Stereochemical assignments were carried out using CD, X-ray and NMR analyses.

**RM_MWGL Regional Meeting 446**

## Total synthesis of (±)-cis-trikentrin B via intermolecular indole aryne cycloaddition and Stille cross-coupling reaction

***Nalin Chandrasoma***[1], *dncx3b@mail.umkc.edu, Neil Brown*[1,2]*, Allen Brassfield*[1]*, Alok Nerurkar*[1]*, Susana Suarez*[1]*, Keith R. Buszek*[1,2]*. (1) Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110, United States (2) Center of Excellence in Chemical Methodologies and Library Development, University of Kansas, Lawrence, KS 66047, United States*

A new total synthesis of the annulated indole natural product (±)-cis-trikentrin B was accomplished via an efficient intermolecular Diels-Alder cycloaddition using our 6,7-indole aryne methodology as the key step. The butenyl side chain was introduced via Stille cross-coupling to complete the synthesis.

**RM_MWGL Regional Meeting 447**

## Hydrogen-bond mediated catalysis in the organic solid state

***Jelena Stojakovic***, *jelena-stojakovic@uiowa.edu.Department of Chemistry, University of Iowa, Iowa City, IA 52242, United States*

The organic solid state provides an access to molecules that are inaccessible or difficult to realize from the liquid phase with strict control of both geometry and stereochemistry. To control reactivity in the solid state, we have developed a linear-template approach in which small-molecule templates direct covalent-bond formations *via* hydrogen bonding. Catalysis is essential for efficient and sustainable organic syntheses. However, catalysis in the organic solid state is expected to be difficult to achieve due to low diffusion rates of molecules in the crystals. A recently reported example of supramolecular catalysis in the organic solid state[1] will be presented, as well as results of expanding the scope to new substrates. The first reported small-molecule supramolecular catalyst, 4,6-dichloro-resorcinol (**4,6-diCl-res**), catalyzes a [2+2] photodimerization of *trans*-1,2-bis-(4-pyridyl)

ethylene (**4,4'-bpe**) to give *rctt*-tetrakis-(4-pyridyl)cyclobutane (**4,4'-tpcb**) *via* hydrogen bonding. To achieve turnover, dry mortar-and-pestle grinding was utilized. A reaction of **2,2'-bpe**, catalyzed by a similar ditopic receptor **res**, is now reported wherein the turnover proceeds spontaneously. The catalyses were investigated using $^1$H NMR spectroscopy, XRPD analysis and single-crystal X-ray diffraction.

Sokolov, A. N., Bučar, D-K., Baltrusaitis, J., Gu, S. X., MacGillivray, L. R. *Angew. Chem. Int. Ed.* 2010, **49**, 4767.

**RM_MWGL Regional Meeting 448**

## Dynamics of networked electrochemical reactions: coupling topology and synchronization

***Mahesh Wickramasinghe**, mwickram@slu.edu, István Z Kiss.Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States*

Complex networks have been found to play important role in the functioning of systems in many scientific disciplines from natural science to social sciences. Previous theoretical and numerical studies indicate that when coupling was introduced along the connections of a network of oscillating elements, synchronization occurred, which could exhibit strong dependence on coupling topology. In this contribution, we perform an experimental study on the relationship between coupling topology and synchronization of small networks of electrochemical oscillators.

Electrochemical nickel dissolution in sulfuric acid was taken as an experimental test bed in the study. The working electrode of the electrochemical cell was an array of Ni wires embedded in an insulating material. The coupling topology of the network was implemented with cross resistances (R) between the Ni wires. The oscillating current of nickel electrodissolution was measured at different coupling strengths (1/R). Small networks (3-4 nodes) with linear, square, star, and global coupling schemes were considered.

At strong coupling (small cross resistance) identical synchronization of chaotic oscillators is obtained. The networks with different coupling topology synchronized at different critical coupling strengths. The experimental data shows that the absolute value of the second largest eigenvalue of the connectivity matrix of the network is inversely proportional to the critical coupling strength at which synchronization occurs.

At weak coupling the oscillators fall into chaotic phase synchronization in which only the frequencies of oscillators are synchronized. A synchrony index based analysis of phases of the oscillators allowed us to differentiate the direct interactions from indirect interactions between two oscillators in the networks. Therefore, a possibility arises for decoding network topology from dynamical measurements. This latter finding has importance in systems biology, for example, in decoding the wiring diagram of the brain based on EEG or MEG measurements of electrical activity of different brain regions.

## RM_MWGL Regional Meeting 449

### Batch pH oscillations in the Belousov-Zhabotinsky reaction

***Glen A. Frerichs**, Glen.Frerichs@westminster-mo.edu, Xiaohe Huang, James Jones, Mulurhab Gebrekidan, Jacob Burch, Mei Yuan.Department of Chemistry, Westminster College, Fulton, MO 65251, United States*

Batch chemical oscillators are extremely rare, with the Belousov-Zhabotinsky (BZ) reaction being the best known and most studied. In 1951 the BZ oscillator was discovered by Belousov, and Zhabotinsky reinvestigated this batch reaction a decade later. The classical BZ system consists of bromate ion, malonic acid, and cerium or manganese ions as a catalyst in $H_2SO_4$. Oscillations in this batch system have been observed previously in the potential of Pt or bromide-selective electrodes, as well as in absorbance at a fixed wavelength. Considerable efforts to discover chemical systems that exhibit pH oscillations in a closed system have met with very limited success. We report here the discovery of batch pH oscillations in the BZ reaction at both 25° and 60°C. Oscillations were obtained using $KBrO_3$ or $NaBrO_3$ with malonic acid and $MnSO_4$. Depending on the concentrations of the main reactants, oscillations were observed both with and without $H_2SO_4$ or NaOH. Maximum amplitude of the oscillations was 0.50-0.55 pH units. Generally, pH oscillations occurred concurrently with oscillations in potential of a Pt electrode, and lasted as long as 5 hours.

During the course of an experiment, the pH drops initially before oscillations begin and the pH gradually increases. When the pH reaches a critical maximum value, oscillations stop. A proposed model for the system will be discussed.

## RM_MWGL Regional Meeting 450

### SAPT calculations: Methods for large system computation

***Charles C. Kirkpatrick**[1], kirkpacc@slu.edu, Michael Lewis[1], Bradley K. Welch[1], Jasmine N. Coleman[1], Jian Wang[1], Keith Hacke[2]. (1) Department of Chemistry, Saint Louis University, St. Louis, MO 63103, United States (2) Advanced Technology Group, Saint Louis Unversity, St. Louis, MO 63103, United States*

Model systems are employed for calculating the contributions of electrostatic, exchange, dipole-induced, and dispersion energies between substituted aromatic molecules and carbon nanotubes using SAPT. The roles of hardware, software, basis sets, and model chemistries on computational time and accuracy will be addressed. The implication of these results for performing SAPT calculations on even larger systems will be presented.

## RM_MWGL Regional Meeting 451

### High level quantum mechanical studies of singlet carbenes HCXH (X=O, S, Se)

***Jean M. Standard**, standard@ilstu.edu.Department of Chemistry, Illinois State University, Normal, IL 61790-4160, United States*

Carbenes of the form HCXH (X=O, S, Se) exist in both *cis* and *trans* isomer forms in the ground singlet state, as well as in a skewed configuration in the lowest triplet state. Hydroxycarbene, HCOH, has received a great deal of recent experimental and computational scrutiny as an isomer of formaldehyde, $H_2CO$, and is thought to play a role in $H_2CO$ photochemistry and in the reaction of C atom with $H_2O$. Thiohydroxycarbene, HCSH, has been previously suggested as a possible product formed in the atmosphere of Jupiter as a result of the collision of Comet Shoemaker-Levy 9 with the planet in 1994. HCSH is also involved as an intermediate in the reaction of C atom with $H_2S$. To the best of our knowledge, there have been no experimental or computational studies of the structure or properties of the selenium-containing analog, HCSeH. In this work, computational studies at the CCSD(T)/cc-pVTZ level and higher have been performed in order to elucidate key features of the potential energy surfaces of HCXH. In particular, the barrier for conversion from *cis*- to *trans*-$^1$HCXH has been computed for each of the analogs, and results have been compared with previous computational results where available. The results indicate that the barriers to rotation are rather high for what would nominally be considered rotation about a C-X single bond, ranging from 26-38 kcal/mol depending upon the level of theory. The origin of the barriers to rotation for conversion between the *cis* and *trans* forms of HCXH has been explored in detail using a variety of techniques.

### RM_MWGL Regional Meeting 452

## Theoretical study of hydrolization of $B_2O_3$

*Thomas A. Holme, **Chamila C De Silva**, chamila@iastate.edu.Department of Chemistry, Iowa State University, Ames, IA 50011, United States*

Importance of boron in plants has gained a considerable interest for many years. Mainly, boron exists in soil as anhydrous oxides ($B_2O_3$). However, plants absorb boron as boric acid, which is a hydrolyzed form of $B_2O_3$. A theoretical study of hydrolization of $B_2O_3$ in to boric acid was carried out. The model structure for $B_2O_3$ was composed with interconnected ribbons of $BO_3^{3-}$. The hydrolyzation reactions were observed on the central $BO_3^{3-}$of the structure with RHF/6-311G(d,p) level. Barrier heights are lower when two water molecules are used for the hydrolization reaction. These barrier heights for the consecutive bond breaking of B−O in the hydrodrolysis of $BO_3^{3-}$ are 12.56, 19.88 and 25.22 kcal/mol.

### RM_MWGL Regional Meeting 453

## Obtaining partial molar quantities from computer simulations

***Elizabeth A. Ploetz**, ploetz@ksu.edu, Paul E. Smith. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

We explore different methods for obtaining partial molar quantities (volume, enthalpy, compressibility, heat capacity, etc.) from computer simulations. Two approaches which both require simulations across a range of compositions are compared, namely, (1) the finite difference method and (2) measuring fluctuations in the bulk properties of the system. These methods both work by fitting the molar property of interest as a function of composition and taking partial derivatives to obtain the partial molar quantities. The results of using these methods to interpolate infinitely dilute partial molar quantities will be presented. Additionally, the ability to use these methods for determining the conformational changes of peptides and proteins is discussed. A third approach, which theoretically requires only one simulation, is introduced. This method is based upon fluctuations in a local, grand-canonical region within a closed simulation system using the Fluctuation Theory of solutions.

**RM_MWGL Regional Meeting 454**

## Application of correlation-gas chromatography to problems in thermochemistry

***James S Chickos***, *jsc@umsl.edu. Department of Chemistry and Biochemistry, University of Missouri-St Louis, Saint Louis, MO 63121, United States*

Correlation–gas chromatography is proving to be a powerful analytical technique that can be applied to the measurement of vaporization enthalpies and vapor pressures of liquids, and solids. In some instances, this technique can provide thermochemical data not available by other means It has been applied to the measurement of vaporization enthalpies of the n-alkanes from $C_{21}$-$C_{92}$, complex fuels, tautomeric and isotopically substituted mixtures. With the use of chiral columns the technique provides a simple method for measuring energetic differences between enantioners and the chiral stationary phase. Most recently, in conjunction with other measurements, it has been used to quantify some unusual intermolecular interactions observed in specific heterocyclic compounds. This technique as applied to some of these systems will be discussed.

**RM_MWGL Regional Meeting 455**

## Solute diffusion in *n*-alkanes and squalane

***Bruce A. Kowert***, *kowertba@slu.edu, Michael B. Watson. Department of Chemistry, Saint Louis University, St. Louis, MO 63103-2010, United States*

The translational diffusion constants, *D*, of the following hydrocarbon solutes have been measured in squalane (2,6,10,15,19,23-hexamethyltetracosane) at room temperature using capillary flow techniques: perdeuterobenzene, toluene, biphenyl, *p*-terphenyl, pyrene, perylene, coronene, tetracene, chrysene, rubrene, 9,10-diphenylanthracene, triptycene, *p*-cyclophane, dodecahydrotriphenylene, bibenzyl, tetraphenylethylene, *trans*-stilbene, 1,4-diphenyl-1,3-butadiene, 1,1,4,4-tetraphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene, diphenylacetylene, 1,4-diphenylbutadiyne, buckminsterfullerene, 1-hexene, 1-tetradecene, and cyclohexene. These same solutes have been studied in the *n*-alkanes hexane through hexadecane. To check the method used to determine the *D* values in squalane, we used it for perdeuterobenzene, biphenyl, *p*-terphenyl, pyrene, *p*-cyclophane, and 9,10-diphenylanthracene in *n*-hexadecane; agreement with the previous results was found. Deviations from Stokes-Einstein behavior were seen in the *n*-alkane results. The deviations, which increased as the solute size decreased, persist in squalane. The deviations are discussed in terms of a modification of the Stokes-Einstein equation and the relative sizes of the solute and solvent molecules.

**RM_MWGL Regional Meeting 456**

## Viscosity and thermal conductivity of potassium atoms at high temperatures

***Louis Biolsi**, louis@biolsi.com. Department of Chemistry, Mo University of Science & Technology, Rolla, MO 65401, United States*

Including the contribution of excited state atoms improves the accuracy of gaseous transport properties at high temperatures. For potassium, experimental and/or theoretical information is available for the potential energy curves of ten electronic states of the potassium dimer; the $X^1\Sigma_g^+$ and $^3\Sigma_u^+$ states that dissociate to two ground state $^2S$ potassium atoms and the four $^1\Sigma_{g,u}^+$, $^3\Sigma_{g,u}^+$, $^1\Pi_{g,u}$, $^3\Pi_{g,u}$ gerade/ungerade pairs of states that dissociate to a ground state $^2S$ atom and an excited $^2P$ atom. When the atoms interact, they can follow any of these electronic potential energy curves and the collision integrals for the various interactions determine the transport properties of the atoms when degeneracy averaged. Results for the viscosity and thermal conductivity of potassium atoms are given over a wide temperature range.

**RM_MWGL Regional Meeting 457**

## Influence of atom recombination and molecular relaxation on the properties of high-enthalpy flows

*Sriram Doraiswamy[1], **J. Daniel Kelley**[2], jdanielkelley@sbcglobal.net, Graham V Candler[3]. (1) Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455, United States (2) Department of Physics and Astronomy, University of Missouri-St. Louis, St. Louis, MO 63121, United States (3) Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, MN 55455, United States*

The high enthalpy flows discussed here are produced by shock heating a gas to high temperature and density. This gas then flows through a nozzle into an expansion chamber where internal energy is converted to translational energy in the bulk flow. This flow, moving at very high speed, encounters an aerodynamic model and the interactions, e.g. heat deposition, shock wave location, are observed and measured. These data are then used to validate and improve computational fluid dynamic studies.

The expansion process in a high enthalpy nozzle is dominated by atom recombination. The recombinied species have substantial internal energy upon formation and then relax towards equilibrium via energy transfer between internal energy and translational energy modes. The prediction of test section conditions is important to accurately calculate the interactions between the flow and test object. An energy bin based coupling model for recombination and relaxation is developed for these flows using oxygen as the test gas. The strong coupling between excited vibrational and rotational motion is included in the bin model. A prior recombination distribution of molecules, dependent on the total recombining system energy, is obtained using information theory. The low lying electronically excited states of oxygen are also considered. The energy levels are obtained considering the molecules to be rotating Morse oscillators. The results from a state-specific model are compared with the lower-resolution energy bin approach. The energy bin approach using only the ground state of the oxygen molecule predicts similar conditions at the test section as the state-specific model. The inclusion of the excited electronic states produces test section conditions with significant chemical nonequilibrium and also predicts non-trivial concentrations of the electronically excited states. The effect of changing the initial recombination distribution and the sensitivity of the test section conditions to the inter-bin relaxation rate constants are investigated.

## RM_MWGL Regional Meeting 458

## Theoretical Investigation of reaction of lactic acid on MgO clusters

***Lila B. Pandey****, lbpandey@ksu.edu, Christine M Aikens. Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Interaction of lactic acid with variable sizes of magnesium oxide clusters $(MgO)_n$ (n = 2, 4, 6, 8, 9, and 12) has been investigated. Density functional theory with the PBE functional and a double zeta basis set has been employed to optimize the structures. Both dissociative and associative adsorption of carboxylic acid, carboxy, hydroxy, and hydroxy-carboxy functional groups are investigated. All the adsorptions are calculated to be exothermic. Dissociative adsorption of lactic acid with the lowest coordinated magnesium is optimized to be the lowest energy structure. Adsorption energies are found to be lower as the size of MgO grows. The geometry of the magnesium oxide cluster changes to a nanorod like structure when lactic acid interacts with higher coordinated magnesium atoms in double layer systems but very little effect is noticed when third layer is added.

## RM_MWGL Regional Meeting 459

## Protein fold determined by paramagnetic magic-angle spinning solid-state NMR spectroscopy

***Christopher P. Jaroniec***[1], *jaroniec@chemistry.ohio-state.edu, Philippe S Nadaud*[1], *Ishita Sengupta*[1], *Jonathan J Helmus*[1], *Charles D Schwieters*[2]. *(1) Department of Chemistry, The Ohio State University, Columbus, OH 43210, United States (2) Division of Computational Bioscience, Center for Information Technology, National Institutes of Health, Bethesda, MD 20892, United States*

We present recent magic-angle spinning solid-state NMR structural studies of paramagnetic analogs of a model 56-residue protein, B1 immunoglobulin binding domain of protein G (GB1). Using a series of GB1 mutants containing EDTA-$Cu^{2+}$ tags at positions 8, 19, 28, 42, 46 and 53 we have determined 231 longitudinal $^{15}N$ paramagnetic relaxation enhancement (PRE) restraints by multidimensional NMR techniques employing rapid data acquisition schemes. The PRE data provide valuable structural information about $^{15}N$-$Cu^{2+}$ distances up to ~20 Å that is inaccessible by conventional methods. We subsequently used the $^{15}N$ PREs and backbone dihedral angle restraints derived from $^{13}C$ and $^{15}N$ chemical shifts for GB1 using TALOS+ to calculate models for the protein backbone fold. This yielded an ensemble of low energy protein structures corresponding to the correct GB1 X-ray structure; the Cα coordinates of the average NMR structure obtained from the 20 lowest energy structures in the ensemble showed a RMS deviation of 1.7 Å relative to the X-ray structure. In addition we will present the preliminary results of our studies aimed at: (i) evaluating the influence of intermolecular electron-nucleus couplings and secondary protein $Cu^{2+}$ binding sites on the accurate measurement of $^{15}N$ PREs and (ii) the development of improved $Cu^{2+}$-chelating tags for SSNMR structural analysis of proteins.

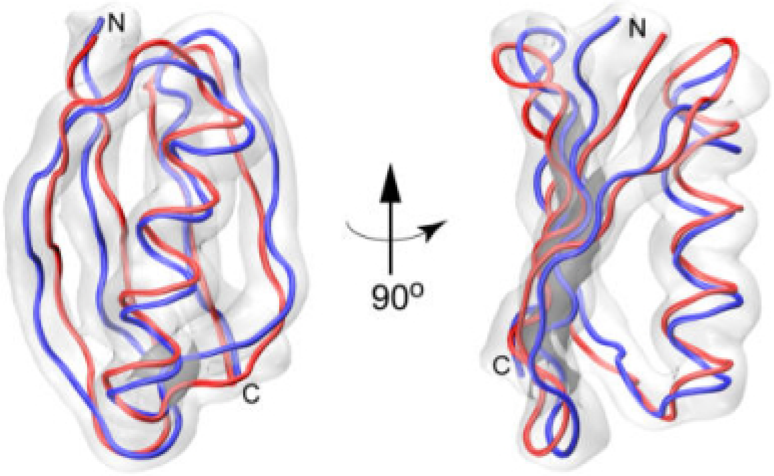


**Figure caption.** Comparison of the average GB1 backbone fold determined by paramagnetic solid-state NMR methods (blue) with the X-ray structure (red).

**RM_MWGL Regional Meeting 460**

## A study of residual solvent in aspirin by variable contact time CRAMPS; shelf lives of drugs

***Bernard Gerstein***, *berniegerstein@aol.com, Xu Hsu. Department of Chemistry, Iowa State University, Ames, IA 50011-3111, United States*

Residual saturated solution in aspirin is detected quantitatively and qualitatively utilizing Variable Contact Time Combined Rotation and Multiple Pulse (VCT CRAMPS) NMR of protons[1]. Concentrations of residual solutions, occluded during crystallization from solution, can be detected to better than 0.01 mol %. Samples from the same newly-opened bottle exhibit quite different finger prints for the occluded mobile phase. Specifically, the NMR signal of the saturated solutions are broadened relative to the NMR of aspirin in non-saturated solution. Because reactions in solution are much more rapid than those in solids, the amounts of saturated solution determine the lifetimes of drugs on the shelf.

1. B.C. Gerstein, *CRAMPS; High Resolution NMR of High γ Nuclei in Solids*, Encyclopedia of Magnetic Resonance, John Wiley, (2009).

**RM_MWGL Regional Meeting 461**

## Carbon partitioning in leaves under elevated $CO_2$ conditions using $^{11}C$ and $^{13}C$ labeling

***Jacob Schaefer***, *jschaefer@wustl.edu, Rebecca Dirks, Manmilan Singh, Gregory S Potter, Lee G Sobotka. Department of Chemistry, Washington University, Saint Louis, MO 63130, United States*

We have labeled soybean leaves with 200- and 600-ppm $^{13}CO_2$ spiked with $^{11}CO_2$ and examined the effect of light intensity on metabolism using a new combination of analytical techniques: direct positron *in vivo* imaging of an intact attached leaf, and solid-state $^{13}C$ nuclear magnetic resonance (NMR) of the same intact leaf. We first made 60-minute movies of the movement of photosynthetically assimilated $^{11}C$ labels. At the end of each movie, the labeled leaf was frozen in liquid nitrogen. After 24 hours when virtually all the radioactivity had decayed ($^{11}C$ half-life is 20 minutes), the leaf was lyophilized and examined by solid-state NMR to determine total label incorporation into sugars, starch, proteins, and protein precursors. This combination of complementary analytical techniques has led to two unexpected conclusions for photosynthetically heterogeneous soybean leaves: (i) transient starch deposition is not the temporary storage of sucrose excluded from a saturated sugar-transport system, and (ii) total peptide synthesis is suppressed under high-$CO_2$ conditions, and in regions of the leaf where starch deposition is most active under low-$CO_2$ conditions.

**RM_MWGL Regional Meeting 462**

## Is it possible to solve a protein structure with one NMR spectrum?

***Chad M Rienstra**, Rienstra@scs.illinois.edu, Anna E Nesbitt, Ming Tang, Michael Brothers, Kristin Nuzzio, Gemma C Comellas, Lindsay J Sperling. Departments of Chemistry and Biochemistry, Center for Biophysics and Computational Biology, University of Illinois at Urbana-Champaign, Urbana, IL 60801, United States*

Solid-state NMR has progressed remarkably in the last decade, yet remains rate-limited in solving protein structures by the large time cost of data collection and analysis. The standard approach requires numerous 3D data sets to be collected in order to assign a protein of significant size, and then many additional samples and data sets to obtain structurally informative and resolved long-range distances. These problems are especially acute in the context of membrane proteins of significant size. In an effort to address this throughput challenge, we are developing a method to screen candidate structures using a single $^{13}C$ two-dimensional CTUC-COSY spectrum. Candidate structures are produced by either an *ab initio* approach (ROSETTA/CS-ROSETTA) or by comparative modeling (MODELLER). A COSY spectrum is predicted for each of the candidates using SHIFTX2 and/or SPARTA+ and then compared with acquired data using algorithms to determine spectral similarity. We compare applicability and success of several approaches, including pattern recognition algorithms, selected to compare either peak positions or spectral intensities, and rigorously benchmark these results against several available structure scoring methods. Of particular note is the utility of SHIFTX2 or SPARTA+ predicted $^{13}C$ shifts, which are considerably more accurate than $^{1}H$ or $^{15}N$ shifts; the relative ease of $^{13}C$ chemical shift predictability opens a unique window of opportunity for $^{13}C$ detected SSNMR experiments. For a test set of approximately a dozen proteins, we find excellent agreement between the best model and the native structure. Scoring models in this manner may also assist with automated assignment and structural refinement.

### RM_MWGL Regional Meeting 463

## Shifting shapes: Seeing a protein's moves

***Ann McDermott**, aem5@columbia.edu. Department of Chemistry, Columbia University, New York, NY 10027, United States*

The plasticity of ion channels is clearly critical to the many essential processes they carry out in all cells. A conformational exchange process in the ion-binding selectivity filter of a simple ion channel, KcsA, will be discussed. This highly conserved region of KcsA exhibits clearly resolved and site specifically assigned NMR chemical shifts. These reporters allowed us to probe site-specific affinities of the ions, and to observe a related slow conformational exchange process. We observe a significant degree of anti-cooperativity in their binding behaviour. Methods for characterizing millisecond and microsecond conformational exchange processes in high resolution SSNMR experiments will also be discussed.

## RM_MWGL Regional Meeting 464

### Numerical analysis of classical free radical additon polymerization: A mathematically stiff system

***Amber M. Brown***[1], *200806422@panthers.greenville.edu, H. Darrell Iler*[1], *George Peters*[2]. *(1) Chemistry, Greenville College, Greenville, Illinois 62246, United States (2) Mathematics, Greenville College, Greenville, Illinois 62246, United States*

Free Radical Addition Polymerization is an important and widely used technique for producing polymers via an accepted four-step mechanism resulting in a set of coupled differential equations generally solved by application of the Steady State Approximation. This work concludes that the accepted mechanism results in a stiff system of coupled differential equations whose numerical analysis requires algorithms designed to accommodate stiffness instability. Mathematical software programs, Mathcad and MATLAB, incorporate necessary stiff solver algorithms and result in solutions for system parameters that are essentially identical to one another and in agreement with steady state predictions. Numerical analysis leads to the determination of system parameters for the polymerization of polymethyl methacrylate (PMMA) that provide numerical rates of polymerization that agree with steady state results and empirical data. This work shows that the numerical analysis of this system makes good pedagogical sense, as it offers the opportunity to introduce Polymer and/or Physical Chemistry students to numerical analysis methods in the context of a simple, yet important, chemical kinetic system and allows for a variety of levels of student engagement.

## RM_MWGL Regional Meeting 465

### Diffusion of Carbon-14 Oxide in Neutron Irradiated Flax Linen

***Arthur C. Lind***[1], *art@artlind.com, Mark Antonacci*[2], *David Elmore*[3], *Giulio Fanti*[4], *James M Guthrie*[5]. *(1) Lind Research and Development, Chesterfield, Missouri 63017, United States (2) RS Foundation, Eureka, Missouri 63025, United States (3) Department of Physics, Purdue University, West Lafayette, Indiana 47907, United States (4) Department of Mechanical Engineering, University of Padua, Padua, Italy (5) University of Missouri Research Reactor, Columbia, Missouri 65211, United States*

Flax linen samples were irradiated with thermal neutrons having a fluence of about $10^{14}$ $n \cdot cm^{-2}$. Since flax contains trace amounts of nitrogen, it was expected that $^{14}C$ would be produced via the $^{14}N(n,p)^{14}C$ reaction. The amount of $^{14}C$ produced was calculated from the neutron fluence, the measured nitrogen content of the linen and the cross section for this reaction. When the linen was irradiated in carbon dioxide gas, the measured $^{14}C$ was in agreement with the calculated value. However, the measured $^{14}C$ was about 4.5 times larger than calculated when the linen was irradiated in air. The $^{14}C$ that was produced by the neutrons reacting with the 78% nitrogen in the surrounding air most likely reacted with oxygen in the air and entered the flax fibers as a carbon oxide, $^{14}C^{16}O$ or $^{14}C^{16}O_2$. The $^{14}C$ content of flax samples was measured after heating in air at

various temperatures from 20˚C to 245˚C for 75 minutes. As the temperature increased, the $^{14}C$ content approached the calculated value, which was based on the nitrogen content of the linen; this indicates that the $^{14}C$ produced within the linen became chemically bound and remained. Thus, the $^{14}C$ that was produced in the air diffused out again. An Arrhenius analysis resulted in an activation energy of 58.9 kJ/mole; this is not an uncommon value for diffusion of carbon dioxide through amorphous polymers, but the pre-exponential factor was about $3 \times 10^6$ times smaller. Thus, it would take about 1.5 years for 75% of this $^{14}C$ to diffuse out at 20˚C. Flax fibers are highly crystalline and diffusion is virtually zero through crystalline material. Thus, the diffusion most likely occurs along the labyrinth of the amorphous lignin between the crystals. This torturous path greatly slows the diffusion and could explain the very small pre-exponential factor.

**RM_MWGL Regional Meeting 466**

## Polymer brush 'nanosponges' for fast protein separation with MALDI mass spectrometry analysis

***Colleen N Scott***, *cscott@chem.siu.edu, Bojan Mitrovic, Stephanie Eastwood, Gary Kinsel, Venney Wong, Daniel Dyer.Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, United States*

We will discuss the synthesis and characterization of weak polyelectrolyte polymer brush films. These films expand and contract from a few nanometers to approximately 100 nm depending on the pH of the solution. During contraction they expel the solvent much like a sponge; therefore, we refer to them as 'nanosponges'. The uptake and release of peptides/proteins will be discussed, along with their structure-property relationships . We have synthesized cationic and anionic brushes and will compare their selectivity for different protein mixtures. The films will be characterized by ellipsometry, FT-IR, and MALDI-TOF.

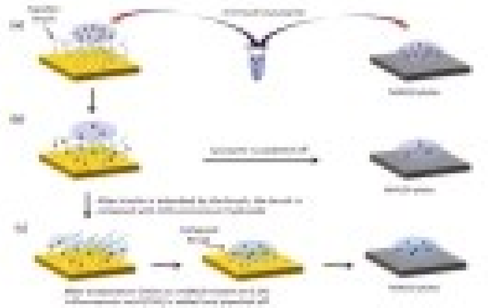


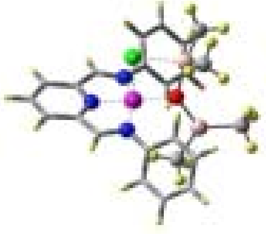
Figure 1 Process of separating and analyzing a mixture of Insulin and Lysozyme

## RM_MWGL Regional Meeting 467

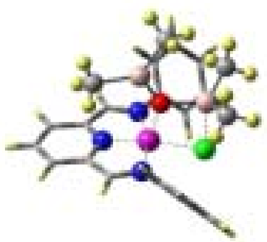
### Fe(II)/MAO catalyzed olefin polymerization: Oxophilicity of cyclic and acyclic aluminoxane ligands in Fe(II) Complexes

***Rainer Glaser***, *glaserr@missouri.edu, Xinsen Sun. Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States*

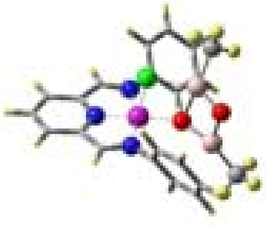
Acyclic aluminoxanes are reversed-polarity heterocumulenes and O-to-Al dative bonding reduces the Lewis donor ability of the central oxygen in acyclic aluminoxanes toward Lewis acids. In cyclodialuminoxanes, on the other hand, intramolecular O-to-Al dative bonding is impeded and dicoordinate oxygen in cyclic aluminoxanes is a strong Lewis donor. This difference between cyclic and acyclic aluminoxanes has important consequences for MAO-assisted Ziegler-Natta olefin polymerization. The Brookhard-Gibson-type transition metal catalysts for olefin polymerization all contain highly oxophilic transition metals, and our previous studies (*JACS* **2011**, *133*, 13323–13336) suggest that these transition metal catalysts should discriminate strongly in favor of cycloaluminoxane-O donors even if these are present only in small concentrations in the MAO cocatalyst. Here we report the results of an ab initio study which was performed to test this hypothesis. The ligand exchange reactions $L(R)_2FeCl_2$ + MAO → $L(R)_2FeCl(MAO) + Cl^-$ have been studied for MAO species $(Me_2Al)_2O$ and $(MeAlO)_2$, two diiminylpyridine ligands ($L(R)_2$, R = Ph, Me) and for both apical and equatorial exchange. The coordination of the cyclic MAO species is preferred by about 15 kcal/mol.



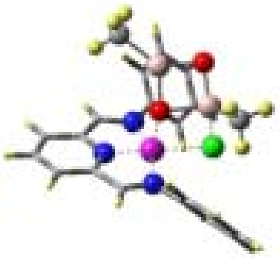
$L(Ph)_2FeCl_{ax}(O(AlMe_2)_2)_{eq}$



$L(Ph)_2FeCl_{eq}(O(AlMe_2)_2)_{ax}$



$L(Me)_2FeCl_{ax}(O(AlMe_2)_2)_{eq}$



$L(Me)_2FeCl_{eq}(O(AlMe_2)_2)_{ax}$

## RM_MWGL Regional Meeting 468

## Stepped growth of sp-sp$^2$ conjugated oligomers and its applications

***Xueyi Chen***[1], *xchen@kumc.edu, Xinyan Bai*[2], *Thomas C. Sandreczki*[2], *Jerry R. Dias*[2]. *(1) Department of biochemistry and molecular biology, University of Kansas-Medical Center, Kansas City, Kansas 66160, United States (2) Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, United States*

Stepwise-expansion of sp-sp$^2$ conjugated systems is of current interest since it is the most efficient way to synthesize the sp-sp$^2$ conjugate oligomers with least complication from side reactions. Although this method has been adopted for more than a decade, to date, its detailed application and limitations remain unclear. In this study, we conducted systematic investigation of stepwise growth of sp-sp$^2$ conjugate oligomers under oxygen free conditions and studied its application in synthesis of comb-like polymers. All products and intermetiates are unambiguously characterized by $^1$H-NMR $^{13}$C-NMR. Single crystals of several products are characterized X-ray diffraction.

**RM_MWGL Regional Meeting 469**

---

## Physic chemical recycling of tyres by modified asphalt formation

***Lorena Eugenia Sánchez Cadena***[1], *hau10@hotmail.com, Zeferino Gamiño Arroyo*[2], *Luis Elías Chávez Valencia*[1], *Angel Romo Uribe*[3]. *(1) Department of Civil Engineering, University of Guanajuato, Guanajuato, Guanajuato 36000, Mexico (2) Department of Chemical Engineering, University of Guanajuato, Guanajuato, Guanajuato 36000, Mexico (3) Physical Institute, UNAM, Cuernavaca, Morelos 62210, Mexico*

The Mexican tyre industries produce 25 million pneumatic annually, but only 9% is recycled. The remainder is not processed nor is it disposed of properly. This gives rise to serious pollution problems, such as “dengue” and VOC. Sometimes tyres are burning in cement factorys, but it is not good for the environment, because when tyre is burned the VOC are produced and due to current environmental regulations, it is mandatory to research ways of recycling tyres. One option is the solvolysis, it consists in a depolymerisation with an appropriate solvent. Where covalent ligands could be cutted for adding crumb rubber into the hot mix asphalt. Crumb- rubber-modified hot mix asphalt (CRM-HMA) has been used in asphalt pavements because it allows for a quiet vehicle flow and it has excellent tyre grip properties. In this study three samples of modified asphalts were characterized using the Marshall Method ASTM D 1559. One controlled sample and three more containing 1wt%, 1.6wt% and 2wt% of crumb rubber were studied. Stability, flow and voids were determined for each sample. It was found that adding tyre into asphalt worked well up to 1.6%. Higher elastomeric concentrations resulted in low-quality asphalt which could not be used. CRM-HMA seems to be a good way of recycling used pneumatics. FT-IR, and DSC analysis show that a despolymerisation process occurs in solvolysis reaction.

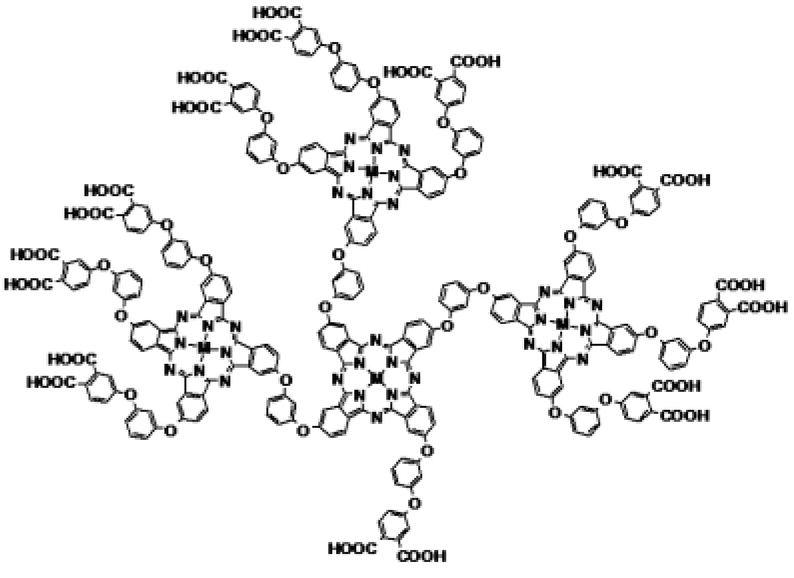
**RM_MWGL Regional Meeting 470**

# Synthesis, photophysical properties, and photovoltaic applications of non-aggregated hyperbranched phthalocyanine dyes

***Yong Li**, yong.li@sdstate.edu, Peifen Lu, Minlin Jiang, Prem Thapaliya, Xingzhong Yan. Department of Electrical Engineering & Computer Science, South Dakota State University, Brookings, South Dakota 57007, United States*

Phthalocyanines have a window of very weak absorption at 400 to 600 nm, which can be treated as a life window for some practical application, such as solar cells for a greenhouse. This absorption gap can also be filled by other light-harvesting materials for more efficient photovoltaic cells. Organic solar cells based on phthalocyanines have been proved successful with efficiencies of up to 5.0%. However, strong aggregation of phthalocyanines and lack of directionality in their excited states have suppressed their photovoltaic performances in DSSCs.

This work presents the synthesis, electrochemical and photophysical properties, and photovoltaic performances of a series of novel non-aggregated hyperbranched phthalocyanine dyes with different metal centers ($H_2$, AlCl, Co, Cu, Zn; **6-10**). The absorption, fluorescence, fluorescence dynamics, electrochemistry, and photovoltaic performances of these hyperbranched phthalocyanine dyes were significantly affected by the metal centers. A power conversion efficiency of 1.15% has been achieved from the Zn substituted hyperbranched phthalocyanine dye sensitized solar cells, a value of at least ~3 times higher than that of any other metal centered counterpart sensitized solar cells in this work. This work provides an avenue to solve the aggregation issue of the phthalocyanine dyes on $TiO_2$ which hinders phthalocyanine dyes from high performances in DSSCs.



HBMPc-COOH
M = 2H, AlCl, Co, Cu, Zn
6-10

## RM_MWGL Regional Meeting 471

## Understanding DNA flexibility *in vitro* and *in vivo*

*Justin Peters[1], Nicole Becker[2],* ***Jim Maher***[2]*, maher@mayo.edu. (1) Mayo Graduate School and Department of Biochemistry and Molecular Biology, Mayo Clinic, Rochester, MN 55905, United States (2) Department of Biochemistry and Molecular Biology, Mayo Clinic, Rochester, MN 55905, United States*

We have broad interests in the fundamental properties of DNA and RNA molecules, and their interactions with proteins. Our laboratory studies electrostatic effects in DNA stiffness and bending as well as enhancement of DNA flexibility by proteins. We are testing the concept that the exceptional stiffness of double-stranded DNA is related to DNA charge. This concept remains controversial almost 60 years after the elucidation of DNA structure. The Maher lab has shown that asymmetric charge neutralization along the DNA backbone induces DNA bending toward the neutralized face. Similar effects are seen for tethered ions and bound proteins with modified charge. Ongoing ligase-catalyzed cyclization kinetics studies monitor the flexibility of DNAs with non-natural charge densities to test the Manning hypothesis that DNA charge density influences flexibility. We are also studying the properties and mechanisms of proteins that enhance the apparent flexibility of DNA by sequence-nonspecific DNA binding and kinking. Eukaryotic HMGB proteins and bacterial HU are of interest. The laboratory re-established an experimentally tractable implementation of the classic Lac repressor-mediated DNA looping model (discovered 50 years ago this summer) in living bacterial cells. This work seeks to understand why the “softness” of DNA appears greater in vivo. Studies are probing the importance of bacterial nucleoid proteins and supercoiling in modifying apparent DNA flexibility. These experiments will help us understand how cells use proteins to assist in managing the local rigidity of DNA.

## RM_MWGL Regional Meeting 472

## DNA as a catalyst for covalent modification of biomolecules

***Scott K. Silverman****, scott@scs.illinois.edu. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

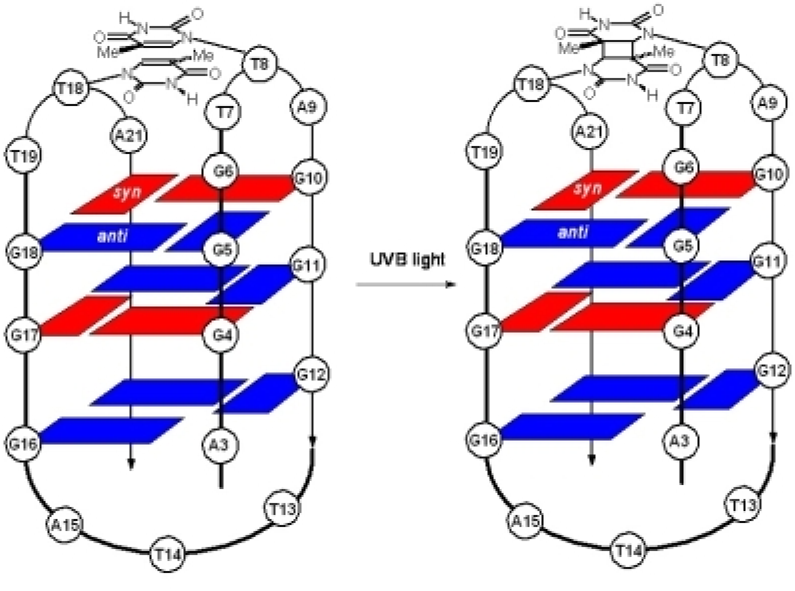
Natural biological catalysts include both protein enzymes and RNA enzymes (ribozymes), whereas nature apparently uses DNA solely for genetic information storage. Nevertheless, the chemical similarities between RNA and DNA lead to consideration of DNA as a catalyst, especially because DNA is more stable than RNA and is less costly and easier to synthesize. Our research group uses in vitro selection to identify new deoxyribozymes for various chemical reactions. We consider DNA simply as a large biopolymer that can adopt intricate three-dimensional structures and, in the presence of appropriate metal ion cofactors, provide the chemical complexity required to achieve catalysis. This presentation describes our efforts to identify deoxyribozymes that covalently modify biomolecules, with particular focus on modifications of amino acid side chains and sequence-specific hydrolysis of DNA strands.

## RM_MWGL Regional Meeting 473

## Structure-activity relationships of G-quadruplex interloop photocrosslinking

***Jillian E. Smith**, jesmith@wustl.edu, John-Stephen A. Taylor. Department of Chemistry, Washington University of St. Louis, St. Louis, MO 63130, United States*

Telomeres are conserved DNA sequences that cap the ends of chromosomes. The human telomere sequence contains a 3' overhang of single stranded DNA of tandem repeats of TTAGGG, short fragments of which form various G-quadruplex structures *in vitro*. Our group has recently discovered that irradiation of the sequence d[AAAGGG(TTAGGG)$_3$AA], Tel26, with biologically relevant light results in the formation of a significant amount of *anti* thymine dimers between the loops of the G-quadruplex structure. The formation of the *anti* thymine dimers suggests that there is rapid equilibrium with the reported structure of Tel26, hybrid-1 that does not contain two TTA loops in close proximity, and another structure that does contain two lateral loops, such as Form III. The current study focuses on elucidating the structural features of G-quadruplexes that facilitate formation of the *anti* thymine dimers by making a series of substitutions and insertions in the sequence to stabilize specific structures. The results with a number of sequence variants are most consistent with an intermediate involvement of the Form III structure.



Form 3 quadruplex

Photocrosslinked

## RM_MWGL Regional Meeting 474

## Targeting dynamic ribosomal RNA sites with small molecules

***Christine S. Chow****, csc@chem.wayne.edu. Department of Chemistry, Wayne State University, Detroit, MI 48202, United States*

Recently, there has been considerable interest in dynamic regions of ribosomal RNA that reside at the subunit interface, contain modified nucleotides, and participate in biomolecular interactions. Such regions include helix 69 of 23S rRNA and the decoding site of 16S rRNA. These RNA helices have been shown to be dynamic and exist in multiple conformations. Conformational flexibility is important for these regions to accommodate various RNA and protein components at different stages of protein biosynthesis by the ribosome machinery. A synthetic chemistry approach was used to produce RNA constructs containing all of the natural modified nucleotides. Structural and stability changes in these RNAs were examined through a variety of biophysical techniques. Ligands that bind to these regions were identified and tested for their ability to regulate conformational changes in the model systems as well as in complete, intact ribosomes. In addition, bioinorganic chemistry approaches were used to identify unique drug-binding sites on the ribosome. These results will contribute to future drug development, with emphasis on targeting dynamic regions of the ribosome.

---

**RM_MWGL Regional Meeting 475**

## Computational Model for Predicting Experimental RNA and DNA Nearest-Neighbor Free Energy Rankings

***Charles A Johnson****, Richard J Bloomingdale, Vikram E Ponnusamy, Conor A Tillinghast, Brent M Znosko, Michael Lewis. Department of Chemistry, Saint Louis University, St. Louis, Missouri 63103, United States*

Hydrogen-bonding, intrastrand base-stacking, and interstrand base-stacking energies were calculated for RNA and DNA dimers at the MP2(full)/6-311G** level of theory. Standard A-form RNA and B-form DNA geometries from average fiber diffraction data were employed for all base monomer and dimer geometries, and all dimer binding energies were obtained via single-point calculations. The effects of water solvation were considered using the PCM model. The resulting dimer binding energies were used to calculate the 10 unique RNA and 10 unique DNA computational nearest-neighbor energies, and the ranking of these computational nearest neighbor energies are in excellent agreement with the ranking of the experimental nearest-neighbor free energies. These results dispel the notion that average fiber diffraction geometries are insufficient for calculating RNA and DNA stacking energies.

---

**RM_MWGL Regional Meeting 476**

## Quantum dynamics of a Morse oscillator in real and imaginary time

***Coral Hanson****, cehanson09@ole.augie.edu, Bijoy Dey. Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

Time-dependent quantum dynamics is essentially about solving the time-dependent Schrödinger equation in real time. When real time is replaced by imaginary time, by the substitution t=-it, one encounters a different realm of dynamics. The former is real time quantum dynamics (RTQD) whereas the latter is imaginary time quantum dynamics (ITQD). Although real time quantum dynamics is an active research area, imaginary time quantum dynamics remains an unchartered territory. In this study, we investigate the ITQD to compute the quantum eigenstates of a general anharmonic oscillator. The quantum ground state obtained from the ITQD study was then allowed to interact with a pulsed laser electric field to study the RTQD of the anharmonic oscillator. We applied this to a CO molecule, yielding various anharmonic states, the transition probability of these states in presence of the laser pulse, the autocorrelation function and the emission spectrum.

**RM_MWGL Regional Meeting 477**

## Periodic and complex waveform current oscillations of copper electrodissolution in phosphoric acid in an epoxy-based microchip flow cell

***Amy Bi****, abi@slu.edu, Yanxin Jia, István Kiss. Department of Chemistry, Saint Louis University, St. Louis, Missouri 63103, United States*

We investigate anodic copper dissolution (electropolishing) in phosphoric acid in an epoxy-based microchip flow cell. The cell was constructed by reversible sealing of a poly (dimethylsiloxane) chip with a 0.1mm height and 0.2mm width flow channel over a 0.1mm diameter Cu wire embedded in an epoxy resin. With the application of proper external resistance, flow rate, and circuit potential, the electrodissolution of copper in the microcell displayed periodic smooth and relaxation oscillations as well as complex waveforms with mixed mode and chaotic oscillations. These experiment thus reproduce the dynamical features of the negative differential resistance electrochemical system previously characterized in macrocell configuration.

In contrast to previous microchip based oscillatory electrochemical systems, the oscillations in the Cu-phosphoric acid system exhibited strong dependence on the flow rate of the electrolyte solution. An increase in flow rate correlated with a decrease in minimum external resistance required for oscillations: for 0.100 μL/min, 1.000 μL/min and 5.000 μL/min flow rates minimum resistances of 555 kΩ, 262 kΩ, and 59 kΩ were measured, respectively. Laboratory data also indicated that the direction of flow affected the observed dynamics of the microcell. Pushing the flow moved the acid through the channel over the recessed Cu electrode to reservoir accommodating the counter and reference electrode; pulling the flow transferred the acid from the reservoir to the electrode. It is likely that the recessed Cu electrode exhibits stronger mass transfer in the pull flow, which contributes to the increased oscillatory potential region and the more complex waveforms of the observed oscillations.

The proposed experiments can be extended to multi-electrode configuration; the epoxy-based substrate thus holds promise for studies of synchronization of multi-electrode systems as well as for electroanalytical and corrosion applications that that require collector-generator multi-electrode wires and controlled flow conditions.

**RM_MWGL Regional Meeting 478**

## Exploring the quantum dynamics of a multi-particle system

***Marcus J Edgington***, *mjedgington08@ole.augie.edu, Bijoy K Dey. Department of Chemistry, Augustana College, Sioux Falls, South Dakota 57197, United States*

Real time quantum dynamics can be studied by solving the time-dependent Schrödinger equation (TDSE). Since an analytical solution is not known, one usually resorts to using a numerical technique; one such numerical technique uses the Split-Operator Method to evaluate the exponential of the Hamiltonian operator. The TDSE can be solved if an initial value for the wave function of the system is known. Finding the initial wave function requires solving a time-independent Schrödinger equation which is a daunting task except for in the case of a one particle system.

An equivalent formulation of the TDSE in the imaginary time can be obtained by replacing time (*t*) with *-it*. The equation is called the imaginary time Schrödinger equation (ITSE) which resembles a classical fluid dynamics equation. When propagated from any arbitrary function, the ITSE yields the stationary states of the system; this is known as the Quantum Monte Carlo Method. We have investigated both the TDSE and ITSE to calculate the stationary states and the dynamic states of a two-particle system. The examples of stationary states include: (i) two particles (distinguishable and non-distinguishable) confined in a quantum well, (ii) two interacting particles (through Coulombic potential) confined in a quantum. While the dynamic states include: (i) two non-interacting free particles (modeled as Gaussian wave packet, and acting as fermions or bosons) undergoing motion, and (ii) two interacting (through Coulomb potential) particles confined in a quantum well and shined upon by an external laser pulse. A large number of results have been obtained, which includes contour maps of the two-particle probability density at different times, single-particle probability density at different times, inter-particle distance as a function of time, auto correlation function, and the emission spectrum.

**RM_MWGL Regional Meeting 479**

## Molecular structural study of thin-film boron carbide

***Wenjing Li***[1], *wlcy9@umkc.edu, Michelle M Paquette*[2], *Sudarshan Karki*[2], *Bradley J Nordell*[2], *M Sky Driver*[2], *A N Caruso*[2], *Nathan A Oyler*[1]. *(1) Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, United States (2)*

*Department of Physics, University of Missouri-Kansas City, Kansas city, Missouri 64110, United States*

Boron-rich carbides have attracted attention of scientists in different fields due to their unique thermal, electrical, and mechanical properties. To date, no clear understanding about the molecular structure and the formation mechanism of thin-film boron carbides have been established.

In this project, amorphous hydrogenated boron carbide thin-film was made by applying plasma-enhanced chemical vapor deposition (PECVD) method from the single-source precursor orthocarborane ($C_2B_{10}H_{12}$). To investigate physical structure of a-$B_xC$:$H_y$ thin-films we applied solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) methods along with elemental analysis and Fourier transform infrared (FTIR) spectroscopy. *Ab initio* calculations were performed to compare with the experimental results in order to propose a structural model.

### RM_MWGL Regional Meeting 480

## Theoretical analysis of surface plasmon resonance of silver and gold nanowires

***Emilie B Guidez***, *emilieg@ksu.edu, Christine M Aikens.Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Gold and silver nanoparticles show tunable surface plasmon resonance depending on the shape and the size of the nanoparticles. The absorption spectra of linear nanowires with up to twenty atoms were studied with Density Functional Theory (DFT). The SAOP and LB94 exchange-correlation functionals were used with a double-zeta basis set. Relativistic effects were described with the zeroth order regular approximation (ZORA). In the silver case, a sharp longitudinal peak corresponding to the HOMO-LUMO transition red shifts as the length of the wire increases. The wavelength increases linearly with the number of atoms in the chain. The intensity of this peak increases linearly with the length of the wire due to the additive collective oscillation of the electrons. A high-energy transverse peak occurs at about 6 eV and its energy does not vary significantly with the length of the nanowire. A small d-band also occurs but does not interact much with those transitions. On the other hand, gold nanowires also show longitudinal and transverse peaks but the interactions with the d-band induce some splitting. The main transverse peak becomes particularly hard to determine. Additionally, a break is observed in the linearity of the wavelength and intensity vs number of atoms between six and eight atoms, which is where the d-band becomes more important. As the length of the nanowire increases, a distinct pattern occurs in the d-band.

### RM_MWGL Regional Meeting 481

## Computational investigation of the electronic structures of polymers used in polymer-fullerene composite solar cells

***Brian P. G. Banks***[1]*, bnks_brn@yahoo.com, Oleg Poluektov*[2]*, Jens Niklas*[2]*, Kristy L Mardis*[1]*. (1) Department of Chemistry and Physics, Chicago State University, Chicago State University, IL 60628, United States (2) Department of Chemistry and Physics, Argonne National Laboratory, Argonne, IL 60439, United States*

Polymer-fullerene composites possess the ability to revolutionize the solar cell industry by serving as the material for inexpensive and easy-to-fabricate solar cells. The goal of this research is to determine why changing the polymer more than doubles the device efficiency. Monomer, dimers, and trimers of the electron-donating polymer 2-ethylhexyl 6-[4,8-bis(2-ethylhexoxy)thieno[2,3-f]benzothiophen-2-yl]-3-fluoro-6H-thieno[3,4-b]thiophene-2-carboxylate (PTB7) and poly(3-hexylthiophene) (P3HT) were constructed using PQSMol. Long alkyl chains were modeled as single methyl groups to reduce the computational time. The electron transfer observed by EPR was modeled by first optimizing the oxidized structures of PTB7 and P3HT using DFT and a 6-31G* basis. The g-tensors of the optimized, charged structures were then calculated using orca (DFT|tzvpp basis). The g values for the PTB7 trimer were determined to be 2.0024, 2.0032, and 2.0041, respectively. Values for the smaller units varied by less than 0.2% and all were within the range of experimental uncertainty. In agreement with experiment, the calculated g-values for P3HT were smaller (2.0019, 2.0022, 2.0030) than those of PTB7. The good agreement between calculation and EPR measurements allows the investigation of the spin density. Comparing the spin densities of P3HT and PTB7 allows the hypothesis that the difference in efficiencies is due to a fluorine atom in PTB7 to be rejected.

---

**RM_MWGL Regional Meeting 482**

## Structures and water dissociation reactions of Mn-doped $TiO_2$ clusters

***Choongkeun Lee****, choong@ksu.edu, Christine M. Aikens. Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

$TiO_2$ clusters are potentially useful materials to be activated by light, but $TiO_2$ is not activated by a wide area of full solar spectrum because of its large band gap, about 3.2 eV. This is in the UV region, which is less than 10% of the solar spectrum. To reduce the band gap and to increase its efficiency, Mn can be doped in $TiO_2$. Small $Ti_nO_{2n}$ ($n$ = 2-6) clusters have been substituted with one or two Mn using density functional theory. When is Mn placed at lower coordinated positions, the structure is more stable. The band gap is reduced by the substitution, but it is not reduced greatly with the second addition of Mn. Since these materials are often in aqueous solution, we also studied the reaction of water with the small clusters. The details of the reaction on the clusters will be presented.

---

**RM_MWGL Regional Meeting 483**

## Recovery of carbochemicals from aqueous biomass hydrolyzates using critical fluid carbon dioxide

***Jenny Phomakay**, jphomaka@uark.edu, Sumio Mori, Jerry W. King, Keerthi Srinivas. Department of Chemical Engineering, University of Arkansas, Fayetteville, AR 72701, United States*

To produce furfural and 5-hydroxymethylfurfural (HMF) from the monomeric sugar feedstocks – glucose and xylose – we have applied both compressed and supercritical carbon dioxide (SC-$CO_2$) to extract and recover the above two carbochemicals from the aqueous reaction medium. The ability of $CO_2$ to solvate and extract these targeted carbochemicals comes from literature studies on liquid $CO_2$–water–furfural system, our own calculations on the negative second mixed virial coefficients for low pressure $CO_2$–furan solute systems, the recorded and calculated high mole fraction activity coefficients for furfural and 5-HMF escaping from aqueous solutions, the relative differences in the respective solubility parameters for furfural, 5-HMF and water, and certain SC-$CO_2$–furan phase and thermodynamic solubility measurements. Utilizing initially various $CO_2$ flow rates (30 – 60 L/min - STP) and extraction temperatures (23 – 50$^o$C), and extraction times (0.5 – 6.0 hrs.); $CO_2$ at 10 psig was sparged through a 50 mL Parr reactor containing ~4-10 wt.% of furfural in an aqueous solution. Secondly, we employed an Applied Separations Spe-ed supercritical fluid extraction (SFE) Spe-ed unit using a specially-designed extraction cell to allow internally the flow of SC-$CO_2$ through the aqueous hydrolyzate mixture contained in an extraction cell. An extraction pressure range of 80 – 140 bars at 40 – 50$^o$C for 5 – 60 min. at 30 – 60 L/hr of $CO_2$ – STP were initially used in SFE experiments. Sparging experiments conducted over a wide range of extraction conditions: $CO_2$ flow rates, extraction times, and temperatures using different stirrer agitation rates have demonstrated that appreciable amounts of the dilute furfural aqueous mixture can be extracted and recovered based on gravimetry. In general, the best extraction and recovery of furfural is achieved by utilizing low extraction temperatures (30 – 40$^o$C), $CO_2$ flow rates (~30 – 40 L/min) and agitation rates (60 rpm).

**RM_MWGL Regional Meeting 484**

## Extensive SAPT and SAPT-DFT energy comparison on small systems:applications towards larger dimers

***Bradley K Welch**[1], bwelch5@slu.edu, Charles C Kirkpatrick[1], Michael Lewis[1], Keith Hacke[2]. (1) Department of Chemistry, Saint Louis University, St.Louis, Missouri 63103, United States (2) Advanced Technology Group, Saint Louis University, St.Louis, Missouri 63103, United States*

SAPT calculations were preformed on small to intermediate sized neutral-neutral and anion-neutral dimeric systems to assess the accuracies of different basis sets and electron correlation methods. The small systems we've computed values for were Rg-Rg (Rg=He,Ne,Ar) and F- -Rg. The systems were extremely studied with the aug-cc-pvxZ (x=d,t,q,5,6) basis sets,a variety of DFT functionals were employed and the energies were extrapolated to
the CBS for DFT and coupled clustered methods. We also looked at some intermediate

sized systems. Our results indicate that DFT-SAPT total energy compares well to CC-SAPT total energy, and that there is no general trend in accuracy for the dft decomposition energies compared to CC-SAPT energies. The application of these results could be used for SAPT decomposition energies on larger systems.

**RM_MWGL Regional Meeting 485**

## Fast Marching algorithm for reaction dynamics: A new perspective for Monte Carlo sampling and reaction paths

***Nathan W. Truex***, *nwtruex07@ole.augie.edu. Department of Chemistry, Augustana College, Sioux Falls, South Dakota 57197, United States*

Chemistry is all about breaking and making bonds. Often we are used to thinking of chemical reactions as the ones where the reactants and products are the only key players. The transformation of reactants into products is a continuous process, with the involvement of a host of chemical species along the way. Some of these chemical species can, indeed, be identified in the experiment; they are the stationary points (transition states, reactive intermediates, complex ions) in the potential energy surface of the reacting system. Others (e.g., valley ridges, valley ridge inflexion points) are not amenable to experimental determination and hence, their role is often ignored in the chemical reactions. The presence of these various species in a given chemical reaction depends on the path it takes. A detail understanding of these requires the exploration of the potential energy surface. We have investigated a wave-front based approach (also called fast marching method) to solve the Hamilton-Jacobi equation. In this method, a wave-front constructed around the reactant state is expanded with the aid of the fast marching method until the wave-front is swept over the most important region of the potential energy surface. At the end we obtain a new surface, called t-surface. This t-surface is then used to calculate the reaction paths. This surface, represented by the “alive” points, resides in the important region of the potential energy surface. Our results show that these “alive” points can be used as the Monte Carlo sampling points, providing an alternative way to carry out Monte Carlo simulation in a mathematically rigorous way. The systems include: hydrogen transfer of malonaldehyde, conformation dynamics of alanine dipeptide, SN2 reaction and bifurcation reaction of methoxy radical to hydroxyl methylene radical.

**RM_MWGL Regional Meeting 486**

## A computational study of the bonding interaction between chromium, molybdenum, or tungsten carbonyl complexes and cyanoethylenes or fluoroethylenes

***Sheryl L Johnson**, sljohn5@ilstu.edu, David L Cedeño. Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160, United States*

The Dewar-Chatt-Duncanson model is widely used to provide a qualitative picture of the bonding interaction between a metal and an unsaturated hydrocarbon (alkene or alkyne). Despite its widespread utilization, the model does not allow proper predictions of bond energy, as it only emphasizes the electronic aspect of the interaction. It is well established that steric factors also influence the bond. Our group further investigated the effect of the alkene's structural reorganization directly resulting from the bonding interaction. A recent study using metal-chloroethylene complexes ($M(CO)_5(C_2H_{4-n}Cl_n)$, n = 0 to 4, M = Cr, Mo, W) demonstrated that the metal-alkene bond strength does not increase in direct proportion to the increase of the electron withdrawing ability of the alkene. Here, we present complementary studies using the analogous $M(CO)_5(C_2H_{4-n}F_n)$ and $M(CO)_5(C_2H_{4-n}(CN)_n)$, n = 0 to 4, M = Cr, Mo, W, in which the effect of steric hindrance is minimized, while the electronic effects dominate. Computational studies were carried out at the DFT level using the Becke-Perdew functional for electron exchange and correlation. Besides calculating metal-alkene bond energies, a bond energy decomposition analysis was carried out to quantify steric, electronic and reorganizational effects on the bond strength.

Similarly to what it was found in the analogous metal-chloroalkene complexes, metal-alkene bond strengths do not increase in proportion to the electron withdrawing ability of the alkene as one would deduct from the Dewar-Chatt-Duncanson model. Reorganizational effects are dominant and correlate with the electron-withdrawing ability of the alkene.

**RM_MWGL Regional Meeting 487**

## Comparison of structures of $CH_2ClF...C_2H_3F$ and $CH_2F_2...C_2H_3F$ as determined by Fourier-transform microwave spectroscopy

***Cori L Christenholz**, clchristenholz@eiu.edu, Daniel A Obenchain, Rebecca A Peebles, Sean A Peebles.Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920, United States*

The structures of $CH_2ClF…C_2H_3F$ (CFM...VF) and $CH_2F_2…C_2H_3F$ (DFM...VF) have been studied by Fourier-Transform Microwave (FTMW) spectroscopy. Optimizations of multiple possible structures were carried out at the MP2/6-311++G(2d,2p) level. Assignments of CFM…VF and DFM…VF were completed using the Chirped-Pulse FTMW broadband spectrometer, as well as the Balle-Flygare FTMW resonant cavity instrument, at Eastern Illinois University. The predicted most stable conformer of DFM…VF was assigned; however, the second lowest energy structure of CFM...VF (22 $cm^{-1}$ higher in energy than the most stable conformer) was observed in the scan. The rotational constants of the most stable structures of both species were determined, as well as the $^{37}Cl$ isotope of the CFM…VF and the three $^{13}C$ isotopes of the DFM…VF. In both species there is a weak interaction between the hydrogen atoms of CFM or DFM and the fluorine atom of the vinyl fluoride. The chlorine atom of $CH_2ClF$ or fluorine atom of $CH_2F_2$ interacts with the hydrogen atom of $C_2H_3F$ that is geminal to fluorine. Both structures are planar with only the hydrogens of CFM or DFM out of the plane. The dipole moments of both species were determined by measuring Stark effects. The total dipole moments range from 1.9 to 2.4 D.

**RM_MWGL Regional Meeting 488**

## Easy as π: Analysis of C-H… π interactions within chlorofluoromethane-acetylene ($CH_2ClF$-HCCH)

***Lena F. Elmuti***[1], *lfelmuti@eiu.edu, Rebecca A. Peebles*[1], *Sean A. Peebles*[1], *Amanda L. Steber*[2], *Justin L. Neill*[2], *Brooks H. Pate*[2]. *(1) Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, United States (2) Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States*

The purpose of this study was to determine the structure of the weakly bound complex chlorofluoromethane-acetylene ($CH_2ClF$-HCCH). This was accomplished using microwave spectroscopic analysis, which involves a supersonic expansion to sustain the weak attraction between chlorofluoromethane and acetylene. The study can provide insight on C-H…π hydrogen bonding between the hydrogen atom within chlorofluoromethane and the π bond within acetylene.

In this study, microwave spectra were collected at the University of Virginia (UVA) and Eastern Illinois University (EIU). The chirped-pulse Fourier transform microwave spectrometer at UVA served as a starting point by providing a full 11 GHz spectrum. One spectrum from the Balle-Flygare resonant-cavity Fourier transform microwave spectrometer at EIU covers about 1 MHz of the range of the spectrum from UVA, offering a higher resolution than seen by the UVA spectrometer. Both spectrometers were used collaboratively to make an assignment for $CH_2ClF$-HCCH. Four isotopes for this complex were analyzed including $CH_2{}^{35}ClF$-HCCH, $CH_2{}^{37}ClF$-HCCH, $CH_2{}^{35}ClF$-$H^{13}C^{13}CH$,and $CH_2{}^{37}ClF$-$H^{13}C^{13}CH$. Structural parameters including angles, distances, and the length of C-H...π interactions were found. This cluster can now be compared with others that possess C-H…π interactions, such as $CH_2F_2$-HCCH, $CHClF_2$-HCCH and $CHF_3$-HCCH.

**RM_MWGL Regional Meeting 489**

## Photovoltaic devices based on porphyrin polymeric donor materials: A computational study of linker effects

***Zachary L Dunn***, *z-dunn@onu.edu, Morgan A Hammer, Trilisa M Perrine.Department of Chemistry and Biochemistry, Ohio Northern University, Ada, OH 45810, United States*

The electronic properties of porphyrin based polymeric systems for use in organic photovoltaic (OPV) devices were studied using DFT with the B3LYP functional and the LANL2DZ basis set. The focus was upon the exploration of using polymers based on porphyrin as donor molecules in the OPV donor-acceptor regime. The goal was to minimize the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in order to optimize the wavelengths and amount of incident light the OPV devices absorb. A variety of possible linker moieties between the porphyrin molecules were explored, including ones based on thiophene and furan heterocycles, phenyl rings, and butadiyne functional groups and which included single, double, or triple bonds between the porphyrin ring and the linker core. The most promising of these included two thiophene heterocycles and two triple bonds.

**RM_MWGL Regional Meeting 490**

## Computational study of substituent effects on the band gap of porphyrin based polymeric systems

***Morgan A Hammer***, *m-hammer@onu.edu, Zachary L Dunn, Trilisa M Perrine.Department of Chemistry and Biochemistry, Ohio Northern University, Ada, Ohio 45810, United States*

Porphyrins have electrical properties that may be utilized as donating materials in photovoltaics. A computational study (DFT with B3LYP and the LANL2DZ basis set) was performed on functionalized zinc-centered porphyrin monomers with the goal of lowering the HOMO/LUMO gap. By narrowing the band gap, a greater portion of the solar spectrum can beabsorbed. Two different substituents that are known to improve porphyrin solubility were tested for their contribution to the band gap. It was determined that their contribution is small, and that these substituents may be truncated as an adequate approximation for more extensive oligomer calculations. The electron donating and electron withdrawing groups, $-NH_2$ and $–NO_2$ respectively, were tested in various combinations at the beta and meso positions. Both substituents proved to lower the band gap, with the amino groups proving most effective at the meso positions and the nitro groups proving most effective at the beta positions.

**RM_MWGL Regional Meeting 491**

## Quantitative structure-property relationship study of the short-circuit current of thiophene dyes for dye-sensitized solar cells based on neural networks

***Seri P. Kamari***, *seri.kamari@gmail.com, Robert LeSuer, Kristy L. Mardis. Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628, United States*

Dye sensitized solar cells (DSSC) are an attractive alternative to silicon-based solar cells due to their prospect of high energy conversion efficiency and low production cost. However, their efficiencies remain low with the best all dyes exhibiting efficiencies of

around 11%. One of the important parameters controlling the efficiency of the solar cell is the short circuit current ($I_{sc}$). $I_{sc}$ is believed to depend on hydrophobicity, molecular weight, pKa, and absorption maximum, however, no obvious linear relationship exists between these parameters and experimental values of $I_{sc}$. In this work, a quantitative structure-property relationship (QSPR) analysis of short-circuit current ($I_{sc}$) and thiophene derivatives was carried out using artificial neural networks. Two hundred twenty-nine thiophenes culled from literature sources were divided into training (169 molecules) and validation (60 molecules) sets which were chosen randomly. The Neural Network algorithm in Mathematica 8 with the feed forward routine was used to create a neural network with 1 hidden layer. Descriptors including hydrophobicity, surface area, and pKa were included to study the influence of solubility, aromaticity, and size on $I_{sc}$. Initial results indicate that a more diverse group of descriptors is necessary to produce a model capable of predicting Isc values. However, the created database is the most complete set of solar cell dye molecules compiled and will be of great benefit for future studies.

### RM_MWGL Regional Meeting 492

## Computational investigation of the conformational preferences of a cytochrome $c_7$ dimer

***Adam O Zayed***[1], *azayed20@csu.edu, David M. Tiede*[2], *Kristy L. Mardis*[1]*. (1) Department of Chemistry and Physics, Chicago State University, Chicago, IL 60628, United States (2) Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL 60439, United States*

Cytochrome $c_7$ from the *G. sulfurreducens* bacteria has been shown to undergo electron transfer (ET) when bound to a variety of molecules. Domains containing polymers of $c_7$-type proteins with up to nine repeats have been identified in the genomic sequence. The packing of the molecules in the crystal structure suggest that the polymers might form a “nanowire”. However, the actual ET properties of the polycytochrome $c_7$-type molecules would be determined by the interactions of neighboring heme groups and thus more information of the actual conformational structure is necessary. The current work presents a computational investigation of the conformations of a cytochrome $c_7$ dimer. The program MOE was used to build the cytochrome $c_7$ dimer from the PDB entry 1RWJ and to create an appropriate homolog to complete the pair. Nanosecond scale NVE simulations were run using CHARMM to simulate the dimer's conformations. During the simulation, the distance between the heme groups decreased from 25.53 Å to 20.5 Å. This significant decrease suggests electron transfer may occur.

### RM_MWGL Regional Meeting 493

## A batch pH oscillator: The Belousov-Zhabotinsky reaction

***James Jones***, *Glen.Frerichs@westminster-mo.edu, Xiaohe Huang, Mulurhab Gebrekidan, Jacob Burch, Mei Yuan, Glen A Frerichs. Department of Chemistry, Westminster College, Fulton, MO 65251, United States*

Batch chemical oscillators are extremely rare, with the Belousov-Zhabotinsky (BZ) reaction being the best known and most studied. In 1951 the BZ oscillator was discovered by Belousov, and Zhabotinsky reinvestigated this batch reaction a decade later. The classical BZ system consists of bromate ion, malonic acid, and cerium or manganese ions as a catalyst in $H_2SO_4$. Oscillations in this batch system have been observed previously in the potential of Pt or bromide-selective electrodes, as well as in absorbance at a fixed wavelength. Considerable efforts to discover chemical systems that exhibit pH oscillations in a closed system have met with very limited success. We report here the discovery of batch pH oscillations in the BZ reaction at both 25° and 60°C. Oscillations were obtained using $KBrO_3$ or $NaBrO_3$ with malonic acid and $MnSO_4$. Depending on the concentrations of the main reactants, oscillations were observed both with and without $H_2SO_4$ or NaOH. Maximum amplitude of the oscillations was 0.50-0.55 pH units.

Generally, pH oscillations occurred concurrently with oscillations in potential of a Pt electrode, and lasted as long as 5 hours. During the course of an experiment, the pH drops initially before oscillations begin and the pH gradually increases. When the pH reaches a critical maximum value, oscillations stop. A proposed model for the system will be discussed.

**RM_MWGL Regional Meeting 494**

## Convenient approach to composition tunable uncapped semiconducting nanocrystals

***Shaohua Li***, *sldm7@mail.umkc.edu, Guolong Tan, Zhonghua Peng. Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, United States*

Ternary $CdSe_{1-x}S_x$ nanocrystals with varied compositions (x = 0~1) can be conveniently prepared by mechanical alloying of the elemental powders in appropriate loadings. Without external heating or applied pressure, the mechanochemical reaction between Cd and S/Se occurs rather quickly and is completed in less than 1 h.

Nanoparticles of homogenous chemical composition with average sizes smaller than 10 nm are obtained after 40 h of the mechanical alloying process. As the content of sulfur (x value of $CdSe_{1-x}S_x$) increases, the lattice parameter of the resulting nanocrystals linearly decreases and the bandgap quadratically increases, demonstrating the composition homogeneity and bandgap tenability through composition variations. These results significantly expand the application scope of the mechanical alloying process and open up an exciting prospect that nanocrystals of ternary, quaternary or even more complicated chemical compositions can be conveniently prepared. Such uncapped nanocrystals are expected to be superior materials in applications such as solar cells, and photocatalytic water splitting.

## RM_MWGL Regional Meeting 495

## Self-Regenerative Redox Catalyst: Palladium Oxide Nanoparticles on Cerium Oxide Nanorods

***Yunyun Zhou**, yunyun.zhou1986@huskers.unl.edu.Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68503, United States*

We report the self-regenerative catalytic activity of palladium oxide ($PdO_y$) nanoparticles on cerium oxide ($CeO_{2-x}$) nanorods support under ambient conditions. These catalysts can regain 60-80 % of their initial catalytic activity for carbon monoxide (CO) oxidation repeatedly for at least ten subsequent runs. X-ray absorption and photoelectron spectroscopy studies demonstrate the oxidation and reduction of the palladium oxide before and after the catalysed reactions and subsequent ambient regeneration process. These results and the observed $Pd^{4+}$ species in the self-regenerated catalysts suggest a strong interaction between the palladium oxide nanoparticles and the cerium oxide nanorod support.

## RM_MWGL Regional Meeting 496

## Quenching of coumarin luminescence by CdSe quantum dots

***Aravind Baride**[1], aravind.baride@usd.edu, Stanley P May[1], Daniel Engebretson[2]. (1) Department of Chemistry, The University of South Dakota, Vermillion, South Dakota 57069, United States (2) Department of Biomedical Engineering, The University of South Dakota, Sioux Falls, South Dakota 57107, United States*

Quenching of coumarin luminescence in the presence of CdSe quantum dots (QDs) was investigated. In our study CdSe QDs quenching effect on two coumarin derivatives, 7-hydroxycoumarin and 7-diethylamino coumarin, was reported. The effect of QDs with different ligands on coumarin emission was studied at various temperatures. The quenching rate constant, derived from a Stern-Volmer plot, was ~$10^4$ times larger than the dynamic quenching rate constant calculated from Stoke-Einstein and Smoluchowski equation. Temperature dependent studies of the quenching process showed a gradual decrease in quenching rate with increase in temperature, indicating a static quenching mechanism. The quenching of coumarin luminescence can have significant influence on the results of the systems containing both coumarin and QDs, such as, photo-induced drug delivery, bio-imaging, and fluoroimmunoassay systems. On other hand, coumarin luminescence quenching can be used to design luminescent probes for the detection and quantification of coumarin labeled proteins.

## RM_MWGL Regional Meeting 497

## Structural diversity in MgSe nanocrystals

***P.J. Morrison***[1,2], *pjmorris@go.wustl.edu, William E. Buhro*[1,2]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, Missouri 63130, United States (2) Center for Materials Innovation, Washington University in St. Louis, St. Louis, Missouri 63130, United States*

Because of its relatively high ionicity, magnesium selenide is a large band-gap semiconductor (Eg = 4.0 eV). The energies of its valence- and conduction-band edges suggest it could be an ideal shell material for electronic passivation of CdSe quantum nanostructures. However, MgSe exhibits a rock-salt crystal structure in the bulk, whereas CdSe nanocrystals exhibit either a wurtzite or zinc-blende structure, suggesting that epitaxy at the CdSe-MgSe interface may be difficult to achieve. We now report that MgSe nanocrystals of various morphologies possess rock-salt, wurtzite, or zinc-blende structures. HRTEM images of recently synthesized MgSe tetrapod nanocrystals establish that they have zinc-blende nanocrystal cores, and wurtzite arms. Significantly, the lattice parameters of the wurtzite and zinc-blende MgSe are within 3% of those of CdSe, indicating that epitaxial MgSe shell growth on CdSe nanocrytals should be achievable.

---

**RM_MWGL Regional Meeting 498**

## Role of Chloride in the growth of Silver nanowires by the polyol synthesis

***Waynie M. Schuette***, *wwolaprath@go.wustl.edu, William E. Buhro. Department of Chemistry and Center for Materials Innovation, Washington University, St. Louis, Missouri 63130, United States*

Various additives are employed in the polyol synthesis of silver nanowires (Ag NWs), which are typically halide salts such as NaCl, $PtCl_2$, AgCl, and AgBr. A variety of mechanistic roles have been suggested for these additives. Chloride ion has alternatively been proposed to be a selective etching agent and electrostatically stabilizing adsorbate. AgCl has been proposed to serve as a buffering agent, or as an ill-defined growth seed. In a few studies, the additives have been suggested to serve as heterogeneous-nucleated agents, although experimental evidence for this proposal is lacking. We now show that the early addition of NaCl in the polyol synthesis of Ag NWs from $AgNO_3$ in ethylene glycol results in the rapid formation of AgCl nanocubes, which induce the heterogeneous nucleation of metallic Ag on their surfaces. Ag NWs subsequently grow from these nucleation sites. The conclusions are supported by studies using ex-situ generated AgCl nanocubes.

---

**RM_MWGL Regional Meeting 499**

## Synthesis and isolation of the pure magic-size CdSe nanocluster $[(CdSe)_{13}(n\text{-octylamine})_{13}]$

***Yuanyuan Wang**, wangyy.nju@gmail.com, Yi-hsin Liu, Ying Zhang, Fudong Wang, Henry Rohrs, Michael L. Gross, William E. Buhro. Department of Chemistry, Washington University in St. Louis, Saint Louis, MO 63130, United States*

We describe a novel method to synthesize and isolate the smallest-known magic-size CdSe nanocluster – $(CdSe)_{13}$. Magic-size nanoclusters, such as $(CdSe)_{13}$, $(CdSe)_{19}$, and $(CdSe)_{33,34}$, are typically generated in mixtures. To our knowledge, this report is the first isolation of a CdSe nanocluster of a single size. The $(CdSe)_{13}$ is generated in an *n*-octylamine-based lamellar-template structure by reaction of $Cd(OAc)_2{\cdot}2H_2O$ and selenourea at room temperature. The stoichiometry of the nanocluster is established by UV-visible spectroscopy and matrix-assisted laser-desorption ionization (MALDI) mass spectrometry. Elemental analysis confirms the composition of the isolated material to be $[(CdSe)_{13}(n\text{-octylamine})_{13}]$. Free $(CdSe)_{13}$ nanoclusters are liberated from the synthetic templates by sonication of $[(CdSe)_{13}(n\text{-octylamine})_{13}]$ in the presence of oleylamine. The growth behavior of free and templated nanoclusters is distinguished by their differing growth kinetics in the presence of polar solvents.

**RM_MWGL Regional Meeting 500**

## Insights into AuSR nanocluster growth via Au(III) chloride

***Brian M. Barngrover**, bribarn@ksu.edu, Christine M. Aikens. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

Using density functional theory with the Becke Perdew (BP86) functional and a Triple Zeta Polarized (TZP) basis set, a theoretical examination was done on gold(III) chlorine precursor with thiols, thiolates, and disulfides to cause reduction of gold(III) to gold(I). A further investigation was carried out into the varying ratios of thiols, thiolates, and disulfides to the gold(III) chlorine precursor. A secondary investigation into the subsequent reactions of electron and hydride additions to gold(I) and gold(0) structures was also analyzed. A barrier height of 0.31 eV was found for the first thiol addition to $AuCl_4^-$. The first and subsequent additions are exothermic overall. Thiol addition results in a doubly protonated $Au(HSR)_2^+$ subunit and a disulfide. For thiolate addition, either reduction to $Au(SR)_2^-$ and a disulfide can occur or ligand exchange occurs and $Au(SR)_4^-$ can form; both reactions are exothermic and the gold(I) structure is slightly more favored. A 3:1 ratio of thiol or thiolate ligands to $AuCl_4^-$ preferentially leads to reduction and a monosubstituted $AuClSR^-$ subunit. These subunits can oligomerize to form anionic chains, which are seen to passivate nanoparticles, or they can form rings. A barrier height of 0.33 eV was found for the formation of the dimer from two of the $AuClSR^-$ subunits. The overall reaction is exothermic allowing for the dimerization reaction to occur with relative ease.

Some gold structures require extra electrons either added directly or by a reducing agent such as borohydride to form dimers or larger clusters with gold-gold bonds. Once gold(I) structures have formed oligomeric chain and cyclic clusters, adding electrons or

hydrides to $(AuSR)_n$ chain and ring structures result in either the formation of gold-gold bond and the removal of a thiol or decomposition into smaller gold(I) structures.

## RM_MWGL Regional Meeting 501

## Binding of formyloxyl radicals to $Au_{20}$: Implications for the growth of gold nanopaticles

***Jacob M. Hull***, *jhull@ksu.edu, Makenzie R. Provorse, Christine M. Aikens. Department of Chemistry, Kansas State Universtiy, Manhattan, KS 66506, United States*

Citrate reduction of gold salts is one of the most common methods of producing gold nanoparticles. It has been previously reported, using density functional theory (DFT), that the incremental binding energies of formate (the simplest carboxylate) bound to $Au_{20}$ decrease sharply as the number of formates bound increases and that electron density builds up on uncomplexed apex gold atoms. These data suggest that $Au_{20}$ cannot accommodate many negative charges and that neutral carboxylates, such as those produced in oxidation-reduction reactions during nanoparticle synthesis using the citrate method, may play a role in the growth of gold nanoparticles and affect their properties. In this study $Au_{20}$-formyloxyl radical interactions were investigated using DFT at the BP86/DZ level of theory to model neutral carboxylate-gold nanoparticle binding. It was found that the incremental binding energy (IBE) of one formyloxyl radical is 56 kJ/mol lower than when one formate is bound. The IBEs of subsequent additions however heavily favor the addition of formyloxyl radicals. The IBE for the most favorable geometry of the addition of a second formyloxyl radical is 210 kJ/mol higher than the IBE for the most favored addition of a second formate. All additions of formate after the second result in non-bonding structures, whereas the additions of formyloxyl radicals remain highly favorable through eight bound formyloxyl radicals (the highest number tested) with a range of binding energies of 154-331 kJ/mol. It was found that the most favorable geometries after the third addition of formyloxyl radical featured a distortion of the tetrahedral structure of the $Au_{20}$. This distortion would likely affect the properties of the nanoparticle. These results suggest that radical carboxylates could play an important role in the formation and properties of gold nanoparticles synthesized using the citrate method.

## RM_MWGL Regional Meeting 502

## Abstract withdrawn

## RM_MWGL Regional Meeting 503

## Towards hybrid nanobiodevice construction: $F_1$-ATP synthase adsorption studies

***Jenifer K Settle***[1], *jsettle@ku.edu, Cindy L Berrie*[1], *Mark L Richter*[2]. *(1) Department of Chemistry, University of Kansas, Lawrence, Kansas, United States (2) Department of Molecular Biosciences, University of Kansas, Lawrence, Kansas, United States*

Hybrid nanobiodevice construction requires controlled incorporation of biomolecules within the device. A tiny molecular motor, $F_1$-ATP synthase (ATPase), is an ideal candidate for such devices. However, nonspecific adsorption of ATPase results in a variety of protein orientations on the surface. To improve the functionality of the immobilized protein within a device, only one orientation (gamma unit upright) is desired. Thus, controlling orientation is also imperative in device fabrication. Several techniques have been utilized to study and control both placement and orientation of ATPase adsorption. Atomic force microscopy was used to create nanopatterned arrays by grafting a dithiol into a resist matrix monolayer, exposing a thiol group. Through maleimide chemistry, a maleimide-nitriloacetic acid (NTA) group was attached to the terminal end of the dithiol pattern. NTA coordinates with nickel ions, which then coordinates with the histidine tag on the ATPase, thus controlling orientation and location. This process has also been studied via surface plasmon resonance. By coordinating these efforts with nanoelectrode construction, a functional nanobiodevice may be engineered.

## RM_MWGL Regional Meeting 504

### Rational design and preparation of polyarginine capped gold nanoparticle for siRNA delivery

***Ziyan Zhang***, *zzhangb@go.wustl.edu, John-Stephen A. Taylor. Department of Chemistry, Washington University in St. Louis, Saint Louis, MO 63130, United States*

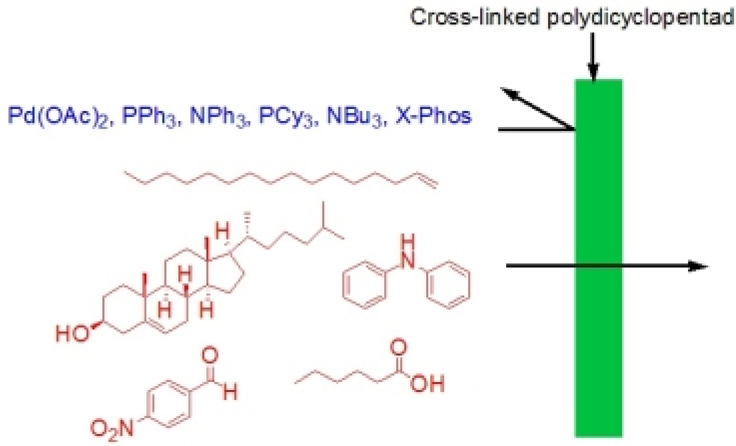
Cationic gold nanoparticles are of interest as potential nonviral gene and siRNA delivery agents because of their ability to bind nucleic acids electrostatically and enter cells via endocytosis. In this study, we designed an arginine-rich peptide capped gold nanoparticle for enhanced particle stability and nucleic acid binding ability. The peptide was designed to have one cysteine for gold attachment, two threonines to enhance peptide self-assembly on the gold surface and multiple arginines for siRNA binding and cell entry. The nanoparticle was synthesized by a one-pot strategy by mixing peptide and $HAuCl_4$ solution together followed by addition of sodium borohydride. The resulting nanoparticles showed much improved stability against high salt concentration and high DNA concentration compared to primary amine capped gold nanoparticles. The physical properties of the nanoparticle were characterized and the DNA binding ability was studied by a gel retardation assay. The cell transfection ability of the nanoparticle is currently under investigation.

## RM_MWGL Regional Meeting 505

### Retention of palladium and phosphine ligands using nanoporous polydicyclopentadiene thimbles

***Abhinaba Gupta***, *gupta.abhinaba@gmail.com, Ned Bowden. Department of Chemistry, University of Iowa, Iowa City, Iowa 52242-1292, United States*

Thimbles composed of polydicyclopentadiene retained Pd and phosphines used in Buchwald–Hartwig and Sonogashira coupling reactions but allowed the products to permeate. The products were isolated in high yields on the exteriors of the thimbles with no detectable contamination from phosphine and with Pd loadings as low as <5.5 ppm.



## RM_MWGL Regional Meeting 506

## Effects of particle size, shape, and temperature on dodecanethiol assisted digestive ripening of Au nanoparticles

***Christopher Parsons***[1], *cjpar@uga.edu, Deepa Jose*[2], *Kenneth J Klabunde*[2]. *(1) Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States (2) Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States*

Digestive ripening, a process which converts an extremely polydisperse colloid into a highly monodisperse one when refluxed or kept at room temperature in the presence of an excess capping ligand, was found to be an efficient route for the synthesis of monodisperse nanoparticles of metals like Au, Ag, Cu, Mg, etc. Gold nanoparticles of various shapes and sizes were prepared by the solvated metal atom dispersion (SMAD) technique in volatile nonaqueous solvents like pentane, toluene, tetrahydrofuran, and acetone. The as-prepared samples were characterized by UV-visible spectroscopy and TEM bright field imaging. The particle size of the as-prepared SMAD Au samples varies from 3 - 40 nm. The digestive ripening of these samples with dodecanethiol was done in different solvents like toluene, 4-tert-butyl toluene, or phenyl ether. This allowed the digestive ripening process to occur at a gradient of temperatures. The course of digestive ripening was followed using UV-Visible spectroscopy and TEM bright field imaging.

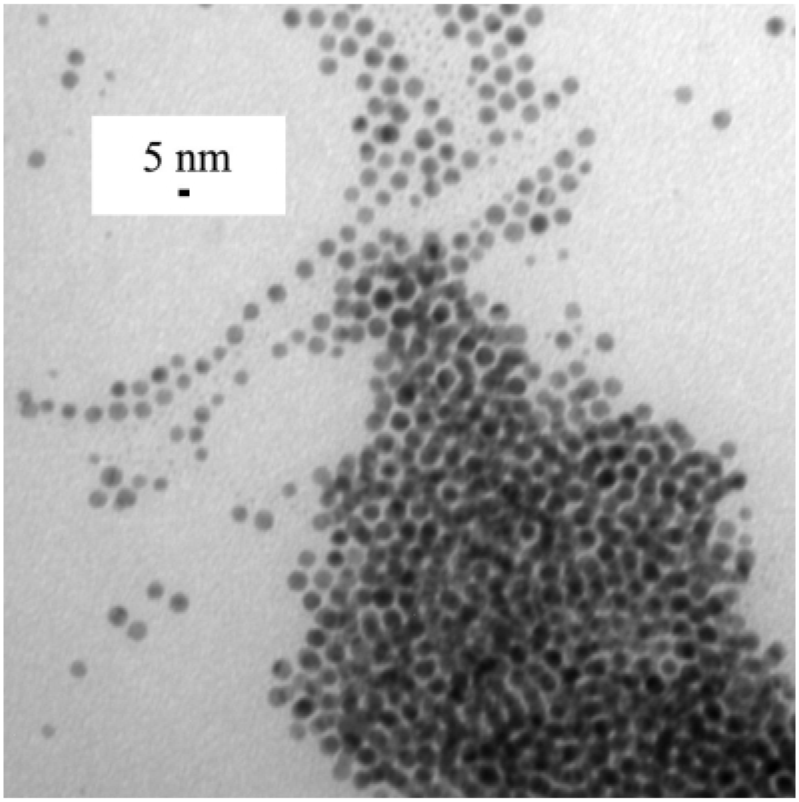


**Figure 1:** TEM image of Au nanoparticles prepared in THF after digestive ripening in toluene.

**RM_MWGL Regional Meeting 507**

## Changes in chemical structure, crystallinity and mechanical properties of LDPE and PP composites reinforced by cellulose fibres after exposure to accelerated photoageing

***Rungsima Chollakup***[1,2,3]*, aaprmc@ku.ac.th, Florence Delor-Jestin*[3,4]*, Agnes Rivaton*[2,3]*, Sandrine Thérias*[2,3]*, Jean-Luc Gardette*[2,3]*. (1) Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI), Kasetsart University, Bangkok, Thailand (2) LPMM BP 10448, Clermont Université, Université Blaise Pascal, Clermont-Ferrand, France (3) LPMM, CNRS, UMR 6505, Aubière, France (4) LPMM BP 10187, Clermont Université, ENSCCF, Clermont-Ferrand, France*

This study is aimed to investigate the effect of cellulose fibre on changes in chemical structure, crystallinity and mechanical properties of LDPE and PP composites resulting from degradation provoked by exposure to UV light. LDPE and PP composites with cellulose fibres (pineapple leaf fibre - PALF, coir fibre - C, and palm fibre - P) were exposed to artificial accelerated weathering. Fourier transform infrared (FTIR) spectroscopy was used to determine the chemistry changes at the surface of the LDPE and PP composites. Carbonyl and vinyl group formation (at 1712 and 908 $cm^{-1}$) at the

surface after weathering was identified as an important index for structural changes for the LDPE composites. Meanwhile, the carbonyl and hydroxyl group formation (at 1712 and 3400 $cm^{-1}$) at the surface after weathering was identified as an important index of the PP composites. Differential Scanning Calorimetry (DSC) was employed to evaluate the crystallinity changes of the LDPE and PP composites. Tensile analyzer was used to test for Young's modulus of the composites. Carbonyl groups were formed at a higher rate in the case of PP, with degradation time around 70 hrs for the PP composite and 300 hrs for the LDPE composites. While, the vinyl group formation found in the LDPE composites and the hydroxyl group formation found in the PP composites were not significantly modified by the fibre type and the fibre content. For the highest fibre content (around 25% by weight) the inclusion of fibres gave significant structural changes for both LDPE and PP composites. We found that Young's modulus and crystallinity of the LDPE composites tend to increase after 100, 200 and 300 hours of photo-ageing. This effect was less pronounced in the case of the PP composites. Due to the higher mobility of shorter chains, an increase of crystallinity was observed.

## RM_MWGL Regional Meeting 508

### Detection of Sphingolipid Biomarkers in a Murine Model of Niemann-Pick Type C1 (NPC1) Disease

***Martin Y. Fan****, myfan@wustl.edu, Hideji Fujiwara, Rohini Sidhu, Daniel S Ory. Department of Biology and Biomedical Sciences, Washington University in St. Louis, St. Louis, Missouri 63105, United States*

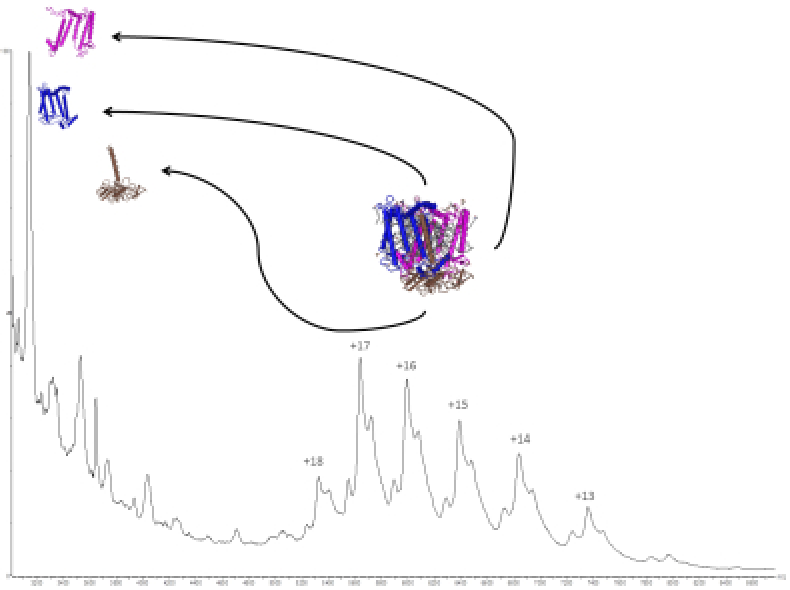
Niemann-Pick Type C1 (NPC1) disease is a rare lysosomal lipid storage disorder for which there are currently no FDA-approved treatments. A major barrier to the development of more effective treatments is a lack of biochemical outcome measures for evaluating efficacy of therapy in clinical trials. We hypothesized that alterations in the lipid profile of human NPC1 subjects will provide biomarkers to follow disease progression and to evaluate potential efficacy of new therapies. Using a mass spectrometry-based approach we have quantified the tissue concentrations of 40 lipid species in an *Npc1*$^{-/-}$ mouse model, and compared these results to those of wild type and heterozygous mice. In *Npc1*$^{-/-}$ mice numerous ceramide species — particularly those with sugar moieties such as lactosylceramides, monohexosylceramides, and gangliosides — were more than ten-fold elevated relative to wild type mice. No significant differences were found between wild type and heterozygous mice. Tissue concentrations of the glycosphingolipid species accumulated as *Npc1*$^{-/-}$ mice aged, correlating with increased disease severity. These findings raise the possibility of using glycosphingolipids as NPC1 disease biomarkers. In future studies, these candidate lipid species will be examined in plasma samples obtained from human NPC1 subjects to assess their utility as possible disease biomarkers.

## RM_MWGL Regional Meeting 509

# Native mass spectrometry of membrane-bound protein-pigment complexes suggests induced pigment dissocation

***Lucas B. Harrington***[1], *harringtonlb@wustl.edu, Hao Zhang*[1], *Michael L Gross*[1], *Robert E Blankenship*[1,2]*. (1) Department of Chemistry, Washington University, St. Louis, MO, United States (2) Department of Biology, Washington University, St. Louis, MO, United States*

Mass spectrometry of large protein complexes in their native form is a developing technology that holds enormous promise as a high-throughput tool for both structural biology and proteomics. Direct analysis of protein complexes in their near native form can provide stoichiometric as well as structural information. However, up to this point its application has largely been restricted to soluble complexes, due to the challenges posed by the requirement for detergent to stabilize membrane-bound complexes in solution. Here, we demonstrate the potential of this technology to characterize membrane-bound protein-pigment complexes, using purified reaction centers from the purple photosynthetic bacterium Rhodobacter sphaeroides as a model. Reaction centers were purified and solution conditions (including the concentration of the protein, ammonium acetate and detergent, as well as detergent type) were optimized. Following introduction of the complex into the gas phase via electrospray ionization, high energy was applied at both the source and collision cells in order to strip away bound detergent molecules. When total energy applied exceeded the optimal desolvation conditions, significant loss of pigment and pigment fragments was observed, suggesting partial unfolding of the complex. These developments open up native mass spectrometry to other membrane-bound photosynthetic complexes.



**RM_MWGL Regional Meeting 510**

## Effects of natural colloids on the adsorption of polycyclic aromatic hydrocarbons (PAHs) by multi-walled carbon nanotubes

***Yang Yang***[1], *rachel.yang.yy@gmail.com, Worlanyo E Gato*[1], *Henok D Abshiro*[1], *Jay C Means*[2]. *(1) Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States (2) College of science, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*

Carbon nanotubes (CNTs) have been widely used materials in both industry as well as in scientific research. These materials have special structures and functions. As a consequence of their pervasive use, their potential adverse effect on the environment is of concern to environmental scientist. For instance, CNTs may enhance the toxicity of polycyclic aromatic hydrocarbons (PAHs) after release to the environment due the fact that they are superior sorbents. In environmental water system, natural colloids widely exist. The interaction between natural colloids and CNTs may change CNTs' adsorption capacity of PAHs. This research investigates adsorption capacity of two different CNTs of PAHs namely, napththalene, phenanthrene and pyrene in water and in the presence of colloids. Adsorption capacity of two multi-walled CNTs was examined in the presence of pure water, 0.5 ppm and 20 ppm of selected PAHs. This is then followed by a study of the interaction between these two CNTs and natural colloids filtered from lake water. The adsorption of PAHs to CNTs equilibrated with colloids will also be determined. Gas chromatography mass spectrometry (GC-MS) was employed to quantify samples. Adsorption isotherms are then fit over the concentration ranges and PAHs analyzed. Results obtained from this planned study will enable the evaluation of the potential environmental impact of CNTs as sorbent materials. Also the nature of the interaction of the colloids with CNTs will be useful in determining their environmental applications. The present work is ongoing. We hope to generate enough data in a few months.

**RM_MWGL Regional Meeting 511**

---

## Study of Lignin by Pyrolysis GC - MS

***Vara Prasad R Sakampally***, *vara.sakampally@sdstate.edu, Raynie Douglas. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57006, United States*

Pyrolysis is one of the thermochemical routes to convert biomass into a useful primary energy sources, focusing dramatically to reduce, or even end, dependence on foreign oil, helping in the creation of a domestic bioeconomy. To achieve this objective, we are trying to produce bio-oil by pyrolysis of lignin produced from feedstocks like prairie cordgrass, miscanthus and switchgrass. The lignin produced by various extraction processes is pyrolyzed by using a pyroprobe and the effect of various factors like temperature, ramp rate, pyrolysis time, and catalyst during pyrolysis are investigated using GC-MS.

**RM_MWGL Regional Meeting 512**

## Analysis of dissolved methylmercury in environmental samples using Hg-complex ion chromatography: A reoptimized method with increased sensitivity and reduced noise

***Anthony C. Yerkes**[1], ayerkes2@illinois.edu, Robert J.M. Hudson[2]. (1) Department of Chemistry, University of Illinois, Urbana, IL 61801, United States (2) Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, IL 61801, United States*

Analysis of methyl mercury (MeHg) is extremely important due to the toxicological properties it holds and the effects it may have. The analysis is difficult due to ultratrace amounts of MeHg that tend to bond strongly to dissolved organic matter. The first part of the system uses thiourea (TU) as a catalyst to release the MeHg from the dissolved organic matter. The analytical method involves eluting a freshwater sample through the system using acidified TU. The MeHg is then analyzed using ion chromatography with cold-vapor atomic flourescence spectrometry detection. Before improvements made to the reagents, the method consistently contained results with sensitivities between 40 and 80. With changes to the reductant, made from KOH and $SnCl_2$, sensitivities increased consistently between 100 and 200. The vast improvement in sensitivity gives the opportunity for very small detection limits. Optimization within the reductant resulted in the improvement. The change in the reductant produced higher sensitivity, but also cleared up the formation of solids within the tubing. The tin concentration in the reductant was a large factor in solid formation and by reducing the concentration, the signal to noise ratio increased due to much smaller noise along the baseline of the chromatogram.

The increased signal to noise ratio allows for smaller detection limits leading to improved detection of MeHg in ultratrace amounts. This system has been used in an analysis study to determine amounts of MeHg in denitrifying bioreactors.

**RM_MWGL Regional Meeting 513**

## Photo-induced dissolution of metal ions from fly ash particles in a nitric acid media

***Nigar J. Hamid**[1], jasmine.hamid@lawrence.edu, Mulu A Kebede[1], Jonas Baltrusaitis[2], Juan G Navea[1]. (1) Lawrence University, United States (2) The University of Iowa, United States*

Fly ash is a particulate matter produced by coal-based power plants that provides a reactive surface for atmospheric heterogeneous processes. Fly ash have a large surface area and a variable chemical composition depending on the source of coal and the combustion process. The chemical composition of fly ash includes many photoactive species such as semiconductor metal oxides and light absorbing species. As a consequence, fly ash can influence the photochemistry of environmental species, such as nitric acid, adsorbed on its surface. In addition, reactions on fly ash surfaces

can cause the dissolution of the ash metal components into atmospheric water.

In this work, we carried out kinetic studies to better understand the photochemical reaction between fly ash and aqueous nitrates ($NO_3^-$). We reacted nitric acid with well-characterized fly ash from different regions, and followed the formation of nitrites ($NO_2^-$) and the leaching of metal ions. Studies were performed under dark conditions, simulated solar radiation, and 310 nm filtered light. The leaching of metal ions from fly ash was found to be affected by both the chemical composition of fly ash and the solar simulated radiation.

## RM_MWGL Regional Meeting 514

### Determination of reactive oxygen species in secondary organic aerosols produced from essential oils

***Megan Czerniejewski****, mdski89@siu.edu, Hardik Amin, Lin Wang, Matthew McCarroll, Kara Huff Hartz. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, IL 62901, United States*

Secondary organic aerosol (SOA) is formed from ozonolysis of monoterpene mixtures and has significant health effects. Toxicity may
be related to the formation of reactive oxygen species (ROS), which is a portion of the ozonolysis products. ROS content of atmospheric aerosols and SOA produced from single precursors have been measured, but it is not known how the composition of monoterpene mixtures impacts the toxicity. The goal of this work is to develop a fluorescence assay for ROS and to analyze filter samples that contain SOA generated from different monoterpene mixtures to determine the amount of ROS present. The fluorescence assay was adapted from Cathcart et al. and Venkatachari et al. The assay uses dichlorofluorescin as a probe, and it is oxidized by $H_2O_2$ and ROS using horseradish peroxidase enzyme to form a fluorescent product. Because there is no standard for ROS, $H_2O_2$ acts as a proxy for determining the ROS content for each sample. For method development, we tested several parameters that impact the quantitation of ROS. Individual components of the blank did not have any contribution towards this fluorescence. Incubation time was
also varied during this research and no significant difference was observed. Two sources of hydrogen peroxide were used: 3% Sigma-Aldrich and 3% United States Pharmacopeia purchased over-the-counter. However, there was no significant difference between the two sources of $H_2O_2$
SOA from filters was extracted with aqueous solution and ROS content was determined. The data shows that our ROS content is higher than expected, which explains why we overestimated the amount of SOA needed to give intensities that fit the calibration curve. Chen et al. found more ROS may form when there is excess ozone, which is similar to the conditions we used to generate the SOA.

## RM_MWGL Regional Meeting 515

## Evaluation of the reduction of nitric acid by humic substances

***Katie L. Boknevitz***, *katherine.l.boknevitz@lawrence.edu, Juan G. Navea. Department of Chemistry, Lawrence University, Appleton, WI 54911, United States*

Humic Substances (HS) are a complex mixture of organic compounds that can be found in the atmosphere as components of aerosols or suspended in water droplets. In addition, HS has been proposed as a source of the Dissolved Organic Matter (DOM) found in rainwater and fog. Because HS are both photoactive and oxidation-reduction-active species, these substances can affect the reduction of nitric acid ($HNO_3$), an important tropospheric compound and a powerful oxidizing agent, generating nitrites ($NO_2^-$). Since nitric acid is also activated by solar radiation, the chemistry of the interaction between HS and nitric acid could differ from daytime to nighttime. The present work contributes with the understanding of the formation of nitrites and DOM, with particular emphasis in the difference between day and night time reactions. Results suggest that oxidation-reduction reactions between HS and nitric acid can produce DOM and nitrites in solution and that, under simulated solar radiation, the rate of product formation is enhanced. The dependence with pH and concentration of nitric acid is also presented.

**RM_MWGL Regional Meeting 516**

## Increasing biochar surface area: Effects of various milling parameters

***Steve C Peterson***[1], *Steve.Peterson@ars.usda.gov, Michael A Jackson*[2]*, Sanghoon Kim*[1]*, Debra Palmquist*[3]*. (1) Plant Polymer Research, USDA - ARS - NCAUR, Peoria, IL 61604, United States (2) Renewable Product Technology Research, USDA - ARS - NCAUR, Peoria, IL 61604, United States (3) Midwest Area Biometrician, USDA - ARS - NCAUR, Peoria, IL 61604, United States*

Biochar produced from corn stover is a renewable, plentiful source of carbon that is a potential source of binder/filter media for water or beverage purification applications. However, to be successful in these applications, the surface area of the biochar must be maximized. In this work, a planetary ball mill was used to increase the surface area of the biochar, and various milling parameters were examined to see which had the largest effect on surface area. The weight ratio of milling media to biochar and the mass of solvent used in wet-milling were the most important milling parameters in maximizing surface area, increasing it by a factor of approximately 60 over unmilled biochar. Additionally, the method of salt-assisted dry-milling was tested and found to increase the surface area of biochar only moderately, but was superior for increasing the micropore surface area of the biochar.

**RM_MWGL Regional Meeting 517**

## Nanoparticles for Mercury Abatement

***Sunil K Thanikanti**, sunil_8714@yahoo.com, Patty K Fu. Department of Chemistry, Governors State University, University Park, IL 60484, United States*

The presence of mercury in the environment is a growing global concern. Electricity generation facilities around the world continue to rely on coal as an abundant and cost-effective energy source. As a result, mercury is released into the atmosphere.

Mercury is a serious toxin linked to developmental problems in children, along with increased health risks to people of all ages and global regulations continue to tighten as a result. One of the key challenges is that, when burned, coal produces two forms of mercury emissions which can typically not be captured by the same control technology.

To solve this difficult problem, we have developed a technology which can be a solution that enables a safer and cleaner method for disposing of the mercury. We believe that the mercury abatement technology we are working on has the potential to capture/decrease about 90 percent of the mercury emissions from all coal types.

**RM_MWGL Regional Meeting 518**

## Synthesis of isosorbide diallyl ether in presence of phase transfer catalysts

***Manmohan Deep Sandhu**, mssandhu@gus.pittstate.edu, Mihail Ionescu.Kansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas 66762, United States*

Isosorbideis a very interesting diol from renewable resources. It is obtained by double dehydration of sorbitol, a product derived from corn starch, in the presence of acid catalysts. Isosorbide has an assymetrical spatial structure with hydroxyl groups of different reactivities. One hydroxyl group having *endo* conformation is less reactive thanthe second hydroxyl group having *exo* conformation. The hydroxyl groups of isosorbide were alkylated by Williamsonreaction with allyl chloride or allyl bromide in the presence of solid KOH andtetrabutylammonium bromideas a phase transfer catalyst.The synthesized isosorbide diallyl ether was obtained in high purity (93-95%) and convenient yields of 65-70%, the unreacted isosorbide and isosorbide monoallyl ether were recycled in the process. The obtained isosorbide diallyl ether was characterized by iodine number, hydroxyl number, acid value, viscosity, density.The structure was confirmed by FT-IR, $^{1}$H NMR, $^{13}$C NMR,GPC, HPLC and GC-MS. Isosorbide diallyl ether is a di-olefinic monomer suitablefor the synthesis of bio-based crosslinked cast polymers, as a co-monomer forvarious crosslinked copolymers by radical polymerization and as co-monomer forthio-ene reactions.

**RM_MWGL Regional Meeting 519**

## Dynamics of zinc-seamed pyrogallolarene capsules: MD and QM/MM studies

***Kathryn E. Brewer**, kebhgf@mail.missouri.edu, Daniel J Shaughnessy, John E Adams.Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211-7600, United States*

Metal-seaming of organic macrocycles has been shown to yield robust nanocapsules, but uncertainties remain about the dynamics of guest species and how the presence of a guest influences the dynamics of the capsules themselves. We have carried out fully classical and QM/MM molecular dynamics simulations of zinc-seamed pyrogallolarene dimeric capsules, focusing on the development of reliable force field parameters for the unusual bonding environments found in these capsules and on the sensitivity of guest molecule motion to these parameter choices. Characterization of the guest dynamics will provide insight into the interpretation of NMR studies of the guests.

### RM_MWGL Regional Meeting 520

## Study of the Distribution and Quantity of Iodine in the Brine Waters of Northwestern Oklahoma

*Jason R. Wickham[1], **Eric C. Pribil**[1], hawker08@flash.net, Katherine A Drouhard[1], Darrell Mason[2]. (1) Northwestern Oklahoma State University, United States (2) Arysta LifeScience Technologies, United States*

In the late 1970's, it was discovered that the brine waters of northwestern Oklahoma contain significant amounts of Iodine (above 60 ppm). However, the exact amounts and distributions of Iodine throughout this brine water formation were unknown. Currently, the majority of the world's supply of Iodine comes from mining Iodate minerals in Chile (~ 65%), brine water aquifers in NW Oklahoma (~ 5%) and Japan (~ 25%), and seaweed extraction. With the growing need for Iodine compounds in the medical and agricultural fields the demand for Iodine is higher than ever. One example of this is the development of a new environmentally safe biodegradable fumigant (methyl iodide) developed by Arysta LifeScience Technology, which is currently poised to replace the non-biodegradable methyl bromide based fumigants. Thus, Arysta LifeScience Technology has recruited the aid of Northwestern Oklahoma State University to quantify the Iodine concentration and distribution throughout the brine aquifer, as well as, determine the longevity of these iodine concentrations. Currently, this has resulted in the discovery of three new sites within the aquifer that contain concentrations above 300 ppm and show that the iodine levels are currently steady within about a 5 ppm fluctuation.

### RM_MWGL Regional Meeting 521

## Abstract withdrawn

### RM_MWGL Regional Meeting 522

## The future of the chemical enterprise

***Joseph E. Sabol**, info@chem-consult.com. Joseph E Sabol, Chemical Consultant, Racine, WI 53408, United States*

The ACS Division of Small Chemical Businesses has objectives "To aid in the formation, development, and growth of small chemical businesses." SCHB helps chemists working in small enterprises, including self-employed, with the legal, social, educational, legislative, regulatory, and economic aspects of their unique professional status. SCHB serves as a clearinghouse of information, a forum for discussion, and a liaison between small businesses and students. SCHB has informative programs at ACS national and regional meetings, featuring small businesses and resources for small businesses, and provides valuable member-only content. See what SCHB is doing and what it can do for you. SCHB is only as strong as its members - contact an SCHB officer for more information on how you can join and help. SCHB: where all the elements come together for a successful chemical business.

**RM_MWGL Regional Meeting 523**

## Analytical sciences digital library – a unifying force for analytical science education

***Thomas Spudich**[1], tspudich@maryville.edu, Cynthia Larive[2]. (1) College of Arts and Sciences, Maryville University, St. Louis, MO 63141, United States (2) Department of Chemistry, University of California-Riverside, Riverside, CA 92521, United States*

The Analytical Sciences Digital Library (ASDL) is a collection of peer-reviewed, web-based resources related to chemical measurements and instrumentation. The collection is a freely accessible website at www.asdlib.org. Materials in the ASDL collection include active learning materials, animations, case studies, lecture slides, on-line texts, simulations, tutorials, and virtual experiments. Sites are categorized to allow for easy browsing or the collection can be searched using a keyword search function. Each web resource in the main collection of ASDL includes a detailed annotation describing the site and its useful attributes. In addition to providing annotated links to web-based content, the ASDL journal, JASDL, publishes online articles in the areas of e-Courseware, e-Labware, e-Educational Practices. Statistics provided by Google Analytics show a global reach with users from around the globe accessing ASDL.

ASDL is more than just a repository of information for the use of analytical chemistry teachers, students and practitioners; it is a site that fosters input and interactions among the analytical science education community. Interactions within the ASDL on-line community foster adaptation of curricular materials already posted on ASDL and development of new resources that can be shared with others. The ASDL on-line community goes beyond social networking to allow users to collaborate on projects, maintain their own blog spot, develop research and curriculum ideas, syllabi, and online texts, connect with colleagues, and work collaboratively in teams of students and/or faculty.

### RM_MWGL Regional Meeting 524

## Medicinal chemistry: Too much to learn in one semester?

***Haizhen Zhong***, *hzhong@unomaha.edu, Victoria Mashinson, Theodor A Woolman. Department of Chemistry, University of Nebraska at Omaha, Omaha, NE 68182, United States*

Medicinal chemistry for professional pharmacy students and medicinal chemistry majoring graduate students is generally a two-semester course. Due to increasing demand on biomedical studies, medicinal chemistry has been offered as a one-semester course to undergraduate students. The health-oriented nature of this course has made it practical and attractive. However, the interdisciplinary nature challenges both students and instructors. Here we report our efforts to incorporate molecular modeling and the top sale drug molecules into our curriculum to study the molecular properties of clinical drugs. Students were asked to draw three-dimensional structures of drug molecules in MOE, a molecular modeling program and to calculate and study their physicochemical properties. It's a satisfying experience for students to learn the complicated physicochemical properties of clinical drugs. This study at the same time also suggests recent research directions of medicinal chemistry.

### RM_MWGL Regional Meeting 525

## Use of in-situ generated *o*-iodoxybenzoic acid (IBX) for oxidation of alcohols: An introduction of undergraduates to hypervalent iodine reagents, catalytic cycles and green chemistry

*Meredith Bertels, Chris LeFever, Kishor K Madne, Sonali R. Pandey, Swetha V. Saraf, Amanda Vanoskey, Lauren Zeman, Jin Jin,* ***Thottumkara K. Vinod****, mftkv@wiu.edu.Department of Chemistry, Western Illnois University, Macomb, IL 61455, United States*

A green oxidation procedure for oxidation of alcohols using catalytic amounts of in-situ generated *o*-iodoxybenzoic acid (IBX) in presence of Oxone as a stoichiometric oxidant is developed. Catalytic amount of commercially available 2-iodobenzoic acid is used as the organoiodine precursor for IBX in the reaction. This convenient procedure for the oxidation of alcohols, completed in a 2.5 h laboratory period, is carried out in aqueous solvent mixtures and involves product isolation by filtration of the crystallized carboxylic acid product. Students are introduced to several pedagogically relevant green chemistry principles including the use of aqueous reaction medium, non-extractive product isolation procedure, and the use of benign and catalytic reagents in this convenient oxidation experiment. Finally, this experiment also allow instructors to discuss the use of

IBX and other hypervalent iodine reagents as benign alternatives to commonly used and frequently discussed transition metal based reagents.

### RM_MWGL Regional Meeting 526

## Preparation of divalent Fe, Co, and Ni tosylate salts

*Hung Nguyen[1], C Joshua Ema[3], Timothy H Ema[1,4],* ***Philip J Janini**[1]*, *pjjm84@mail.umsl.edu, Yuanzhu Zhang[1], Nigam Rath[2], Stephen M Holmes[1,2]. (1) Department of Chemistry and Biochemistry, University of Missouri-Saint Louis, Saint Louis, Missouri 63121, United States (2) Center for Nanoscience, University of Missouri-Saint Louis, Saint Louis, Missouri 63121, United States (3) Lutheran High School South, Saint Louis, Missouri 63123, United States (4) McLuer High School, Florissant, Missouri 63031, United States*

A synthetic procedure appropriate for high school and undergraduate chemistry courses is described. Use of expensive glassware and equipment has been eliminated and the procedures optimized to produce large, colored crystals in reasonable yield (ca. 20 %) within 1-2 lab periods. The high school module introduces techniques including refluxing, filtration, and crystallization. The experiment also introduces students to redox chemistry, reactivity of d block metals, and basic spectroscopy. Undergraduates can further characterize the product by UV/vis and IR spectroscopy, magnetic susceptibility measurements, and single crystal x-ray diffraction. Preparation of an N,N-dimethylformamide adduct is also described using schlenk line techniques. The experiment also provides undergraduates with a physical system to observe redox chemistry, crystal field splitting and its effects on spectra.

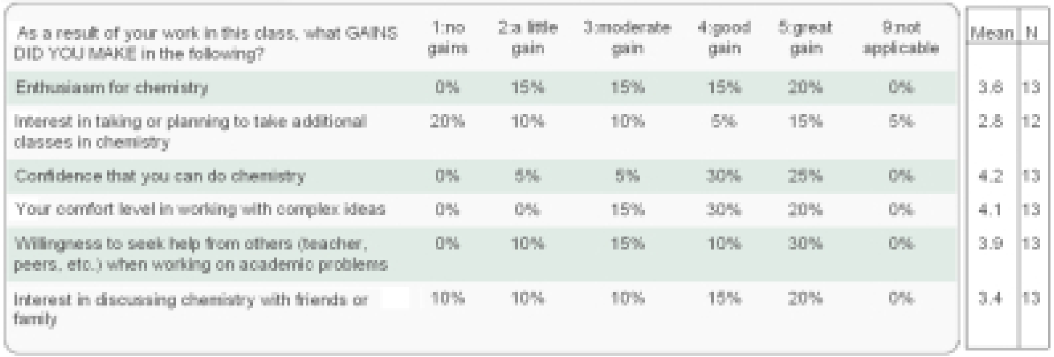
### RM_MWGL Regional Meeting 527

## Guided inquiry laboratory projects built upon endothermic reaction demonstrations

*Andrew O Ward,* ***Richard L Petersen**, rlpetrsn@memphis.edu. Department of Chemistry, University of Memphis, Memphis, TENNESSEE 38152, United States*

We have developed a collaborative, guided inquiry laboratory project for General Chemistry students based on the demonstration of two endothermic reactions between solids. The first has barium hydroxide octahydrate, ammonium chloride, and phenolphthalein provided as solid unknowns which, when mixed together in a sealable bag as prescribed, turn into a red liquid at a dramatically lowered temperature accompanied by evolution of a gas. The second has solid citric acid monohydrate and sodium bicarbonate reacting in a minimal volume of water which generates a cold, effervescent solution. Students pool and compare their observations on solubility, conductivity, acid/base properties, and mutual interactions of the unknowns, then collaboratively propose, design, and carry out further characterization experiments over the next three periods. Qualitative analysis of the salts and pH and spectroscopic

analysis of the indicator give rise to further quantitative analytical experiments largely based on techniques and concepts learned earlier in the laboratory course. A writing team produced a single class report summarizing the collective research, the class discussion, and conclusions that could be drawn. Students' learning gains and attitudes about chemistry were assessed through surveys



| As a result of your work in this class, what GAINS DID YOU MAKE in the following? | 1:no gains | 2:a little gain | 3:moderate gain | 4:good gain | 5:great gain | 9:not applicable | Mean | N |
|---|---|---|---|---|---|---|---|---|
| Enthusiasm for chemistry | 0% | 15% | 15% | 15% | 20% | 0% | 3.6 | 13 |
| Interest in taking or planning to take additional classes in chemistry | 20% | 10% | 10% | 5% | 15% | 5% | 2.8 | 12 |
| Confidence that you can do chemistry | 0% | 5% | 5% | 30% | 25% | 0% | 4.2 | 13 |
| Your comfort level in working with complex ideas | 0% | 0% | 15% | 30% | 20% | 0% | 4.1 | 13 |
| Willingness to seek help from others (teacher, peers, etc.) when working on academic problems | 0% | 10% | 15% | 10% | 30% | 0% | 3.9 | 13 |
| Interest in discussing chemistry with friends or family | 10% | 10% | 10% | 15% | 20% | 0% | 3.4 | 13 |

## RM_MWGL Regional Meeting 528

## Impact of the first-year implementation of process oriented guided inquiry learning in an organic chemistry course on students' attitudes and learning

***Tony Chase**, tonychase@gmail.com, Marilyne Stains. Department of Chemistry, University of Nebraska Lincoln, Lincoln, NE 68588, United States*

Research has shown that poor teaching in college science courses is one of the main reasons for students to leave the science pipeline. Finding a way to engage students and better foster the learning environment is essential to keeping students interested in pursuing careers in Chemistry. Process Oriented Guided Inquiry Learning (POGIL) is an emergent instructional method, in which students are engaged in solving complex, multifaceted chemistry problems as a team. Several research studies have shown the effectiveness of POGIL on student learning but few have reported short-term impact on learning and on students' attitudes toward chemistry, their learning environment, and their self-efficacy toward chemistry. The goal of this study was thus to evaluate these issues within the context of a first-year trial of this pedagogy. Specifically, POGIL was implemented for the first time in two-thirds of the recitations of an organic chemistry course at a public university in the fall of 2010. Students' changes in attitudes about chemistry and their learning environments and changes in their self-efficacy towards chemistry were evaluated through two surveys - The Attitude toward the Subject of Chemistry Inventory (ASCI), and the Chemistry Attitudes and Experiences Questionnaire (CAEQ) – which were collected at the beginning and end of the semester. Analysis of the ASCI survey for non-POGIL students revealed an 11% increase in fear towards chemistry as a field of study while POGIL students' fear did not change. A similar trend was observed with anxiety, in which non-POGIL students reported 9% more anxiety towards chemistry than POGIL students. The new pedagogy also favorably impacted attendance in discussion. However, no impact on learning as measured by exam grades was observed. Limitations to the implementation that may explain this result will be discussed along with results from the analysis of the CAEQ survey.

### RM_MWGL Regional Meeting 529

## Modifying POGIL to Improve Student Perception of Relevance of Organic Chemistry

***Ehren Bucholtz**, ebucholtz@stlcop.edu. Division of Basic and Pharmaceutical Sciences, St. Louis College of Pharmacy, St. Louis, MO 63110, United States*

A problem facing chemical education is the perceived irrelevance of chemistry to the everyday lives and future careers of non-major students taking those courses. The perceived lack of relevance may be rooted in how we teach it. Focus is placed on chemical principles that need to be learned while minimizing their applications to the students' future endeavors. Chemistry becomes a set of ideas to be memorized and recalled rather than understood and applied. Without application practice, students may not internalize the concepts to use them in future learning or professional settings.

One methodology that has been used to increase learning outcomes in the organic chemistry curriculum is Process Oriented Guided Inquiry Learning (POGIL). POGIL uses the learning cycle format and constructivist theory to help students learn key concepts, but models and data presented may not apply to real life situations.

Baseline data was obtained using the Individual Development and Educational Assessment (IDEA) Teaching Evaluation form which assesses student perception of: a) progress on learning objectives, b) instructor excellence, c) course excellence, and d) relevance to real life situations. The POGIL only methodology used in an organic chemistry course produced student perceptions in the bottom 30% of chemistry courses contained in the national IDEA database. To increase relevance of the course, a problem was added to each class day that could be answered with the concepts being covered with the day's POGIL based materials. These were presented as “Who gives a darn?” questions. Over a three year period, this change resulted in increased ratings on the IDEA evaluation, culminating in a course evaluation in the highest 10% of chemistry courses in the database.

### RM_MWGL Regional Meeting 530

## Development and implementation of streaming online media to enhance pre-lab instruction in first semester organic chemistry laboratory courses

***James T Fletcher**, jamesfletcher@creighton.edu. Department of Chemistry, Creighton University, Omaha, NE 68178, United States*

This presentation will describe the recent usage (2007-2010) of streaming online media to enhance the delivery of pre-lab instruction for first semester Organic Chemistry

Laboratory at Creighton University. In 2007, consumer-grade hardware and software products were utilized to capture and edit video footage for preparing online streaming media modules corresponding to five different experiments performed in Creighton University's *CHM 321: Organic Chemistry Laboratory I* course. Featuring dynamic footage of experimental techniques combined with background information, this approach aimed to both improve delivery of pre-lab instruction and reallocate limited lab time. Using iMovie and Flip4Mac software, six media streams ranging from 10-15 minutes each corresponding to five different experiments were made available for student viewing via Creighton's Winstream server. Implementation of this instructional resource has varied by instructor over the past four years, including viewing during pre-lab lecture time or student viewing outside of pre-lab lecture time, coupled with or without traditional lecturing. Assessment of student opinions indicated that they felt viewing this media significantly improved their preparation for performing experiments. Instructor assessment indicated students viewing the media streams worked with increased confidence and competence relative to prior years without this resource. This institutionally well-regarded method of pre-lab instruction has impacted more than 1200 students over the past four years, and this integrated technological approach is likely amenable to a variety of laboratory courses that emphasize instruction of hands-on techniques. The motivation behind this project, the tools used to create the streaming media, the implementation of such media, the results of student assessment of such media and examples of the finished product will be presented.

**RM_MWGL Regional Meeting 531**

## Comparison of phenanthrene and 1,10-phenanthroline derivatives as potential sensors

***Jackson J. Whitcomb****, jackson.j.whitcomb@wmich.edu, Lars Kohler, Sherine Obare, Elke Schoffers.Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008-5413, United States*

1,10-Phenanthroline is a well-known ligand for supramolecular chemistry. For example, we found that the introduction of 2-aminopyridine in the 6-position caused a change in absorption when it was titrated with diethyl chlorophosphate. In order to identify the binding mechanism we investigated the role of the diimino moiety of 1,10-phenanthroline through comparison with related phenanthrene derivatives.

**RM_MWGL Regional Meeting 532**

## The Viscosity Lowering of Ionic Liquids

***Brad Anderson****, baanderson9096@jacks.sdstate.edu, Douglas E Raynie. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57007, United States*

The process for fermentation of biomass to create biofuels involves the fractionation of the biomass to isolate the carbohydrates. Fractionation of the biomass separates the biomass into its three major components: cellulose, lignin and hemicellulose. One way to fractionate the biomass is by the use of ionic liquids. However, ionic liquids have a high viscosity, making the separation of the fractionated biomass more difficult. The ionic liquids 1-ethyl-3-methylimidazolium acetate (Emim Ac), Emim benzenesulfonate, Emim toluensulfonate, Emim xylenesulfonate and Emim alkylbenzenesulfonates (a mixture of the toluene and xylene sulfonates) were investigated as ionic liquids of interest. The research performed was aimed at lowering the viscosity of each ionic liquid by two methods. The first method involved increasing the temperature over a temperature range of 25 to 100°C and the second method involved the addition of a less viscous solvent, dimethyl sulfoxide (DMSO). The importance of this research is that it will allow the process of fractionating biomass to become more efficient, which will directly benefit biofuels production.

### RM_MWGL Regional Meeting 533

## The effect of 1-methyl-3-butylimidazolium tetrafluoroborate BMIMBF$_4$ ionic liquid as mobile phase additive on the peak shapes and resolution of nitroaromatics and nitroanilines on reversed phase liquid chromatography

***Bartlomiej Redlinski***, *b-redlinski@wiu.edu, Tarab Ahmad, Tariq Ahmad, Craig Utterback.Chemistry, Western Illinois University, Macomb, IL 61455, United States*

The identification of explosives and their degradation products is important in forensic and environmental applications. Complete separation of these structurally similar compounds using reversed-phase liquid chromatography has proven to be a challenge. Room temperature ionic liquids RTILs are salts with melting points at or close to room temperature. They are good solvents, highly polar, environmentally benign, nonvolatile, nonflammable, and stable in air or water. Because of these particular properties, they are currently, of considerable interest in the separation and analysis. RTILs can be used to adjust the selectivity as well as to enhance the resolution by improving the peak shapes. In the present work we will investigate the effect of using BMIM salts as a mobile phase additives on the retention behavior, peak shapes and resolution of the explosives using two C$_{18}$ reversed phase columns.

### RM_MWGL Regional Meeting 534

## The effect of counter ion of 1-methy,3-butyl imidazolium ionic liquid as a mobile phase additive on the adsorption behavior of tryptophan on reversed phase liquid chromatography

***Tarab Ahmad***, *tj-ahmad@wiu.edu, Bartlomiej Redlinski, Ahlam Alalwiat.Chemistry, Western Illinois University, Macomb, IL 61455, United States*

Ionic liquids (IL) or room temperature ionic liquids (RTIL) are a type of salts that are liquid at low temperature(100$^{o}$C). Common ionic liquids, are composed of 1,3-dialkylimidazolium and 1-alkylpyridinium cations combined with $Cl^{-}$ /$AlCl_3$,, $BF_4{}^{-}$ (TFB), $PF_6^{-}$ (HFP), and $NO_3^{-}$ anions. Because RTIL are good solvents for both inorganic and organic materials, they are non-volatile, nonflammable, thermally stable, and recyclable solvents. Currently they are being investigated widely as “green chemistry” solvents. In this study two ionic liquids that contains the 1-methyl, 3-butyl imidazolium (MBMIM) salts with different counter-ions; chloride and tetrafluoroborate are investigated as a mobile phase additive for the adsorption behavior of tryptophan on reversed phase liquid chromatography. The adsorption isotherms were determined by the frontal analysis method and the adsorption data are fitted to a Langmuir model. An excellent agreement was found between the experimental overloaded band profiles and t the calculated profiles.

### RM_MWGL Regional Meeting 535

### Analysis of Color Degradation in Paper and Artwork Using VISNIR

***Jeffrey Cornelius**, jeff.cornelius@principia.edu, Brian Kamusinga. Department of Chemistry, Principia College, Elsah, Illinois 62028, United States*

An undergraduate lab was written to monitor the effects of sunlight or other interactions that alter the appearance of paper color. We analyzed the changes after the paper was exposed to sunlight in varying amounts and showed how this can be applied to the study of the degradation, protection restoration of art work. In this study, different types and colors of paper were exposed to direct sunlight, and the rate and state of degradation was quantitatively measured using a USB4000 VISNIR spectrometer from Ocean Optics between 350-1000 nm.Additionally the instrument can also be used to observe the emission lines of gas spectral tubes and the
spectral profiles of different sources of light.

### RM_MWGL Regional Meeting 536

### Determination of phenol concentration in spiked wastewater samples through multivariate regression modeling of UV-visible spectral data

***Emily Gripka**, ingle88@stmary.edu, Mariah Vaughn, Jemima Ingle. Department of Natural Sciences and Mathematics, University of Saint Mary, Leavenworth, Kansas 66048, United States*

The Environmental Protection Agency (EPA) designates 126 pollutants as priority pollutants, mandating acceptable levels for wastewater; many others are regularly monitored. One such pollutant, phenol, is acceptable at levels less than 0.3 ppm. In this paper, we describe continuing studies in the development of a method for determining concentration of phenol in wastewater using multivariate regression modeling of UV-visible spectral data. Although established methods currently exist for these

determinations, these methods involve time-consuming, costly, and/or environmentally unfriendly complexation steps. The goal of this project is to devise a more efficient and cost-effective method of determining the concentration of these pollutants.

Previous work had demonstrated the viability of this technique for samples of phenol in distilled water and tap water. In this study, samples of effluent wastewater were taken from a local wastewater plant. These samples were analyzed for their phenol content, and the samples were then spiked with additional phenol. The UV-visible spectrum of each sample was obtained, and the spectral data subjected to a PLS-1 regression analysis. The regression models were used to predict the concentration of phenol in unknown samples. The results of these studies continue to be promising, showing RMS absolute errors of less than 1. This paper will discuss the methods and results for the compounds and conditions studied to date.

**RM_MWGL Regional Meeting 537**

## Characterization of tannins from *Quercus actissma* leaf extracts by LC-ESI-MS and bioassay directed HPLC fractionation

***Lawrence Rudolf**[1], james.chapman@rockhurst.edu, Christina Zanaboni[2], Kaela Severa[2], Chad M Scholes[2], James M Chapman[1]. (1) Chemistry, Rockhurst University, Kansas City, Missouri 64110, United States (2) Biology, Rockhurst University, Kansas City, Missouri 64110, United States*

Hydrolyzable and condensed tannins are representatives of a large group of polyphenolic compounds found in plants. There is great speculation as to the importance and function of these secondary metabolites in plant-predator relationships. The identification of and characterization of these molecules from plant materials could greatly increase the likelihood of elucidating a role and mechanism of action. Fresh green and wintered leaves from *Quercus actissma* (Sawtooth Oak) were extracted with a solution of methanol:water. The extract was concentrated and subjected to semi-preparative HPLC to fractionate the chemical constituents. Fractions were examined by several assay methods and those of interest were analyzed by LC-ESI-MS to characterize the tannins present. The primary fractions were further separated by analytical HPLC in an attempt to isolate single tannins for further evaluation in the bioassays. Initial results have indicated that while the whole leaf extracts are bioactive not all subsequent fractions possess activity in the assays, thereby indicating selectivity for certain chemical constituents with regards to biological activity.

**RM_MWGL Regional Meeting 538**

## HDXMS reveals folding of calcineurin upon binding calmodulin

***Farai I Rusinga**[1], rusingaf@ku.edu, Trevor Creamer[2], David D Weis[1]. (1) Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States (2)*

*Department of Molecular and Cellular Biochemistry, University of Kentucky, Lexington, Kentucky 40536, United States*

Calcineurin is a protein phosphatase involved in the regulation of cellular processes via calcium signaling. This enzyme is highly conserved from yeast to man and is the only Ser/Thr phosphatase known to be under $Ca^{2+}$/calmodulin control. Calcineurin possesses a regulatory domain to which calmodulin binds upon elevation of intracellular calcium and is thereby activated. The regulatory domain consists of an intrinsically unfolded protein segment comprising the calmodulin binding region and an auto-inhibitory domain. Calmodulin binding induces folding in this region that provides free energy to displace the auto-inhibitory domain thereby exposing the calcineurin catalytic site. The folding is proposed to involve the formation of an α-helix within the calmodulin binding domain, a conformational change known to occur in other calmodulin-binding partner interactions.

Using HD exchange mass spectrometry, we have shown that the unbound regulatory domain of calcineurin is indeed unstructured but adopts structure when calmodulin binds to it. Analysis of peptic digest fragments of the regulatory domain reveal that complete amide backbone H/D exchange occurs within 5s in the absence calmodulin. This results shows that all labile hydrogens are exposed to deuterium exchange within this time frame. Introducing a two-fold excess of calmodulin in the presence of $Ca^{2+}$ induces protection from exchange within the binding domain. Even after 24hrs of exposure to deuterating conditions a significant proportion of labile hydrogens remain un-exchanged. Peptide fragments adjacent to and C-terminal of the binding domain also show evidence of protection. This suggests that structuring is not only restricted to the binding domain but, to some extent, other regions of the regulatory domain.

These data will contribute towards elucidating the mechanism of calcineurin activation and more broadly, highlighting the importance of intrinsically unfolded proteins.

## RM_MWGL Regional Meeting 539

### Characterization of the chemical constituents of Chinese and Korean Jakyak root and correlation to medicinal activity

*Isabella Fuentes, **Natasha Frost**, james.chapman@rockhurst.edu, James M Chapman.Chemistry, Rockhurst University, Kansas City, Missouri 64110, United States*

The Korean Jakyak root, Paeoniae Radix (PR), is the root of the white peony plant, *Paeonia lactiflora* Pallas. Jakyak is a traditional Korean medicinal plant that is often used to treat common colds as well as liver diseases in China. Additional claims include its ability to open the lungs, calm coughing, and that it possesses anti-tumor activity, neuroprotective antioxidants, and anti-inflammatory properties. The purported medicinal activities of Korean Jakyak root were correlated with the chemical constituents analyzed by GC-MS and compared with that of Chinese Jakyak root (Bai Shao Yao). The samples for analysis were obtained by utilizing the traditional Korean tea method of preparation which involves steeping the root in hot water. Liquid and headspace samples of both teas were collected and analyzed to reveal medicinally relevant compounds with regards to antimicrobial, anti-inflammatory, and analgesic properties. The Korean and Chinese roots both possessed constituents of medicinal importance, but did not have complete overlap in the compounds identified.

**RM_MWGL Regional Meeting 540**

## Optimization of ETD parameters for top-down proteomics analysis with an ultrahigh-resolution QTOF mass spectrometer

***James R. Unverferth***[1,2]*, jrubr9@mail.missouri.edu, Justin B. Sperry*[2]*, James A. Carroll*[2]*. (1) Biochemistry Department, University of Missouri, Columbia, MO 65211, United States (2) BioTherapeutics Mass Spectrometry, Pfizer, Chesterfield, MO 63017, United States*

Top-down proteomics is a contemporary MS-based method used to characterize intact proteins and their inherent post-translational modifications. The top-down MS approach is advantageous because minimal sample preparation is required, minimal sample is consumed, and data collection and analysis is rapid. Electron Transfer Dissociation (ETD), an emerging tandem MS (MS/MS) technique in top-down proteomics, has been recently adapted to the ultrahigh-resolution Bruker Daltonics maXis QTOF mass spectrometer. ETD is advantageous over other MS/MS techniques because it does not cleave post-translational modifications from the protein backbone, allowing for site-specific characterization. As well, ETD is more efficient than collision-induced dissociation at fragmenting the higher charge states that intact proteins exhibit upon analysis by electrospray ionization. The purpose of the experiments was to determine the optimal ETD parameters, such as analyte accumulation time, reagent injection time and extended reaction time, to yield the most extensive (and interpretable) protein fragmentation results. Proteins of different molecular masses ranging from 8 kDa up to 60 kDa were investigated in order to identify common trends in the results. The various ETD parameter sets and corresponding data were evaluated via TD Mascot (Matrix Science) database searches such that the “scores” were correlated to the total amino acid sequence coverage and the number of contiguous peptide bond cleavages. Ultimately, we want to create a templated ETD-based protein sequencing and characterization approach for the laboratory.

**RM_MWGL Regional Meeting 541**

## Method development for structural characterization of sulfated steroids with mass spectrometry: Applications in animal communication

***Yuetian Yan***[1]*, yuetianyan@go.wustl.edu, Timothy Holy*[2]*, Michael L Gross*[1]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Anatomy and Neurobiology, Washington University in St. Louis, School of Medicine, St. Louis, MO 63110, United States*

The general class of sulfated metabolites found in female mouse urine provides important ligands for the pheromone-sensing neurons. Of those compounds, two of the highest amounts were previously structurally characterized with Mass Spectrometry and NMR to be sulfated steroids. Given that the physical and chemical properties of the large number of unknown compounds are similar, it is reasonable to propose that there are more communicants that have the sulfated steroid ring structure. Here, we describe our efforts to develop mass-spectrometry tools to resolve the structures of those sulfated steroids. Because these compounds occur in trace amounts, it is unlikely that we will isolate sufficient amounts for NMR. Thus, MS methods may be the primary approach for determining structure.

Using 4-pregnene-11β,21-diol-3,20-one 21-sulfate as a standard compound, we explored different mass spectrometric approaches, including high-resolution mass spectrometry (HR-MS), H/D exchange followed by ESI mass spectrometry, tandem mass spectrometry, high-resolution tandem mass spectrometry, and gas chromatography mass spectrometry (GC/MS). We included GC/MS because steroids undergo rich fragmentation by EI although we had to derivatize first the sulfate group, the carbonyl group, and the hydroxyl group. The derivatization was successful for nanomoles of sample. ESI-MS with direct infusion, done in the negative-ion mode, required only tenths of nanomole of sample. With this mass spectrometry kit of structural tools, we are now able to determine the chemical formula of a compound by HR-MS. Following that, we obtained an EI spectrum by GC/MS, and this spectrum could be searched in the steroid database, leading to several structure candidates. Combining this information with that from tandem MS, where the ring structure can be well characterized by its rich fragmentation, a possible structure of the compound can be proposed.

**RM_MWGL Regional Meeting 542**

## Focusing of bacteria and fungi from mixed samples using the isotachophoresis mode of capillary electrophoresis

***James Bennett**, bennjame@mail.gvsu.edu, Andrew W. Lantz. Department of Chemistry, Grand Valley State University, Allendale, MI 49401, United States*

In this experiment we attempt to use the isotachophoresis mode of capillary electrophoresis to focus and potentially separate bacterial and fungal species. Isotachophoresis is typically used in biochemistry to concentrate and separate protein samples based on their electrophoretic mobilities as compared to the other components in a multi-electrolyte system. The same basic principle may be applied to the analysis of whole cells by exploiting their differences in size and surface charges. Different bacteria such as gram positive and gram negative have different surface characteristics as well as being vastly different from that of fungi. By focusing the cells into distinct zones based on these surface characteristics it would be possible to differentiate between species and thus have a fast and inexpensive test to determine the cause of sample contamination. Initial data shows success in focusing individual samples of gram

positive (*Bacillus subtilis*) and gram negative bacteria (*Escherichia coli*), as well as single celled fungi (*Candida albicans*) in a two electrolyte system. In this system, the cells themselves act as a third “electrolyte” component which is highly focused between the leading and terminating electrolytes. Cell focusing typically was accomplished in under 10 minutes of isotachophoresis. Current work focuses on the separation of these model species in a mixed bacterial or fungal sample. This may be accomplished by utilizing an electrolyte system with increasing numbers of components having mobilities that “bracket” each species in the sample. The speed of this test could potentially allow for faster analysis in many settings such as medical centers, food processing facilities, and water treatment plants.

**RM_MWGL Regional Meeting 543**

## Binding Studies of Dopamine Imprinted Polymers

***Alexander Goffeney***, *alexander.goffeney@usiouxfalls.edu, Drew Goede, George Mwangi. Department of Chemistry, University of Sioux Falls, Sioux Falls, SD 57105, United States*

The goal is to form a polymer that is dopamine specific in its nature. This dopamine specific polymer can be introduced to a system, both chemical and biological to detect and extract dopamine from the system. Clinical significance in this study aids in the research of various brain disorders such as Parkinson's and Schizophrenia. In these experiments, dopamine is introduced to a solution containing various functional monomers and cross-linkers. The subsequent reactions form molecularly imprinted polymers (MIP). After the MIP has been formed the application 4:1 methanol: acetic acid removes the template from the MIP. Once the template is extracted the now empty MIP is introduced to the system containing dopamine to determine its rebinding capacity. The template removal led to an extraction of 85 percent of the template with 4:1 methanol: acetic acid. When the polymers are washed in 4:1 methanol: water, only 62 percent of the template was extracted. The polymers synthesized from itaconic acid (ITC) and trimethylolpropane trimethacrylate (TRIM) demonstrated the greatest ability to rebind to dopamine.

**RM_MWGL Regional Meeting 544**

## Hydrogen-deuterium exchange mass-spectrometry study of troponin C dynamics and binding within the troponin complex

***Richard Yu-Cheng Huang***[1], *ryhuang@wustl.edu, Brady J. Summers*[2], *Henry W. Rohrs*[1], *Michael L. Gross*[1]. *(1) Department of Chemistry, Washington University in St. Louis, United States (2) Department of Chemistry, University of Missouri-Kansas City, United States*

The troponin protein complex is part of the thin filament in striated muscle myocytes (along with tropomyosin and actin) and plays a regulatory role in muscle contraction by

binding calcium ions released by nerve impulses. The relationship between troponin complex and muscle contraction disorders has implications in cardiac-related diseases. The complex is composed of three subunits; troponin C (TnC), the calcium binder; troponin I (TnI), the inhibitor; and troponin T (TnT), the anchor and structural support. We used solution phase hydrogen/deuterium exchange (H/D exchange) monitored by mass spectrometry at both the global and peptide level to understand better the structural dynamics within the rabbit skeletal troponin complex. We determined that the major affecter of structure in calcium-activated TnC is TnI, and that TnT plays only a minute role in the structure of TnC. We also compared the binding affinity between TnC and TnI in the presence or absence of TnT by using PLIMSTEX (protein-ligand interaction by mass spectrometry, titration, and H/D exchange). Given that there are two interaction sites between TnC and TnI, our titration curves, when fit with 1:2 binding model, yield two binding constants: $K_{a1}= (2.1 \pm 0.1) \times 10^{6}\ M^{-1}$; $K_{a2}= (2.7 \pm 0.6) \times 10^{3}\ M^{-1}$. The product of these values agrees with the affinity of intact TnI and TnC ($\sim 10^{9}\ M^{-1}$) reported previously. The outcomes further confirm that TnT has little effect on the binding between TnC and TnI and demonstrate the utility of H/DX in protein biophysics.

**RM_MWGL Regional Meeting 545**

## Characterization of human apolipoprotein E3 and E4 isoforms' interactions with amyloid β42 by the mass spectrometry-based FPOP protein footprinting method

***Brian Gau***[1]*, briancgau@gmail.com, Kanchan Garai*[2]*, Carl Frieden*[2]*, Michael Gross*[1]*.*
*(1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Biochemistry and Molecular Biophysics, Washington University School of Medicine, St. Louis, MO 63110, United States*

The amyloid beta peptide 1-42 (Aβ42) may be the most important biomolecule implicated in Alzheimer's disease (AD) pathogenesis. Cerebral plaques comprised of the insoluble fibrillar form of this peptide are found in all patients diagnosed with AD. The soluble oligomers of Aβ42 are neurotoxic. The amyloid hypothesis suggests that the clearance of this peptide in the brain is central to affecting the likelihood of AD onset. One protein known to interact with this peptide in its fibrillar and soluble forms is apolipoprotein E (apoE). Strikingly, the apoE4 isoform of this protein confers a 12-fold greater risk for AD for people with two copies of this allele than for people with no copies. The molecular characterization of Aβ42 interaction with apoE isoforms has thus been an important goal of many studies; owing to the oligomeric properties of these biomolecules, no high resolution structure of the complex or of the WT isoforms of apoE exist. We have used the fast photochemical oxidation of proteins (FPOP) method of mass spectrometry-based protein footprinting to provide an intermediate-resolution picture of the Aβ42 interaction with apoE4 and the more common apoE3 isoform. We find that both proteins exhibit Aβ42 binding in their N-terminus domains, involving residues W34 and Y36, and R167. Proline 293 is also involved in a C-terminal domain interaction in apoE3, but the overall footprinting signals in the C-terminal domain suggest that this interaction is not as strong as the N-terminal domain. These results are consistent with several studies which have examined the N- and C- domain interactions with Aβ using domain-truncated apoE.

### RM_MWGL Regional Meeting 546

## Correlation of Mass Spectrometric Analysis of Heat-Treated Glutaraldehyde Preparations to Their 235 nm/280 nm UV Absorbance Ratio

***Atish D Sen***[1], *sena@abclabs.com, Richard Dunphy*[1]*, Ian Handley*[2]*, Ron Dieck*[2]*,*
*Leonard Rosik*[1]*. (1) ABC Laboratories, Inc., Columbia, Missouri 65201, United States*
*(2) Tenaxis Medical, Mountain View, CA, United States*

The 235 nm/280 nm UV absorbance ratio (UV Ratio) is widely used as a measure of the degree of polymerization of glutaraldehyde. Conventional practice is to measure the UV absorbance of bulk material at 235 nm (C=C absorption) and at 280 nm (C=O absorption). Gel permeation chromatography of preparations of heat-treated glutaraldehyde (HTGA) did not have sufficient mass discrimination to explain the variation in the UV Ratio of HTGA. Preparations of HTGA were analyzed by direct infusion ion trap mass spectrometry (IT-MS) and time of flight mass spectrometry (TOF-MS). Structures were assigned to the masses found. The structures of the UV-absorbing species were used to calculate absorbance contributions from each species found in the preparations at greater than 5% relative abundance. The contributions were weighted and summed. A MS-based 235 nm/280 nm ratio was calculated and compared to the experimentally determined 235 nm/280 nm ratio for the HTGA preparations. A very good correlation was obtained.

### RM_MWGL Regional Meeting 547

## Localized Structural Analysis of CBP with Millisecond Timescale Hydrogen Deuterium Exchange MS

***Theodore R. Keppel****, trkeppel@ku.edu, David D. Weis. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

The hydrogen/deuterium exchange mass spectrometry (H/D-MS) technique is useful for studying protein conformation and dynamics, especially for proteins with extended regions which lack stable structure in solution. Using H/D-MS, the protein is diluted in a large excess of deuterium oxide buffer for a specific length of time. The exchange of amide hydrogens for deuterium is quenched by a rapid decrease in pH and temperature. When the sample and buffers are mixed by hand, exchange kinetics can be measured starting from about a minimum of 3-5 seconds of $D_2O$ exposure. To detect residual structure in highly disordered or molten globular proteins, rapid mixing of sample with deuterium oxide and quench, as possible with a stopped or quench-flow mixer, allows for millisecond-scale exchange times. Here, we present the construction and validation of a syringe driven, quench-flow mixing apparatus to study deuterium exchange kinetics of CREB binding protein (CBP). Protein sample is combined with

deuterium oxide in a 1:20 ratio in a micro-T. This deuterated sample then flows through the delay line and into a second micro-T which mixes in the acidic quench solution. The flow of these solutions is driven by a single syringe pump. Eluent is collected in a centrifuge tube held in liquid nitrogen for rapid freezing and storage. The reaction time is calibrated using the base-catalyzed hydrolysis of benzylidenemalononitrile, a pseudo-first-order reaction. H/D-MS information is localized along the protein sequence by using a peptic digest prior to introduction of deuterated sample into the ionization source. Our mass spectrometry analysis of deuterium exchange labeled CBP reveals the properties of residual structure in the protein.

## RM_MWGL Regional Meeting 548

### UHPLC-MS-MS analysis of pesticides in aqueous environmental samples: An educational outreach program

***Mitchel T. Popko****, mtpopko@jacks.sdstate.edu, Randy E. Jackson, Brian A. Logue. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota Box 2202, SAV 131, Brookings, SD 57007, United States*

When pesticides are used for agricultural purposes, they can make their way into nearby water sources. These pesticides are not only harmful to the insects or plants they are intended to kill, but can also cause unintended harm to other species. A UHPLC-MS-MS method for the simultaneous detection of 12 pesticides in environmental water samples was developed, for use in an undergraduate laboratory setting. By using this method, students are exposed to a powerful analytical technique and the importance of Analytical Chemistry in determining water quality. Environmental water samples were prepared by filtering with a 0.22 µm nylon syringe filter prior to UHPLC-MS-MS analysis. The chromatograms of spiked water samples showed well-defined peaks for each pesticide of interest. The method was then applied to a non-spiked environmental water sample from six mile creek in Brookings County, SD several pesticides were identified including ametryn, atrazine, and propazine. The method will be used by undergraduate Analytical Chemistry students to analyze water samples of interest submitted by high school students from the region.

## RM_MWGL Regional Meeting 549

### Paper-based microfluidic devices in colorimetric tests

***Michelle E Clevenger****, michelleclevenger@creighton.edu, Kalani Parker, Connor Neuville, Erin Gross. Department of Chemistry, Creighton University, Omaha, NE 68178, United States*

Paper-based microfluidic devices are portable, cost-effective means for on-site diagnosis. The devices are ideal for in-field testing and in limited-resource locations. We adapted a literature procedure for incorporation into an undergraduate teaching laboratory. We show the fabrication process of the devices from wax printing and the optimization of the design. The design of each device enables two bioassays to be simultaneously run. The two bioassays detect disease states related to glucose and protein content in urine. The colorimetric reactions were quantified with Adobe Photoshop software to produce standard curves, allowing for unknown samples to be quantified. This process was converted into a microfluidics experiment for the quantitative analysis laboratory in which students diagnosed an unknown artificial urine sample. Students made standard solutions of glucose and protein in ranges relevant to the disease state. Students also prepared the microfluidic devices by spotting each test zone with the appropriate colorimetric reagent. The data was analyzed visually and electronically via Adobe Photoshop. The results were accurate and reasonable for quantitative analysis students. This experiment creates a multi-disciplinary atmosphere in which students are exposed to chemical analysis, bioanalytical chemistry, medicine and the social issues involved in healthcare disparities.

This work was funded by a Creighton University College of Arts and Sciences Summer Faculty Development Grant and by the Ferlic Summer Research Program.

**RM_MWGL Regional Meeting 550**

## Alternative fragmentation pathways of a model glycopeptide

***Venkata Karthik Kolli***, *venkata.kolli@huskers.unl.edu, Eric D Dodds.Department of Chemistry, University of Nebraska Lincoln, Lincoln, Nebraska 68588, United States*

Structural analysis of glycoproteins has always been a challenging problem. The use of tandem mass spectrometry (MS/MS) to identify glycopeptides derived from proteolysis of a glycoprotein is one of the most important approaches for characterizing protein glycosylation. However, there remains a need to better understand the varied MS/MS fragmentation behaviors of glycopeptide ions in order to maximize the analytical value of these experiments. Here, we have studied the collision-induced dissociation (CID) behavior of a model glycopeptide derived from coral tree (*Erythrina cristagalli*) lectin. The lectin was digested with trypsin to yield a mixture of peptides and glycopeptides. The glycosylated fraction of peptides was then enriched using HILIC-based solid-phase extraction. The glycopeptide preparation was then analyzed by MS and MS/MS using a Waters Synapt G2 HDMS instrument. MS/MS experiments were performed on the glycopeptide [SKPAQGYGYLGVFNNSK + 2 GlcNAc + 3 Man + Fuc + Xyl] under a variety of conditions. For example, CID of the triply protonated ion of this glycopeptide was performed at a number of different collision energies. These energy-resolved CID results depicted a remarkable pattern in cleaving both the carbohydrate group and the peptide group, thus allowing determination of both the glycan connectivity and the full peptide sequence. This finding is intriguing, given that this glycopeptide ion has been well-studied in the past and was not previously found to exhibit significant peptide backbone fragmentation. The present data indicate that the peptide backbone fragment ions are products of secondary dissociation, produced by glycan elimination, followed by the fragmentation of the peptide. These results suggest that choice of CID collision energy can be tuned to yield orthogonal information regarding the glycopeptide

sequence. Ongoing efforts are aimed at determining the effects of charge state and charge carrier on the dissociation of this model glycopeptide.

## RM_MWGL Regional Meeting 551

### Gas-phase release and sequencing of subunits from non-covalent protein complexes

***Deepali Rathore***, *deepali@huskers.unl.edu, Eric D. Dodds. Department of Chemistry, University of Nebraska, Lincoln, Lincoln, Nebraska 68588-0304, United States*

In recent years, mass spectrometry (MS) has become a valuable tool for measuring masses and subunit stoichiometries of non-covalent protein complexes. The gas-phase dissociation of these protein assemblies via tandem mass spectrometry (MS/MS) can further support subunit stoichiometry assignments and can, in some cases, yield information on the arrangement of subunits within the complex; however, subunit sequence information must usually be determined in a separate experiment. Here we show, for two well-studied non-specific protein dimers (glucagon, monomer mass 3.5 kDa; and cytochrome C, monomer mass 12.4 kDa), that subunit sequence information can be directly obtained from the protein aggregate in a single gas-phase experiment. This was accomplished using stepwise stages of collision-induced dissociation (CID) in combination with ion mobility (IM) separation. Solutions of the two proteins were nanosprayed to give gas-phase ions using a home-built nanoflow electrospray ionization (ESI) source operated in static mode. MS, MS/MS, and IM were performed using a Waters Synapt G2 HDMS instrument. Quadrupole selection of the glucagon dimer (5+ charge state) or cytochrome C dimer (11+ charge state) was followed by CID-IM-CID-TOF analysis. This strategy allowed dimers to first be separated into monomers, which were then separated by IM. The monomers were then further fragmented in a second stage of CID, resulting in b and y ions that were consistent with the known monomer sequences. Hence, this approach shows promise for sequencing subunits directly from unknown protein complexes. Future work will focus on extending this strategy to the identification of protein subunits from biologically relevant assemblies using top-down proteomics approaches.

## RM_MWGL Regional Meeting 552

### HPLC method to monitor methylcarbonate/acid reaction progress

***Erika E. Arens***, *duane.weisshaar@augie.edu, Sarah J.M. Jamison, Duane E. Weisshaar, Gary W. Earl. Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

Methylcarbonate quaternaries are produced by a green reaction in which the anion is cleanly exchanged by reacting methylcarbonate with an acid. In aqueous solution, methylcarbonate is converted to bicarbonate which reacts similarly. An anion-exchange HPLC method employing indirect detection was developed. Two unidentified interfering

peaks were present when 0.5 mM sodium naphthalene disulfonate (NDS) in 20% methanol/water was used as the mobile phase. The pH of the mobile phase was increased to avoid the interference, but the pH was difficult to reproduce and did not circumvent the interference. The interfering peaks disappeared when the NDS concentration was lowered to 0.25 mM. Samples dissolved in methanol produced a split peak for bicarbonate. A bicarbonate calibration curve was linear for 25 to 750 µM.

## RM_MWGL Regional Meeting 553

## Investigation of methylcarbonate/acid reaction as a function of pKa

***Kai T. Jacobson**, duane.weisshaar@augie.edu, Nicholas A. Sveiven, Duane E. Weisshaar, Gary W. Earl. Department of Chemistry, Augustana College, Sioux Falls, SD 57197, United States*

Methylation of 3° amines with dimethyl carbonate provides a green synthesis of quaternary ammonium compounds (quats). Reaction of the resulting methylcarbonate anion with acids provides a clean route for exchange of the anion on the quat. This study examined the rate of exchange as a function of pKa. Phenol (pKa 9.99) required 20+ hours to reach completion even with a continuous purge of $N_2$ to remove $CO_2$. Anion HPLC proved to be more sensitive for following the reaction than NMR, but HPLC column efficiency deteriorated significantly after several injections. Reaction of alanine (pKa 9.87) occurred at a similar rate, but HPLC column efficiency also deteriorated after several injections. Freshly prepared methylcarbonate quat was required to eliminate the efficiency problem. The reaction rate for acids with pKa 10 is too slow to be practical. Future work will examine the rates for slightly stronger acids.

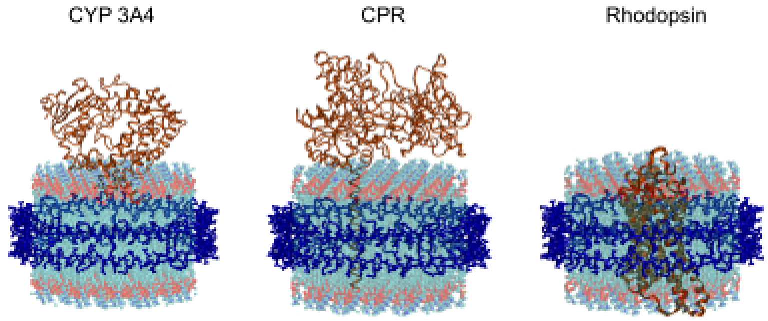
## RM_MWGL Regional Meeting 554

## MALDI mass spectrometry of membrane proteins in Nanodiscs

***Michael T. Marty**[1], mmarty2@illinois.edu, Aditi Das[2,5], Stephen G. Sligar[1,2,3,4]. (1) Deptartment of Chemistry, University of Illinois Urbana-Champaign, Urbana, IL 61801, United States (2) Deptartment of Biochemistry, University of Illinois Urbana-Champaign, Urbana, IL 61801, United States (3) Center for Biophysics and Computational Biology, University of Illinois Urbana-Champaign, Urbana, IL 61801, United States (4) College of Medicine, University of Illinois Urbana-Champaign, Urbana, IL 61801, United States (5) Department of Comparative Biosciences, University of Illinois Urbana-Champaign, Urbana, IL 61801, United States*

Over the last decade, Nanodiscs have emerged as a leading technology for solubilizing membrane proteins for structural, functional, and enzymatic studies. Nanodiscs are nanoscopic, self-assembled lipid bilayers encircled by membrane scaffold protein (MSP) belts. They provide a platform for analyzing membrane proteins in a native-like lipid membrane environment and have been used with a wide range of analytical techniques.

Conventional methods for MALDI mass spectrometry of full-length membrane proteins in Nanodiscs are severely limited by strong MSP signal and weak signal from the membrane proteins. This is likely due to higher concentrations of MSP and interference from lipids surrounding the protein. We present here an optimized ultra-thin layer sample preparation technique, which enhances membrane protein signal and nearly entirely suppresses MSP signal. The suppression effect is investigated further with different matrices, first shot MALDI experiments, and MALDI mass spectrometry imaging. We show that this method can be successfully applied to Nanodiscs containing membrane proteins of different sizes and membrane topologies, and we apply this ultra-thin layer method to mixtures of membrane proteins in Nanodiscs. These results demonstrate the general applicability of this method and open new possibilities for future structural and functional mass spectrometry studies of membrane proteins in Nanodiscs.



## RM_MWGL Regional Meeting 555

## H/DX-Mass Spectrometry Study of Amyloid beta (Ab 1-42) peptide oligomer

***Ying Zhang***[1,2], *ying.zhang@go.wustl.edu, Liviu Mirica*[2], *Michael Gross*[1,2]*. (1) Center for Biomedical and Bioorganic Mass Spectrometry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Amyloid deposits involving various proteins are composed of fibrils that may be responsible for several diseases. For example, amyloid beta (Aβ) peptide has well known implications in Alzheimer's disease. There are several forms of Aβ peptide of which Aβ (1-42) is the most neurotoxic and disease-related. Recent evidence suggests that oligomers populated during fibril assembly are more responsible for the neurotoxicity. Identifying the oligomer interfaces could be the basis for drug design to prevent oligomerization. To understand better the oligomerization of Aβ (1-42), we applied hydrogen-deuterium exchange (H/DX) and mass spectrometry to different forms of Aβ peptide. In all experiments, pre-oligomerized peptide was diluted in $D_2O$ buffer

(PBS, pH 7.4). Then, the exchange was quenched by lowering the pH to 2.5 and the temperature to 4℃. Information at the peptide level was achieved by digesting online with pepsin and analyzing by LC/MS (Agilent 1200 Series LC, Bruker MaXis Q-TOF mass spectrometer). We studied the oligomerization at different temperatures (4℃ vs 25℃) and observed no difference in H/DX at 4˚C in 30 hours. This indicates that Aβ(1-42) does not undergo significant oligomerization at this temperature. At 25˚C, however, H/DX extent decreases dramatically as time increases, indicating that Aβ (1-42) undergoes oligomerization and possibly aggregation within 30 min with accompanying conformational changes or increases in protection. The results show that H/DX coupled with MS may be an important tool for understanding the oligomerization and aggregation of various proteins.

## RM_MWGL Regional Meeting 556

### Investigating insulin oligomers by native spray H/D exchange and top-down mass spectrometry

***Yining Huang**, yininghuang@wustl.edu, Weidong Cui, Michael L Gross. Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Human insulin can form various oligomers, and this property is dictates whether diabetes treatment must have a slow or fast response. By utilizing an online HDX native-spray device in conjunction with FTICR MS, we can introduce oligomers to gas phase, isolate (purify) them, and submit them to electron-capture dissociation (ECD). Thus, instead of measuring an average pattern contributed by all the oligomers presented in the solution, we can interpret the oligomer-specific deuterium incorporation at the single amide-bond level and provide insight into the oligomer interface.

The apparatus was constructed by connecting two syringes to a three-way junction, one syringe holding a deuterated sample and another some $H_2O$ buffer. Reaction times were controlled by using variable flow rates and various lengths of tubing. MS and MS/MS analysis were done on a Bruker 12 T SolariX FTICR mass spectrometer.

*r*-Humaninsulin at 5 μM nanosprayed from 10 mM ammonium acetate $H_2O$ buffer (pH=7.4) gave mainly monomer ions; ECD without isolation cleaved disulfide bonds effectively and gave full coverage for B-chain. Consecutive c and z ions indicate that 80% of the residues on B-chain can be resolved. At 1M, the insulin monomer, dimer, trimer and hexamer can be readily and simultaneously introduced to the gas phase; the monomer and dimer could be isolated and fragmented, affording spectra from which mass shifts of single residues could be resolved, showing the presence of D/H at individual amide linkages. Both monomer and dimer showed distinctive patterns of deuterium incorporation, suggesting conformational changes upon dimerization and the interface of protein-protein interaction.

## RM_MWGL Regional Meeting 557

### Phthalocrowns: New macrocycles for metal binding

***Ingrid-Suzy Tamgho**, it7@zips.uakron.edu, Christopher J Ziegler. Department of Chemistry, The University of Akron, Akron, Ohio 44325, United States*

Crown ethers and phthalocyanines are both important molecules in organic and coordination chemistry. With regard to metal coordination, crown ethers can selectively bind alkali and alkali earth metal ions based on size for organic solvent applications, and the metal complexes of the phthalocyanines have many uses in materials applications. In this poster, we present a new class of molecules we call the phthalocrowns, which can be considered as fusions between the crown ether and phthalocyanine macrocycles. These compounds are synthesized via Schiff base-type condensation reactions between polyetherdiamines and diiminoisoindoline or phthalonitrile (catalyzed based). Alternatively, we can generate these compounds from trichloroisoindoline and from phthalonitrile. We are currently producing macrocycles with two and three ether groups appended to diiminoisoindoline, and are characterizing these compounds with methods including X-ray crystallography. *The purpose of this project is then to study the ability of these new molecules to bind cations, including main group and/or transition elements.*

### RM_MWGL Regional Meeting 558

### Effect of different oxidants on epoxidation of alpha olefines

***Jian Hong**, jhong@pittstate.edu, Darin DeGruson, Zoran S. Petrovic.Kansas Polymer Research Center, Pittsburg, Kansas 66762, United States*

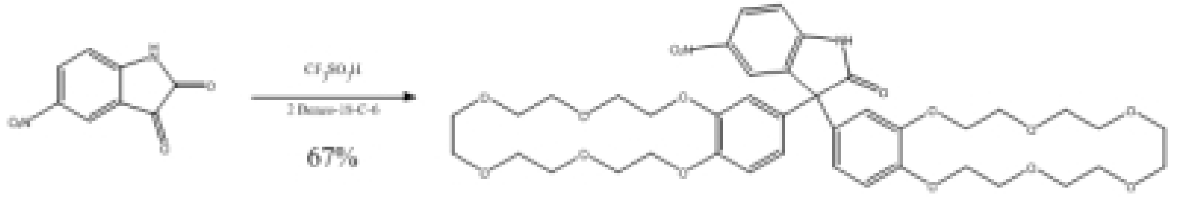
Although epoxidation of internal double bonds such as in vegetable oils is a well controlled process, the preparation of epoxidized terminal olefins in high yield is challenging due to side reactions. We investigated epoxidation of 1-decene as a model compound using different peroxides and catalysts as well as different reaction conditions. The systems used were acetic acid/$H_2O_2$/Amberlit 120H, peracetic acid, m-chloroperbenzoic acid and $H_2O_2$/methyltrioxorhenium. The products were characterized with FT-IR and the yields were measured by epoxy oxygen content (EOC) and gas chromatography (GC). Both EOC and GC results showed that m-chloroperbenzoic acid is the best oxidant for epoxidation of 1-decene.

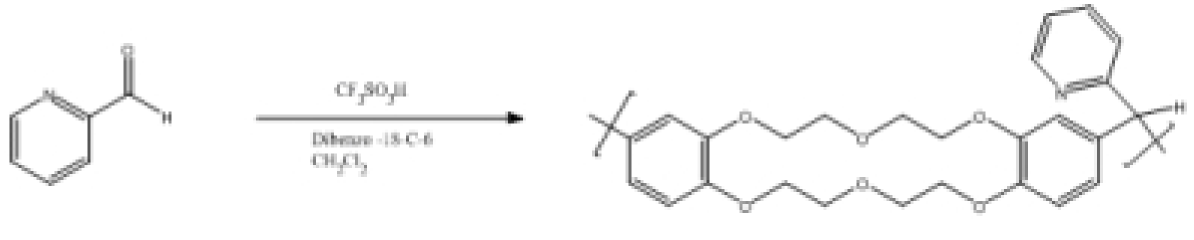
### RM_MWGL Regional Meeting 559

### Utilizing the hydroxyalkylation reaction to prepare bis(benzocrown ethers)

***Matt E Zielinski**, mz4000@gmail.com, Adam F Tracy, Douglas A Klumpp*.Chemistry and Biochemistry, Northern Illinois, De Kalb, Illinois 60115, United States*

The hydroxyalkylation reaction can be used to condense benzo crown ethers with an array of aldehydes and ketones. These hydroxyalkylation reactions are catalyzed by sulfuric or trifilic acid. The products from the reactions are bis(benzocrown ethers) and they are formed in good yields. Furthermore we can exploit this hydroxalkylation reaction to generate polymers using dibenzocrown ethers and various ketones and aldehydes.





## RM_MWGL Regional Meeting 560

## Fluorinated dienes in the Diels-Alder reaction

***Nasim Ehterami***, *nehtera@siue.edu, Timothy Patrick.Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026, United States*

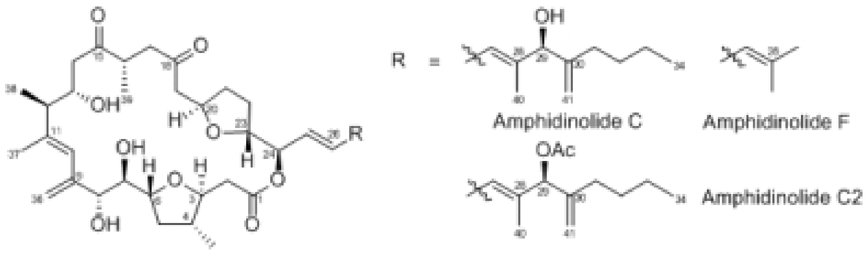
Compounds with one or more fluorine have become importnat in medical chemistry. The Special nature of fluorine imparts a variety of properties to medicine, including enhanced binding interactions, metabolic stability, chnage in physical properties. Here, as it is shown Diels-Alder reaction occure to combine 1-benzylidene-3-oxopyrazolidine-1-ium-2-ide and fluoro butenone to yield N-hetrocycles. [Figure 1]

## RM_MWGL Regional Meeting 561

## Synthesis of the C(10)-C(17) unit of amphidinolides C, C2, & F, potent cytotoxic macrolides

***Sudeshna Roy***, *srb5c@umsl.edu, Christopher D. Spilling. Department of Chemistry & Biochemistry, University of Missouri-St. Louis, St. Louis, Missouri 63121, United States*

The amphidinolides are an important family of 36 unique anti-tumor macrolides. They are isolated from a symbiotic marine dinoflagellate *Amphidinium sp.* found in Okinawan aceol flatworms in Japan. Amphidinolide C, one of the most cytotoxic molecules in this family, exhibits *in vitro* cytotoxicities against murine lymphoma and human skin cancer cells in the nano-molar range. Surprisingly, amphidonolides F and C2, which have the same core structure of amphidinolide C but vary merely in the side chain structure, are about 1000-fold less active. Hence, the diversity in the structure of the side chains can be instrumental in determining the biological activity. Herein, we present our ongoing synthetic efforts toward amphidinolides C, C2 and F with emphasis on the synthesis of the western fragment (C10-C17) from commercially available (*S*)-roche ester.



## RM_MWGL Regional Meeting 562

## Application of 6,7-indolyne aryne cycloaddition and Pd(0)-catalyzed Suzuki-Miyaura and Buchwald-Hartwig cross-coupling reactions for the preparation of annulated indole libraries

*Paul D. Thornton[2], Neil Brown[1,2], David Hill[2], Ben Neuenswander[2], Gerald H. Lushington[2], Conrad Santini[2], **Keith R. Buszek**[1,2], buszekk@umkc.edu. (1) Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110, United States (2) Center of Excellence in Chemical Methodologies and Library Development, University of Kansas, Lawrence, KS 66047, United States*

The construction of an unprecedented class of an indole-based library, namely, a 6,7-annulated-4-substituted 93-member indole library, using a strategic combination of 6,7-indolyne cycloaddition and cross-coupling reactions under both Suzuki-Miyaura and Buchwald-Hartwig conditions is presented. This work represents the first example of library development that employs the indole aryne methodology. Annulated indoles, with the exception of only a few biologically active natural products (i.e., the trikentrins, herbindoles, teleocidins, and nodulisporic acids), have no representation in the PubChem or MLSMR databases. These structural entities are therefore predicted to have unique chemical property space characteristics and a high probability of exhibiting interesting biological activity.

## RM_MWGL Regional Meeting 563

## 1,10-Phenanthroline derivatives as potential organophosphate sensors

***Marcus N. Moses***, *marcus.n.moses@wmich.edu, Lars Kohler, Sherine Obare, Elke Schoffers. Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008-5413, United States*

The goal of this project was to modify the substituents in the 5- and 6-position of 1,10-phenanthroline and to study whether hazardous organophosphates could be detected. The molecules were prepared via nucelophilic addition of different aromatic amines to 1,10-phenanthroline-5,6-epoxide which served as key intermediate. Fluorescence measurements were conducted with diethyl chlorophosphate (DCP). A molecule derived from 2-aminopyridine displayed interesting changes in absorption during the titration of the analyte.

**RM_MWGL Regional Meeting 564**

---

## Synthetic studies of dipyrromethene ligand systems for the discovery of manganese (III)-based peroxynitrite decomposition catalysts

***Andrew Kamadulski***[1], *wneuman@siue.edu, Smita Rausaria*[1], *Daniela Salvemini*[2], *William L Neumann*[1]. *(1) Pharmaceutical Sciences, Southern Illinois University Edwardsville School of Pharmacy, Edwardsville, IL 62026, United States (2) Pharmacology and Physiology, St. Louis University, St. Louis, MO 63104, United States*

We have shown that Mn(III)-bishydroxyphenyldipyrromethene complexes are potent orally active peroxynitrite reductase catalysts in vivo. Preliminary results reveal that these complexes operate via a 2-electron mechanism for the reductive decomposition of peroxynitrite. Thus, Mn(III) species are oxidized to the Mn(V)oxo form with concomitant reduction of peroxynitrite to the relatively innocuous nitrite. Our current work involves the synthesis of new functionalized dipyrromethene ligand systems for continued structure-activity relationship (SAR) studies. Herein we describe our recent synthetic progress, SAR work and in vivo studies of the resulting Mn(III) complexes in models of inflammatory pain, neuropathic pain and opioid analgesic tolerance (conditions known to be driven by the overproduction of peroxynitrite).

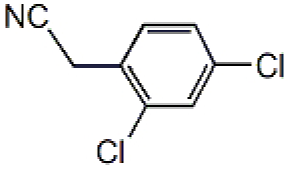
**RM_MWGL Regional Meeting 565**

---

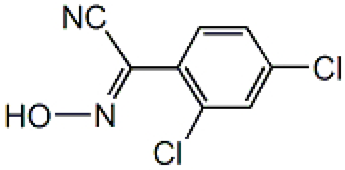
## Preparation, characterization and *Human Carbonyl Reductase* (HCBR) inhibition studies of 2,4-dichlorophenyl-cyanoxime, H(2,4-diCl-PhCO)

*Michael Hilton*[1], ***Nikolay N. Gerasimchuk***[1], *NNGersaimchuk@MissouriState.edu, Henry Charlier*[2]. *(1) Department of Chemistry, Missouri State University, Springfield, Missouri 65897, United States (2) Department of Chemistry and Biochemistry, Boise State University, Boise, Idaho 83725, United States*

A high-yield synthesis of 2,4-dichlorophenyl-cyanoxime from respective 2,4-dichlorophenyl-acetonitrile was developed using room temperature nitrosation reaction with gaseous methylnitrite. The cyanoxime was characterized by spectroscopic ($^{1}$H,$^{13}$C NMR, IR-, UV-visible) methods and X-ray analysis. The H(2,4-diCl-PhCO) adopts non-planar *trans-anti* geometry in a solid state. Colorless cyanoxime in solutions forms pale-yellow anion upon addition of a base. The H(2,4-diCl-PhCO) was found to be very potent uncompetitive inhibitor of HCBR at the level of 10-12 micromoles. The HCBR is responsible for development of cardiotoxicity and resistance during the anticancer treatment using antracycline drugs.



**2,4-diCl-Ph**



**H(2,4-diCl-PhCO)**

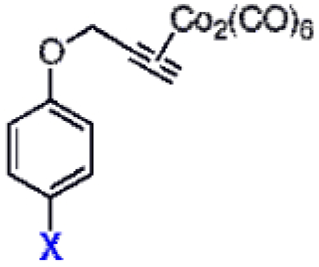
## RM_MWGL Regional Meeting 566

## Organometallic anticancer compounds: Synthesis and biological activity of a new class of simple alkyne hexacarbonyl dicobalt complexes

***Stefan L. Debbert***, *debberts@lawrence.edu, Sydonie D. Schimler, Meareg G. Amare. Department of Chemistry, Lawrence University, Appleton, WI 54911, United States*

While platinum complexes such as cisplatin find wide use in cancer chemotherapy, organometallic chemistry still provides an underscreened population of compounds with potentially interesting medicinal properties.

Recently, some alkyne hexacarbonyl dicobalt complexes have been found to exhibit notable anticancer activity. In order to investigate the role of the organometallic complex in this bioactivity, we have designed and synthesized several novel cobalt-alkyne complexes. These compounds were obtained easily by reacting dicobalt octacarbonyl with propargyl aryl ethers and other alkynes. Cobalt-alkyne complexes are known to stabilize positive charge on an adjacent carbon, as in the Nicholas reaction; to probe whether this charge stabilization is important in the bioactivity of this class of compounds, we varied the electron distributions of the compounds by appending either electron-donating or electron-withdrawing moieties onto the aromatic ring. After their synthesis and characterization, these cobalt-alkyne compounds were assayed for antiproliferative activity against MDA-MB-231 and A549 cell lines. The most active of our compounds rival cisplatin for antiproliferative activity. Furthermore, the trend in antiproliferative activity among the compounds derived from *p*-substituted propargyl aryl ethers indicates that charge stabilization by the cobalt-alkyne complex may be important in the bioactivity of these compounds.



| X | IC$_{50}$ (MDA-MB-231) |
|---|---|
| H | 10.3 μM |
| Br | 8.9 μM |
| CN | 5.3 μM |
| NO$_2$ | 1.8 μM |

## RM_MWGL Regional Meeting 567

## Synthesis of several ionic liquid perbromides for the regioselective bromination of polyalkylated aromatic hydrocarbons

***Michael L Miller***, *michaelmiller@creighton.edu, Michael J Kulig, Adam Zeiszler. Department of Chemistry, Creighton University, Omaha, Nebraska 68178, United States*

Ten novel ionic liquid ammonium perbromides were successfully synthesized and characterized using NMR, IR and mass spectroscopies. Of these, two show a high degree of regioselectivity for the bromination of dialkylated arenes at either the *α*,*α*′-benzylic or isomeric aromatic positions, providing a new and efficient synthetic pathway for the preparation of tetrabrominated *o*-xylene derivatives, important building blocks for the construction of larger polycyclic aromatic hydrocarbons. The bromination of buckminsterfullerene using several of the liquid perbromides is also described.

## RM_MWGL Regional Meeting 568

## Investigation of ruthenium complexes, with the introduction of a novel chiral phopshinooxazoline ligand, to be employed as a catalyst in the Mukaiyama Aldol reaction

***Nichole Curvey***, *nsck95@mail.umsl.edu, Andria Widaman, Eike Bauer. Dept. of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

The versatility of oxidation states as well as the inherent stability of ruthenium has made it a widely researched transition metal utilized as a catalyst for organic reactions. Previously the synthesis of sterically and electronically tuned P^N bidentate phosphinooxasoline (PHOX) ligands have been optimized. The work displayed here will show the synthetic pathway from easily accessed amino acids to the PHOX ligands (L) shown in **Figure 1**. A new method of oxazoline formation allows the synthesis of $L^e$, with a phenyl group alpha to the oxygen, and ruthenium complexes of the architecture [RuCl$_2$L$_2$] shown in **Figure 2** will be presented. X-Ray crystallographic analysis revealed that the phosphorus is trans to the nitrogen of the opposite ligand in the isomer isolated.

The surprising dynamics of these complexes will also be discussed. Finally, the best catalytic results were obtained for the Mukaiyama Aldol reaction when $AgPF_6$ or $Et_3OPF_6$ was used to extract two, rather than one chloride ion.

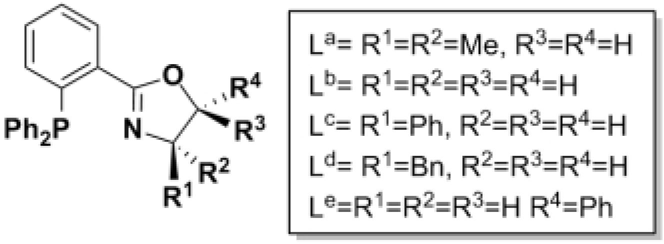


**Figure 1.** Phosphinooxazolines synthesized

$L^a$= $R^1$=$R^2$=Me, $R^3$=$R^4$=H
$L^b$= $R^1$=$R^2$=$R^3$=$R^4$=H
$L^c$= $R^1$=Ph, $R^2$=$R^3$=$R^4$=H
$L^d$= $R^1$=Bn, $R^2$=$R^3$=$R^4$=H
$L^e$=$R^1$=$R^2$=$R^3$=H $R^4$=Ph

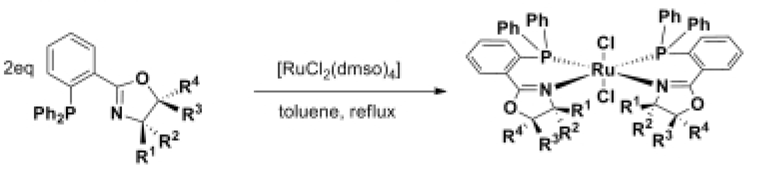


**Figure 2.** Ruthenium complexes synthesized

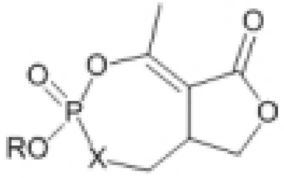
## RM_MWGL Regional Meeting 569

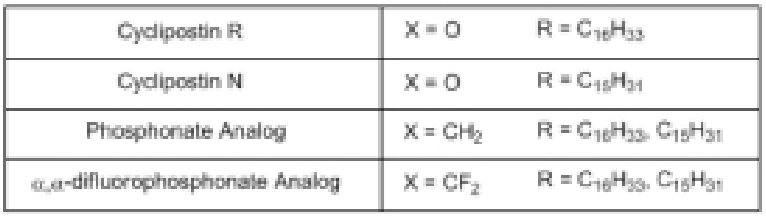
## Structure-activity relationship studies of the cyclipostins and their analogs: A means of probing hormone sensitive lipase active site morphology toward the development of new inhibitors

***Benjamin P. Martin**, bpmfzf@mail.umsl.edu, Christopher D. Spilling.Department of Chemistry & Biochemistry, University of Missouri - St. Louis, St. Louis, Missouri 63121, United States*

Hormone sensitive lipase (HSL) is a key enzyme in the breakdown of stored lipids in adipose tissue and freeing fatty acids for metabolism. Because of the role of elevated free fatty acid plasma levels in insulin resistance, inhibition of HSL has been targeted as an alternative means of regulating type II diabetes. The cyclipostins are a family of bicyclic phosphate triesters which inhibit HSL at nanomolar concentrations. By exploring the importance of their structural motifs on binding and inactivation, much can be learned about the structure of HSL's active site and toward the design of a more ideal inhibitor. This process has been initiated by preparation of various structural analogs of the cyclipostins. Synthesis of phosphonate analogs has been accomplished, and that of

α,α–difluorophosphonate analogs is currently underway.





| | | |
|---|---|---|
| Cyclipostin R | X = O | R = $C_{16}H_{33}$ |
| Cyclipostin N | X = O | R = $C_{15}H_{31}$ |
| Phosphonate Analog | X = $CH_2$ | R = $C_{16}H_{33}$, $C_{15}H_{31}$ |
| α,α-difluorophosphonate Analog | X = $CF_2$ | R = $C_{16}H_{33}$, $C_{15}H_{31}$ |

## RM_MWGL Regional Meeting 570

## Influence of aromatic amines on the spectroscopic properties of 1,10-phenanthroline

***Kim Lien Huynh**, kim.l.huynh@wmich.edu, Sherine Obare, Elke Schoffers. Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008-5413, United States*

The B-ring of 1,10-phenanthroline was functionalized by introducing different aromatic amines such as aniline, 1-naphthylamine, and 1,5-diaminonaphthalene via nucleophilic addition to 1,10-phenanthroline 5,6-epoxide. The properties of the resulting amino alcohol derivatives were examined using UV and fluorescence spectroscopy. In addition, their interaction with DCP was studied by monitoring changes in absorbance.

## RM_MWGL Regional Meeting 571

## Modulating supramolecular reactivity using covalent “switches” on a pyrazole platform

***Evan P. Hurley**, ehurley@k-state.edu, Christer B. Aakeroy, John Desper. Department of Chemistry, Kansas State University, Manhattan, KS 66506-0401, United States*

Co-crystallizations between halogen- and methyl- substituted pyrazoles and twenty aromatic carboxylic acids have been carried out via melt and solution-based experiments. The solids resulting from all reactions were screened using infer-red spectroscopy in order to determine if a reaction (co-crystal or salt) had taken place, or if the two components failed to yield a multi-component product. The halogenated pyrazoles, including the dimethyl analogs, gave a success rate 55-70%. Substituting the halogen (R-X, X= Cl, Br, I) for a nitro (R-$NO_2$) group drops the reaction success rate significantly to 10%. Single crystal data obtained from solution-based experiments yielded co-crystals and salts with varying architectures: dimers (9/14), trimers (3/14), and tetramers (2/14). In all of the crystal structures, the primary driving force for co-crystal or salt formation is O-H---N interactions between carboxylic acid---azole and secondary N-H---O interactions. Our conclusions are the overall charge on the pyrazole can be modulated by using specific halogen-based covalent handles, which in turn can

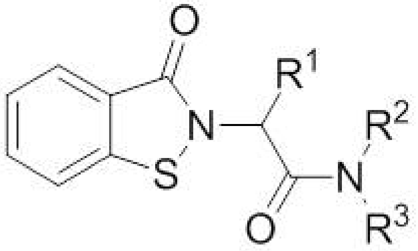
increase (or decrease) the success rate for a reaction and yield co-crystals 9/14 (64% supramolecular yield) times.

## RM_MWGL Regional Meeting 572

## Antifungal activity of a series of 1,2-Benzisothiazol-3(2H)-one derivatives

***Sridhar Aravapalli***[1]*, sxaravapalli@wichita.edu, Dengfeng Dou*[1]*, Deepu Alex*[2]*, Bingfan Du*[1]*, Kok-Chuan Tiew*[1]*, Sivakoteswara Rao Mandadapu*[1]*, Richard A Calderone*[2]*, Wiiliam C Groutas*[1]*. (1) Department of chemistry, Wichita State University, Wichita, Kansas 67260, United States (2) Microbiology and Immunology, Georgetown University Medical Center, Washington DC, United States*

Invasive fungal infections are an emerging health problem and the leading cause of morbidity and mortality in immune-suppressed patients. Current therapy for fungal infections involves the use of polyenes, azoles, echinocandins, allylamines, and antimetabolites. These agents exert their antifungal effects through different mechanisms, including compromising membrane integrity and altering membrane permeability by binding to fungal cell membrane sterols,blocking the production of ergosterol, inhibiting lanosterol C-14α-demethylase, arresting fungal cell wall synthesis by inhibiting 1,3-β-D-glucan synthase, and blocking the biosynthesis of fungal cell wall sterols through the inhibition of squalene epoxidase. The use of these agents is plagued by toxicity, limited efficacy, and the emergence of resistance, consequently, there is a pressing need for new and effective antifungal therapeutics that are fungicidal, fungal-specific, and have a broad spectrum of activity and novel mechanisms of action.



Structure (I)

Screening of a subset of compounds from an in-house library of compounds resulted in the identification of a series of compounds represented by structure(I) that exhibited noteworthy antifungal activity against Candida species, Aspergillus fumigatus and Cryptococcus neoformans. Based on these observations, structure-activity relationship studies aimed at delineating the structural elements in structure(I) responsible for its antifungal activity and identifying drug-like antifungal coumpounds that display optimal potency, selectivity, pharmacokinetics and oral bioavailability, were undertaken.

The synthesis and screening results of structure (I) derivatives will be presented

## RM_MWGL Regional Meeting 573

# Progress towards the synthesis of a long wavelength fluorescent biosensor for citrate metabolite

***Chuangjun Liu**, Narsimha Sattenapally, Quinn` A Best, Lichang Wang, Matt McCarroll, Colleen G Scott. Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*

The measurement of metabolites, e.g. citrate, maleate, and pyruvate, plays an important role in our understanding of certain biological processes. Though quantitative measurements of these metabolites using the present techniques such as mass spectrometry (MS), NMR and chromatography are helpful, a highly sensitive system capable of detecting low concentrations of metabolites, i.e. pM to μM concentrations, would be highly useful. Since fluorescence is a highly sensitive technique capable of detecting single molecules, we are working towards the development of a novel fluorescence based sensor for detecting metabolites. Importantly, a fluorescent probe with long absorption and emission wavelength in the red or near infrared region of the spectrum is of advantage to biological systems because of the absence of auto fluorescence from the biological medium. Herein we present our progress towards the synthesis, characterization and fluorescence analysis of a biosensor for the citrate metabolite.

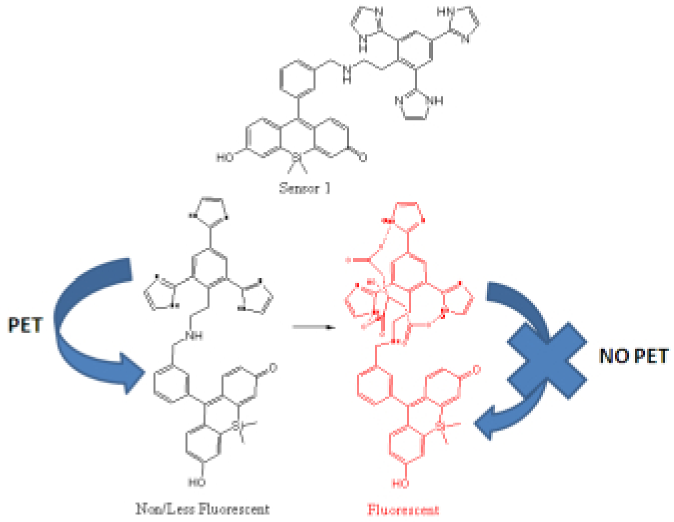


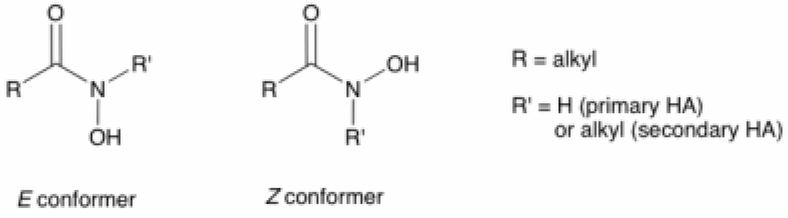
Figure 1. Structure of fluorescence sensor and schematic diagram of sensor interaction with bioanalyte

## RM_MWGL Regional Meeting 574

## Synthesis and conformational characterization of *N*-alkyl hydroxamic acids

***Heather L. Schenck**, hschenck@uwlax.edu, Rose Zolondek. Department of Chemistry, University of Wisconsin - La Crosse, La Crosse, WI 54601, United States*

The preparation and NMR structural characterization of *N*-alkyl hydroxamic acids (HA's) are described. These structures are small molecule models of microbial siderophores. Siderophores are used by micro-organisms to harvest ferric iron, and often employ HA's as iron-binding functional groups. An HA has two favored conformations, labeled *E* and *Z*.



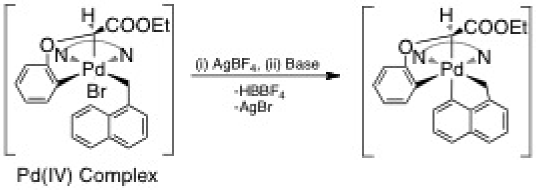
The *Z* conformation is required in order for an HA to bind iron via both oxygen atoms. This study examines the effect on the *Z/E* ratio of the *N*-alkyl substituent in secondary HA's, employing an unbranched 3-carbon chain. The 3-carbon chain is in analogy to several native siderophores that use *N*-acetyl-*N*-hydroxyornithine as an HA. NOESY experiments will be used to attempt to assign signals to specific conformers. Results will be compared to the existing *N*-methyl HA reported in the literature. The effect of solvent polarity on the *Z/E* ratio is explored by NMR spectroscopy.

**RM_MWGL Regional Meeting 575**

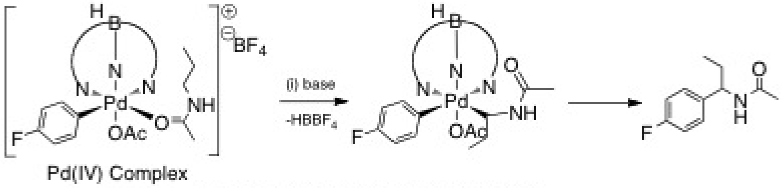
## Seeking evidence for electrophilic C-H activation at palladium(IV) centers

***Rachel Ruffie**, rruffie@gmail.com.Department of Chemisty, University of Kansas, Lawrence, Kansas 66049, United States*

Reaction pathways mediated by Pd in higher oxidation states have the potential to effectively realize the most challenging C-C coupling events including formation of C(sp$^3$)-C(sp$^3$) bonds. Herein, we report the synthesis of unique Pd(IV) complexes and the describe the investigations of intra- and intermolecular C-H activation pathways available to these Pd(IV) centers. Following C-H activation, conditions for reductive elimination leading to C-C bond coupling are being studied.



Proposed Intramolecular C-H Activation



Proposed Intermolecular C-H Activation

## RM_MWGL Regional Meeting 576

## Chemical constituents of the Burmese python (*python molurus bivittatus*) sexual attractiveness pheromone

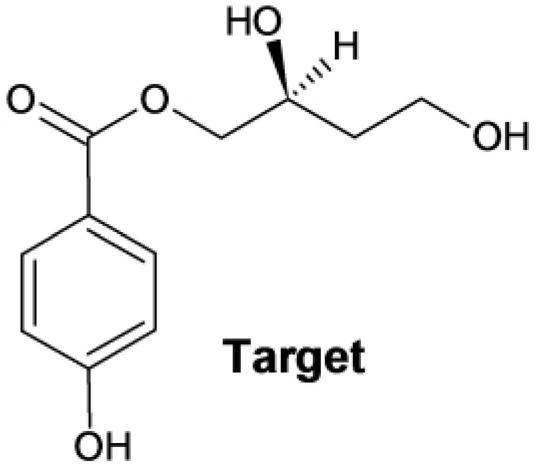
***Allison Balloon***[1,2], *ajballoon1@malone.edu, Jeff Goff*[1], *Chris Carmichael*[1,2], *Skip Snow*[3]*. (1) Department of Natural Science, Malone University, Canton, OH 44709, United States (2) The Herbert W. Hoover Foundation, Canton, OH 44702, United States (3) The Everglades National Park, Homestead, FL 33034, United States*

In recent years the population of the invasive Burmese python (*Python molurus bivittatus*) has threatened several endangered species and the balance of the ecosystem in the Everglades National Park. By extracting, identifying, and synthesizing the sexual attractant pheromone, we will explore its use as a lure and population control for invasive species management. The objective of this project was to separate and characterize the structure of the female pheromone that stimulates male courtship and trailing behavior. Chemical separation was accomplished after extraction of neutral skin lipids from the female shed skin in hexanes. Preparative flash chromatography and semi-preparative HPLC were used to further separate specific lipid classes. Using Y-maze, tongue flick density, and vector analysis the suspected pheromone fraction was shown to elicit natural courtship behaviors with statistical significance over the remaining skin lipid fractions and controls. This demonstrates that an intrinsic chemical in the shed skin lipids successfully elicits male sexual attraction behavior. Isothermal GC-FID analysis of the pheromone fraction shows that the compound peaks elute during regularly spaced intervals in a staggered pattern suggesting the presence of both saturated and mono-unsaturated long chain ($C_{25}$-$C_{38}$) fatty acid derivatives. Preliminary spectroscopic methods and previous research in similar snake species suggest that the pheromone consists of aliphatic and olefinic methyl ketones differing in carbon chain length and double bond location. This will be confirmed using $H^1$, $C^{13}$, and 2-D NMR methods.

## RM_MWGL Regional Meeting 577

## The total synthesis of (S)-2,4-dihydroxy-1-butyl (4-hydroxyl)benzoate

***Samuel David**, davids@uwosh.edu, Joel Seagren, Atanas Radkov. Department of Chemistry, University of Wisconsin, Oshkosh, WI 54901, United States*



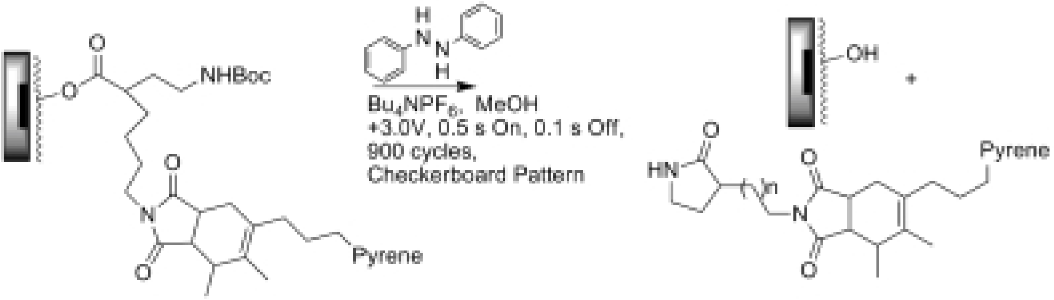
This study is the first synthesis of (*S*)-2,4-dihydroxy-1-butyl (4-hydroxy)benzoate, a newly discovered natural product with anti-tumor properties from the fungus, *Penicillium auratiogriseum*. The key steps are a 1,3 diol protection followed by the coupling of *p*-anisic acid to the protected alcohol and subsequent de-protection steps.

**RM_MWGL Regional Meeting 578**

## Site-selective, cleavable linkers: Quality control and the characterization of small molecules on microelectrode arrays

***Bo Bi**[1], bbi@go.wustl.edu, Richard Y-C Huang[1], Karl Maurer[2], Ceng Chen[1], Kevin D Moeller[1]. (1) Department of Chemistry, Washington University in St.Louis, Saint Louis, MO 63130, United States (2) CombiMatrix Corporation, Mukilteo, WA 98275, United States*

A “safety-catch” linker strategy has been used to characterize the stereochemistry of a Diels-Alder reaction conducted on a microelectrode array. Following formation of the Diels-Alder product on the array, the product was cleaved from the surface of selected electrodes in the array by site-selectively generating acid at the electrode. The product was then compared to independently synthesized material using LC-MS.



It was found that the surface of the array had a minor influence on the stereochemistry of the Diels-Alder reaction leading to slightly more of the exo-product relative to a similar solution-phase reaction.

## RM_MWGL Regional Meeting 579

### Metal oxide interferences on lead analysis in tungsten filament atomic absorption spectrometry

***Derek Poci**, dpoci@siue.edu, Edward C. Navarre .Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026, United States*

Several interferences that decrease lead (Pb) absorbance were investigated using a laboratory-built tungsten filament electrothermal atomizer. The study focused on interferences relevant to the analysis of Pb in physiological samples. Raman microscopy was used to track the formation of metal oxides *in situ* during the drying and pyrolysis stages of analysis. Metal oxide formation was correlated to the temperature of each step and subsequent nonspecific spectral interference during atomization. Rhenium was studied as a permanent modifier for the analysis of Pb-containing samples. Atomic absorption results showing the effectiveness of rhenium for reducing interferences from organic matrix components will be presented.

## RM_MWGL Regional Meeting 580

### Kinetic performance comparison of a capillary monolithic and a fused-core column

***Tunde A. Dioszegi**, tunde.dioszegi@sdstate.edu, Douglas E Raynie.Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57006, United States*

The kinetic performance of two capillary C18 columns (a 15cm 0.3 mm ID Eksigent, Halo fused-core and a 15 cm 0.2 mm ID, Phenomenex, Onyx monolith) was compared in isocratic-elution liquid chromatography. The experiments were performed on a micro-liquid chromatography system(Eksigent LC100, Dublin, CA). Heptanophenone was chosen as a test compound. The ($u_0$, H) couple obtained in a column with permeability $K_{v0}$ was transferred into a (N,$t_0$) couple and the kinetic plots were achieved by using the

Kinetic Method Plot Analyzer template (Gert Desmet, Vrije University, Brussels, Belgium). The $u_{0,opt}$ (0.98 mm/s for the monolith and 1.05 mm/s for the fused-core column) and $H_{min}$ (17.58 µm for the monolith and 18.08 µm for the fused-core column) values determined from the van Deemter curve were found to be almost identical, whereas the $N_{opt}$ (the plate number for which the support achieves its best analysis time/pressure cost ratio) (152,416 for monolith and 40,708 for fused-core column), $N_{max}$ (the maximum plate number that can ever be reached with a support) (547,117 for monolith and 115,789 for the fused-core column) and $t_{opt}$ (the time needed to obtain $N_{opt}$ plates) (2,527 s for the monolith and 1,293 s for the fused-core column) performance numbers determined from the kinetic plots werefound to be significantly different.

## RM_MWGL Regional Meeting 581

## Characterization of deep eutectic solvents and comparison with room temperature ionic liquids

***Ganesh Degam**, Ganesh.Degam@sdstate.edu, Douglas Raynie.Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57006, United States*

Deep Eutectic Solvents (DESs) are eutectic mixtures of quaternary ammonium or metal salts with hydrogen bond donors (HBDs), comprised of bulky cations and smaller anions which are bound to a HBD. Physical properties of a wide variety of DESs were measured by altering the quaternary ammonium salt, HBD and their composition. DESs of urea as HBD and choline chloride as ammonium salt has the lowest density of the mixtures we tested. Viscosity of DESs as a function of temperature was studied by varying temperature from 25°C – 150°C. DESs with smaller cations such as ethyl/methyl ammonium have less viscosity. DESs and Room Temperature Ionic Liquids (RTILs) have similar behavior with increase in temperature. The density and viscosity of DESs is lesser than RTILs. Solubility of various compounds in DESs was studied. Lignin is extracted from grasses with DESs. FTIR analysis was used to analyze the extracted and recovered lignin. DESs were evaluated as switchable solvents, simply by the addition of $CO_2$ to precipitate lignin out of DESs in place of acids. The pH of DESs decreases by saturating with $CO_2$, but it is not enough to precipitate lignin completely from DESs.

## RM_MWGL Regional Meeting 582

## Cavity ring-down spectroscopy of liquids using standard cuvettes

***Bryan J. Culbertson**, bjc179@msstate.edu, Stephen C Foster.Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, United States*

Cavity ring-down spectroscopy (CRDS) has emerged as a sensitive analytical technique. In this method, a laser pulse is injected through one of two highly-reflective mirrors which form a stable optical cavity and the rate that the light leaves the cavity is monitored by a detector placed behind the second mirror. Once entrapped, the light pulse makes many round trips as it slowly leaks back through the mirrors to be lost from the cavity. If an absorber is present inside the cavity, the "storage time" for the light will be reduced; the absorber removes light and hastens the decay of the trapped light.

It is a relatively straightforward procedure to apply CRDS to gas-phase samples. It has seen much less application to samples in the liquid phase. There are two obvious approaches to the study of liquid samples: completely filling the cavity with the liquid (which can lead to mirror contamination), or the insertion of a liquid-filled sample cell into the cavity (with the potential for reflection and scattering losses). In a recent paper, Zare and coworkers used a custom cell mounted at Brewster's angle to minimize reflection losses.

The current study used a standard 1-cm quartz cuvette mounted at normal incidence to the cavity axis. No attempt was made to reduce reflections from the cell surface because they are on-axis and are not lost from the cavity. 10-ns, 532-nm frequency-doubled Nd:YAG laser pulses were injected into a cavity formed with a pair of 1-m radius high-reflectivity mirrors. The mirror spacing was varied between 15 cm and 50 cm to examine the effect of cavity length on scattering and reflection losses. Ring-down times for pure solvent and dye solutions will be discussed as a function of cavity length and minimum detectable absorptions for the system will be presented.

### RM_MWGL Regional Meeting 583

## Determination and quantification of dimethyl methylphosphonate from activated carbon particles

***Brendan L. Mitchell****, brendan.mitchell@sdstate.edu, Brian A Logue.Department of Chemistry and Biochemistry, South Dakota State University, Brookings, SD 57007, United States*

Carbon particles are utilized as an adsorbent in protective equipment for binding hazardous gases including chemical warfare agents (CWAs). Although an activated carbon matrix makes it difficult to simply and quickly quantify bound substances, the effectiveness of activated carbon particles can be tested by exposing them to a chemical of interest and quantifying the bound concentration. We have developed a simple and effective method for the quantification of dimethyl methylphosphonate (DMMP), a simulant for CWAs (e.g. sarin), from activated carbon particles using static headspace gas chromatography mass-spectrometry (SHS-GC-MS). DMMP exposed activated carbon was spiked with internal standard (DMMP-$d_6$) and analyzed after headspace extraction was performed. The method produced a dynamic range between 2.48 and 620 g DMMP/kg carbon and a detection limit of 1.24 g DMMP/kg carbon. Furthermore, the method produced a coefficient of variation of less than 4% (intra- and inter-assay) and mean recoveries of 92.9, 88.5, and 96.8% for three sets of quality control (QC) samples. Overall, the method developed provides a simple and effective

procedure for quantifying DMMP from activated carbon particles and can be applied to test the effectiveness of protective equipment.

## RM_MWGL Regional Meeting 584

## Beeswax processing and refining in supercritical carbon dioxide

***George N. Gachumi****, george.gachumi@sdstate.edu. Department of Chemistry & Biochemistry, South Dakota State University, Brookings, South Dakota 57007, United States*

Supercritical carbon dioxide was explored as an alternative to organic solvents in extracting and bleaching beeswax. Beeswax, which consists primarily of a mixture of esters of fatty acids and long chain alcohols, has versatile applications in the cosmetic, pharmaceutical and food processing industries.
Temperature and pressure are very critical parameters in supercritical fluid extraction and their optimization was investigated using crude beeswax
sample. A subsequent study was carried out to investigate the dependence of extraction time. This study showed that, at a temperature and pressure of $70^0$C and 10000 psi respectively, highest yields were obtained with a dynamic extraction time of 30 minutes at a flow rate of approximately 1-2 mL/min. For effective utilization of $SCO_2$, it is key to operate at temperatures above the melting point of wax. These optimized conditions were then applied in
extracting beeswax from slum gum, capping and filter cakes. Bleaching studies were also investigated to determine the ratio of wax to adsorbent required to discolor wax.

## RM_MWGL Regional Meeting 585

## Application of 1-ethyl-3-methylimidazolium acetate (EmimAc) in the isolation of lignin and hemicellulose

***Victor Essel****, victor.essel@sdstate.edu, Douglas Raynie. Dept. of Chemistry and Biochemistry, South Dakota State University, Brookings, SOUTH DAKOTA 57007, United States*

Our earlier work investigated the isolation of cellulose and protein from soybean meal and flakes using the ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate (EmimAc). In this work, we used the same solvent system to explore the extraction of lignin and hemicelluloses from these feedstocks. Cellulose and protein were coprecipitated as a complex by diluting the IL-dissolved biomass in excess deionized water. By adding ethanol to the filtrate sample in a ratio of 2:1, persistently dissolved protein was isolated. After recovering the precipitated protein, we isolated the lignin component of the IL-dissolved biomass using concentrated $H_2SO_4$. Finally, the hemicellulose component was recovered with ethanol in a ratio of 2:1. We characterized the isolated lignin and hemicellulose using FTIR, MALDI-TOF, Py-GC-MS and elemental analysis.

## RM_MWGL Regional Meeting 586

### Synthesis and characterization of 1-ethyl-3-methylimidazolium alkylbenzene sulfonate (EMIM ABS) ionic liquids

***Hiranmayee Kandala***, *hiran.kandala@sdstate.edu, Douglas Raynie. Department of Chemistry and Biochemistry, South Dakota State University, Brookings, South Dakota 57006, United States*

In this study, low melting EMIM ABS ionic liquids have been synthesized which can be handled under ambient conditions and can be used as green solvents to isolate lignin from the biomass feedstock. Characterization has been done to determine the physical and thermal properties like viscosity, melting point and thermal stability of these ionic liquids. To confirm structural integrity of the synthesized ionic liquids and to make sure that the sodium acetate was completely eliminated from the ionic liquids after synthesis, a proton NMR analysis was performed. All the EMIM ABS ionic liquids had high viscosities and a significant change in the viscosity has been noticed with increasing the bulk of functional groups on the anion in the ionic liquid. Thermo gravimetric study of the synthesized ionic liquids has been done to attribute the thermal stability of ionic liquids majorly to either degradation or evaporation. Differential scanning colorimetric study was performed to determine the glass transition and melting points of the ionic liquids. Further, the purity of lignin isolated from the biomass using ionic liquids has been determined using FTIR.

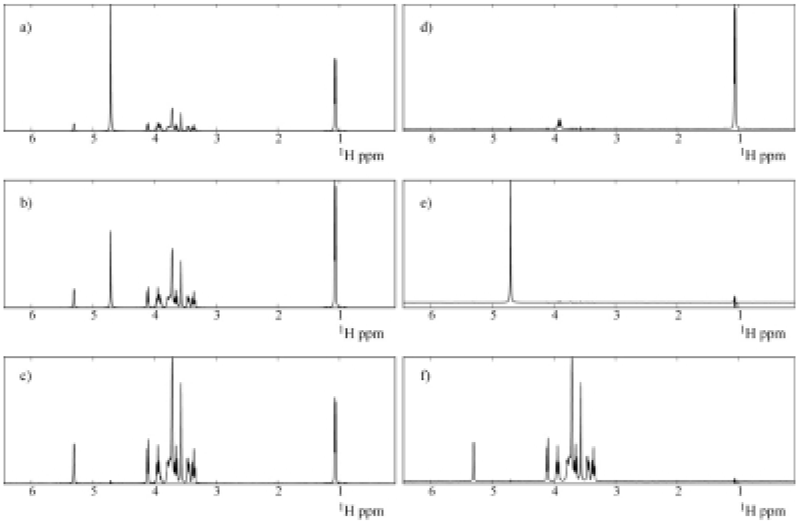
## RM_MWGL Regional Meeting 587

### Diffusion-ordered independent component analysis: Separating nuclear magnetic resonance spectra of analytes in a mixture

***Junyan Zhong***[1], *jzhong@odu.edu, Nicole DiDonato*[2]*, Patrick G Hatcher*[2]*. (1) College of Sciences Major Instrumnetation Cluster, Old Dominion University, Norfolk, VA 23529, United States (2) Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, United States*

Nuclear magnetic resonance (NMR) spectrum in a mixture contains the overall peaks of all the analytes. It is impossible to perform structural assignment on the mixture without the knowledge of individual spectra of the components. Spectral separation is thus an important means of teasing out pure components before spectral assignment. We propose a strategy called diffusion-ordered independent component analysis (DIFFICA) to achieve this task. The strategy applies ICA algorithms to diffusion ordered spectroscopy (DOSY) to extract spectra of pure components in a mixture. It is a combination of experimental and computational designs. DIFFICA was applied in both simulated and experimental data. Not any diffusion parameters will work, the selection of diffusion parameters to guarantee pure spectra is governed by the distance correlation between separated spectra. To investigate the effects of the diffusion parameters such as diffusion time on the effectiveness of the spectral extraction, a

series of 2D DOSY spectra were experimentally acquired, and the best range of diffusion times were determined by the lowest distance correlation values. As an example, the three spectra on the left column (a-c) of the following figure correspond to the three $^1$H spectra acquired experimentally from a mixture containing water, isopropanol and sucrose, and the three individual spectra on the right column (d-f) are DIFFICA-separated spectra from (a-c). They are identified as isopropanol (d), water (e) and sucrose (f).



## RM_MWGL Regional Meeting 588

## Top-down fragmentation of protein assemblies: Native electrospray and electron-capture dissociation in FTICR MS

***Hao Zhang***[1], *zhanghao@wustl.edu, Weidong Cui*[1]*, Jianzhong Wen*[1]*, Robert E. Blankenship*[2]*, Michael L. Gross*[1]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Chemistry and Biochemistry, Washington University in St. Louis, St. Louis, MO 63130, United States*

Native ESI mass spectrometry and ion mobility are playing an increasingly important role in structural studies of protein assemblies. Although the stoichiometry, shape, and dissociation of protein assemblies can be probed, the sequence information of the subunits still heavily relies on independent, bottom-up proteomics. We report here a top-down approach that integrates Electron-Capture Dissociation(ECD) and native ESI of protein assemblies in a 12 tesla FTICR mass spectrometer. The MWs. subunit identities, ligand-binding sites, and some structural information can be obtained in one experiment. ECD fragmentation patterns and ion mobilities of the protein assemblies activated at different collision energies are also useful pieces of information. We find that unfolding of flexible regions of the assembly occurs upon ECD. The results provide the new experimental evidence supporting the charge asymmetric partitioning model for complex dissociation. We conducted ECD top-down experiments on protein assemblies of different sizes and oligomeric states. The results from human hemoglobin tetramer (hHb 64 kDa), yeast alcohol dehydrogenase tetramer (ADH, 147 kDa), concanavalin A tetramer (ConA, 103 kDa) and photosynthetic Fenna-Matthews-Olson protein trimer (FMO, 140 kDa) show that the relatively free and flexible regions of the subunits can be sequenced by ECD or by activated ion ECD in which the protein ions are collisionally activated prior to ECD. The effectiveness of the activation/unfolding process induced by this strategy is revealed by the increase in ECD fragmentation. The fragments correlate well with the B-factor from X-ray crystallography, which is a measure of the extent an atom can move from its coordinated position as a function of temperature or crystal imperfections. This approach provides not only top-down proteomics information of the assembly subunits but also details on the unfolding pathways of protein complexes. Those results and the results of the ion mobility study are in good agreement.

### RM_MWGL Regional Meeting 589

## ACS CHAS: Where chemistry and safety meet

***Kenneth P. Fivizzani****, kfivizzani@wowway.com.CHAS Division, Naperville, IL 60564, United States*

The American Chemical Society Division of Chemical Health and Safety (CHAS) provides expertise in laboratory safety, chemical management, and safe chemical work practices to the Society and the general public. The division organizes technical symposia at ACS National and Regional Meetings and offers workshops in specific areas of chemical safety. Two CHAS Awards recognize outstanding contributions to the field of chemical health and safety; a third award recognizes comprehensive lab safety programs in higher education. The CHAS Website and Listserv offer on-line information and discussion of relevant topics. The division publishes the *Journal of Chemical Health and Safety* six times per year.

### RM_MWGL Regional Meeting 590

## Development, advantages, educational value, challenges, and implementation of a green, microscale organic chemistry laboratory

***Thomas E. Goodwin****, goodwin@hendrix.edu.Department of Chemistry, Hendrix College, Conway, AR 72032, United States*

At Hendrix College, we have been practicing microscale green chemistry for over 20 years in our introductory Organic Chemistry lab. I will discuss the development of our laboratory program, as well as its challenges and benefits. Examples of the experiments that we have developed will be discussed. We are currently focused on developing new solventless or aqueous-based experiments. This presentation will focus on several of these, including a solventless Diels-Alder reaction and a solventless imine formation (neither of which requires a solvent for product isolation), an aqueous Suzuki cross-coupling, and the synthesis of new amino acid derivatives from isatins. I will also discuss a stereochemical exercise based upon the biosynthesis of beetle aggregation pheromones.

## RM_MWGL Regional Meeting 591

## Improving safety education in undergraduate chemistry programs

***David C. Finster***, *dfinster@wittenberg.edu.Department of Chemistry, Wittenberg University, Springfield, OH 45501, United States*

The argument is presented that safety instruction in undergraduate chemistry programs in the United States is inadequate. The multiple reasons for this circumstance will be examined. It is proposed that an enhanced level of safety instruction can only be achieved by holding academic chemistry programs accountable for the level of safety education demonstrated by their students and graduates and by taking additional steps to improve the culture of safety in academic settings. Methods for such assessing accountability and effecting a cultural change will be explored.

## RM_MWGL Regional Meeting 592

## Laboratory safety and management for teaching assistants

***Barbara L. Foster***, *bfoster@wvu.edu.C. Eugene Bennett Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States*

At West Virginia University, safety is our first priority, both in our academic and research laboratories. It is with a keen sense of responsibility that we prepare our students for their careers in laboratory settings in academia, industry, government, law enforcement, and the health sciences. We realize that what our students learn about safety in our laboratories will have a significant impact on all of the people who will share their work environments in the future. This talk will focus on various methods to instill a culture of safety within your department and within the teaching assistants in your academic laboratories. Topics include: Principles of Laboratory Safety, Laboratory Procedures, Chemical Management, Emergency Preparedness, and Laboratory Facilities.

## RM_MWGL Regional Meeting 593

## Developing nanoparticles as mercury eliminating agents

***Lalitha Amarapalli***, *amarapalli.lalitha@gmail.com, Patty K. Fu. Department of Chemistry, Governors State Univesity, University Park, IL 60484, United States*

Mercury is considered to be a global contaminant because it is toxic, does not break down in the environment and can build up in living things. Mercury can be carried long distances on wind currents, staying in the atmosphere for long periods of time, when in

its vapor form. High mercury exposure results in permanent nervous system and kidney damage. Mercury exists in three different chemical forms elemental, inorganic and organic and the routes of exposure can be inhalation, ingestion or skin contact. Vapor from liquid elemental mercury and methyl mercury are more easily absorbed than inorganic mercury salts and can, therefore, cause more harm. This problem can be solved by the use of nanoparticles. This was achieved by creating a special filter which was used to trap the mercury. The chemistry of metal alloying can be utilized for sequestration of mercury from water.

## RM_MWGL Regional Meeting 594

### Study of the photochemistry of adsorbed nitrate on different components of mineral dust aerosols

*Rachel M Welch, Ellen M Coddens,* ***Juan G Navea****, juan.g.navea@lawrence.edu. Chemistry Department, Lawrence University, Appleton, Wisconsin 54911, United States*

Mineral dust aerosols are known to provide an active surface for tropospheric gases, including nitrogen dioxide and nitric acid. In fact, recent studies suggest that photochemistry of adsorbed nitrate may contribute with the renoxification of the atmosphere. In addition, mineral dust contain a variety of photoactive components such as semiconductive or chomophore species. However, several questions still remain about the role of these components in the heterogeneous photochemistry of adsorbed nitrates, especially at early stages of the reaction.

To better understand the role of these different components of mineral dust, we carried out individual kinetic studies using alumina and iron oxide for the photochemistry of chemisorbed nitrate with simulated solar radiation. The surface reaction was studied using an ATR-FTIR flow cell, which was coupled to a long-path cell for the analysis of gas-phase products. This novel setup allowed the characterization of the reaction at early stages, when chemisorbed nitrate photolyzes to yield gas-phase products such as NO, $NO_2$, $N_2O_4$, and $N_2O$. The rate of these reactions on the different surfaces are contrasted, as well as the complex dynamic balance between adsorbed nitrate and its gaseous nitrogen-containing products.

## RM_MWGL Regional Meeting 595

### Assessment of bigoenic secondary organic aerosol in the Kathmandu Valley, Nepal

***Elizabeth Stone****, Tony Nguyen. Department of Chemistry, University of Iowa, Iowa City, Iowa 52242, United States*

Secondary organic aerosol (SOA) is suggested to be a major source of organic aerosol in the Southeast Asian regional haze. In this study, we assess biogenic contributions to SOA by measurement of particle-phase isoprene, monoterpene, and sesquiterpene

photooxidation products in fine particles ($PM_{2.5}$) in the Kathmandu Valley. Organic species were measured in solvent-extracts of filter samples using gas chromatography mass spectrometry (GCMS) and chemical derivatization. Organic speciation targeted molecular markers for primary aerosol sources—including motor vehicles, biomass burning, and detritus—and SOA products. As authentic standards of many SOA products are not commercially available, the uncertainty introduced to measurement by use of surrogate species for quantification is estimated. Biogenic SOA contributions to $PM_{2.5}$ mass and organic carbon content and their seasonal variations are presented. High concentrations of isoprene derivatives in aerosol, particularly in the late summer months, point to biogenic SOA as a major aerosol source in the Himalayan region.

**RM_MWGL Regional Meeting 596**

## Effects of biodiesel composition on pollutant emissions from a single cylinder diesel engine

***Yue Zhong***[1], *dana0610@ku.edu, Edward Peltier*[1], *Michael Mangus*[2], *Christopher Depcik*[2], *Andrew Duncan*[3], *Susan Williams*[3]. *(1) Department of Civil, Environmental and Architectural Engineering, University of Kansas, Lawrence, Kansas 66045, United States (2) Department of Mechanical Engineering, University of Kansas, Lawrence, Kansas 66045, United States (3) Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States*

Due to concerns over the availability and environmental impact of petroleum fuels, interest of biodiesel use is increasing. In this study, we analyzed biodiesels prepared from seven different feedstocks: waste cooking oil, rapeseed oil, olive oil, palm oil, coconut oil, canola oil, and soybean oil. Exhaust emissions of gas-phase compounds ($CO_2$, CO, $NO_2$, NO, THC) and particulate matter were measured for each biodiesel and Ultra Low Sulfur Diesel (ULSD) during combustion in a diesel generator operating under different engine loads (0, 25, 50, 75, 100%). The composition of each biodiesel was also analyzed using a variety of chemical and physical tests to investigate the relationship between fuel properties and pollutant emissions. The results showed that both engine performance and biodiesel composition affected emissions levels. All of the biodiesels produced fewer CO and THC emissions than ULSD, with the lowest emissions observed at high loads due to improved combustion. Particulate matter emissions were also reduced for all biodiesel fuels compared to ULSD. However, brake-specific $CO_2$ emissions increased because of the lower energy content of the biodiesel fuels. NO emissions increased with increased engine loads while $NO_2$ emissions decreased, resulting in highest total NOx emissions at 50% to 75% load, depending on the fuel. ULSD had lower NOx emissions at 0% loads than the biodiesels, but at 50% loading and above, ULSD NOx emissions were equivalent to or greater than all of the biodiesels tested. The H: C ratio of biodiesels had a substantial effect on NOx emissions, with higher H: C ratios leading to lower brake specific NOx emissions. The average hydrocarbon chain length and the number of double and triple bonds were also significant in determining $NO_x$ emissions.

## RM_MWGL Regional Meeting 597

### Speciation and Formation of SOA Generated from Ozonolysis of Realistic Terpene Mixtures

***Hardik S Amin**, hardik@siu.edu, Kara E Huff Hartz. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, IL 62901-4409, United States*

Secondary organic aerosol (SOA) is generated by reaction between volatile organic compounds (VOCs), and oxidants such as hydroxyl radical and nitrogen oxides and ozone. Previous laboratory studies on SOA formation and speciation are largely limited to oxidation of a single VOC. In the atmosphere, however, multiple precursor VOCs co-exist and concurrently undergo oxidation reaction to generate SOA. Hence, laboratory studies that are used to explain SOA formation and the species that are generated from oxidation of multiple precurors are necessary. Air fresheners are excellent candidates for SOA sources as they contain multiple VOCs. In this research, SOA is generated in a 5.5 $m^3$ Teflon bag by volatilizing VOC mixtures or air freshener in an ozone atmosphere. The aerosol mass concentration is estimated by a scanning mobility particle sizer. The goal of these experiments is to compare the species generated and SOA formed by VOC mixtures to a commercially available air freshener. Hence, the VOC mixtures are made to match the percent mass composition as present in air freshener. Comparative analysis between SOA yields generated from single precursor to SOA yields generated from precursor mixtures and air fresheners are found to be similar. Condensed phase SOA is collected onto quartz filters for speciation. The SOA on filters samples are solvent extracted. The extract, which contains a mixture of chemical species, like carboxylic acids, dicarboxylic acids, ketones, and alcohols, is concentrated and derivatized by silylation. The derivatized samples are then analyzed by gas chromatography-mass spectrometry (GC/MS) in electron impact ionization and chemical ionization modes. The GC/MS results show equal amount of each chemical species generated during SOA formation reaction by precursor mixtures and air freshener. The results of this research provide knowledge on SOA generated by ozonolysis of near realistic terpene mixtures and composition for a portion of indoor condensed phase SOA.

---

## RM_MWGL Regional Meeting 598

### Determination of Monoamine Neurotransmitters and their Metabolites by Liquid Chromatography - Tandem Mass Spectrometry

***John F Gemoules**[1], jgemoules@aol.com, Joseph H Bisesi[2], Lauren E Sweet[2], Steven J Klaine[2,3], Kevin A Johnson[1,4]. (1) Environmental Science Program, Southern Illinois University Edwardsville, Edwardsville, Illinois 62026, United States (2) Clemson University Institute of Environmental Toxicology, Clemson University, Pendleton, South Carolina 29670, United States (3) Department of Biological Sciences, Clemson*

*University, Clemson, South Carolina, United States (4) Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, Illinois 62026, United States*

Pharmaceuticals are continuously released into the environment due to inefficiencies in wastewater treatment, as well as other processes. The neurochemical mode of action of antidepressants warrants the investigation of the effects these chemicals may have on fish behavior. Using a predator prey bioassay previously designed in our collaborators' lab, we have shown that the antidepressants fluoxetine (Prozac®) and venlafaxine (Effexor®) individually increase the time it takes for a predator to capture its prey. In the environment these antidepressants could be found in complex mixtures with other antidepressants, as well as chemicals of varying modes of action. Since the effects of mixtures are not well understood, the objective of the study was to characterize monoamine (MA) neurotransmitter (NT) profiles associated with the behavioral effects of a simple mixture of the two antidepressants (previously investigated individually), fluoxetine and venlafaxine.

In this study fish brains were collected throughout the exposures to determine the MA NT profiles. Previous work has shown that antidepressant exposure decreases brain serotonin, which can be correlated with an increase in time to capture prey. However, in order to assess/confirm the effects caused by these antidepressants, analytical techniques needed to be developed for the MA NTs dopamine, epinephrine, norepinephrine, serotonin, as well as a few of their metabolites. The analytical method developed uses LC/MS/MS to determine the concentrations of NTs in the subject fish brain. The steps involved in this study included determining an effective procedure to extract the neurotransmitters from the brain tissue; removal of co-extracted interfering matrices, along with the chromatographic separation, mass spectral identification and quantitation of the neurotransmitters.

**RM_MWGL Regional Meeting 599**

### Development of an *in situ* remediation strategy for a metals-contaminated, alkaline groundwater: Initial amendment screening and effect of pH

***Aaron S. King***[1], *aaronking95@gmail.com, Edward Peltier*[1], *Mandy M. Michalsen*[2]. *(1) Department of Civil, Environmental, and Architectural Engineering, University of Kanas, Lawrence, KS 66045, United States (2) Seattle District, U.S. Army Corps of Engineers, Seattle, WA, United States*

Groundwater beneath a former industrial site contains dissolved metals and organic material at high levels, as well as elevated pH (10-12). Migration of metal contaminants to site-adjacent waterways must be controlled to avoid impacting endangered species. In this study, the efficacy of five amendments (chitin, apatite, granular activated carbon, Thiol-SAMMS®, and limestone) was examined for the removal of copper, lead, vanadium, and arsenic for both unaltered and pH-adjusted (pH = 8) site groundwater in laboratory batch studies. Dissolved metals and dissolved organic carbon (DOC) concentrations were measured in samples taken from the raw groundwater sample,

after pH adjustment, and after application of amendments. Simply reducing the groundwater pH with hydrochloric acid accounted for the majority of arsenic removal, but did little for the removal of other contaminants.
However, pH adjustment generally improved amendment performance. The greatest reductions in dissolved copper (68%), lead (58%), and vanadium (62%) concentrations were observed under pH-adjusted conditions in the presence of apatite. Thiol-SAMMS® also performed well under pH-adjusted conditions (Cu: 67% reduction, Pb: 41% reduction, V: 24% reduction), and also removed both copper (57% reduction) and lead (36% reduction) at the original pH. GAC was somewhat effective at removing lead under all conditions (20-25% reduction) and copper (28% reduction) when the pH was adjusted. Chitin was effective only for vanadium removal at lowered pH, while limestone was not effective for any metals. GAC was effective at reducing DOC concentrations under all conditions (22% reduction). These results suggest that a strategy using pH adjustment and some combination of apatite, Thiol-SAMMS®, and/or GAC may be best suited for remediation at this site.

## RM_MWGL Regional Meeting 600

### Determination of pharmaceuticals and personal care products, endocrine disrupting compounds and metabolites in Illinois groundwater by LC/MS/MS

***Matthew Salske***[1]*, msalske@siue.edu, Kevin A Johnson*[1,2]*. (1) Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, IL 62026, United States (2) Environmental Sciences, Southern Illinois University Edwardsville, Edwardsville, IL 62026, United States*

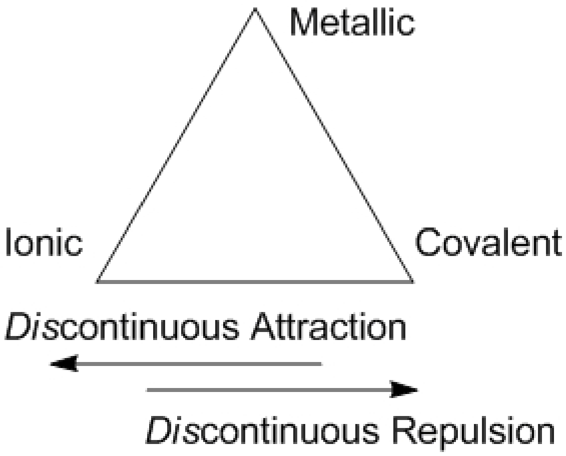
Pharmaceuticals and personal care products (PPCP's) and endocrine disrupting compounds (EDC's) are continuously released into the environment due to inefficient wastewater treatment and through other processes. As a result quantifiable levels of these chemicals have been detected in waterways worldwide. Many studies report concentrations of the PPCP's and EDC's around the level of low ppb (μg/L) for surface, drinking, and sewage treatment waters (influent and effluent). However, modern analytical techniques now allow for detection and quantitation below ppt (ng/L). Considering the low detection limits of these methods, few studies have reported on PPCP's and EDC's in groundwater. To the best of our knowledge, no studies have been conducted analyzing groundwater in rural Illinois for PPCP's and EDC's.
The focus of this study is to analyze rural Illinois groundwater for 26 PPCP's, EDC's and metabolites. Water samples were obtained from wells in southern Illinois and analyzed for these compounds by LC/MS/MS. The analytes were extracted from 1L well water samples by solid phase extraction. Of the 26 analytes, at least 9 were detected within limits of quantitation. Of the 9 PPCP's and EDC's detected 7 compounds (acetaminophen, caffeine, fluoxetine, ciprofloxacin, doxycycline, carbamazepine epoxide, and β-estradiol) were above 0.1ng/L. DEET and ketoprofen were detected above 0.08 ng/L.

## RM_MWGL Regional Meeting 601

## “Tensegrity” as an organizing architecture for covalent molecular structure

***J. David Van Horn**, vanhornj@umkc.edu, Charles Smith, Jami Wade, Dayu Wang. Department of Chemistry, University of Missouri-Kansas City, United States*

Macroscopic architecture (bridges, buildings, etc.) can be understood in terms of combinations of compressive and tensile forces ranging from continuous to discontinuous in their degree. At the molecular level, these structural forces may be considered to be repulsive and attractive, respectively. Molecular bonding (metallic, ionic, and covalent) as typified by the van Arkel-Ketelaar triangle is compared to the limiting cases of these opposing forces (see Figure). Specifically, a covalent bonding network consists of *discontinuous* repulsive forces and continuous attractive forces; ionic bonding is the opposite limiting case with *discontinuous* attractive forces. Between these discontinuous limiting cases lies metallic bonding—a case with continuous repulsive and attractive forces. Other molecular arrangements fit into varying degrees and combinations of these forces. Within this framework, the covalent bond may be considered a “molecular tensegrity”. At its idealized limit, covalent bonding is comprised of a continuous network of attractive interactions through electrons and a discontinuous set of repulsive interactions through the nuclei. Models for two-particle systems are presented as a way to accommodate basic particle interactions, and models of dihydrogen, methane, water, diborane, and benzene are derived from the simpler interactions. Molecular tensegrity is compared and contrasted with the development of bonding theory since the discovery of the electron and early nuclear models.



## RM_MWGL Regional Meeting 602

## Enhancing the Thermal Barrier to Reversible Electron Transfer in Cyano-Bridged {$Fe_2Co_2$} Squares

***Yuan-Zhu Zhang**[1], yuanzhuzhang@gmail.com, Diana Siretanu[3], Rodica Ababei[3], Rodolphe Clérac[3], Corine Mathonière[4], Stephen M. Holmes[1,2]. (1) Chemistry &*

*Biochemistry, University of MIssouri-St. Louis, St. Louis, MO 63121, United States (2) Center for Nanoscience, University of MIssouri-St. Louis, St. Louis, MO 63121, United States (3) UPR 8641, Centre de Recherche Paul Pascal, Université de Bordeaux, Pessac, France (4) Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), Université Bordeaux 1, Pessac, France*

Over the past five years we have strived to systematically prepare several examples of discrete molecular Fe/Co squares and boxes that exhibit reversible changes in their optical and magnetic properties. Over this timeframe various factors such as intermolecular interactions (hydrogen bonding, p-p stacking, etc.) and electronic environment of the polynuclear complexes (solvation, ancillary ligands, & anions) have been investigated. Considering that electron transfer and spin state changes within Fe($\mu$-CN)Co units are entropy driven, and that the difference of Gibbs free energy between the two valence tautomeric states is related to the redox potentials of the Co and Fe ions; we believe that chemical modifications of either Co(II) or Fe(III) site should be an efficient means to design materials that exhibit magnetic and optical bistability at more technologically relevant temperatures (e.g. 300 K). A new iron(III) building block and two molecular square derivatives are described. We find that the new tetranuclear complexes exhibit thermally-induced transitions that are dependent on their crystal packing and counterions ($T_{1/2}$ ~ 230 and 240 K) suggesting that this is a promising approach for engineering materials with tunable properties.

**RM_MWGL Regional Meeting 603**

## Dithiocarbamate ligands bearing amino functionality for polyoxometalate functionalization

***Kanika Sharma***, *kanika@ksu.edu, Jeffery Karcher, Eric A Maatta, John Desper. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

Polyoxometalates (POMs) are an interesting class of compounds because of their desirable attributes including redox activity, oxidative and thermal stability, photochromism and magnetism among others. Hence, these are widely used in the fields of optics, electrochemistry, catalysis and medicine. In a bid to modify their properties, several attempts have been made to synthesize covalently hybridized POMs in order to introduce multi-functionalities within these systems, but only a few have been successful due to synthetic difficulties. We are trying to develop a new class of covalent hybrid POMs that contain multimetallic centers. In order to achieve this, we have designed and synthesized bifunctional organic ligands that have an amino end, enabling an oxo-imido exchange at the POM, and a dithiocarbamate functionalized end for coordination to various metals. Dithiocarbamate ligands exhibit a versatile coordination chemistry with virtually all metallic cations and have recently been employed to create supramolecular architectures capable of electrochemical sensing applications. Our goal is to employ these new organic ligands in the synthesis of POM hybrids possessing unprecedented structures and functionality. These systems have been characterized using IR, $^1$H and $^{13}$C NMR spectroscopy and by X-ray crystallography.

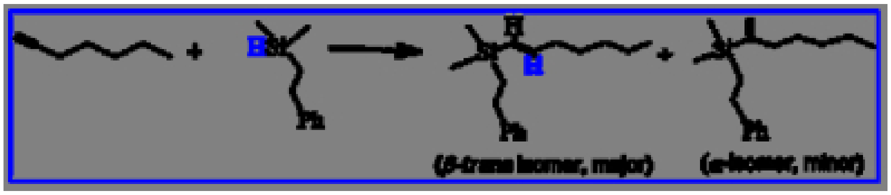
## RM_MWGL Regional Meeting 604

## Some novel phosphine complexes of platinum and palladium and their catalytic applications

***Sitaram Acharya***, *Janet Braddock-Wilking, Nigam P. Rath. Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, Missouri 63121, United States*

Some water-soluble platinum(II) and palladium(II) alkyl, halide, and alkynyl complexes bearing the 1,3,5-**t**riaza-7-**p**hospha**a**damantane (PTA) and DAPTA (DAPTA = 1,3-**di****a**cetyl-1,3,5-**t**riaza-7-**p**hospha**a**damantane) ligands have been synthesized utilizing a simple synthetic route. Utilization of these Pt or Pd complexes containing the PTA and DAPTA ligands as catalysts for the metal-mediated hydrosilylation and hydrogermylation reactions has been investigated for the first time. The catalytic activity of *cis*-Pt(Me)$_2$(PTA)$_2$ (**1**) in hydrosilylation reactions with different unsaturated organic systems such as alkenes, alkynes, alkadienes/diynes, and ketones has been explored utilizing different tertiary hydrosilanes as well as siloles and silafluorenes. Compound (**1**) was found to exhibit a good catalytic activity for these reactions forming predominantly the desired regioselective hydrosilylated products. The *β-trans* isomers were selectively formed during the hydrosilylation of alkynes and alkadiynes (fig 1) . The PTA complexes, *trans*-Pd(Me)Cl(PTA)$_2$ and *cis*-PdCl$_2$(PTA)$_2$ were also applied as pre-catalysts in Suzuki-Miyaura cross-coupling reactions and copper-free Sonogashira cross-coupling reactions, respectively and were found to exhibit a good catalytic activity with minimal side reactions. These metal complexes have their potential applications to use in the biphasic catalytic reaction system for efficient recycling of the catalyst.

The synthesis of the metal complexes and the results from the metal-catalyzed hydrosilylation and hydrogermylation reactions as well as cross-coupling reactions will be presented.

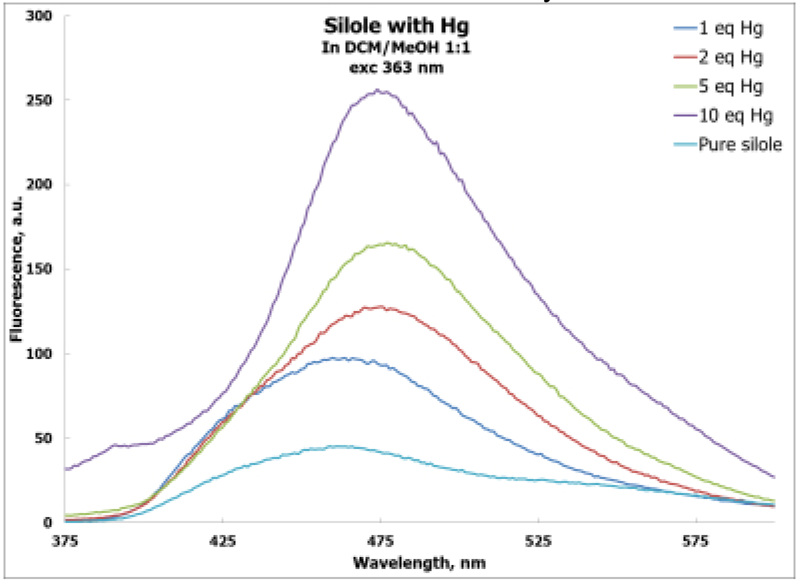


## RM_MWGL Regional Meeting 605

## Study of siloles and optical properties related to coordination with metal ions

***James B. Carroll***, *jbc6wc@mail.umsl.edu, Janet Braddock-Wilking. Department of Chemistry and Biochemistry, University of Missouri - Saint Louis, Saint Louis, Missouri 63121, United States*

Siloles (silacyclopenta-2,4-dienes) are an important class of compounds, with unique optical properties due to a small HOMO-LUMO gap and conjugation with aromatic substituents. Such features make this compound class attractive to many applications, including chemical sensing, organic light-emitting diodes (OLEDs), and photovoltaic devices. Most chemical sensing applications developed with siloles have centered on detecting volatile organic compounds. However, there exists a need for detection of environmentally harmful metals, such as nickel, copper, and mercury. This presentation will focus on the interaction of siloles containing moieties that can coordinate with metal ions (e.g., bipyridine). Several siloles have been synthesized and characterized by multinuclear NMR, UV-visible and fluorescence spectroscopies. The optical spectra of these compounds will be compared for both the free siloles and their interaction with metal ion solutions to test for selectivity and fluorescence enhancement or quenching



.

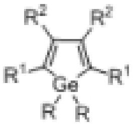
## RM_MWGL Regional Meeting 606

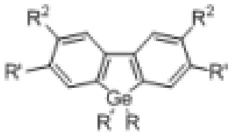
## Synthesis and characterization of a series of cyclic germanium compounds for potential use as fluorescent biological probes

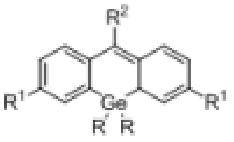
***Teresa Bandrowsky***, *tlb4h5@umsl.edu, Janet Braddock-Wilking. Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri-St. Louis, St. Louis, MO 63121, United States*

Of the many probes that have been developed for the detection of biological molecules, fluorescence (FL) biosensors are forerunners in the field as they demonstrate ultra-high

sensitivity, low background signals, and wide dynamic ranges. Despite their efficiency, conventional FL biosensors suffer from concentration dependent aggregation-caused quenching (ACQ) of light emission. As a result, dilute solutions of the fluorophore molecule are required in order to minimize contact between adjacent molecules and prevent aggregation; however, this limits sensitivity and strength of the FL signal.
Our research efforts involve the synthesis of a series of five, six, and seven membered cyclic germanium compounds and the investigation of their potential as label-free fluorescent turn-on sensors and assays for the detection of biomolecules. Several of our published germoles are weakly emissive but exhibit enhanced emission upon aggregation (AIE effect) and thus, do not fall victim to the limitations of the ACQ effect. Our aim is to design and screen cyclic germanium compounds for the AIE effect and to test their ability to generate stable, highly fluorescent signals for use as efficient biosensors. The synthesis and characterization of these cyclic germanium compounds will be presented.





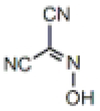


## RM_MWGL Regional Meeting 607

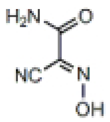
## Synthesis, characterization and applications of light-insensitive silver(I) cyanoximates.

*Steven Gross[1], Robert Hougas[1],* ***Nikolay N. Gerasimchuk[2]****,*
*NNGerasimchuk@MissouriState.edu. (1) Department of Chemistry, Creighton University, Omaha, Nebraska 68178, United States (2) Department of Chemistry, Missouri State University, Springfield, Missouir 65897, United States*

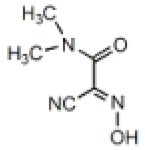
Ten AgL coordination polymeric compounds of silver(I) with cyanoximes – small organic molecules with general formula NC-C(=NOH)-R, where R is an electronwithdrawing group – were synthesized and characterized using a variety of spectroscopic methods and X-ray analysis. Crystal structures of 8 complexes were determined and revealed that cyanoxime anions act as bridges of different complexity in formed 2D coordination polymers. All ten complexes have demonstrated a remarkable visible light stability due to the short, covalent bonds between Ag and N atoms of bridging cyano- and nitroso-groups. There are three areas of potential practical applications of these unusual complexes: 1) battery-less detectors of UV-radiation, 2) non electrical sensors for gases of industrial importance, 3) antimicrobial additives to light-curable acrylate polymeric glues, fillers and adhesives used during introduction of indwelling medical devices. Chemical, technological and biological aspects of these applications are described in this presentation. Three complexes – Ag(CCO), Ag(ACO) and Ag(ECO) – were intensely studied as additives to polymeric composites used in dentistry.



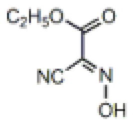
**1**, CCO



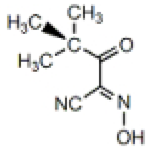
**2**, ACO



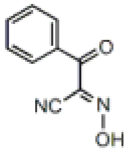
**3**, DCO



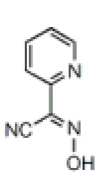
**4**, ECO



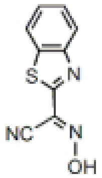
**5**, PiCO



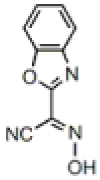
**6**, BCO



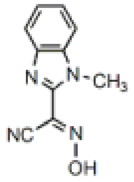
**7**, 2PCO



**8**, BTCO



**9**, BOCO



**10**, BIMCO

---

## RM_MWGL Regional Meeting 608

## Redox chemistry of cationic [$\eta^5$-$C_5H_5Ru(PPh_3)_2]^+$ vinylidene complexes.

***Michael J. Shaw**, michsha@siue.edu, Andrew Hansen, Brian M. Schutte.Department of Chemistry, Southern Illinois University Edwardsville, Edwardsville, Ilinois 62026, United States*

The conversion of an internal alkyne to a terminal vinylidene ligand via a Ru-mediated C-C activation reaction makes available [$\eta^5$-$C_5H_5Ru(PPh_3)_2$(vinylidene)]$^+$ complexes which feature disubstituted vinylidenes. The redox chemistry of monosubstituted and disubstituted vinylidene complexes will be presented. The structural consequences of electron-transfer to and from these complexes has been probed chemically through $^1$H, $^{13}$C, and $^{31}$P NMR reactions, and electrochemically through CV and fiber-optic infrared spectroelectrochemical measurements. Digital simulations of CV data recorded under different conditions of concentrations and scan rates provide supporting evidence for the proposed structural changes.

---

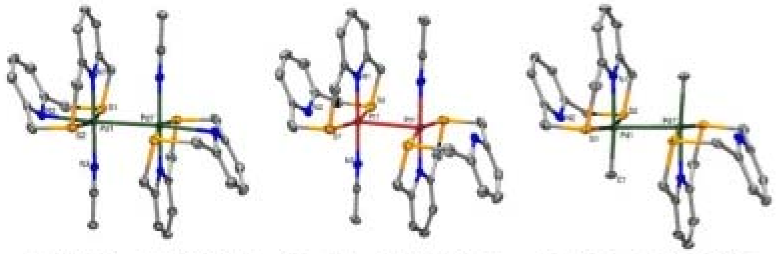
## RM_MWGL Regional Meeting 609

## Non-bridging ligand supported $d^8$-$d^8$ bond in the $Pd^{II}$ and $Pt^{II}$ complexes

***Jia Luo**[1], luojia@go.wustl.edu, Nigam P Rath[2], Liviu M Mirica[1]. (1) Department of Chemistry, Washington University, St. Louis, Missouri 63130-4899, United States (2) Department of Chemistry and Biochemistry, University of Missouri - St. Louis, St. Louis, Missouri 63121-4400, United States*

Numerous natural and synthetic metal-containing systems employ binuclear and multinuclear metal clusters for catalyzing difficult reactions such as small molecule activation and multielectron reactions. In such multinuclear complexes, the presence of

metal-metal interactions plays an important role in their reactivity. While several $Rh^{I}$, $Ir^{I}$ and $Pt^{II}$ dinuclear complexes that exhibit weak $d^8$-$d^8$ interactions have been characterized, only a few $Pd^{II}$ dinuclear species with metal-metal interactions have been reported up to date and all are supported by either dinucleating or bridging ligands. Reported herein are the rare examples of dinuclear Pd and Pt complexes that display $d^8$-$d^8$ interactions supported by a mononucleating tetradentate ligand, 2,11-dithia[3.3](2,6)pyridinophane (N2S2). The variable-temperature $^1H$ NMR and UV-vis spectroscopy studies in different solvents imply that these dinuclear complexes may convert to mononuclear analogs in solution. Density Function Theory (DFT) analysis supports the presence of $d^8$-$d^8$ interactions in these Pd and Pt complexes, which could play an important role in the reactivity of these complexes based on our preliminary reactivity studies on $Pd^{II}$-monomethyl dimer.



Pd···Pd = 3.0657(3) Å Pt···Pt = 3.0768(3) Å Pd···Pd = 3.1132(2) Å

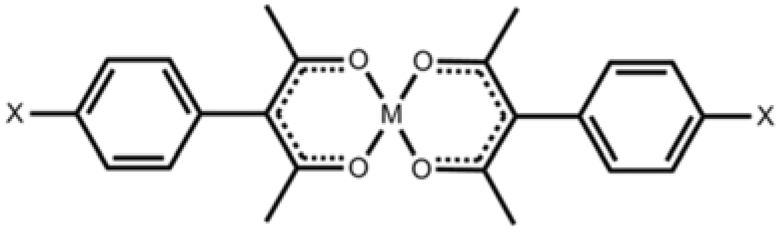
Figure 1. X-ray crystal structures of Pd and Pt dimers.

**RM_MWGL Regional Meeting 610**

## Halogen bonding or close packing? Examining the structural landscape in a series of Cu(II)-acac complexes

***Abhijeet S Sinha**, sinha@ksu.edu, Prashant D Chopade, Christer B Aakeroy, John Desper. Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States*

Coordination chemistry is an ever growing field in inorganic chemistry due to its widespread applications and thus, there is always a need to modulate the properties of coordination compounds. Apart from coordinate covalent bonds, even hydrogen bonds have been used as a functional tool to fine-tune the properties of these complexes. Recently, halogen bonds are also emerging as a possible control because; they do not necessarily compete with the coordination sites for metals, which is possible in case of some hydrogen bond donors and acceptors. In order to study the feasibility of halogen bonds to compete with other forces in crystal packing, we synthesized a series of four bifunctional ligands based on $\beta$-diketonate moieties bearing methyl, chloro, bromo and iodo substituents and their corresponding copper(II) complexes. The compounds were characterized by $^1H$, $^{13}C$ NMR and IR spectroscopy and by single crystal X-ray diffraction. This presentation will examine the structures displayed by the ligands as well as by several Cu(II) coordination complexes thereof, and analyze them in the context of a balance between identifiable intermolecular interactions and close-packing forces.



X = $CH_3$, Cl, Br, I

## RM_MWGL Regional Meeting 611

## New iPrN4 Pd complexes

***Fengrui Qu***, *fqu22@wustl.edu, Liviu Mirica.department of chemistry, washington University in st louis, st louis, MO 63130, United States*

A new ligand N,N'-di-iso-propyl-2,11-diaza[3,3](2,6)pyridinophane ($^{iPr}$N4) was synthesized by a modified procedure reported for its t-butyl analog $^{tBu}$N4. A series of new $^{iPr}$N4Pd$^{II}$XY complexes were synthesized, where X and Y are different ligands such as chloride and methyl group. The iPrN4 ligand was found to stabilize Pd$^{II}$, Pd$^{III}$ and Pd$^{IV}$ oxidation states. Specifically, $^{iPr}$N4Pd$^{II}$Cl$_2$, $^{iPr}$N4Pd$^{II}$MeCl, and $^{iPr}$N4Pd$^{II}$Me$_2$ were oxidized to their Pd$^{III}$ and Pd$^{IV}$ analogs, and their spectroscopic properties(X-ray, UV-vis, CV, EPR and NMR) are described. A comparison within $^{iPr}$N4Pd$^{III}$XY series showed how the coordinating ligands (methyl or chloride) affected the electrochemical properties of the complexes. These data were also used to compare the $^{iPr}$N4Pd$^{II}$XY and $^{tBu}$N4Pd$^{III}$XY series, and provide insight into the stabilization of the different Pd oxidation states.

## RM_MWGL Regional Meeting 612

## Direct measurement of exchange rate of hydrogen and deuterium between gas and hydride phases

***Mark S Conradi***[1], *msc@wuphys.wustl.edu, Robert L Corey*[2]*. (1) Department of Physics, Washington University, Saint Louis, MO 63130, United States (2) Department of Physics, South Dakota School of Mines and Technology, Rapid City, SD 57701, United States*

The rate of exchange of H (or D) between $PdH_x$ and the surrounding $H_2$ gas at thermal equilibrium has been measured from the apparent relaxation rate of the hydride resonance. The intrinsic relaxation in the gas is very fast, compared to the intrinsic rate in the hydride. Thus, exchange between the phases opens up a second, parallel relaxation path for the hydride spins. Over a wide range of exchange rates, the

exchange rate is essentially equal to the measured apparent relaxation rate. A key requirement of the method is that each particle of the hydride be surrounded by a large excess of spins in the gas phase. Results from $PdH_x$ agree well with earlier isotope exchange results. In $PdD_x$, the exchange rate is followed over 3 decades. The measurement is performed entirely at thermal equilibrium, allowing access to very fast rates.

## RM_MWGL Regional Meeting 613

### Local physical structure in hydrogenated boron carbide materials

***Nathan A. Oyler***[1]*, oylern@umkc.edu, Wenjing Li*[1]*, Michelle Paquette*[2]*, Anthony Caruso*[2]*. (1) Department of Chemistry, Univ. of Missouri-Kansas City, Kansas City, MO 64110, United States (2) Department of Physics, Univ. of Missouri-Kansas City, Kansas City, MO 64110, United States*

Magic angle spinning solid-state NMR techniques are applied to the elucidation of the local physical structure in the products of the plasma-enhanced chemical vapor deposition of thin-film amorphous hydrogenated boron carabide from orthocarborane. Experimental 1H, 13C, and 11B chemical shifts and dipolar recoupling methods are used in conjuction with ab initio calculations of model molecular compounds to assign chemical environments and determine atomic connectivities. The results of these studies and a discussion of various complicating factors will be presented.

## RM_MWGL Regional Meeting 614

### *In situ* high pressure and temperature NMR analysis of metal carbonate formation from $CO_2$ with implications for carbon capture, conversion, and sequestration

***J. Andrew Surface***[1]*, jasurfac@wustl.edu, Philip A Skemer*[3]*, Sophia E. Hayes*[1]*, Mark S. Conradi*[2]*. (1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, United States (2) Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, United States (3) Department of Earth and Planetary Sciences, Washington University in St. Louis, St. Louis, MO 63130, United States*

Carbon dioxide geological sequestration is currently being explored and used as a long-term $CO_2$ storage alternative as part of the growing international carbon capture, conversion, and sequestration (CCCS) initiative. The safety of this method relies on successful magnesium and calcium carbonation reactions at moderately high pressures and temperatures like those in deep underground brine-soaked, semi-porous magnesium- and calcium-containing rock beds. Much is still to be learned about the reaction rates, pathways, physical transport of reactants and products, and spatial pH variation once the supercritical $CO_2$ is pumped underground. The problem is even more complex as most models and experiments on these systems have been done in well-mixed conditions which can enhance the reactions rates and change the observed reaction pathways. To date, modeling, accumulation of field data, and *ex situ* reaction

observations have been used to understand these systems, but all of these may differ in some form from "real world" conditions. Herein we describe a new state-of-the-art solid state NMR method which allows *in situ* observation of these reactions in near-geological reaction conditions (high pressure and high temperature). We will also discuss the spatial pH variation that has been observed during preliminary carbonation reactions and its effect on successful rock dissolution, carbonate precipitation, reaction pathways and products.

## RM_MWGL Regional Meeting 615

### Studies of atomic and molecular interactions of laser-polarized xenon and parahydrogen for magnetic resonance applications

***Boyd M. Goodson***[1]*, bgoodson@chem.siu.edu, Nicholas Whiting*[2]*, Ping He*[1]*, Panayiotis Nikolaou*[3]*, Laura Walkup*[1]*, Aaron Coffey*[3]*, Kirsten Groome*[1]*, Hayley Newton*[2]*, Brogan Gust*[1]*, Kaili Ranta*[1]*, Allie Hunter*[1]*, Neil Eschmann*[1]*, Michael J Barlow*[2]*, Eduard Chekmenev*[3]*. (1) Department of Chemistry and Biochemistry, Southern Illinois University-Carbondale, Carbondale, IL 62901, United States (2) Sir Peter Mansfield Magnetic Resonance Centre, University of Nottingham, Nottingham, United Kingdom (3) VUIIS, Vanderbilt Medical School, Nashville, TN, United States*

NMR/MRI methods enjoy wide applicability but suffer from notoriously low detection sensitivity, owing in part to typically low nuclear spin polarization (~$1\text{x}10^{-5}$ or lower, providing a major obstacle to many applications). We will focus on two methods for improving polarization and NMR detection sensitivity: (1) spin-exchange optical pumping (SEOP); and (2) para-hydrogen induced polarization (PHIP).

We have utilized newly-available high-power laser diode arrays (LDAs) to study the generation of hyperpolarized xenon-129 (HPXe) via SEOP under conditions of high xenon density and high resonant laser flux. We have found an unexpected, inverse relationship between the optimal temperature for performing SEOP and the xenon density—an effect that can be exploited to achieve unexpectedly high xenon polarizations at high xenon densities. Separately, while it has long been predicted that cesium would offer greater efficiency for polarizing $^{129}$Xe compared to the standard choice (rubidium), these predictions had never been realized. However, using diode lasers now available at Cs lines, we found that a ~2-fold average improvement in xenon polarization may be obtained using cesium—particularly at high xenon densities. We will report on our efforts to understand these different effects and to translate our results to larger- (e.g. human-)scale HPXe production.

We have also begun investigation of polarization enhancement via SABRE (signal amplification by reversible exchange), an approach recently developed by Duckett and co-workers. Whereas previous PHIP techniques rely on irreversible chemical processes, SABRE utilizes a catalyst that transiently binds both para-hydrogen ($p\text{H}_2$) and the target substrate molecule, thereby allowing the target spins to be hyperpolarized without permanent chemical alteration. We are investigating the effects of catalyst / substrate choice and other experimental parameters on SABRE. We have performed an in-house synthesis of an efficient Ir-based SABRE catalyst, allowing us to observe $^1H$ NMR enhancements of nearly ~100-fold in small organics like pyridine.

---

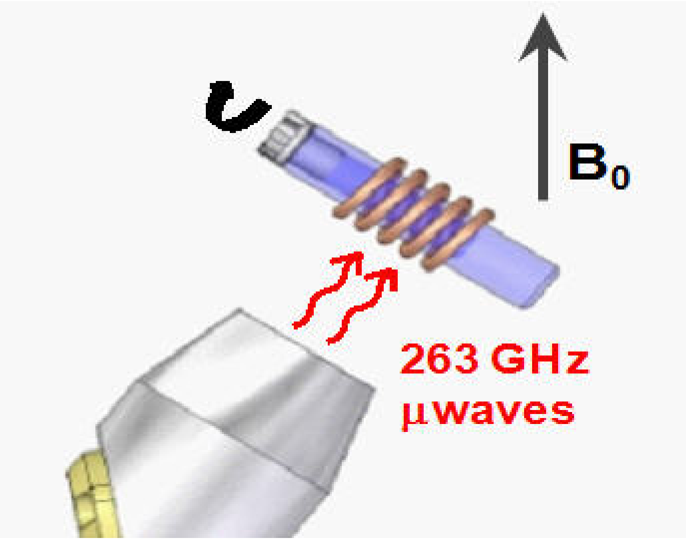
**RM_MWGL Regional Meeting 616**

## Dynamic nuclear polarization for enhanced sensitivity in solid-state NMR experiments

***Melanie Rosay***[1], *melanie.rosay@bruker-biospin.com, Shane Pawsey*[1], *Richard J Temkin*[2], *Robert G Griffin*[3], *Werner E Maas*[1]. *(1) Bruker BioSpin Corporation, Billerica, MA 01821, United States (2) Department of Physics and Plasma Science and Fusion Center, Massachusetts Institute of Technology, Cambridge, MA 02139, United States (3) Department of Chemistry and Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*

Dynamic Nuclear Polarization (DNP) experiments transfer the higher Boltzmann polarization of unpaired electron spins to nuclear spins for large gain in sensitivity and dramatic reduction in signal averaging time. This sensitivity gain opens the door to applications in solid-state NMR that may not have been achievable otherwise. The polarization transfer is driven by microwave irradiation of the electron spins near their Larmor frequency. For DNP experiments at $^1H$ frequencies in the range of 400-800 MHz, microwave sources operating in the range of 263-527 GHz are required with high output power, frequency and power stability, and reliability.

We report on the development of a DNP spectrometer for solid-state NMR applications with a microwave frequency of 263 GHz, 400 MHz $^1H$ frequency. Microwaves are generated with a continuous-wave gyrotron and transmitted to the NMR sample via corrugated waveguide. The sample is then irradiated for DNP-NMR experiments while spinning at the magic angle in a 3.2 $mm^3$ rotor. DNP signal enhancements of up to a factor of 80 at 100 K using the biradical TOTAPOL have been measured and a broad range of samples have been successfully polarized spanning from small molecules to large biological complexes and materials. Examples will be shown and future directions discussed.



## RM_MWGL Regional Meeting 617

### Chemical and biochemical reactions investigated by dynamic nuclear polarization

***Christian Hilty***, *chilty@chem.tamu.edu.Department of Chemistry, Texas A&M University, College Station, TX 77843, United States*

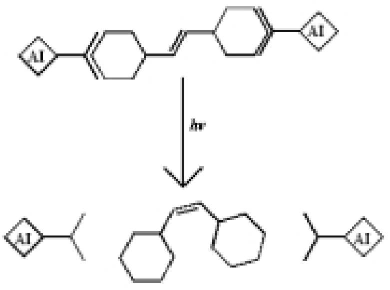
Solid-to-liquid state dynamic nuclear polarization (DNP) affords a sensitivity gain sufficient to enable single-scan acquisition of NMR spectra at low concentration of insensitive nuclei or of nuclei with low natural abundance. Combined with a rapid injection and mixing system, it becomes possible to obtain time-resolved data characterizing dynamic processes far from equilibrium. Kinetics and intermediates can be observed in various types of reactions, including enzyme-catalyzed reactions of small-molecule substrates, fast organic reactions and polymerization reactions. By observing nuclei with large chemical shift dispersion, such as $^{13}$C, even closely related reactants and products can be distinguished, such as different anomers of sugars. Quantitative analysis of the signal evolution additionally reveals information on relaxation rates, which are dependent on structural and dynamic properties of the molecular species involved. Interactions of small molecule ligands with proteins can be investigated by observing the effect of binding on the ligand signals, which allows the determination of dissociation constants, and can also be used to determine competitive binding of two ligands to a binding pocket. Further, protein resonances can be enhanced by transfer of magnetization through nuclear Overhauser effect from hyperpolarized ligands. Finally, data will be presented showing that substantial signal enhancements can be obtained when polarizing polypeptides directly, potentially opening a new avenue for the study of protein folding.

## RM_MWGL Regional Meeting 618

### Co-Crystals of Photochromic Compounds

*__Baillie A. DeHaven__, baillied@ksu.edu, Christer B. Aakeroy, Sheelu Panikkattu, John Desper.Department of Chemistry, Kansas State University, Manhattan, Kansas 66502, United States*

Methods used to control the release of active ingredients via external stimuli are scarce in practical applications. The purpose of this research project is to develop new solid structures - co-crystals - which combine both a photoactive molecule and a mimic of an active ingredient (AI). The preliminary part of this research is to synthesize and characterize co-crystals of a library of photoactive molecules. In order to form co-crystals, we combined various photoactive molecules with appropriate co-crystallizing agents in a series of mechanical grinding experiments. Once the grinding experiments were completed, an infrared (IR) spectrum was taken on the solids to ensure that the two molecules formed a co-crystal. If the IR showed positive results, we then attempted to generate single crystals using slow evaporation with a series of solvents (e.g. methanol and ethanol). From the single crystal data received from X-ray diffraction (XRD), we were able make inferences about predictability of intermolecular interactions between both components. This presentation will discuss both the experimental protocol and the results that we have obtained to date.



## RM_MWGL Regional Meeting 619

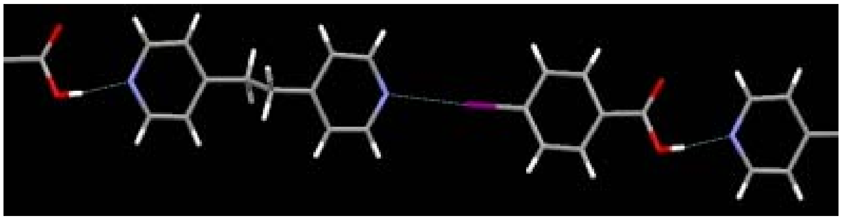
## Balancing hydrogen and halogen bonding in co-crystal assembly

*__Sean K. Dembowski__, sdembows@oberlin.edu, Christer B. Aakeröy, Prashant D. Chopade, John Desper.Department of Chemistry, Kansas State University, Manhattan, KS 66506, United States*

Co-crystallization has recently gained interest as a potential method of adjusting or even customizing the physical properties of a compound without changing its chemical characteristics. However, unlike recrystallization, a key laboratory separation technique that occurs frequently and precisely, co-crystal formation is still a rare and relatively poorly understood phenomenon.

Hydrogen bonding is by far the most common tool in crystal engineering; however, a complex synthetic scheme relying solely on hydrogen bonds has the potential for undesirable competition and crossover interactions between incorrect donor-acceptor pairs. Our research introduces halogen bonding into the synthetic scheme to determine whether co-crystal engineering using both hydrogen and halogen bonding simultaneously will allow for more control in co-crystal formation.

By correlating computed electrostatics and bonding patterns of molecules containing both hydrogen and halogen bond donors, we can determine the relative strengths of different donor groups and establish hierarchies for bonding schemes using hydrogen and halogen bonding in parallel.



### RM_MWGL Regional Meeting 620

## An exacting test of whether activation energy controls regioselectivity of competitive nucleophilic aromatic substitutions from an excited state

***Gene G. Wubbels**, wubbelsg@unk.edu, Ryo Tamura, Emmett J. Gannon.Department of Chemistry, University of Nebraska at Kearney, Kearney, Nebraska 68849, United States*

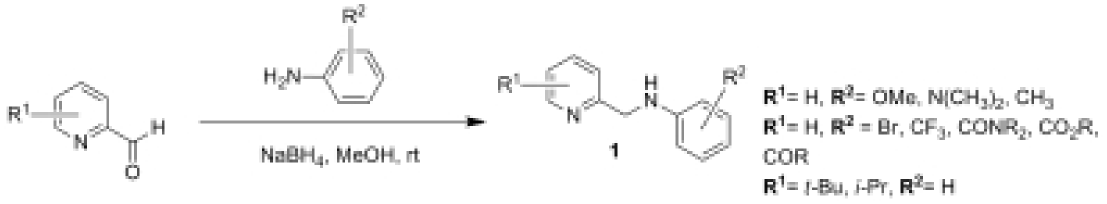
Photolysis of 2-chloro-4-nitroanisole (**1**) with hydroxide ion in water gives three products from the triplet state, namely, 2-methoxy-5-nitrophenol (**2**), 2-chloro-4-nitrophenol (**3**), and 3-chloro-4-methoxyphenol (**4**), in nominal yields of 70, 15, and 15% at room temperature. Quantitative analysis of photolyses at various temperatures gave product yields of: 72.6, 14.3, and 13.2% at 0 $^oC$; 69.4, 14.9, and 15.8% at 35 $^oC$; and 66.7, 15.9, and 17.5% at 70 $^oC$, respectively. From the net product-forming rate constant from the excited triplet (1.96 e8 $M^{-1}s^{-1}$) and the assumption that a precursor of **3** reverts to starting material to the extent of about 50%, the rate constants for each nucleophilic attack can be determined and the Arrhenius activation energies calculated. The product ratios can then be calculated according to Arrhenius theory for each temperature, which are: 72.4, 14.2, and 13.3% at 0 $^oC$, 69.4, 15.1, and 15.5% at 35 $^oC$, and 66.8, 15.9, and 17.4% at 70 $^oC$, respectively. The agreement of the observed yields with those predicted with Arrhenius theory is impressive. Especially notable is that the odd variations in the yields of **3** and **4** are reproduced. Because of the partitioning of **3,** its activation energy is lower than that of **4** despite the similarity of yield. As expected, higher temperature favors the competing reactions with higher activation energies. Here, the range of increase of **3** is only about half that of **4** in both experiment and theory**.** Others have reported that density functional calculations fail to detect the intermediacy of the triplet sigma complex in the displacement of chloride ion. We report that the sodium counter ion must be included to find the intermediate, that Hartree-Fock calculations at high levels of theory are successful, and that density functional calculations fail to detect the intermediate even with the counter ion.

## RM_MWGL Regional Meeting 621

# New iron pyridyl amine complexes and their catalytic activity in oxidation reactions

***Matthew Lenze**, matt.chemguy@gmail.com, Eike Bauer. Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, Missouri 63121, United States*

Oxidation is a powerful and versatile method to rapidly and strategically functionalize a wide range of substrates. However, the use of oxidation reactions in industry is limited on large scales due to the use of hazardous oxidants and precautions needed to be taken in order to properly handle the oxidants. Another limiting feature of oxidations in the pharmaceutical industry is the stoichiometric use of highly toxic metals such as chromium, osmium, and ruthenium which need to be removed from the final product to meet food and health standards. Accordingly, non-toxic alternatives to the current methodologies are being investigated. Our goal is to develop an environmentally friendly, iron based, catalyst systems that are capable of efficiently oxidizing unactivated substrates using hydroperoxides as the oxidant. Reported herein is the preparation of a series of sterically and electronically modified bis and trisdentate *N*-donor pyridyl amine ligands, L, such as **1** (Scheme 1).



These ligands were then successfully employed in the synthesis of their respective metal complexes of the general formula $[Fe(OTf)_2L_2]$ or $[FeL_2]^{2+}(OTf)_2$. The respective complexes of these pyridyl-based ligand systems **1** have been isolated in 78-99% yields and have displayed efficacy in the of oxidation secondary alcohols and activated methylene groups to the corresponding ketones (37-93% isolated yields) using aqueous *tert*-butylhydroperoxide as the oxidant. The substrate scope of these oxidation reactions will be presented as well as mechanistic and kinetic investigations.

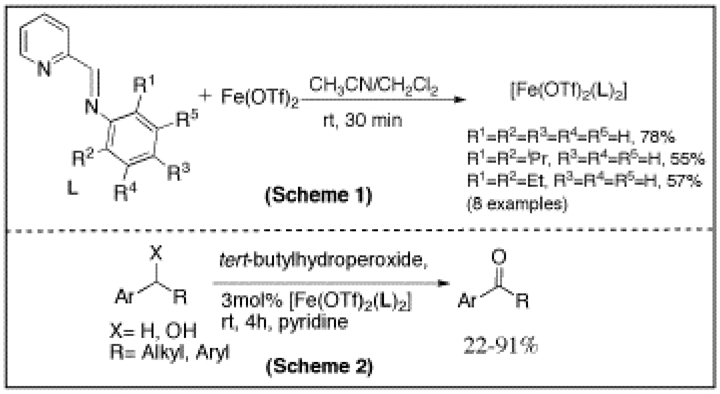
## RM_MWGL Regional Meeting 622

# Synthesis and characterization of Iron(II) complexes of α-Imino pyridine and their catalytic application in oxidation of activated methylene group and secondary alcohols

***Pushkar Shejwalkar***, *pshejwalkar2004@gmail.com, Eike Bauer. Department of Chemistry and Biochemistry, University of Missouri Saint Louis, St. Louis, MO 63121, United States*

Oxidation of relatively inert C-H bonds catalyzed by iron complexes has been a 'hot topic'of research in catalysis for a while. Current research is directed towards improvement in selectivity, relative ease and milder reaction conditions for the reactions. Iron complexes mimicking motifs found in nature have already shown to be catalytically active in the title reaction. Our group is particularly interested in nitrogen-based ligands that are easy to synthesize, tunable (sterically and electronically), and give better conversion towards the oxidation of C-H bonds.

Here we report the use of 'imine based' bi-dentate ligand systems that are easy to access and can be tuned electronically and sterically. We synthesized a set of sterically and electronically tuned Fe(II) complexes of α-iminopyridines (**L**) of the general formula [Fe(OTf)$_2$**L**$_2$] (Scheme 1) by mixing Fe(OTf)$_2$ and ligand **L** in acetonitrile/CH$_2$Cl$_2$ solvent mixture at room temperature.



The new complexes were subsequently employed as catalysts in oxidations reactions utilizing tert-butylhydroperoxide (TBHP) at room temperature in 4 hr. The yields ranged from 22-91% (Scheme 2). The new complexes specifically oxidize benzylic CH$_2$ groups as well as secondary alcohols to the corresponding ketones. Primary alcohols and methyl groups are not oxidized under these conditions.

Preliminary mechanistic investigations revealed a radical pathway and that the oxidation of benzylic CH$_2$ groups goes through a different pathway than the oxidation of secondary alcohols. We also present UV-Vis spectroscopic evidence for the formation of an [Fe-O-O-$^t$Bu] intermediate.

---

## RM_MWGL Regional Meeting 623

## Efforts toward the synthesis of high oxidation state iridium complexes

***Sean Whittemore***, *swhittem@chemistry.osu.edu, James Stambuli. The Ohio State University, United States*

In some instances, the C-H bond activation of alkanes using cationic iridium(III) complexes is believed to proceed via iridium(V) intermediates. Although there are several reports of iridium(V) complexes in the literature, they are still considered to be rare. Therefore, the synthesis of high oxidation state iridium complexes may potentially lead to new catalysts for the activation of alkane C-H bonds. Synthetic efforts, as well as initial reactivity studies of these complexes, will be presented.

### RM_MWGL Regional Meeting 624

## Measuring Energy Transfer Processes Among Cyanine Dyes

***Colette Robinson***[1], *cdr2007@k-state.edu, Dinusha Udukala*[1], *Mausam Kalita*[2], *Hongwang Wang*[1], *Deryl L. Troyer*[2], *Stefan H. Bossmann*[1]. *(1) Chemistry, Kansas State University, Manhattan, Kansas 66506-0401, United States (2) Anatomy&Physiology, Kansas State University, Manhattan, Kansas 66506, United States*

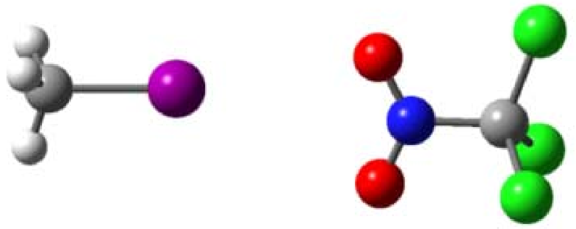
The early detection of cancer is crucial with regard to proper treatment. Cancer cells are known to over-express various matrix metalloproteinases (MMPs) such as MMP1, MMP2, MMP7, as well as urokinase-type plasminogen activator (uPA) and several cathepsins. The objective of our research is to develop a Fe/Fe3O4 nanoparticle-based system, which has the potential to identify the presence of these proteases in cancer cells and tissue. Our nanoplatform for protease detection consists of dopamine-tetraethylene glycol coated Fe/Fe3O4 nanoparticles to which cyanine dyes are attached by means of specific peptide sequences. These cleavage (consensus) sequences can be cleaved in the presence of the right protease, releasing the fluorescent dyes. Photodonor/acceptor pairs are an important component for optical biosensors, for instance for the measurement of the in-vivo activities of cancer-related proteases. The aim of these studies was to quantify photoinduced energy transfer reactions occurring between cyanine dyes in dependence of their differences in excited state energies and redox potentials. Foerster-type energy transfer has been studied between pairs of water-soluble and hydrophobic cyanine dyes of the types 3.0, 3.5, 5.0, 5.5, 7.0, and 7.5. The highly fluorescent dyes were excited in their resp. excitation maxima and their fluorescence was monitored. The rates of energy transfer and the so-called Foerster-radii have been determined.

### RM_MWGL Regional Meeting 625

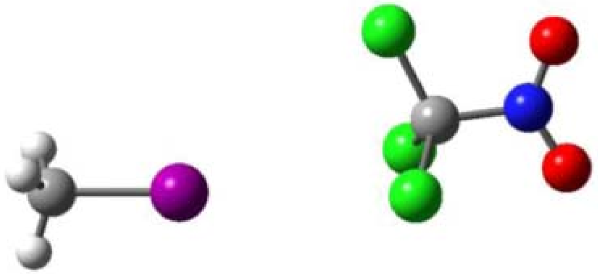
## Iodine bonding stabilizes methyl iodide in Midas pesticide

***Kaitlan Prugger**, glaserr@missouri.edu, Rainer Glaser. Department of Chemistry, University of Missouri, Columbia, Missouri 65211, United States*

Following the phaseout of the fumigant methyl bromide, the EPA approved methyl iodide for use as plant pesticide in 2007. MeI is commonly applied as Midas®, a pesticide containing both MeI and chloropicrin ($Cl_3C–NO_2$). Here we report the results of an ab initio study of the structures and stabilities of aggregates formed between $CH_3I$, **1** and chloropicrin, **2**, and of some of their addition products at the UQCISD(full)/6-31G*//MP2(full)/6-31G* level. We have determined the structures and stabilities of the iodine bonded molecular aggregates (IBMA) **3** and **4** and the hydrogen bonded molecular aggregates (HBMA) **5** and **6**. The aggregation between iodomethane and chloropicrin results in two iodine bonded molecular aggregates (IBMA). Aggregate **3** involves genuine iodine bonding (oxygen-charge induced iodine polarization) and aggregate **4** involves some iodine bonding in the broader sense (chlorine-charge induced iodine polarization) and significant iodine-chlorine bonding (dispersion). Aggregates **5** and **6** with hydrogen bonding between methyl-Hs of iodomethane and chloropicrin's O or Cl acceptors also exist on the potential energy surface. The mixed aggregates **3** - **5** are bound on the free enthalpy surface relative to the homodimers of **1** and **2**, and the IBMA structures **3** and **4** are most stable. This result suggests that the liquid mixture of chloropicrin and iodomethane is a good choice to reduce the volatility of iodomethane because of thermodynamically stabilizing iodine bonding.



IBMA(O), **3**



IBMA(Cl), **4**

**RM_MWGL Regional Meeting 626**

**Protease assays for the detection of cancer**

***Dinusha N Udukala***[1], *dinu@ksu.edu, Hongwang Wang*[1], *Stefan H Bossmann*[1], *Deryl Troyer*[2], *Olga Koper*[3], *Franklin Kroh*[3], *Gayani Abayaweera*[1], *Leonie Bossmann*[1], *Colette Robinson*[1]. *(1) Deparment Of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States (2) Department Of Anatomy and Physiology, Kansas State University, Manhattan, Kansas 66506, United States (3) Nano Scale Corporation, Manhattan, Kansas, United States*

Cancer cells are well-known to over express various matrix metalloproteinases (MMPs) as well as urokinase-type plasminogen activator (uPA). The goal of the research is to develop a Fe/$Fe_3O_4$ nanoparticle-based system, which has the potential to recognize the existence of these proteases in cancer cells and tissue. This nanoplatform for protease recognition consists of aminosilane coated Fe/$Fe_3O_4$ nanoparticles to which cyanine dye 5.5 is directly attached and TCPP is attached by means of specific peptide sequences.

These consensus (cleavage) sequences can be cleaved in the presence of the correct protease, thus releasing the fluorescent dye that is linked via the consensus sequence. Upon escape from the Fe/$Fe_3O_4$ nanoparticle, the emission intensity of the organic dye will significantly increase, which can be detected using fluorescence spectroscopy, in blood, tissue or urine samples. This diagnostic nanoplatform can be applied for the recognition of different stages of various solid tumors. Whereas MMP2 is over expressed in early stages of cancer, urokinase is dominant in later stages. Urine samples from canine cancer subjects were used to demonstrate the protease assay for recognition of several enzymes. A distinct relationship was observed between the stage of the cancer and the fluorescence intensities of the assay. The results obtained to date are very promising and may lead to a simple assay for the early diagnosis of various cancers.

**RM_MWGL Regional Meeting 627**

## Long Wavelength Fluorophores for the Generation of Singlet State Oxygen

***Quinn A Best***, *qbest@siu.edu, Colleen Scott, Matthew McCarroll. Department of Chemistry and Biochemistry, Southern Illinois University Carbondale, Carbondale, Illinois 62901, United States*

The synthesis and characterization of a series of longer wavelength far-red fluorophores capable of generating singlet state oxygen will be described. These fluorophores may be useful in photodynamic therapy (PDT), where red/near-IR absorption and emission is potentially more beneficial because those wavelengths have deeper penetration in tissue.

**RM_MWGL Regional Meeting 628**

## Chemically directed assembly of charge-transferring hybrid nanostructures

***Robert J. Hamers**, rjhamers@wisc.edu.Department of Chemistry, University of Wisconsin - Madison, Madison, WI 53706, United States*

The increasing interest in renewable energy is leading to a need to develop robust, low-cost methods of forming charge-transporting interfaces. Examples include interfaces of molecules with metal oxide nanoparticles, and formation of dyadic nanoparticle-nanoparticle junctions. Metal oxides are of particular interest because of their electronic properties and chemical stability. We have been investigating the use of chemical self-assembly methods, particularly the use of "click" chemistry, as a versatile means to assemble novel nanostructures on metal oxide nanoparticle films for applications in photovoltaic energy conversion and photocatalysis. A key element has been to develop robust chemical methods for functionalization of metal oxides with alkyne groups and with azide groups, enabling formation of junctions by the Cu-catalyzed Azide-Alkyne Cycloaddition (CuACC) reaction, also known as "click" chemistry. Initial experiments focused on using click chemistry to form junctions between Ru coordination complexes and metal oxide nanoparticles, while more recent efforts have been placed on making nanoparticle-nanoparticle heterojunctions. In both cases we have succeeded in using click chemistry to assemble charge-transferring hybrid junctions. To test whether the resulting structures support charge transfer, we using time-resolved surface photovoltage (TR-SPV) measurements, a non-contact method of measuring charge-transfer dynamics at surfaces. In this talk we will discuss these and other recent studies of the chemical assembly of charge-transferring nanostructured interfaces and their resulting charge-transfer properties.

**RM_MWGL Regional Meeting 629**

## Synthetic pathway to and optical properties of CdSe quantum belts

***William E. Buhro**, buhro@wustl.edu. Department of Chemistry, Washington University, St. Louis, MO 63130, United States*

Pseudo-1D nanocrystals such as quantum wires (QWs) and quantum belts (QBs) are in principle capable of transporting energy (excitons) and charge over long distances, and thus may have applications in solar-energy conversion and other technologies. However, excitons and charge carriers in QWs and QBs sample extremely large surface areas and thus have a high probability of encountering surface trap sites, precluding efficient transport.

Photoluminescence (PL) efficiencies provide a convenient measure of surface trap-site populations, with high PL efficiencies indicating well-passivated surfaces having low trap-site densities. The PL efficiencies for QWs reported to date are disappointingly low (0.1-0.3%), indicating defective surfaces at which photogenerated electron-hole pairs recombine non-radiatively.

I will describe semiconductor QBs in which excitons are efficiently delocalized over the entire length of the nanocrystals and the PL efficiencies rise to 40%, rivaling those of

quantum rods. These very good optical properties result from synthetic and passivation schemes that limit surface trap-site populations. The results establish that pseudo-1D semiconductor nanocrystals can effectively transport excitons and presumably charge carriers with minimal losses to non-radiative-recombination pathways.

## RM_MWGL Regional Meeting 630

### Controlled assembly of nanoparticles to superlattice crystals

*Deepa Jose, John Matthiesen, Chris Parsons, Yijun Sun, Chris Sorensen, **Ken Klabunde**, kenjk@k-state.edu. Departments of Chemistry and Physics, Kansas State University, Manhattan, KS 66506, United States*

An emerging theme of modern science is that uniform nanoparticles (NPs) can serve as the atoms and molecules of a new class of NP based materials. Our long term research goal is to mimic nature's atomic and molecular solids with materials based on NPs. To achieve our goal there are three key issues that must be addressed: 1) novel synthesis to create a library of NPs with thermally stable ligand shells that can interact and bond together in a wide variety of ways, 2) develop assembly methods based on an understanding and control of the potentials of interaction to guide the assembly of macroscopic quantities of NPs into any imaginable form, and 3) the ability to induce and control the formation of a wide variety of strong interparticle bonds in the assembled material that mimic those used by nature for atomic and molecular solids.

We have discovered a remarkable process called digestive ripening or nano-machining which causes particles to be “nanomachined” in the presence of a surface active ligand at elevated temperatures to the same, equilibrium size or, reversibly, into a variety of polygonal structures. This process yields quasimonodisperse NPs in multi-gram quantities that form beautiful NP superlattices and can be applied to Ag, Co, In, Pd, CdSe, CdTe, as well as Au.

We will discuss how digestive ripening happens and compare different ligands (thiols, amines, silanes) and different techniques (inverse micelle reduction of metal salts vs. solvated metal atom dispersion (SMAD)). The tendencies to form very small clusters, such as $[Au_{25}SR_{18}]^-$ vs. $[Au_{3800}(SR)_{360}]$ will be discussed. The overall importance of digestive ripening to achieve substantial amounts of monodisperse nanocrystals, which can be used to grow large nanocrystals superlattices, will be discussed and evaluated.

## RM_MWGL Regional Meeting 631

### Wrapping up nanorods

***Catherine J. Murphy**, murphycj@illinois.edu. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States*

Gold nanorods have potential applications as chemical sensing, biological imaging, and photothermal therapeutics. Our laboratory has developed the syntheses of these materials, in controlled size and shape, over the last few years. Surface modification of these nanomaterials is a key step to enable applications. In this talk I will describe our recent efforts to wrap up nanorods with layer-by-layer polyelectrolyte deposition in aqueous solution, in a way that allows for “capture coating” of small molecules at defined distances from the surface.

**RM_MWGL Regional Meeting 632**

## Plasmonic nanomaterials for disease diagnostics

***Amanda J Haes***, *amanda-haes@uiowa.edu, Marie Carmelle S. Pierre, Binaya Shrestha, Anna Volkert. Department of Chemistry, 204 IATL, University of Iowa, Iowa City, IA 52242, United States*

Precise control over the shape, size, and local environment of nanoparticles is vital for the development of new nanotechnology applications. This is especially important in understanding how these size-dependent properties impact the detection of biological and chemical targets. In this presentation, the architecture, stability, and surface chemistry of solution-phase gold and silver nanoparticles will be correlated to nanoparticle function for improved disease treatment strategies and for the direct detection of disease biomarkers. Nanoparticle concentration, core composition, and surface chemistry will be shown to play important roles in these sensing schemes. The most rugged and reproducible nanoparticle sensors will utilize silica membrane encapsulation of gold or gold-coated silver nanoparticles. The silica membrane prevents electromagnetic coupling between the nanoparticle cores without blocking the active metal surface for surface enhanced Raman scattering and refractive index sensing. Applications related to the direct and quantitative detection of small molecules will be discussed. Improvements in understanding what is on the surface chemistry of a nanoparticle and how that surface chemistry influences the activity of the nanoparticles will have ultimate implications on the detection of target biological and environmental toxins.

**RM_MWGL Regional Meeting 633**

## Direct observation of conformational exchange in the small multidrug resistance transporter EmrE

*Emma A. Morrison[1], Gregory T. DeKoster[1], Supratik Dutta[1], Michael Clarkson[3], Reza Vafabakhsh[2], Dorothee Kern[3], Taekjip Ha[2], **Katherine A. Henzler-Wildman**[1], khenzler@biochem.wustl.edu. (1) Department of Biochemistry and Molecular Biophysics, Washington University School of Medicine, St. Louis, MO 63110, United States (2) Department of Physics and Howard Hughes Medical Institute, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (3) Department of*

*Biochemistry and Howard Hughes Medical Institute, Brandeis University, Waltham, MA 02454, United States*

Small multidrug resistance (SMR) transporters provide an ideal system to study the minimal requirements for active transport across a membrane. EmrE is an *E. coli* SMR transporter that exports a broad class of polyaromatic cation substrates, thus conferring resistance to drug compounds matching this chemical description. As a secondary active antiporter, EmrE drives the uphill export of each substrate molecule by coupling it to the downhill import of two protons across the inner membrane. EmrE is proposed to function via a single-site alternating access model. In this well-established model, transporters are inherently dynamic proteins, converting between inward- and outward-facing conformations in order to move substrate molecules across a membrane barrier.

There is general agreement that the minimal functional unit is an EmrE homodimer, but a great deal of controversy remains regarding its structure, topology, and detailed mechanism. We have used a combination of solution NMR and FRET experiments to directly follow the kinetics and structural changes occurring during individual steps in the transport cycle. Our results reveal that EmrE forms an antiparallel homodimer and exchanges between inward- and outward-facing states at a rate of 5 $s^{-1}$ when bound to the substrate tetraphenylphosphonium. Furthermore, the inward- and outward-facing states are identical except that they have opposite orientation. These findings reconcile the controversial asymmetric EmrE crystal structure with the functional symmetry of residues in the active site and have important implications for the energetics of proton-driven coupled antiport.

**RM_MWGL Regional Meeting 634**

## Structural and biophysical studies of proline catabolic enzymes

***John J Tanner***, *tannerjj@missouri.edu. Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States*

Proline catabolism is an important pathway in energy metabolism. There are two enzymes in the pathway, proline dehydrogenase (PRODH) and pyrroline-5-carboxylate dehydrogenase (P5CDH), and together they catalyze the 4-electron oxidation of proline to glutamate via the intermediate P5C. In some bacteria, the PRODH and P5CDH catalytic activities are combined into a single polypeptide chain known as proline utilization A (PutA). Defects in proline catabolism result in the metabolic disorders hyperprolinemia I and II. Furthermore, proline catabolism is important in apoptosis, tumor suppression, and pathogen virulence.

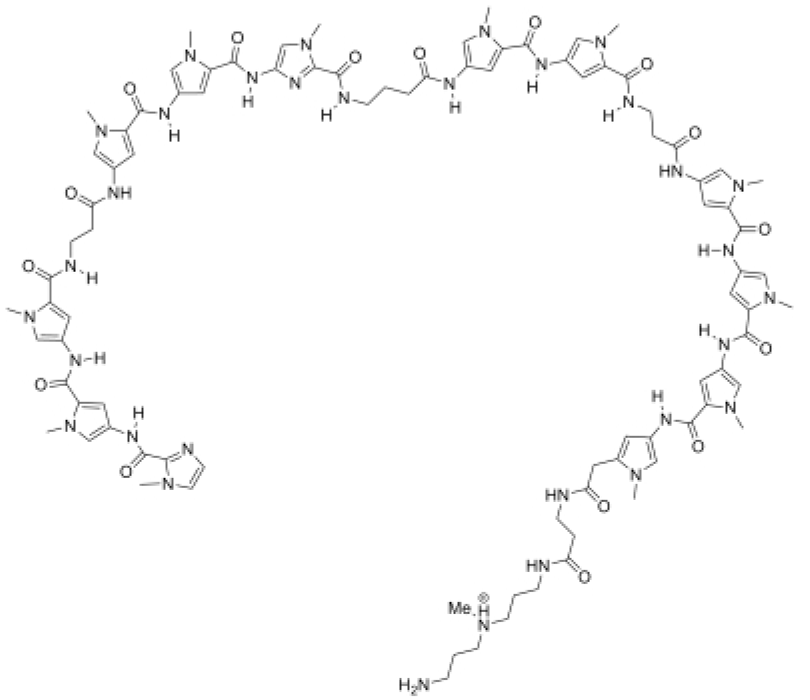
Over the past several years, we have used crystallography, small-angle X-ray scattering, and a variety of biophysical and biochemical tools to probe sequence, structure, and function relationships within the proline catabolic enzyme family. In this presentation, I will describe the first crystal structure of a full-length PutA protein as well as a low resolution SAXS-based model of a trifunctional PutA that combines PRODH, P5CDH, and transcriptional repressor activities into a single polypeptide chain.

**RM_MWGL Regional Meeting 635**

## DNA binding properties of a large antiviral polyamide

***Gaofei He***, *ghe.cmu@gmail.com, Kevin J Koeller, Cynthia M Dupureur, James K Bashkin. Department of Chemistry & Biochemistry, Center for Nanoscience, University of Missouri-St. Louis, St. Louis, MO 63123, United States*

PA1 is a large 14-ring polyamide (PA) that is active against eliminating HPV16 in cell culture (Edwards, T. G.; *et al.*, Antivir. Res. 2011, 91, 177–186). To better understand the basis of this behavior, we have undertaken biophysical studies of its DNA binding behavior. Using both hydroxyl radical and DNase I footprinting as detected by capillary electrophoresis, we have characterized a number of low nM $K_d$ binding sites in a 524 bp region of the HPV16 genome. Single nucleotide (nt) mismatch sites are bound by this PA in addition to the cognate sites predicted by well-known DNA recognition rules (Dervan, P. B.; Edelson, B. S. Curr Opin Struct Biol 2003, 13, 284.), and the present report permits additional comparisons of sequence selectivity in a range of sequence contexts. Further binding details are currently being pursued using affinity cleavage and PA1 conjugated to iron EDTA. Using a simple fluorescence binding assay, we have also demonstrated that while DNA binding affinity is poor in the absence of additives ($K_d$>150 nM), low nM affinity ($K_d$) for a short cognate DNA hairpin is consistently observed in the presence of a wide variety of additives. Such tight binding closely matches affinities obtained *via* footprinting on a long DNA molecule.



## RM_MWGL Regional Meeting 636

# Chasing fluorescence lifetimes in complex biological systems. What can fluorescence lifetime imaging microscopy (FLIM) tell us?

***Robert M Clegg***[1,2,3,4]*, rclegg@illinois.edu, Yi-Chun Chen*[3]*, John Eichorst*[2]*, Kai Wen Teng*[2]*, (nfn) Govindjee*[2,5]*, Shizue Matsubara*[6]*. (1) Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (2) Center for Biophysics and Computational Biology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (3) Department of Bioengineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (4) Department of Biochemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (5) Department of Plant Biology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States (6) Institut für Pflanzenwissenschaften, Jülich, Germany*

To resolve changes in different molecular components in highly complex, intact, functional biological systems, which adapt rapidly to changing conditions, we have developed rapid nanosecond fluorescence lifetime imaging (FLI) to follow these processes in real time (sub-second to many minutes). We have used FLI to investigate non-photochemical quenching (NPQ) mechanisms used by plants to protect themselves from over exposure to light, which can produce destructive reactive oxygen species (ROS). Plants possess the two central mechanisms of NPQ, the xanthophyll and lutein cycles, which allow plants to react rapidly to variable light conditions. Lifetime-resolved fluorescence emission from chlorophyll "brings to light" underlying mechanisms, such as energy transfer, photochemical and non-photochemical quenching, photoinhibition, and state changes (shuttling of components of antennae systems between photosystems PSI and PSII). Some aspects of bioassays based on FRET and fluorescence lifetimes for measuring intracellular oxidation reduction potentials and the enzymatic activity of a matrix metalloproteinase will be discussed, as well as FLIM applications to protoporphyrin IX aggregation in vivo (produced in cells from the precursor for PpIX, ALA ) and in vitro. Fluorescent protein hybrids have played a central role in the development many of these bioassay probes. The overview and examples will emphasize some analysis techniques specific to FLIM that provide rapid and detailed multi-parameter analysis of complex systems.

**RM_MWGL Regional Meeting 637**

## Mass spectral studies of intrinsically disordered proteins

***David D. Weis***, *dweis@ku.edu. Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States*

Intrinsically disordered proteins are highly flexible and lack secondary and/or tertiary structure, yet participate in functional interactions. Over the past decade, bioinformatic approaches have uncovered a vast universe of functional protein interactions involving intrinsically disordered proteins, but much less is known about the atomic-level details of how these proteins function. MS-based labeling strategies such as amide H/D exchange and hydroxyl radical labeling can provide such information. Here, work on two protein systems will be presented: (1) ACTR and CBP, disordered proteins that co-fold upon binding and (2) calcineurin, a disordered protein that undergoes partial folding upon binding to calmodulin. H/D exchange revealed residual structure in the random coil protein ACTR. Although molten globular CBP is mostly folded, rapid inter-conversion between folded and unstructured conformations causes exchange by molecules in unstructured conformations to dominate the observed H/D exchange kinetics. Based on its H/D exchange kinetics, the calcineurin autoinhibitory and regulatory domains are completely unstructured. However, upon binding to calmodulin in the presence of $Ca^{2+}$, the calmodulin binding domain of calcineurin becomes highly protected from H/D exchange, consistent with the assignment of the region as the calmodulin binding domain. There is also significant protection well beyond the limits of the calmodulin binding domain suggesting that calmodulin induces structuring in parts of calcineurin that are distal to the calmodulin binding domain.

**RM_MWGL Regional Meeting 638**

## Tryptophan substitutions as fluorescent probes of amyloid-β structure

***Michael R. Nichols***[1], *nicholsmic@umsl.edu, Jillienne C. Touchette*[1], *Laura L. Williams*[1], *Deepa Ajit*[1], *Fabio Gallazzi*[2], *Ryan T. McDonough*[1], *Geeta Paranjape*[1]. *(1) Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, United States (2) Structural Biology Core, University of Missouri-Columbia, Columbia, MO 65211, United States*

A signature feature of Alzheimer's disease is the accumulation of plaques composed of fibrillar amyloid-β protein (Aβ) in the brain parenchyma. Structural models of Aβ fibrils reveal an extensive β-sheet network with a hydrophobic core extending throughout the fibril axis. In the current studies, phenylalanines in the Aβ(1-40) sequence were substituted with tryptophan residues at either position 4 (F4W), 19 (F19W), or 20 (F20W) to probe the fibril environment. The F4W and F20W substitutions did not alter self-assembly kinetics, while the F19W change slightly lengthened the lag phase without hindering fibril formation. The tryptophan fluorescence of Aβ(1-40) F19W, but not Aβ(1-40) F4W or Aβ(1-40) F20W, underwent a marked blue shift during fibril formation and this shift was temporally correlated with thioflavin T binding. Isolated Aβ(1-40) F19W fibrils exhibited the largest fluorescence blue shifts consistent with W19 insertion into the Aβ(1-40) fibril inner core. Blue shifts were considerably smaller for F4W and F20W fibrils. Fluorescence quenching experiments with water-soluble acrylamide and KI demonstrated that both W19 and W20 were much less accessible to quenching in fibrils compared to purified monomer. Lipid-soluble TEMPO quenched Aβ(1-40) F19W fibrils more effectively than F20W fibrils thus strengthening the conclusion that while W20 accessibility is compromised in Aβ fibrils it resides in a much less hydrophobic environment than W19. The overall findings are consistent with previous structural models of Aβ fibrils, provide new information on residue accessibility, and illustrate the value of tryptophan as a protein folding probe for amyloids.

**RM_MWGL Regional Meeting 639**

## Incorporating peer-led team learning (PLTL) into lower-level chemistry courses: implementation and insights

***Regina F Frey***, *gfrey@wustl.edu. Department of Chemistry, Washington University in St Louis, Saint Louis, MO 63130, United States*

Active-learning strategies can help improve student learning and participation. One approach to incorporate active learning into your class is to include peer-led team learning (PLTL) study groups. This workshop will explore the philosophy and implementation of PLTL into lower-level chemistry courses. Participants will learn how to initiate and structure a PLTL program, design PLTL group activities, and interview and train peer leaders. We will also discuss the evaluation study of our program and give insights into what we have learned over the years.