

## ***Chemical Education: General, Organic, and Biochemistry***

**Organizer:** Dharshi Bopegedera The Evergreen State College

**Organizer:** Carole Berg Bellevue Community College, Bellevue, WA

### **1. Distance Learning GOB, Lec and Labs; What Works, What Doesn't!**

**Kathleen Carrigan, Chemistry Instructor** and Carol Handy, Allied Health, Portland Community College, Portland, OR

We are teaching a Chemistry course taught as a distance learning option with a totally at home lab component that has been a successful, positive experience for both students and instructors. We will share our model that is presently being offered at Portland Community College. We will share the successful aspects that are well received by students, enhance learning, and use interactive instruction. We will show some of the latest technology; tablet laptops, Elluminate®, online homework, and "Jing" for recording instructional media.

There have been many bumps in the road and we would like to help you avoid them by sharing a few of the difficulties in the development and the delivery of a distance learning chemistry course. We will bring the lab kits we use from Lab Paq will be on hand for show and tell and inspection. We will be more than happy to share our model for developing new courses and supporting new instructors.

### **2. Adding Food and Drug Adulterants Into a GOB Chemistry Curriculum**

**Ron Swisher, Ph.D.**, Natural Science Department, Oregon Institute of Technology, Klamath Falls, OR

General/organic/biological chemistry is typically taken by freshman nursing and allied health students. Recent media attention about adulteration of pet food and baby formula with melamine provide opportunity to illustrate basic organic chemistry of melamine and protein to nursing students. Similarly the adulteration of heparin provides the opportunity to discuss the biochemistry of heparin and chondroitin sulfate, two molecules which have widespread medical and dietary supplement use. Other examples will be discussed as time permits

### **3. Examining Protein Structure in a GOB Chemistry Class: An Activity about Alzheimer's Disease**

**Deanna Dahlke Ojennus, Ph.D.**, Department of Chemistry, Whitworth University, Spokane, WA

A computer modeling activity is described in which health science students in a General, Organic, and Biochemistry course examine protein structures related to Alzheimer's disease. The activity focuses on defining each level of protein structure, identifying important stabilizing intra- and inter-molecular forces at each structural level, and establishing the relationship between amino acid sequence and protein structure/function. The value of this hands-on modeling activity is assessed by pre- and post-activity quizzes and by a student survey.

### **4. World Health as a Context for Teaching Chemistry and Biology**

**James J. Neitzel, Ph.D.**, Chemistry, The Evergreen State College, Olympia, WA, Kevin Francis, History of Science, The Evergreen State College, Olympia, WA and Mike Paros, Biology, The Evergreen State College, Olympia, WA

This talk will describe an experimental, year long, full time, team taught interdisciplinary program. The thematic organizing concept in the class was the examination of diseases that have a large impact on global health, based on the World Health Organization's list of the top ten causes of death. Case studies based on this list of diseases were used as the contexts to teach fundamental concepts in chemistry and biology. These cases included cancer and perinatal conditions,

cardiovascular diseases, stroke, and diabetes, and infectious diseases focusing on HIV/AIDS, tuberculosis, malaria, influenza, and diarrheal diseases. Bioethics, history, and public policy were explored as they related to these diseases. Students also participated in community based learning, in which they linked with clinics, hospitals, government public health departments, or other health-related organizations for volunteer service

The goal of this chemistry component of this program was to cover the normal topics covered in a general-organic-biochemistry one year sequence. Examples will be presented of specific contexts for chemistry that included physiology, diagnosis, and medicinal chemistry.

### ***Chemistry, Energy, and Sustainability 1***

**Organizer:** Justin Lytle Pacific Lutheran University

**Presider:** Justin Lytle Pacific Lutheran University

### **5. Solar Water Oxidation by Composite Catalyst/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Photoanodes**

**Diane K. Zhong**, Jianwei Sun, Hiroki Inumaru and Daniel R. Gamelin, Department of Chemistry, University of Washington, Seattle, WA

Capture of solar energy as hydrogen fuel by photocatalytic water splitting is a major thrust in solar energy conversion research. Recently we have shown that, electrodeposition of an amorphous cobalt catalyst layer over a high-surface-area  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode causes a more than 350 mV cathodic shift in the onset potential for photoelectrochemical water oxidation. The catalyst layer is shown to deposit conformally onto the mesostructured  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, leading to a large contact area at the interface between the two halves of the composite photoanode. Photoelectrochemical measurements show that the photocurrent generated from this composite photoanode still derives from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> excitation but is now accessible at an external bias several hundred millivolts below what is typically required for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes alone, indicating a reduced external bias would be needed to drive overall water splitting. These results demonstrate modification of this prototypical photoanode material with a conformal layer of a competent electrocatalyst to separate the tasks of photon absorption and redox catalysis, a strategy that may have important and general ramifications for solar photoelectrochemical hydrogen generation.

### **6. Solar Reaction for One-Way Trans to Cis Photoisomerization**

**Robert S. H. Liu, Professor, emeritus**, Yao-Peng Zhao and Roger O. Campbell, Department of Chemistry, University of Hawaii, Honolulu, HI

Triplet sensitized reaction is ideal for solar reaction because it conveniently taps the abundant long-wavelength light of solar radiation. We have developed conditions for preparation of hindered cis isomers of olefins. In selected cases, condition for one-way trans to cis isomerization has been found yielding exclusively the higher energy isomer. The compounds we have studied include stilbene, styrene, diene and triene derivatives. We have also investigated photoisomerization of compounds in the vitamin A series and showed that the hindered 7-cis isomers can be obtained in high yield (in excess of 80%), compounds previously used in the synthesis of the rare hindered 7-cis isomers of vitamin A. In the process, we have developed a green-&-fun floating solar reactor that made possible such photochemical synthetic reactions without the need of electric energy to

power such reactions nor running water to remove excess heat from solar radiation. In cases where the red-dye Rose Bengal was used as a photosensitizer, the reaction was complete within a short surfing session (i.e. in half an hour) on the beach of Waikiki.

(Ref. *Green Chem.*, **2008**, *10*, 1038-1042; *ibid*, **2009**, *11*, 000-000)

## **7. Resonance Raman and Photocurrent Imaging of Polymer/Fullerene Photovoltaic Devices: Uncovering the Role of Morphology-Dependent Aggregated and Unaggregated Species**

**John K. Grey** and Yongqian Gao, Department of Chemistry, University of New Mexico, Albuquerque, NM

Polymeric photovoltaic materials have long been known to exist in both aggregated and unaggregated forms, however, the specific structural factors that modulate their densities of states (DOS) and contributions to photocurrent generation remains poorly understood. We have recently introduced a new Raman and photocurrent imaging technique that can spatially map local chemical structure and the relative DOS of aggregated/unaggregated species to photocurrent generation in functioning device structures. This approach provides the basis for correlating the local chemical and structural properties to charge transfer yields, which are usually averaged over in conventional device characterization studies. The data also suggests that greater planarity of the polymer chains leads to closer pi-pi stacking distances (H-aggregated form) resulting in higher photocurrents. This trend is rationalized in terms of lower reorganization energies for aggregated species since charge is more delocalized across these regions. We are currently reconciling both experimental data and theory to develop predictive models for reliable control of local structure to optimize overall device performance.

## **8. Development of a Supercritical Water Microchannel Reactor for Reforming Biomass to Hydrogen Gas**

**Aaron K. Goodwin** and Gregory L. Rorrer, Department of Chemical Engineering, Oregon State University, Corvallis, OR

Thermochemical conversion of renewable, CO<sub>2</sub> neutral biomass feed stocks to hydrogen gas is a promising technology for the production of chemicals and fuels that may significantly contribute to the worlds energy supply. Supercritical water (SCW) at temperatures greater than 374°C and pressures greater than 220 bar is an effective medium for reforming biomass to hydrogen rich gas. However, SCW gasification of biomass in traditional flow through reactors is limited by heat transfer to the reacting fluid, resulting in long residence times, and the formation of recalcitrant byproducts and coke precursors. Microchannel reactors can intensify heat transfer to endothermic reforming reactions, and minimize the fluid heating period due to small diameter reactor channels. A SCW Hastelloy C-276 microchannel reactor was developed to gasify soluble and liquefied biomass constituents including hemicellulose/lignin rich alkaline pretreatment streams and biocrude. Biomass constituent model compounds were used to benchmark the performance of the microreactor. For example, xylose, a hemicellulose model compound, was stoichiometrically reformed to hydrogen rich gas (67% H<sub>2</sub>, 33% CO<sub>2</sub>) within a 1 second residence time at 650°C and 250 bar without any byproduct formation. A hydrogen yield greater than 9 moles of hydrogen per mole of xylose reacted was obtained. This study shows that microchannel reactors have considerable promise for intensifying thermochemical conversion of biomass to chemicals and fuels.

## **9. Creating Nanostructured Materials for Enzymatic Biofuel Cells**

Nicolas Cirigliano<sup>1</sup>, James Lim<sup>2</sup>, John Wang<sup>3</sup> and **Bruce Dunn**<sup>1</sup>, (1)Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA, (2)Corning Glass, Corning, NY, (3)HRL Laboratories, Malibu, CA

The flexible solution chemistry of the sol-gel process has been used to synthesize bio-hybrid materials in which a wide variety of biomolecules are encapsulated in a transparent, inorganic matrix. It is now well established that the dopant biomolecules possess enhanced stability and retain

their characteristic reactivities despite being immobilized in the pores of the inorganic matrix. We have used sol-gel encapsulation methods as the basis for the electrode architecture used in enzymatic biofuel cells. In this paper, we review our work on the fabrication and characterization of an enzymatic glucose-oxygen biofuel cell that incorporates nanostructured silica sol-gel/carbon nanotube composite electrodes. With this immobilization approach, the silica sol-gel is sufficiently porous that both glucose and oxygen have access to enzymes and yet provide a protective cage that preserves biological structure and function. Recent work on direct electron transfer with these electrodes will also be presented.

## **10. What Goes around Comes around: Tracking Persistent Organic Pollutants From the Beijing Olympics to the Pacific Northwestern U.S**

**Staci L. Simonich, Associate Professor**, Environmental and Molecular Toxicology and Department of Chemistry, Oregon State University, Corvallis, OR

Emissions of some Persistent Organic Pollutants (POPs) have been increasing in parts of Asia due to increased combustion. During the 2008 Beijing Olympics, atmospheric particulate matter (PM) was collected to determine the effect of increased combustion emission controls on PM concentrations relative to meteorology. Our results suggest that precipitation and wind direction played a larger role in decreasing PM concentrations during the Beijing Olympics than traffic restrictions. In addition, using a series of remote sites in the Pacific Northwestern U.S. at different elevations, we have traced the episodic trans-Pacific atmospheric transport of some POPs to parts of Asia and determined the chemical composition of trans-Pacific and regional U.S. airmasses.

## ***Novel Polymer Science for Modern Applications 1***

**Sponsor:** ACS Division of Polymer Chemistry

**Organizer:** Mark Dadmun University of Tennessee, Knoxville, TN

**Organizer:** Dean Waldow Pacific Lutheran University, Tacoma, WA

**President:** Dean Waldow Pacific Lutheran University, Tacoma, WA

## **11. Poly(vinyl ester) Block Copolymers: New Avenues in Degradable Soft Materials**

**Mahesh K. Mahanthappa, Professor**, Department of Chemistry, University of Wisconsin-Madison, Madison, WI

An important challenge in modern polymer science is the development of new degradable polymeric materials derived from commodity monomers that exhibit tunable physical properties comparable to those of well-known commodity polyolefins. Well-known biodegradable polymers such as poly(lactide) and poly(3-hydroxyalkanoates) exhibit limited thermal stability under melt processing conditions as well as poor mechanical properties. Derived from relatively inexpensive petrochemicals, vinyl ester homopolymers are known and widely used materials in applications ranging from paper coatings and chewing gum bases to biomedical materials. Based on the properties of their parent homopolymers, poly(vinyl ester) block copolymers are expected to have desirable properties associated with known soft materials, while exhibiting the possibility for degradation under a variety of environmental conditions to produce relatively benign byproducts. Herein, we disclose our recent results on the controlled radical polymerization of vinyl ester monomers and the synthesis of the first vinyl ester diblock and triblock copolymers along with preliminary morphological characterization of these new soft materials.

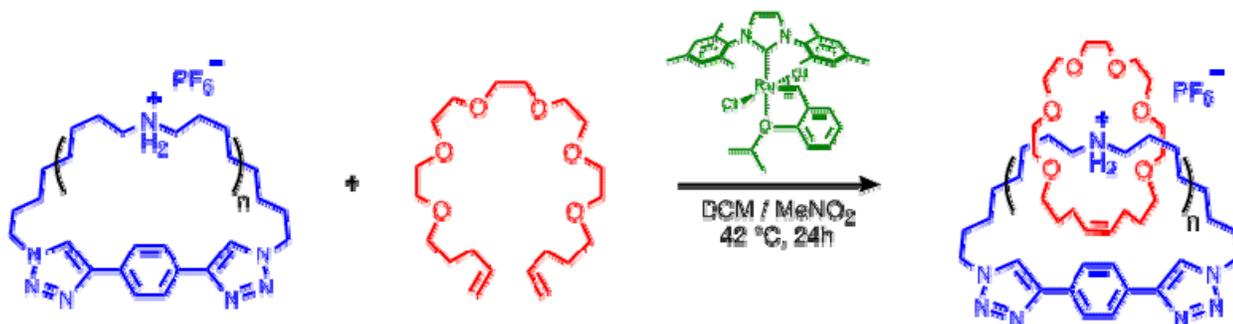
## 12. Quasiliving Cationic to RAFT Polymerization: Synthesis of a Novel Block Copolymer

Andrew J. D. Magenau and **Robson F. Storey**, School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, MS

A novel block copolymer, composed of polyisobutylene (PIB) and poly(N-isopropylacrylamide) (PNIPAM) segments, was synthesized. The PIB block was prepared via quasiliving cationic polymerization and end functionalized by in-situ quenching to yield telechelic halogen-terminated PIB. Azido functionality was obtained by displacement of the terminal halogen through nucleophilic substitution, which was confirmed by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Coupling of an alkyne-functional chain transfer agent (CTA) to azido PIB was successfully accomplished through a copper catalyzed click reaction. Structure of the resulting PIB-based macro-CTA was verified with  $^1\text{H}$  NMR, FTIR, and GPC; whereas coupling reaction kinetics were monitored by real time  $^1\text{H}$  NMR. Subsequently, the function of this macro-CTA was demonstrated by RAFT polymerization of NIPAM for synthesis of the second block. RAFT kinetics were investigated under a variety of reaction conditions using VT NMR, and the resulting block copolymers were characterized by  $^1\text{H}$  NMR and GPC. Aqueous solution properties were briefly probed by dynamic and static light scattering confirming the presence of self assembled aggregates with reversible temperature sensitive responsiveness.

## 13. Synthesis of a Cyclic Charm Bracelet

**Paul G. Clark** and Robert H. Grubbs, Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA

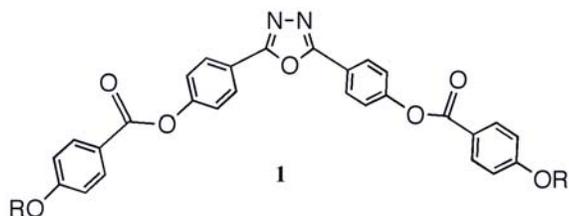


Ring-opening metathesis polymerization of a cyclic boc-amine monomer with Grubbs-Hoveyda 2<sup>nd</sup> generation ruthenium olefin metathesis catalyst in the presence of a chain transfer agent facilitated the synthesis of a dibromo-telechelic linear boc-amine polymer. End-group substitution with sodium azide followed by a high-dilution copper-catalyzed alkyne-azide 'click' cyclization with 1,4-diethynylbenzene yielded the corresponding macrocyclic analogue. Hydrogenation and conversion to the polyammonium species prepared the macrocycle for "clipping". Coordination of diolefin polyether crown-type compounds to the polyammonium backbone and subsequent ring-closing metathesis with Grubbs-Hoveyda 2<sup>nd</sup> generation ruthenium olefin metathesis catalyst afforded the cyclic catenane "charm bracelet" polymer. The cyclic nature of the post-'click' polymer was confirmed with a variety of techniques, including IR spectroscopy, proton and carbon NMR end-group analysis, gel permeation chromatograph elution-time comparison, and topology-based chemical techniques. Analysis and confirmation of the interlocked nature of the "charm bracelet" polymer was accomplished with proton NMR and diffusion-ordered NMR spectroscopy (DOSY).

## 14. In Search of the Biaxial Nematic Phase at Low Temperatures: Effects of Lateral Methylation

**Eric Scharrer**<sup>1</sup>, Jane Lindborg<sup>1</sup>, Nikki LaFemina<sup>1</sup> and Edward T. Samulski<sup>2</sup>, (1)Department of Chemistry, University of Puget Sound, Tacoma, WA, (2)Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC

The existence of the biaxial nematic ( $N_b$ ) phase was first proposed in 1970. Since that time, researchers have sought compounds that might exhibit this unique phase due, in part, to the potential applications; displays created with a  $N_b$  phase might show faster switching times and lower power consumption. In 2004, a series of liquid crystals possessing the 2,5-oxadiazole bisphenol core (ODBP), **1**, was shown to possess the elusive biaxial nematic phase. However, the onset of the nematic phase in these derivatives is impractically high (near 200 °C). This has led to further research into ways to reduce the nematic onset temperature in oxadiazole containing systems, and our recent approach has been to focus on the incorporation of lateral methyl groups at a variety of positions on the aromatic rings. Derivatives with one, two, and three lateral methyl groups show significant reductions in the nematic onset temperatures, while the incorporation of four lateral methyl groups completely destroys mesomorphism. Synthetic details and the phase behavior of a variety of methylated ODBP derivatives will be discussed.



## 15. Controlling Structure and Properties in Conjugated Block Copolymers

**Rachel Segalman**, Chemical Engineering, University of California, Berkeley, Berkeley, CA

Pattern control over polymeric structures on a molecular through nanoscopic lengthscale is a vital tool to optimizing properties. For example, while molecular structure affects the electronic properties of semiconducting polymers, the crystal and grain structure greatly affect bulk conductivity, and nanometer lengthscale pattern of internal interfaces is vital to charge separation and recombination in photovoltaic and light emission effects. In this seminar, I will discuss our work to both understand the effects of structure on properties and gain pattern control in this inherently multidimensional problem. While the 10nm lengthscale is most easily accessed via block copolymer self-assembly, the thermodynamics of these materials is distinct from classical block copolymers due to the conformational asymmetry of a rigid, conjugated polymer chain and liquid crystallinity. We have created a weakly segregated rod-coil block copolymer system by minimizing enthalpic interactions and maximizing conformational asymmetry. The accessible phase transitions of this unique system allow us to explore the thermodynamics of self-assembly. Further, this main chain liquid crystalline block copolymer system has numerous handles which we can use to control the orientation of the internal interfaces within the active layer of a device.

## 16. Morphology, Charge Transport and Photovoltaic Properties of Diblock Copolymers

**Guoqiang Ren**, Pei-Tzu Wu and Samson A. Jenekhe, Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, WA

Polymer solar cells represent a clean and cost-efficient way to utilize the solar energy. Block copolymers, due to the engineered electronic structures and microphase separation properties, have

received much attention as potential candidates for polymer solar cells. Our studies of solar cells based on diblock copoly(3-alkylthiophene)/fullerene blends have shown that block copolymer solar cells can outperformed their parent homopolymers in both charge transport and photovoltaic properties. One- and two-order of magnitude increase in space-charge limited current (SCLC) hole mobility have been achieved compared with homopolymers. The power conversion efficiency (PCE) of block copolymer solar cells was found to be substantially increased compared to the best devices made from the parent homopolymers. Our results showed that block copolymer with tailored structures are promising materials for polymer photovoltaic applications.

### ***General Session - Analytical 1***

**Organizer:** Gary Christian University of Washington

**President:** Bo Zhang University of Washington, Seattle, WA

#### **17. Selective Electrochemical Detection of Triacetone Triperoxide**

**Yuqun Xie** and I. Francis Cheng, Department of Chemistry, University of Idaho, Moscow, ID

There is a dire need for a rapid, selective, portable and inexpensive detection scheme for the explosive Triacetone-triperoxide (TATP). It is of particular concern in major transportation hubs and its precursors are the source of the liquids ban by the TSA. We propose an electrochemical detection method, based on the redox reactions between peroxides and bromide. With the exception of TATP these reactions produce  $\text{Br}_2$ . Reaction with TATP differs in that it produces bromoacetones in place of  $\text{Br}_2$ . A TATP selective detector therefore can sense this peroxide by the loss of bromide without the appearance of  $\text{Br}_2$ . Both  $\text{Br}^-$  and  $\text{Br}_2$  are monitored by double step chronoamperometry through the oxidation of  $\text{Br}^-$  to  $\text{Br}_2$  ( $E_{\text{step}} = 960$  mV vs. Ag/AgCl) and reduction of  $\text{Br}_2$  to  $\text{Br}^-$  ( $E_{\text{step}} = 700$  mV vs. Ag/AgCl). Initial chronoamperometric results yielded a detection limit of  $8.5 \mu\text{M}$  for TATP. We also report results with another improvised explosive, hexamethylene triperoxide diamine and common probable interferences, benzoyl peroxide, and  $\text{H}_2\text{O}_2$  all of which generate  $\text{Br}_2$ . The proposed method offers unique selectivity of triacetone triperoxide (TATP) detection without any interference.

#### **18. Investigation of the Role of the Membrane Material in a Wire Based Electrochemical Sensor for the Detection of Hydrogen Peroxide**

**Drew M. Budner**, James Lagucik and Christopher Fenton, Department of Chemistry, Whitworth University, Spokane, WA

The role of a membrane in a wire based electrochemical sensor has been investigated. The membrane material was varied to determine if the sensor performance was affected by the membrane material. In addition the, thickness of the material was investigated in an attempt to improve sensor performance. It was found that a thicker membrane increased sensor response but the type of material generally had no direct effect on sensor performance.

#### **19. The Electrochemistry, Electrocatalysis and Photoenergy Conversion of Single Nanoparticles**

**Jonathan T. Cox**, Yongxin Li and Bo Zhang, Department of Chemistry, University of Washington, Seattle, WA

We are exploring the fundamental electrochemical properties of individual metal/semiconductor nanoparticles using metal electrodes of true molecular dimensions. Nanodisk metal electrodes of radii ranging from 1 to 3 nanometers have been fabricated using a laser-assisted pulling process. Chemical modification at such small surfaces allows for the immobilization of single Au or  $\text{TiO}_2$  nanoparticles. This allows for the electrochemical properties of different types of materials to be characterized. In one experiment, single gold nanoparticles have been found to exhibit excellent catalytic activities to the reduction of oxygen. This experiment allows for the size/shape dependent electrochemical properties and electrocatalytic activities to be investigated at a single-nanoparticle

level. In a second experiment, in collaboration with the Gamelin group in our department, we are studying the photovoltaic activity of different semiconductor nanoparticles. As one example, a single TiO<sub>2</sub> nanoparticle is immobilized on the surface of the Au nanoelectrode. When UV light is emitted onto the nanoparticle, quantifiable photocurrent is generated by the electron transfer between the nanoparticle and the electrode. The study of this conversion of energy allows a better understanding of photovoltaic cells because the electrochemical properties of single colloidal nanocrystals can be directly analyzed.

## **20. Single Neurotransmitter Sensing and DNA Transport Utilizing Molecular Scale Nanopores and Nanochannels**

**Jin H. Chen, Graduate Student Chemistry**, Marissa Wood and Bo Zhang, Department of Chemistry, University of Washington, Seattle, WA

Nanopores and nanofluidic channels have attracted extensive interest in recent years due to their unique applications in single-molecule sensing and transport studies. We are interested in bioanalytical applications of solid-state nanopores and nanochannels of molecular dimensions. In one project, nanopore-type sensors are developed to study neuronal secretion at a single cell level. Conical-shaped quartz nanopores have been prepared using a simple laser pulling process on a quartz capillary. In a recent experiment using a thermal evaporator, quartz nanopores with radii of 5 nm were coated with a thin gold film, partially sealing the orifice to create nanopores with radii below 2.0 nm. Using this method, we were able to sense single neurotransmitter molecules. In a separate project, silica nanochannels with radii in the range of 5-100 nm were utilized to study molecular transport of double-stranded DNA. Electroosmosis-driven molecular translocation has been observed for genomic-length  $\lambda$ -DNA through a 9-nm radius nanochannel.

## **21. Immunochromatographic Strip-Based Immunosensors for Rapid Detection of Biomarkers**

**Zhexiang Zou**<sup>1</sup>, Hungchi Nian<sup>2</sup>, Jun Wang<sup>2</sup>, Hua Wang<sup>2</sup>, Yaoqun Li<sup>1</sup>, Chuck Timchalk<sup>2</sup> and Yuehe Lin<sup>2</sup>, (1)Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China, (2)Pacific Northwest National Laboratory, Richland, WA

Immunochromatographic strip technique (IST) combines the excellent separation ability of chromatography with high specificity and sensitivity of conventional immunoassay. The advantages of such IST include easy operation, short analysis time, less interference and relatively low cost. We developed several immunosensors that involve immunochromatographic strip technique for rapid detection of biomarkers, such as Hepatitis B surface antigen (HBsAg), 3,5,6-trichloro-2-pyridinol (TCP), and cotinine. Sandwich immunoassay was developed for determination of HBsAg while competitive immunoassay was developed for determination of TCP and cotinine. Both horseradish peroxidase (HRP) and quantum dots (QDs) were used for labeling during the immunoassay. Besides the sensitive electrochemical detection of HRP labeled, QDs exhibit much better stability. More over, QDs can be used for ultrasensitive and rapid fluorescence detection because of their unique optical properties. These novel immunosensors offer a promising new analytical tool for biomarker detection.

## **22. Glycosphingolipid Metabolism in Single Cells**

**Colin D. Whitmore**<sup>1</sup>, Jillian Prendergast<sup>2</sup>, Ronald L. Schnaar<sup>2</sup> and Norman J. Dovichi<sup>1</sup>, (1)Department of Chemistry, University of Washington, Seattle, WA, (2)The Johns Hopkins School of Medicine, Baltimore, MD

We have developed a method for analyzing the metabolism of glycosphingolipids in primary single cells. Our process relies upon the uptake and conversion of a fluorescently labeled substrate. Metabolites of this substrate that retain the fluorescent tag can then be detected with laser induced fluorescence. Dorsal root ganglia were harvested from rats, and dissociated. The neurons were

plated, then were incubated in the presence of our fluorescent ganglioside analogue. During incubation, the substrate was metabolized into fluorescent products. The cells were formalin fixed, which allowed them to be shipped for analysis. Analysis was accomplished with a home built capillary electrophoresis instrument with laser induced fluorescence detection. We observed remarkable heterogeneity among the neurons, in both the quantity of substrate and in the relative quantities of metabolites.

### ***General Session - Biochemistry***

**Organizer:** Dean Waldow Pacific Lutheran University, Tacoma, WA

**Presider:** Stacia M. Rink, Ph. D. Pacific Lutheran University, Tacoma, WA

#### **23. M314H Mutant of Peptidylglycine $\alpha$ -Hydroxylating Monooxygenase (PHM)**

**Brenda A. Broers, Ph.D. Candidate**, Andrew Bauman and Ninian Blackburn, Department of Science and Engineering, Oregon Health and Science University, Beaverton, OR

Peptidylglycine  $\alpha$ -hydroxylating monooxygenase (PHM) catalyzes the first-step of a two-step post-translational modification in which neuropeptides are converted to their active form. This two copper protein, consisting of a CuH with three His ligands and a CuM with two His and one Met ligand, reacts by a mechanism which is not fully understood. It is believed that the coppers cycle through an oxidized and a reduced phase in which O<sub>2</sub> is activated at the CuM site. It has been shown that PHM exists in two forms, Met-off (active) and Met-on (inactive) which involves the dissociation of a methionine S donor at one of the Cu centers. This study investigates whether these on-off effects are due to the CuM Met ligand through analysis of the M314H mutant. M314H is 5% as active as the wild-type (WT) but has a similar pH profile with maximum activity at pH 5.5. Results from FTIR and X-ray Absorption Spectroscopy of fully reduced- and CO-bound forms show the same Met-off, Met-on transition as seen in the WT. Therefore, it is unlikely that the sulfur involved is from the M314 CuM ligand. This ligand may play more of a role in stabilizing an intermediate such as Cu(I)-O<sub>2</sub>.

#### **24. The Copper Binding Histidine - Methionine (HM) Rich Luminal Loop Between TM1 and TM2 of ATP7A: A Spectroscopic Approach**

**Adenike A. Otoikhian**<sup>1</sup>, Amanda Barry<sup>2</sup>, Svetlana Lutsenko<sup>2</sup> and Ninian J. Blackburn<sup>1</sup>, (1)Department of Science and Engineering: Division of Environmental and Biomolecular Systems, Oregon Health and Science University, Beaverton, OR, (2)Department of Biochemistry and Molecular Biology, Oregon Health and Science University, Portland, OR

ATP7A is a human Cu<sup>+</sup>-ATPase, which drives the efflux of copper from the cytoplasm into the secretory pathway, for insertion into the active sites of cuproenzymes. However, little is known about the mechanism by which ATP7A hands off its copper to the acceptor protein. We hypothesize that the luminal loop between transmembrane segments 1 and 2 of ATP7A acts as an important sensor for acceptor-protein loading, and may be involved in direct ATPase-acceptor interaction. This loop is rich in histidine and methionine residues which often signal areas of sequence involved in Cu(1) binding. To investigate this hypothesis, a recombinant system of the luminal His-Met rich loop of ATP7A was constructed. The loop binds 2-2.5 coppers in the Cu(II) and Cu(I) states respectively. EPR and EXAFS data indicate noncoupled dinuclear copper centers. EXAFS data are best interpreted by an average of 2-3 histidines and 1-2 O/N in the Cu(II) coordination. The Cu(I) coordination involves a maximum 2.5 histidine ligands, together with 0.5 sulfur. The coordination chemistry mirrors the H and M centers of the target peptidylglycine  $\alpha$ -hydroxylating monooxygenase (PHM). These findings suggest that the His-Met Rich loop might function like other metallochaperones which mimic the coordination of their target proteins.

## 25. Fluorine Substituted Adenosines as Probes of Nucleobase Protonation in Catalytic RNA

**Ian T. Suydam** and Scott A. Strobel, Molecular Biophysics and Biochemistry, Yale University, New Haven, CT

We have developed a new series of fluorine substituted adenosine analogs to identify sites of adenosine protonation in functional RNA by nucleotide analog interference mapping (NAIM). These analogs make fluorine for hydrogen substitutions in the adenine ring of adenosine or 7-deazaadenosine with resulting N1 pKa values spanning more than four pKa units. To demonstrate the utility of these analogs we have conducted a NAIM study on a ligating construct of the Varkud Satellite (VS) ribozyme. We find that each of the analogs is readily incorporated by T7 RNA polymerase and produce fully active transcripts when substituted at the majority of sites. Strong interferences are observed for three sites known to be critical for VS ribozyme function, most notably A756. A similar interference pattern is observed at A38 of the Hairpin ribozyme, suggesting these sites may be functionally equivalent. The structural similarity of these analogs, combined with their even incorporation and selective interference, provides an improved method for identifying sites of adenosine protonation in a variety of systems.

## 26. Investigation of the Link Between Mitochondrial Function and Diabetes

**Stephanie Bryner**<sup>1</sup>, Carin Thomas<sup>1</sup> and Lucindia Carnell<sup>2</sup>, (1)Department of Chemistry, Central Washington University, Ellensburg, WA, (2)Department of Biology, Central Washington University, Ellensburg, WA

Type II diabetes is a worldwide epidemic affecting over 246 million people, but the cellular mechanism that initiates the disease is still unclear. Recent research shows a link between mitochondrial function and type II diabetes. The aim of this research is to investigate one specific aspect of that link. In particular, we will investigate the role of a mitochondrial enzyme, Nicotinamide Nucleotide Transhydrogenase (NNT), and its impact on maintaining mitochondrial function in animals exposed to a high-fat diet. Three genetically distinct populations of the roundworm, *Caenorhabditis elegans* (wild type and two mutants that lack the *nnt* gene) are grown on high-fat and normal diets and the function of mitochondria in these worms is compared using analytical and imaging techniques. Preliminary data show lower respiratory rate and mitochondrial membrane potential in the nematode lacking *nnt*.

## 27. Rational Enhancement of NKG2D-MICA Affinity in the Undergraduate Laboratory

**Benjamin J. McFarland**, Department of Chemistry and Biochemistry, Seattle Pacific University, Seattle, WA

Many immune responses are governed by tight, highly specific protein-protein interactions. We use the computational method RosettaDesign to redesign the interaction between the immunoreceptor NKG2D, found on natural killer cells, and its MHC-like ligands, which are expressed on stressed, infected, or transformed cells.

We are currently pursuing two design strategies: *i.*) The NKG2D-ligand interface structure is dominated by 2 pairs of central tyrosine residues at positions 152 and 199. We mutated these residues to smaller and larger amino acids in order to investigate the role of the tyrosines in NKG2D-ligand complexes and to compare them with tyrosine-mediated antibody-protein interactions.

*ii.*) We are rationally enhancing MICA binding affinity for NKG2D with designed point mutations at MICA-NKG2D protein-protein contacts. RosettaDesign was used to predict which contact mutations would be most beneficial at the MICA-NKG2D interface. We produced multiple point mutants of MICA and measured NKG2D binding kinetics and thermodynamics using surface plasmon resonance. In

the first round of design, 4 out of 6 mutations enhanced NKG2D affinity by 0.5 kcal/mol or more, up to 1.2 kcal/mol.

In addition to independent undergraduate research projects, we also have adapted this research to undergraduate lecture/lab courses. Protein production is a seven-week sequence of second-quarter biochemistry laboratories, while collection of binding data using surface plasmon resonance and construction of plots to determine thermodynamics of binding are incorporated into a five-week sequence of physical chemistry laboratories. As a result, students accomplish protein design goals while learning the fundamental techniques of biochemistry.

## **28. Coexpression of Human $\alpha$ - and Circularly Permuted $\beta$ -Globins Yields a Hemoglobin with Normal R State but Modified T State Properties**

Anna L. Asmundson<sup>1</sup>, Alexandria M. Taber<sup>1</sup>, Adella van der Walde<sup>1</sup>, Danielle H. Lin<sup>1</sup>, John S. Olson<sup>2</sup> and **Spencer J. Anthony-Cahill<sup>1</sup>**, (1)Department of Chemistry, Western Washington University, Bellingham, WA, (2)Department of Biochemistry and Cell Biology, Rice University, Houston, TX

For the first time, a circularly permuted human  $\beta$ -globin (cp $\beta$ ) has been coexpressed with human  $\alpha$ -globin and shown to associate to form  $\alpha$ -cp $\beta$  hemoglobin in solution. Flash photolysis studies of  $\alpha$ -cp $\beta$  show biphasic and rapid CO and O<sub>2</sub> association kinetics with the amplitudes for the fast association phases being dominant due the presence of large amounts of hemoglobin dimers. Extensive dimerization of liganded but not deoxygenated  $\alpha$ -cp $\beta$  was observed by gel chromatography. The rate constants for O<sub>2</sub> and CO binding to the R state forms of  $\alpha$ -cp $\beta$  are almost identical to those of native HbA, and the rate of O<sub>2</sub> dissociation from fully oxygenated  $\alpha$ -cp $\beta$  is similar to that observed for HbA. When the deoxyHb form of  $\alpha$ -cp $\beta$  is reacted with CO in rapid mixing experiments, the observed time courses are monophasic and the observed bimolecular association rate constant is intermediate between the R state rate and that observed for T state. Thus the deoxygenated permuted  $\beta$  subunits generate an intermediate, higher affinity, deoxyHb quaternary state. This conclusion is supported by equilibrium oxygen binding measurements. See: Asmundson *et al.*, *Biochemistry*, in press (DOI:10.1021/bi900216p)

### ***General Session - Physical***

**Organizer:** Dean Waldow, Ph. D. Pacific Lutheran University, Tacoma, WA  
**President:** David L. Patrick Western Washington University, Bellingham, WA

## **29. Kinetics and Mechanism of One-Electron Oxidation of L-Cysteine by Tris(1,10-phenanthroline)Iron(III) Complex**

**Risikat O. Ajibola**, Department of Chemistry, PORTLAND STATE UNIVERSITY, Portland, OR and Reuben H. Simoyi, Department of Chemistry, Portland State University, Portland, OR

The kinetics of oxidation of cysteine by tris(1,10-phenanthroline)iron(III) complex (ferriin) has been studied spectrophotometrically in aqueous acidic medium under pseudo-first order conditions of excess cysteine. The products of the reaction are strictly ferriin and dimeric cystine. The orders of reaction with respect to ferriin and cysteine, observed rate constants, overall rate constants as well as thermodynamic parameters of the reaction were determined. Acid was found to have inhibitory effect on the reaction. The reaction is first order in both ferriin and cysteine in the initial stages of the reaction. Bimolecular rate constant was deduced to be  $7.15 \text{ M}^{-1}\text{s}^{-1}$ . The reaction is characterized by saturation in cysteine dependence which deviates from first order dependence. Possible explanation is the formation of an initial intimate complex between ferriin and cysteine which further forms an inert complex with another molecule of cysteine through a rapid equilibrium. Activation parameters determined ( $\Delta S^\ddagger = -217.02 \pm 0.03 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $\Delta H^\ddagger = 35.85 \pm 0.38 \text{ KJmol}^{-1}$  and  $\Delta G^\ddagger = 100.52 \text{ KJmol}^{-1}$ ) are indicative of formation of an associative intermediate prior to product formation.

### **31. Sub-Wavenumber CCD Spectrometer Calibration Using Molecular Iodine Laser-Induced Fluorescence**

Joseph G. Lambert, Department of Physics, Drexel University, Philadelphia, PA, Carlos Hernandez-Diaz, Department of Physics, Willamette University, Salem, OR and **J. Charles Williamson**, Department of Chemistry, Willamette University, Salem, OR

Replacement of conventional photomultiplier tube detectors with charge-coupled devices (CCD) or other array-based detectors can greatly accelerate data collection with spectroscopic instruments. However, in most instruments the conversion from CCD pixel coordinate to vacuum wavelength is nonlinear, and the spectral coordinate must be recalibrated whenever the grating is rotated to a new position. We have developed a method for spectrometer CCD calibration based on the laser-induced fluorescence spectrum of room-temperature, gas-phase molecular iodine.  $B \leftarrow X$  excitation at 514.5 nm of the  $P(13)$  43-0,  $R(15)$  43-0, and  $R(98)$  58-1 transitions results in a series of sharp emission lines spaced approximately  $200 \text{ cm}^{-1}$  apart, spanning a spectral range from 509 nm into the infrared. Collision-induced changes in the rovibrational states of excited-state iodine lead to additional calibration peaks in between the dominant emission lines. With our instrument, the iodine reference spectrum and the signal spectrum are recorded simultaneously with no cross talk by separating the two signals spatially along the vertical axis of the CCD imager. Calibration based on the iodine spectrum has been tested against laser line and Raman spectral standard signals, and the accuracy is  $0.05 \text{ cm}^{-1}$  or better.

### **32. Electron Transport and Sensor Characteristics of Tin Dioxide Based Nanocrystalline Materials**

**Allen Chaparadza** and Shankar Rananavare, Department of Chemistry, Portland State University, Portland, OR

Wide band gap, transparent semiconductor  $\text{SnO}_2$  is an n-type conductor and is widely used as a sensor material. Recent discovery of p-type doping with Li has opened exciting possibilities in new classes of sensor as well as transparent nanoelectronic devices. Li-doping in  $\text{SnO}_2$  nanoparticles was explored through a gel-sol method of synthesis to examine the influence of reaction conditions such as pH, dopant concentration, and calcination temperature. The Li doping in nanoparticles was characterized using nuclear reaction analysis and the nanostructure with HR-TEM and XRD techniques.

Direct current conductivity of the nanocrystals was investigated from 25 to 350 °C. Efros-Shklovskii Variable Range Hopping conduction mechanism was observed at temperatures below 100 °C with a cross over to 2D-Mott Variable Range Hopping conduction at temperatures above 250 °C. Thick film conductive  $\text{Cl}_2$  sensors were fabricated using nanoparticulate  $\text{SnO}_2$  doped with Sb. The fabricated sensors were tested against gases like  $\text{Cl}_2$ ,  $\text{Br}_2$ , HCl, NO,  $\text{NO}_2$ ,  $\text{CHCl}_3$ ,  $\text{NH}_3$  and  $\text{H}_2$ . The highest response to  $\text{Cl}_2$  was achieved in 0.1 % Sb doping where an exposure to 3ppm of  $\text{Cl}_2$  gas led to 500 fold increase in device resistance. The high sensitivity to  $\text{Cl}_2$  is accompanied by minor interference due to other gases at room temperature. It was found that the  $\text{SnO}_2$  doped with 0.1% Sb exhibited high response, selectivity ( $>100$  in comparison to the gases described above) and short response time ( $\sim 60\text{s}$ ) to  $\text{Cl}_2$  at 3 ppm level at room temperature.

Using a compression technique, porous diodes consisting of n-type (antimony doped) and p-type (lithium doped)  $\text{SnO}_2$  nano-particulate films were prepared. Their sensor capabilities were measured through alternating and direct current measurements. These porous diodes were capable of detecting 400 ppb  $\text{Cl}_2$  at room temperature and had a 40s response time.

### 33. Mechanistic Investigation Into the Formation of S-Nitrosocysteine

**Moshood Kayode Morakinyo**, Sovathana Ly and Reuben H. Simoyi, Department of Chemistry, Portland State University, Portland, OR

The kinetics and mechanism of the nitrosation of cysteine (CySH) to produce S-nitrosocysteine (CySNO) has been studied in acidic medium by using nitrous acid prepared *in situ*. The stoichiometry of the reaction was  $\text{CySH} + \text{HNO}_2 \rightarrow \text{CySNO} + \text{H}_2\text{O}$ . Only two nitrosating agents were detected; nitrous acid itself and protonated nitrous acid which is the hydrated form of the nitrosonium cation,  ${}^+\text{N}=\text{O}$ . Nitric oxide, NO, itself was not detected as a nitrosant. The bimolecular rate constant for the direct nitrosation of cysteine by nitrous acid was determined to be  $6.4 \pm 1.1 \text{ M}^{-1} \text{ s}^{-1}$ , while nitrosation by the nitrosonium cation has a rate constant of  $6.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . CySNO is short-lived, and decomposes completely to cystine and nitric oxide within 100 s in the presence of micromolar quantities of Cu(II) ions. Since the physiological environment contains many metal ions and metalloenzymes, it is unlikely that CySNO will be an effective carrier of NO.

### 34. Pickering Emulsion Stability and Interfacial Structure

**Kjersta L. Larson-Smith** and Danilo C. Pozzo, Department of Chemical Engineering, University of Washington, Seattle, WA

Particle-stabilized emulsions (Pickering Emulsions) are formed when small particles adsorb at the interface between the oil and water phases. The focus of this study is the interfacial structure and stability of oil in water emulsions that are stabilized by silica nanoparticles. These Pickering emulsions are examined using a combination of small-angle x-ray scattering, dynamic light scattering and microscopy. Small-angle x-ray scattering provides the ability to examine the particle arrangement at the oil-water interface *in situ*. The particle organization at the interface can be correlated to the stability and drop coalescence of the emulsions. Dynamic light scattering and microscopy are used to quantitatively relate the oil droplet size and macroscopic stability of the emulsion to changes in the nano-scale structure. Pickering emulsions of micron sized particles are known to be sterically stabilized by close-packed microparticles that form an elastic shell. In contrast, nanoparticles are not close-packed at the oil-water interface and the emulsion is found to be electrostatically stabilized.

### *Chemical Education: Green Chemistry*

**Organizer:** Carole Berg Bellevue Community College, Bellevue, WA

**Organizer:** Dharshi Bopegedera The Evergreen State College

### 35. Greening of First Year Chemistry Labs-Part I

**Brooke E. Taylor**, Gary E. Mort and John E. Thompson, Science, Lane Community College, Eugene, OR

Introductory and general chemistry classes provide an opportunity to expose a significant number of students to the principles of green chemistry. The goal of green chemistry is to ensure a healthy planet and includes the elimination of pollution by preventing it in the first place. Green chemistry is sustainable chemistry so green processes and labs are "benign by design". While organic chemistry labs have undergone significant green improvements, revisions and developments, general and introductory chemistry labs have not yet been revised to meet the goals of green chemistry. This presentation will focus on the improvement, revision and development of green labs in general and introductory chemistry courses. Strategies used to assess the lab curriculum, to identify stealth green labs, to revise brown labs and to develop new green labs will be discussed along with details of a new green lab for introductory and/or general chemistry.

## **36. Greening of First Year Chemistry Labs-Part II**

**Gary E. Mort**, Brooke E. Taylor and John E. Thompson, Science, Lane Community College, Eugene, OR

Continuing with the theme of greening the general, introductory and high school chemistry lab curriculum, this presentation will discuss specific improvements to stealth green labs, revisions to brown labs and the development of new green labs made at Lane Community College. Labs which we have adopted will be compared to our old labs, as will before and after labs we have greened. We will also share our revisions to our stealth green curriculum. An annotated bibliography of green or readily greenable labs, which already exist in the literature, will be available.

### ***Plenary Session 1***

**President:** Justin Lytle Pacific Lutheran University

**Session Overview:** A committed science and engineering research effort could make the home into a solar power station and solar gas station in the near future. In pursuing the goal of personalized energy, science and engineering drives inextricably to the heart of the energy challenge. Professor Nocera (Massachusetts Institute of Technology) will discuss his efforts toward the triumvirate: secure, carbon neutral and plentiful low-cost energy.

## **37. Personalized Energy: A Carbon-Neutral Energy Supply for 1 (× 6 Billion)**

**Daniel G. Nocera**, Department of Chemistry, 6-335, Massachusetts Institute of Technology, Cambridge, MA

A committed science and engineering research effort could make the home into a solar power station and solar gas station in the near future. In pursuing the goal of personalized energy, science and engineering drives inextricably to the heart of the energy challenge by addressing the triumvirate: secure, carbon neutral and plentiful low-cost energy. Because energy use scales directly with wealth, point-of-use solar energy will put individuals, in the smallest village in the developing world and in the largest city of the developed world, on a more level playing field. And the individual will be energy secure as they will control the energy on which they live. More powerfully, the possibility of generating terawatts of carbon-free energy may be realized by making available personalized energy to the 3 billion low-energy users and 3 billion people to inhabit our planet over the next half century.

Personalized energy at low cost presents new basic research targets, many of which are squarely centered in the endeavors of chemical and materials research. Because personalized energy will be possible only if solar energy is a 24/7 available supply, the key enabler for personalized energy is inexpensive storage. Studies of multielectron chemistry and proton-coupled electron transfer have led to the creation of a new catalyst that captures many of the functional elements of photosynthesis and in doing so provides a highly manufacturable and inexpensive method to effect a fuel-forming reaction that provides a carbon-neutral and sustainable method of solar storage - water-splitting. By developing an inexpensive 24/7 solar energy system for the individual, science and engineering can make available a carbon-neutral energy supply for 1 × 6 billion.

### ***General Poster Session 1***

**Organizer:** Kerry W. Fowler, Ph.D. Past-Chair, Puget Sound Local Section, Seattle, WA

**Session Overview:** Monday Poster Session: Presenters for odd numbered posters should be by their posters during the first half of the session and even numbered posters during the second half.

### **38. Polychromatic Emission and Limitations to Beer's Law**

**Timothy L. Sorey**, Amanda Christensen and Robert Rittenhouse, Department of Chemistry, Central Washington University, Ellensburg, WA

The goals of this project are to find a repeatable non linear graph at non  $\lambda$  max wavelengths, form a mathematical equation that fits the graph, and use this mathematical equation to obtain research grade results. In order to reach this goal, there are four solution colors that are going to be analyzed with concentrations that, with standard conditions, have absorbances near 1.0. These colored solutions will be analyzed using both high resolution ( $\pm 1$ nm) UV-VIS CARY and polychromatic Light Emitting Diode (LED) Spectroscopy instrumentation to study proposed mathematical fit equations for absorbance curves. If non  $\lambda$  max wavelengths have repeatable non linear graphs then a mathematical model could be created to reproducibly fit this calibration graph. This mathematical model can be used by anyone, teachers in particular, who do not have access to monochromatic spectrometers and may wish to make mathematical corrections to polychromatic analytical wavelengths to obtain research grade results.

### **39. Chemical Clues From Fatty Acid Analysis of Prehistoric Fire Pit Remains**

**John Malamakal, BS** and Jeffrey J. Rosentreter, Department of Chemistry, Idaho State University, Pocatello, ID

In archaeological studies, fire pits are referred to as features because they can be seen and recorded as part of the site but cannot be moved without being altered or destroyed. However the charcoal fragments contained in the fire debris hold chemical clues to the foods that have been heated on that fire. Controlling fire is major attribute of civilization and it allows people to cook food, increasing the variety and availability of nutrients. The elucidation of the specific foods, plants and animals, cooked over ancient fire pits aids in the archeological study of an area's ecosystem and civilization. The goal of our research is to develop analytical methodologies capable of examining fire-pit charcoal for trace fatty acids, which may reveal the types of foods cooked over these fires. This investigation focuses on fire debris from the US Great Basin. Implementation of modern GC /MS to quantify fatty acid ratios provided keys useful in elucidating food types prepared with these fires. Analytical method development has focused on the challenge of removing fats sorbed onto charcoal fragments. Quantitative partition coefficients were determined to aid in identifying efficient extraction solvents. Additional method development criteria, including economic and environmental factors, have been evaluated.

### **40. Real-Time Comparison Polarimeter for Data Acquisition In Determination of 0th, 1st, and 2nd Order Rate Constants**

**Timothy L. Sorey**, Edgar Perez and Devlin Forrester-Shipman, Department of Chemistry, Central Washington University, Ellensburg, WA

Currently it is difficult for students to experimentally determine stereocenter chemistry mechanisms without an expensive device that offers precision and accuracy in a time efficient manner. In fact, it is usually the instructor that manipulates the device which acquires data for the students to analyze. The purpose of this research is to have undergraduate chemistry students explore optically active chemical systems using a kinetic polarimeter to acquire and analyze data in real-time in the determination of kinetics rate constants in the lab. If this real-time comparison polarimeter can be used to support students' inquiry and data acquisition of optically active chemicals, then students will construct a better understanding of both chiral molecules and kinetic molecular mechanisms. This proposed device will afford students to easily adjust experimental parameters, make accurate and precise measurements, and use their time more efficiently in the learning laboratory. This proposed analytical instrument will be based upon student accessibility, ease of use, affordability, and offer research quality measurements. This instrument will be assessed experimentally by a known chemical reaction (the hydrolysis of sucrose) and compared with accepted experimental

values. Finally, a prototype of this instrument will be implemented and assessed in an undergraduate teaching laboratory (Fall Quarter 2009, CHEM 361 Lab).

#### **41. Toxic Effects of Urban Particulate Matter of Various Size Fractions On An in Vitro Model of *Saccharomyces Cerevisiae***

**Annika Nieber**<sup>1</sup>, Anne Johansen<sup>1</sup> and James Johnson<sup>2</sup>, (1)Department of Chemistry, Central Washington University, Ellensburg, WA, (2)Department of Biology, Central Washington University, Ellensburg, WA

Particulate components of industrial and commercial emissions suspended in ambient air can enter the human body via the respiratory system. They are known to cause various health effects, which may be controlled by the particle size and redox potential. Aerosol particles were collected near I-5 in Seattle and separated into three different size fractions: Ultrafine (UFP) with a diameter of < 0.1 µm, Fine (FP) with a diameter of 0.1 µm to 2.5 µm, and Coarse (CP) with a diameter of 2.5 µm to 10 µm. The correlation between particle size, redox potential, and toxicity was investigated in a whole cell *in vitro* experiment using the yeast *Saccharomyces cerevisiae* as the model organism. The particles were extracted from the substrates using sonication and the yeast was exposed to different sized particulates. The cytotoxic effects of the particles were evaluated by measuring the viability of the yeast, as well as the mutation rate. Cyclic voltammetry was used to determine the redox potential of the collected particulates. These data showed that the UFP fraction has a negative effect on cell survival and the mutation rate increased with decreasing particle size. The role of the redox potential is still being investigated.

#### **42. MTSL Labeling of Cysteine 93 in Cytochrome P450 Eryf**

J. Zac Peeler<sup>1</sup>, Dmitri R. Davydov<sup>2</sup> and **Jeffrey S. Grinstead**<sup>1</sup>, (1)Department of Chemistry, University of Puget Sound, Tacoma, WA, (2)Skaggs School of Pharmacy and Pharmaceutical Sciences, UCSD, La Jolla, CA

Cytochrome P450s are responsible for the oxidation of many chemicals the human body encounters. Complex interactions between ligands have been proposed that account for the observation that some ligands cooperatively influence the binding and oxidation of substrate molecules. The details of how one ligand molecule can influence the oxidation of another substrate is only beginning to be studied, and previous research has suggested that it may involve the ligand binding to a discrete position within the P450 active site, not necessarily near the heme iron. We are presently developing a method to determine the position of ligands within the active site of the bacterial P450 eryF using NMR spectroscopy of ligand molecules in the presence of a P450 with a paramagnetic label attached to it. The results presented here demonstrate labeling of Cytochrome P450 eryF double mutant S93C/C154S with the MTSL (methanethiosulfonate- paramagnetic spin label). We have used LC-MS to identify intact protein labeled with MTSL, and LC-MS/MS to identify the Cys93-containing tryptic peptide labeled with MTSL. This chemically labeled protein will be used to determine the position of ligand molecules within the active site of solution-phase P450 enzyme.

#### **43. Greening of First Year Chemistry Labs**

**John E. Thompson**, Gary E. Mort and Brooke E. Taylor, Science, Lane Community College, Eugene, OR

Introductory and general chemistry classes provide an opportunity to expose a significant number of students to the principles of green chemistry. The goal of green chemistry is to ensure a healthy planet and includes the elimination of pollution by preventing it in the first place. Green chemistry is sustainable chemistry so green processes and labs are "benign by design". While organic chemistry labs have undergone significant green improvements, revisions and developments, general and introductory chemistry labs have not yet been revised to meet the goals of green chemistry. This poster will focus on the process of improving, revising and developing of green labs in general and

introductory chemistry courses. Strategies used to assess the lab curriculum, to identify stealth green labs, to revise brown labs and to develop new green labs will be shared along with examples of new green labs for introductory and general chemistry.

#### **44. Adding An Explicit Solvent Molecule to Polarized Continuum Model for Computational Study On the Conformational Population of a Highly Fluorinated Hydrazone**

**Shih-I Lu**, Department of Chemistry, Soochow University, Taipei City, Taiwan

In this work, we examined the conformational population of a highly fluorinated hydrazone, 2H-perfluoro-2-methyl-3-pentanone, by density functional theory computations in four Lewis basic solvents: acetonitrile, diethyl ether, tetrahydrofuran and dimethyl sulfoxide. Various 1:1 hydrogen-bonded clusters of rotamer and solvent were embedded in the solvent employing the polarized continuum model in the computations. The calculated results showed the strength of the intermolecular interaction between the hydrogen bonding acceptor of solvent and the hydrogen atom of amino group in the fluorinated hydrazone played an important role in the experimental observation for the relative population. The combined approach that involves attaching a single explicit solvent molecule to the hydrazone, and then surrounding the resulting 1:1 cluster by a dielectric continuum, significantly improves the agreement between the calculated relative Gibbs energy and experiment, whereas, the implicit treatment of solvent gave an error in the prediction of relative stability for the fluorinated hydrazone in the four Lewis basic solvents.

#### **45. Persistence of Fertilizer-Derived Heavy Metals in Oregon Soils and Its Implications for Sustainable Farming**

**Fungai Mukome** and William Fish, Environmental Science and Resources, Portland State University, Portland, OR

According to the USDA, organic farming is one of the fastest growing segments in US agriculture this past decade. Organic farming has become a multimillion dollar industry and while much emphasis is put on the fertilizer inputs onto these fields, very little consideration is given to the prior fertilization activities of these soils and the associated effect of cadmium accumulation from phosphate fertilizer application. The goal of this study was to determine the importance of soil characterization, soil chemistry, and adsorption coefficients on the prediction of the persistence of cadmium-derived fertilizer in agricultural soils. Persistence of heavy metals soil is important for risk assessment modeling, organic farming and transport studies. The buffer capacity of the soils was 17.8, 12.8, 9.2 and 7.4 cmol/kg/ pH unit for Hyslop, Pendleton, Klamath, and Hermiston respectively. This was highly correlated to the clay content ( $R^2 = 0.98$ ). The  $K_d$  values (in parentheses) and adsorption trend of the soil sites was Pendleton (277.6 L/kg) > Klamath (167.5 L/kg) > Hyslop (195.0 L/kg) > Hermiston (93.8L/kg). The cadmium  $K_d$  values were most correlated to the pH of the soils ( $R^2 = 0.94$ ). The adsorption coefficients were important for predicting the doubling times of cadmium in the soils (Hermiston, 4.8 yrs > Hyslop, 3.7 yrs > Klamath, 2.9 yrs > Pendleton 2.3 yrs). Soil texture was the most important parameter in predicting the mass loss due to leaching (46.2, 19.9, 16.7 and 8.3 mg/ha-yr for Hyslop, Hermiston, Pendleton and Klamath respectively). Based on the modeling results, the three year waiting period for certification was predicted to have a negligible effect on reducing background concentrations of cadmium in agricultural soils.

#### **46. WITHDRAWN:**

## 47. Development and Characterization of Conductive Amyloid Fibril Nanowires

Alexandria M. Taber, **Rachel A. Werther**, Jennifer C. Liddle and Spencer J. Anthony-Cahill, Department of Chemistry, Western Washington University, Bellingham, WA

The goal of our project is to create nanoscale conductive wires that will self-assemble from protein subunits composed of fused SH3 and cytochrome  $b_{562}$  protein domains. SH3 is known to readily form amyloid fibrils at low pH, and cytochrome  $b_{562}$  is a protein that can reversibly bind electrons via a heme cofactor. The immediate goal of our research is to understand what factors influence the morphology of these fibrils. To study this, we have used molecular cloning techniques to create fibril proteins that vary by the number of SH3 domains and by the length of the amino acid linker connecting the SH3 and cytochrome  $b_{562}$  domains. Fibril morphology has been studied by imaging with atomic force microscopy (AFM). Future work includes monitoring growth kinetics with fluorescence spectroscopy and studying conductivity and mechanical properties using AFM.

## 48. The Role of Hydroxyl Groups On the $\text{NH}_x$ ( $x=1\sim 3$ ) Adsorption On $\text{TiO}_2$ Anatase (101) Surface by First Principles Study

**Jee-Gong Chang**<sup>1</sup>, Hsin-Tsung Chen<sup>1</sup> and Shin-Pon Ju<sup>2</sup>, (1)National Center for High-Performance Computing, Tainan, Taiwan, (2)Department of Mechanical and Electro-Mechanical Engineering; Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan

We have investigated the adsorption of  $\text{NH}_x$  species ( $x=1\sim 3$ ) on  $\text{TiO}_2$  anatase (101) surface in the presence of hydroxyl groups by using the first principles calculations. The molecular structures, bonding energies, and detailed bonding interactions between the adsorbates and the surfaces were analyzed. It was found that the bidentate adsorbate of  $\text{Ti}-(\text{H})\text{N}-\text{O}(\text{a})$  has the highest adsorption energy of 41.7 kcal/mol, whereas the monodentate adsorbate of  $\text{H}_2\text{N}-\text{Ti}(\text{a})$  with an adsorption energy of 24.5 kcal/mol is the least on the clean surface. Nevertheless, the  $\text{H}_2\text{N}-\text{Ti}(\text{a})$  becomes the most stable one with an adsorption energy of 55.7 kcal/mol on the hydroxylated surface. We carried out the Mulliken charge and density of states (DOS) analyses to study the nature of the surface— $\text{NH}_x$  bonding on the intrinsic role of hydroxyl groups. All these  $\text{NH}_x$  bonds to  $\text{TiO}_2$  surface atoms involve electron donation of their  $2p$  orbitals. The presence of the hydroxyl group can only facilitate the adsorption of  $\text{NH}_2$ , but not  $\text{NH}_3$  and  $\text{NH}$ . This facilitation of  $\text{NH}_2$  is because the donation of the co-adsorption H is to fill the LUMO of  $\text{NH}_2$ , resulting in electron gain in  $\text{NH}_2$  from the bonding. In addition, the upper valance band, which is originally constituted by the mixing of O  $2p$  and Ti  $3d$  orbitals, has been broadened due to the two adjacent H  $1s$  and  $\text{NH}_2$   $\sigma_y^b$  orbitals joined to the bottom of the original  $\text{TiO}_2$  valance band.

## 49. The Toxicity of Buckminster Fullerenes

**Sara Rosario**, Department of Chemistry, Central Washington University, Ellensburg, WA

Since the discovery of Buckminster Fullerenes ( $C_{60}$ ), countless hours have been devoted to the study of this carbon nanoparticle.  $C_{60}$  has been investigated in context of photodynamic therapy of cancer, photovoltaic cells, semiconductors, and enzyme inhibition. However, the biological effects of  $C_{60}$  remain a mystery. The intention of this study was to examine the effects of Buckminster Fullerenes on mitochondrial function to determine the concentration of  $C_{60}$  as well as the time frame of exposure that cause maximum dysfunction. Bovine heart mitochondria were exposed to different doses of  $C_{60}$  (2 -35 ppm). To determine if  $C_{60}$  dosages result in mitochondrial dysfunction hydrogen peroxide and lipid peroxidation were also measured as indicators of oxidative stress and membrane oxidation. This study determined that at low concentration (2 ppm),  $C_{60}$  enhanced electron function and caused little oxidative stress, while at higher concentrations (10-35 ppm)  $C_{60}$  caused no electron transport chain inhibition, or oxidative stress and lipid peroxidation. This study shows that  $C_{60}$  has no deleterious effects over a thirty minute time frame.

## 50. Effects of Heterogeneous Binding Affinity in Molecular Adsorption

**Bojung Park**, Won Jung and Jaeyoung Sung, Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea, South Korea

We investigate the effects of surface heterogeneity on molecular adsorption. From an exact model study, we find that  $(1-\theta)^{-1}$  with  $\theta$  being the surface coverage as a function of density of ligand molecules has a negative curvature of which magnitude increases with the surface heterogeneity. We also propose a novel experimental observable,  $\chi$ , which can be used to quantify the surface heterogeneity.

## 51. Synthesis and Characterization of Dendrimer Encapsulated Transition Metal Nanoparticles

**Hannah S. Halliday** and John D. Gilbertson, Department of Chemistry, Western Washington University, Bellingham, WA

The buildup of carbon dioxide in the atmosphere is a serious scientific and social problem. Finding a commercially viable method for transforming  $CO_2$  into an economically useful product would help immensely in the effort to minimize global warming. One such method is the production of methanol via the hydrogenation of carbon dioxide. Copper catalysts have shown potential for this reaction, but present challenges due to the variance in catalytic activity based on different synthetic protocols. Starburst polyamidoamine (PAMAM) dendrimers are a specific class of nearly monodisperse, hyperbranched polymers that can be employed in nanoparticle syntheses. PAMAM dendrimers can be used to both template and stabilize a wide variety of mono- and bimetallic metal nanoparticles (NPs). Metal cations are first absorbed and stabilized by the interior of the dendrimer, and the NPs are formed inside of the dendrimer through reaction with a reducing agent. The metal uptake by PAMAM dendrimers in  $H_2O$  was explored and quantified using UV-visible spectroscopy. A method for chemically anchoring the dendrimers to a silica support was established, and the ability of these supported dendrimers to uptake  $Cu^{2+}$  was investigated.

## 52. Kinetics and Possible Mechanism of Thiourea-Based Toxicities in Aerobic and Anaerobic Environment

**Merfat M. Alsabban**, Wilbes Mbiya, Moshood K. Morakinyo, Tinashe B. Ruwona, William DeBenedetti, Adeniyi A. Adenuga and Reuben H. Simoyi, Department of Chemistry, PORTLAND STATE UNIVERSITY, Portland, OR

The kinetics and mechanism of decomposition of thiourea dioxides, aminoiminomethanesulfinic acid (AIMSA), methylaminoiminomethanesulfinic acid (MAIMSA) and dimethylaminoiminomethanesulfinic

acid (DMAIMSA) have been studied in alkaline solutions under aerobic and anaerobic conditions. In aerobic conditions, the decomposition of thiourea dioxides is characterized by an induction time followed by the formation of dithionite,  $S_2O_4^{2-}$ . The induction period persists until there was no more molecular oxygen present in the solution. However, in strictly anaerobic environment, no dithionite was formed. The proposed mechanism involves the cleavage of C-S bond to give a urea residue and sulfoxylate ion,  $SO_2^{2-}$ . The sulfoxylate ion is rapidly oxidized by oxygen to give the sulfoxyl anion radical,  $SO_2^{\cdot -}$ , followed by the formation of dithionite via a rapid equilibrium. The C-S bond in DMAIMSA is the longest, that of MAIMSA is the shortest, and their rates of decomposition follow the same trend with DMAIMSA having the fastest rate. In aerobic environment, the dithionite ion can produce a series of reactive oxygen species which may be responsible for the toxicities associated with the most thioureas.

### **53. Incorporation of Bacteriorhodopsin in a Dye Sensitized Solar Cell**

**Jeffery Mottishaw**, Lisa Lau, Caryn Evilia and Rene Rodriguez, Department of Chemistry, Idaho State University, Pocatello, ID

Dye-sensitized solar cells have recently gained much attention as an alternative to standard n-p semiconductor photovoltaic materials. Efficiencies for small area cells have been reported to be greater than 10%. Much research has focused on finding new, less expensive, more robust dyes for use in the DSSC cells. Several researchers have studied the use of dyes found in nature such as extracts of blueberries, black rice, and others, as the absorber in the DSSCs. Solar cells employing these dyes have less than 25% of the efficiency of the Ru-based dyes used in commercial cells.

*H. salinarium* utilizes bacteriorhodopsin (bR) as a light-activated proton pump. Due to the efficiency of the process and its absorbance of multiple wavelengths of visible light, we explored its ability to be used as a sensitizer in a dye sensitized solar cell (DSSC). Bacteriorhodopsin would be an ideal dye for DSSC. It is environmentally friendly, biodegradable and inexpensive dye for this process. The results of these studies indicate that it does in fact function in a DSSC, though the efficiency, for the present, is low.

### **54. QM-MM Simulations and Measurement of Tryptophan Fluorescence Wavelengths and Lifetimes for Trp-X and X-Trp Dipeptides**

**Carl A. Fahlstrom**<sup>1</sup>, Patrik R. Callis<sup>1</sup>, Lee H. Spangler<sup>1</sup> and Greg Gillispie<sup>2</sup>, (1)Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT, (2)Fluorescence Innovations, Inc., Bozeman, MT

The two most common explanations for non-exponential decay of tryptophan (Trp) fluorescence are rotamer subpopulations and excited state dynamics. Trp containing dipeptides provide a robust system for the evaluation of rotamer contributions. The extensive study of the Trp fluorescence wavelengths and non-exponential decay in Trp-X and X-Trp dipeptides by Chen et al., [Biochemistry 1991, 30, 5184-5195] revealed remarkable correlations. At pH 5.5, the fluorescence maximum for Trp-X dipeptides was consistently blue shifted from that of the X-Trp counterpart by 10 nm. The average lifetimes and quantum yields were found to be consistently larger by 50 % for the Trp-X with both exhibiting marked quenching relative to Trp zwitterion. At pH 9.3 the Trp-X show little quenching and the fluorescence is red shifted ~10 nm, while the fluorescence is unshifted and quenching remains strong for the X-Trp. We are applying our QM-MM method that has been successful for predicting Trp wavelengths and fluorescence quenching [Callis et al. J. Phys. Chem. B. 2007, 111, 10335] for the purpose of understanding the robust patterns seen experimentally for the dipeptides. Early results for Trp-Gly and Gly-Trp on a subset of rotamers predict a 10 nm shorter wavelength for Trp-Gly relative to Gly-Trp, in agreement with experiment. Computed lifetimes and wavelengths show good qualitative correlation with experiment at this point in the study. Time resolved measurements at the nanosecond time scale will be presented for Gly-Trp, Trp-Gly, and Leu-Trp at pHs 5, 7, 9, and 11. Fluorescence properties at a variety of excitation wavelengths will be presented in hopes of detecting rotamer subpopulations with differing absorbance properties.

## 55. The Use Plasma Cleaning in the Preparation of Dye-Sensitized Solar Cells

**Michael Fernandez, Undergraduate student**<sup>1</sup>, Gibril Omar, High School student<sup>1</sup>, Lisa Lau<sup>2</sup>, Dr. Rene G. Rodriguez<sup>2</sup> and Dr. Joshua J. Pak<sup>2</sup>, (1)Department of Chemistry, Idaho state University, Pocatello, ID, (2)Department of Chemistry, Idaho State University, Pocatello, ID

The Use of Plasma Cleaning in the Preparation of Dye-Sensitized Solar Cells  
Michael Fernandez, Gibril Omar, Lisa Lau, Rene Rodriguez, Joshua Pak

There have been several reports related to the preparation and cleaning of the nanocrystalline TiO<sub>2</sub> surface needed for the formation of dye-sensitized solar cells, DSSCs. In some cases the use of an rf-plasma to help clean the surface has been attempted. Plasma processing should provide a way to clean the surface of hydrocarbons through oxidation to carbon dioxide and water or perhaps by reduction of oxygen containing species such as alcohols or carbonyl containing species that may be bonded or hydrogen bonded to the surface. Removal of the hydrocarbons and oxygen containing hydrocarbons provided a more reactive and larger surface for the dye to chemisorb on the TiO<sub>2</sub>.

Plasma cleaning of the post-deposited TiO<sub>2</sub> was performed in an oxygen-rich environment, a hydrogen rich environment, and in an inert environment for various exposure times. Experiments were also performed where the TiO<sub>2</sub> layer was subjected to selected combinations of these three environments. The other variable studied was the effectiveness of the different treatments as a function of TiO<sub>2</sub> film thickness by employing TiO<sub>2</sub> deposited in several layers either plasma cleaning each layer after deposition, or plasma treatment only after all the layers were deposited. Results on effectiveness of the different treatments will be presented. The effectiveness was assessed by comparing the relative solar efficiencies of the DSSCs made from the TiO<sub>2</sub> subjected to the different plasma treatment

## 56. DFT / iMCP as a Tool for Organometallic Chemistry

**Christopher C. Lovallo**<sup>1</sup>, Tao Zeng<sup>2</sup> and Mariusz Klobukowski<sup>2</sup>, (1)Department of Chemical and Biological Sciences, Mount Royal College, Calgary, AB, Canada, (2)Department of Chemistry, University of Alberta, Edmonton, AB, Canada

DFT calculations were performed to evaluate the structural and energetic changes during the reactions of Group 7 transition metal (Mn, Tc, Re) decacarbonyls with chlorine and bromine. In addition, the rotation barriers of the decacarbonyls were evaluated. The iMCP model core pseudopotentials were used along with three density functionals (BLYP, B3LYP, M06), covering both hybrid and non-hybrid, as well as gradient-corrected and meta-GGA functionals. The structures were not found to be heavily basis set-dependent, but there was a small (no more than 10%) effect on the reaction energetics. The gradient-corrected functionals consistently underestimated the dissociation energies, whereas the meta-GGA functional overestimated the same. The results here involving the iMCPs agree well with previous all-electron calculations, indicating the validity of these potentials for predicting the energetics of organometallic reactions.

## 57. Ab Initio Study of Ultrafast Phonon-Induced Plasmon Dephasing in Silver Quantum Dots

**Zhenyu Guo** and Oleg Prezhdo, Department of Chemistry, University of Washington, Seattle, WA

Electron-phonon coupled pure-dephasing of plasmon resonance in silver quantum dots (QDs) at room and low temperatures is investigated with ab initio molecular dynamics. Three types of electronic state are studied, which are named as bulk, surface and plasmon states respectively. The dephasing in non-plasmon states occurs faster than that in plasmon states. The dephasing time for plasmon state is about 40-50 femtoseconds.

## **58. Following the Photochemical Formation of Benzene in Complex Aqueous Samples Using Membrane Introduction Mass Spectrometry as a Direct Real-Time Reaction Monitor**

**Cameron C. Newhook**, Erik T. Krogh and Chris C. Gill, Department of Chemistry, Applied Environmental Research Laboratories, Vancouver Island University, Nanaimo, BC, Canada

Trace levels of benzene have been found in a number of commercial food and beverage products, and are thought to arise from the photochemical and/or thermal decarboxylation of sodium benzoate, a common food preservative. In this study, we investigate the production of benzene by directly following its production by passing a reaction mixture over a membrane interface coupled to an ion-trap mass spectrometer in a re-circulated closed loop. Aqueous solutions of sodium benzoate were photolyzed at 300 nm at pH 3 and 7 in the presence and absence of ascorbic acid, added as an auxiliary reducing agent. Benzene concentrations were quantified in-situ ranging from 0.01 – 100 ppb (~0.1 nM – 1  $\mu$ M). We report benzene formation rates ranging from 0.015 nM/min at pH 7 in the absence of ascorbic acid up to 130 nM/min at pH 3 in the presence of ascorbic acid. This work provides direct evidence that the protonated form of benzoic acid is more reactive than benzoate ion and that the production of benzene is enhanced further by two orders of magnitude in the presence of an equimolar concentration of ascorbic acid. Preliminary data directly monitoring benzene formation in complex beverage solutions will also be presented.

## **59. Coumarin-Derivative-Based Artificial Enzyme Functioning as off-On Catalytic Chemodosimeter for Cu<sup>2+</sup>**

**Sujung Yi**, Mi Hee Kim, Hyun Hye Jang, Suk-Kyu Chang and Min Su Han, Chemistry, Chung-Ang University, Seoul, South Korea

Most of conventional Cu<sup>2+</sup> sensors show decreased emission upon Cu<sup>2+</sup> binding, due to quenching of fluorescence by mechanisms inherent to paramagnetic species; such decreased emission is undesirable for analytical purposes. In this study, a new hydrazone derivative that is easily prepared in single step from coumarin 334 and 4-methoxyphenyl hydrazine is a highly effective fluorescent sensor with strong fluorescence enhancement in the presence of paramagnetic Cu<sup>2+</sup> ions. This sensor is catalytically hydrolyzed by Cu<sup>2+</sup>, and the catalytic process induces a large increase in the fluorescence intensity, due to signal amplification. Importantly, this compound has high selectivity for Cu<sup>2+</sup> over other metal ions; moreover, this selectivity is retained even in presence of an excess of other metal ions. In addition, the detection limit for Cu<sup>2+</sup> is below an aqueous Cu<sup>2+</sup> concentration of 100 nM and this detection limit is acceptable within the U.S. EPA limit.

## **60. Stamping Oriented Molecular Monolayers Using Liquid Crystal Inks**

**Jennifer Novotney**, Robert Thompson, Cory Lund, Steven Hickman and David L. Patrick, Advanced Materials Science & Engineering Center, Western Washington University, Bellingham, WA

Self-assembled monolayers (SAMs) are an important class of systems with a wide range of applications, from high resolution photoresists to biochemical sensors. Although a variety of techniques have been developed for spatially patterning SAMs, such as microcontact printing and dip pen lithography, currently no method exists for controlling azimuthal molecular orientation in these films. Such control could open the door to important new applications such as the use of SAMs as alignment films in liquid crystal (LC) displays, polarization-dependent optoelectronic devices, and anisotropic surfaces exhibiting directional flow and friction effects. This poster describes a new approach that for the first time allows control over the orientational properties of SAMs based on printing using patterned stamps and LC inks. Results from two classes of systems will be presented: 1) silane onto glass slides; and 2) physisorbed organic monolayers on graphite. Stamping with LC inks produces monolayers imprinted with the orientational order of the stamp. Data are presented from polarizing optical microscopy, atomic force microscopy, and infrared and polarized UV-Vis spectroscopy quantifying the nature extent of the order.

## **61. Efficient Modulating the Optical Properties of a Dimetallic Coordination Fluorescent Chemosensor for Adenosine-5'-Triphosphate Based Upon Competitive Assay Approach**

**Hyun Hye Jang**, Sujung Yi, Mi Hee Kim, Sudeok Kim, Na Hee Lee, Suk-Kyu Chang and Min Su Han, Chemistry, Chung-Ang University, Seoul, South Korea

Numerous fluorescent sensors with two Zn<sup>2+</sup>- dipicolylamine moieties as anion recognition site were developed. These sensors are effective fluorescent sensors of phosphate derivatives such as ATP, pyrophosphate, and peptide with phosphotyrosine residues but some of these sensors have some background fluorescence in the absence of analytes, which was undesirable for analytical purposes. In research, based upon competitive assay, we simply improved the sensing properties of dimetallic coordination fluorescent chemosensor ([Zn<sub>2</sub>(9,10-bis[(2,2'-dipicolylamino)methyl]anthracene)]<sup>2+</sup>) for ATP by eliminating the background fluorescence of the sensor using pyrocatechol violet as a quencher. The improved sensing ensemble can detect less than 0.5 μM of ATP easily and have a selectivity to ATP over various anions include ADP. Moreover, because of no background fluorescence of our system, in the presence of analyte, the fluorescence in our system was dramatically enhanced over initial state.

## **62. Organic Semiconductor Thin Film Growth Using Organic-Vapor-Liquid-Solid Deposition**

**Kevin Bufkin**, Dan Shaw, Brad Johnson and David L. Patrick, Chemistry, Western Washington University, Bellingham, WA

Interest in using organic semiconductors (OS) in applications such as large area displays, photovoltaic devices, and radio frequency ID tags stems in part from their prospects for enabling significantly reduced manufacturing costs compared to traditional inorganic semiconductors. However many of the best performing prototype devices produced so far have involved expensive or time-consuming fabrication methods, such as film deposition under high vacuum conditions. We present a new approach for growing low molecular weight organic crystalline films at ambient conditions based on a vapor-liquid-solid growth mechanism using thermotropic nematic liquid crystal (LC) solvents. An OS film is deposited via atmospheric-pressure plasma spray onto substrates coated by a thin LC layer oriented using rubbed polyimide, producing films that are highly crystalline, with large grain sizes, and possessing macroscopic uniaxial orientation. This poster will describe the APPS method, and present results for two archetypal OS materials: tetracene and sexithiophene.

## **63. Hg<sup>2+</sup>-Selective Chromogenic and Fluorogenic Chemodosimeter Based On Thiocoumarins**

**Hye Lim Jeon**, Myung Gil Choi, Ji Eun Namgoong and Suk-Kyu Chang, Department of Chemistry, Chung-Ang University, Seoul, South Korea

Coumarin derivatives are widely used as both signaling units and imaging handles for a variety of biological events. However, the simple thio-analog of coumarin, thiocoumarin, has received relatively little interest. We report a new thiocoumarin-based chemodosimeter **1** and show how Hg<sup>2+</sup>-promoted desulfurization of thiocoumarin into coumarin derivative functions in the signaling of Hg<sup>2+</sup> ions in aqueous media. Pronounced Hg<sup>2+</sup>-selective chromogenic and fluorogenic signaling behaviors were observed from the Hg<sup>2+</sup>-triggered transformation of thiocoumarin to a coumarin derivative in aqueous media. The Hg<sup>2+</sup>-selective signaling process of **1** was examined by NMR, fluorescence, and mass measurements. The signaling of Hg<sup>2+</sup> ions by **1** was very fast for a chemodosimeter and completed in less than 2 min. The fluorescence of the **1**-Hg<sup>2+</sup> system was affected by less than 10% in the presence of 100 equiv of other physiologically or environmentally important metal ions as a background. The transformation could potentially be used for the design of other supramolecular

systems that have selective and sensitive signaling and visualizing behaviors for Hg<sup>2+</sup> ions in aqueous environments.

#### **64. Characterization of Adhesive Properties of Home Made Explosives (HME) On Material Surfaces**

**Kendell Horman** and Carla Miller, Chemistry, Idaho National Laboratory, Idaho Falls, ID

The ability to remove home made explosives (HME) from the surface of various material substrates is critical for detection by means of vapor/particle explosive trace detection systems. This study evaluated the effectiveness of using changes in temperature, vibration, and air flow rates to remove HME. A series of experiments were performed in an attempt to characterize the adhesive properties of trace levels of HME deposited on various types of materials ranging from metals to cloths. The materials consisted of 1" x 1" samples of seven different material types: leather, vinyl, metal, cotton, canvas, shrink wrap, and cardboard. The HME used for these tests were ammonium nitrate, triacetone triperoxide (TATP), and hexamethylene triperoxide diamine (HMTD). A known amount of HME was deposited on a Teflon strip, dried, and swiped onto the surface of the substrate of interest. The substrates were photographed using a Zeiss Discover V12 stereoscope with Axiocam ICc1 3 megapixel digital camera prior to being placed on the vibration table, in the environmental chambers, or through the air flow tests. The substrates were photographed after the experiment and an optical comparison was made from pre-test to post-test samples. The particles were also viewed using scanning electron microscopy. In addition fluorescent dyes were used to determine the movement of the explosive on the substrate surface. The results of these experiments appear on this poster.

#### **65. Fluorescent Peptide Labeling Characterization with Capillary Electrophoresis and Mass Spectrometry**

**Roza Wojcik**<sup>1</sup>, Martin Sadilek, Dr.<sup>2</sup> and Norman Dovichi<sup>1</sup>, (1)Department of Chemistry, University of Washington, Seattle, WA, (2)Chemistry, University of Washington, Seattle, WA

Fluorescent labels enable sensitive protein and peptide analysis with capillary electrophoresis coupled with laser induced fluorescence detection. However, labeling reaction often results in the presence of multiple fluorophores on a single analyte.

In this work, we characterized peptide labeling by the pyrylium ion based Chromeon PY-503 dye - a novel fluorophore which doesn't alter the positive charge of primary amines. Capillary electrophoretic separation of PY-503 labeled peptides was performed under alkaline conditions, on a lab-built instrument. Different reaction conditions and localization of the labels in peptides were investigated by a quadrupole time-of-flight instrument equipped with a MALDI source. PY-503 label was also screened for its usefulness as a "flyability enhancer" in MALDI analysis.

#### **66. Single Isomer Sulfoalkyl $\beta$ -Cyclodextrins as Chiral Resolving Agents for CBI-Amino Acids by Capillary Electrophoresis**

**Thomas K. Green** and Daniel L. Kirschner, Department of Chemistry & Biochemistry, Institute of Arctic Biology, University of Alaska Fairbanks, Fairbanks, AK

Single-isomer anionic 2,3-dialkyl-6-sulfoalkyl- $\beta$ -cyclodextrins were investigated for their ability to analytically resolve cyanobenz[f]isoindole (CBI) amino acid enantiomers by capillary electrophoresis. Amino acids (ser, glu, asp, ala, thr, his) were derivatized with naphthalene dicarboxaldehyde (NDA) and cyanide to form highly fluorescent CBI-amino acids. Separation was carried out using reverse polarity with low pH phosphate buffer using laser induced fluorescence detection (410 nm excitation). Baseline resolution was obtained for all CBI-amino acids at 0.2 mM single-isomer sulfoalkyl  $\beta$ -CD in the background electrolyte, an order of magnitude less than the optimum concentration required for commercially-available sulfated  $\beta$ -CD. Single-isomer sulfoalkyl  $\beta$ -CDs interact more strongly with CBI-amino acids compared to sulfated  $\beta$ -CD, resulting in shorter

migration times. Evidence will be presented to support the concept of an extended hydrophobic cavity of the sulfoalkyl  $\beta$ -CD, with its sulfato groups extended away from the primary face of the cyclodextrin. Enantioseparations with single-isomer sulfoalkyl  $\beta$ -CDs are therefore less sensitive to electrostatic interactions between the analyte and anionic sulfato groups of the CD.

### **67. Bioanalysis of Ribavirin in Rat Plasma by High Pressure Liquid Chromatography – Tandem Mass Spectrometry (HPLC-MS/MS)**

Lou Anne McKown and **Lori Payne, Ph.D.**, Bioanalytical Chemistry, Bioanalytical Systems, Inc., McMinnville, OR

Ribavirin is an antiviral prodrug used for the treatment of Hepatitis C and respiratory syncytial virus (RSV) among other common viruses. A method for the analysis and quantification of ribavirin in rat plasma utilizing HPLC-MS/MS with updated HPLC column technology has been developed and validated according to the FDA guidance to the industry. The assay displays good linearity with correlation coefficient  $>0.99$  over a range of 10 – 5000 ng/mL using a 25 mL sample precipitated with 5mM ammonium acetate in 95% acetonitrile in water after the addition of a stable label internal standard. The supernatant is analyzed by HPLC utilizing a HILIC column with detection by MS/MS incorporating a turbo-ionspray interface in positive mode. The choice of HILIC column was essential for adequate retention and acceptable peak shape of ribavirin within 2 minutes of total analysis time. This method greatly facilitated the high throughput analysis of preclinical samples.

### **68. Development and Validation of An LC-MS/MS Method for the Quantification of Rapamycin in Porcine Whole Blood and Tissues**

**Zahuindanda M. DeForrest**<sup>1</sup>, Scott D. McConkie<sup>1</sup>, Peter J. Mann<sup>2</sup> and Melissa M. Kiser<sup>1</sup>, (1)Bioanalytical, BASi, McMinnville, OR, (2)BASi

Rapamycin is a mTOR inhibitor with powerful immunosuppressive properties used to prevent rejection of organ transplants. Rapamycin's advantage over calcineurin inhibitors such as tacrolimus and cyclosporine is its low renal toxicity. BASi has developed and validated an LC-MS/MS method for the quantification of rapamycin in porcine whole blood and tissues.

Analysis of rapamycin uses a unique combination of protein precipitation and column switching. A 0.1 mL aliquot of blood or tissue homogenate is extracted with a precipitating solution containing internal standard. After centrifugation, the supernatant is transferred to 96-well format. Column-switching is utilized by injecting samples onto a Zorbax SB-C18 cleanup column before switching to an YMC-ODS-AQ analytical column for the final gradient separation using acetonitrile/formic acid/NaI. Detection is by ESI+ MS/MS.

Inter-run accuracy ranged from 4.0% to 7.0% for blood and -4.8% to 3.8% for tissues (liver, kidney, myocardial and lung). Inter-run precision ranged from 7.8% to 13.0% for blood and 3.3% to 10.8% for tissues.

A robust, high throughput, unique, and sensitive method was validated for the quantification of rapamycin per FDA guidelines for linearity, precision, accuracy, specificity and stability. The range of the assay is 0.1 – 100 ng/mL in whole blood and 0.5 – 500 ng/g in tissues.

### **69. Investigation of Some Possible Ionic Interference to a Prussian Blue Modified Electrochemical Sensor in the Detection of Hydrogen Peroxide in Natural Waters**

**Devin Merrill**, Emilio Sulpisio and Drew M. Budner, Department of Chemistry, Whitworth University, Spokane, WA

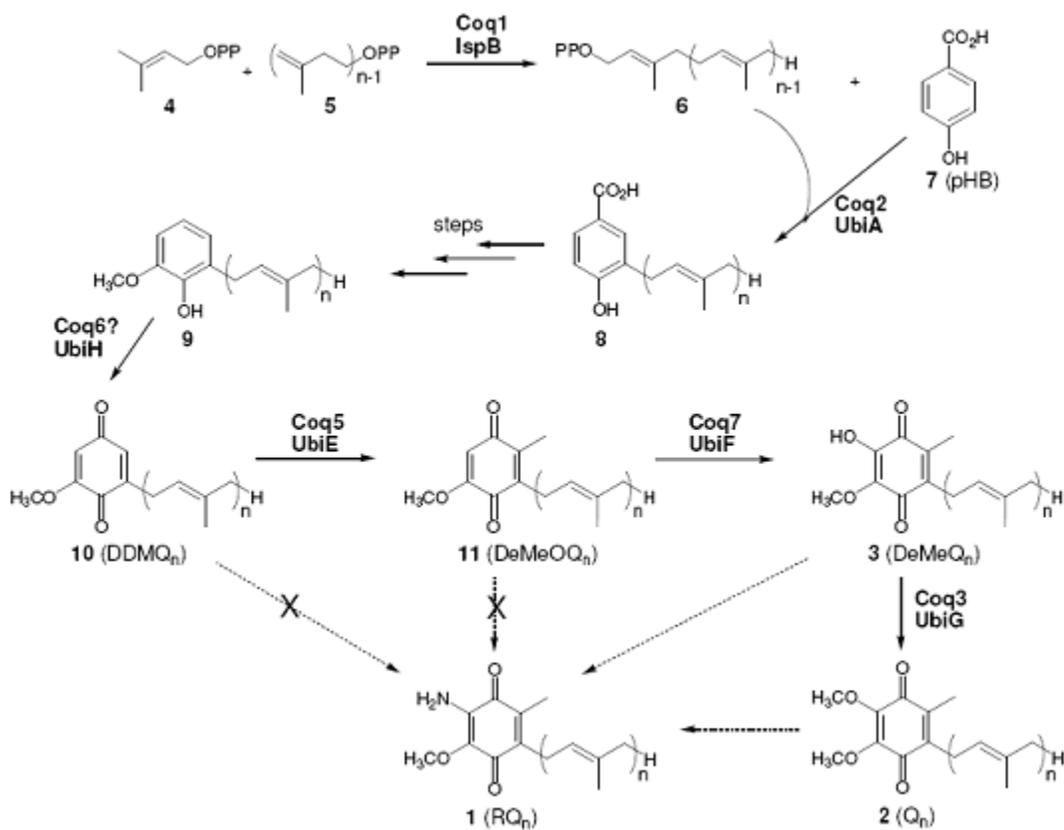
Recent research has shown Prussian Blue to be an effective electrocatalyst for the reduction of hydrogen peroxide and can be used as an electrode modifier for the detection of aqueous hydrogen peroxide. These modified electrodes exhibit relatively long operating lifetimes and low detection limits, indicating that these Prussian Blue sensors are of the desired sensitivity for detection of

hydrogen peroxide in natural water samples. Initial investigations into several possible ionic interferences in the detection of hydrogen peroxide by these electrodes modified with Prussian Blue have been performed.

## 70. Investigation Into the Biosynthetic Pathway of Rodoquinone Using the Model Organism *Rhodospirillum Rubrum*

**Brian C. Brajcich**, Andrew L Iarocci and Zachary T. Lonjers, Department of Chemistry, Gonzaga University, Spokane, WA

Rodoquinone (RQ, **1**) is a necessary electron shuttle that assists in the reduction of fumarate to succinate in the anaerobic metabolism of organisms such as the parasitic helminthes. Through this conversion, ATP is synthesized allowing these organisms to thrive in anaerobic environments. By determining the biosynthetic pathway of RQ, we have hypothesized that selective antihelminthic drugs can be designed that inhibit the RQ pathway. Assays were performed to determine the biological precursor from which RQ is synthesized. Similar to parasites, the bacteria *Rhodospirillum rubrum* (*R. rubrum*) synthesizes both ubiquinone (Q, **2**) and RQ, constituents that are necessary for survival in aerobic and anaerobic conditions. It is already known that demethylubiquinone (DeMeQ, **3**) is the immediate precursor to Q. *In vivo* feeding assays of *R. rubrum* with proposed precursors, DeMeQ<sub>3</sub> and Q<sub>3</sub>, were performed to test for RQ<sub>3</sub> production. Also, methyltransferase inhibition assays were performed that tested different concentrations of S-adenosylhomocysteine (SAH) and its effect on RQ<sub>3</sub> and Q<sub>3</sub> production from DeMeQ<sub>3</sub>. Production of RQ<sub>3</sub> and Q<sub>3</sub> was determined by performing lipid extractions on each assay which were then subjected to LC-MS quantitation. The results of the SAH assays have indicated that Q is required for the production of RQ.



## **71. Infrared Spectroscopy of the Site-Specific Carbon-Deuterium Labeled Acylated Proline**

**Matthew Delsman**, Andrew Durgan and Matthew E. Cremeens, Department of Chemistry, Gonzaga University, Spokane, WA

Neuropeptides are signaling molecules within the brain and gastrointestinal tract. Problems with signaling often cause health problems. Neuropeptides within the brain are often poorly characterized under physiological conditions. Our research aims to provide key structural characteristics of neuropeptides under physiological conditions to aid in the design of therapeutics. The amino acid proline (Pro) has significant structural and functional characteristics in peptides due to its ring structure. Proline's presence within neuropeptides makes it an ideal target for assessing neuropeptide structure.  $^{13}\text{C}$  NMR of N-acylated proline (Ac-Pro) has aided in providing key structural data for Pro by showing cis-trans amide isomerization. IR measurements of Ca deuterated Ac-Pro can help clarify IR data of Pro and provide a better indication of what will be observed for site-specific deuterium labeled Pro in neuropeptides.

## **72. Infrared Spectroscopic Examination of L-Proline in Peptide Signaling**

**Andrew Durgan**, Department of Chemistry, Gonzaga University, Spokane, WA

Like serotonin, neuropeptides are signaling molecules within the brain and gastrointestinal tract. Problems with signaling often cause health problems. Despite the prevalence of neuropeptides within the brain and their importance, they are often poorly characterized under physiological conditions. Our research aims to provide key structural characteristics of neuropeptides under physiological conditions for the sake of aiding the rational design of therapeutics.

Proline, one of the twenty one amino acids, has significant structural and functional characteristics as it pertains to the overall structure of a peptide chain. Based upon these unique characteristics, proline can be used as an ideal target molecule. However, the infrared (IR) spectrometer was used to detect a specifically deuterium-labeled (C-D) site as an active location for direct probing. The IR data collected on the zwitterionic form of L-Proline indicate the possibility of more than one structure conformations, possibly from the detection of carboxylate rotamers. However, the  $\text{C}^{13}$  NMR measurements of L-Proline only indicate one conformation, as presented within. Further, examination of the IR spectrum will be performed to determine the proper identity of the proline conformations.

## **73. Production of Isotopically-Labeled Myoglobins for NMR Backbone Dynamics Studies**

**James M. Hall**, Danielle J. Slaughter and Spencer J. Anthony-Cahill, Department of Chemistry, Western Washington University, Bellingham, WA

Our research goal is to study the backbone dynamics of permuted myoglobins and relate the findings to the observed stability changes seen in permuted globins. Soluble  $^{15}\text{N}$ -labeled permuted myoglobins must be produced despite the low expression of soluble protein in *E coli* cells. An alternate approach is the high-level expression of the permuted proteins in the apo-form as inclusion bodies. The challenge faced in this case is the reconstitution of the apoprotein with the heme prosthetic group. We have expressed labeled apo-myoglobin and reconstituted it with heme. HSQC spectra of reconstituted wild-type and permuted myoglobins have been collected at 500 MHz. The HSQC spectrum of the permuted globin is less well-resolved than that of the wild-type; but, shows many similar crosspeaks.

## 74. Capping Beta Sheets

**Brandon L. Kier** and Niels H. Andersen, Dr., Chemistry, University of Washington, Seattle, WA

We have developed a motif that specifically caps the ends of beta sheets, stabilizing beta sheet structure even more effectively than a covalent cross-strand disulfide bond. This beta cap motif consists of two cross-strand tryptophan residues interacting edge-to-face, and a tight network of H-bonds including a glycine backbone amide proton with one of the tryptophan indole rings as the H-bond acceptor. It bears no structural similarity to well-known alpha helix caps, though it achieves a similar result (improving fold stability and reducing fraying.)

The usefulness of this beta cap has been highlighted by analysis (via NMR and circular dichroism) of highly stabilized, non-frayed versions of previously reported beta hairpins of varying lengths, as well as a novel family of stable homodimeric beta sheets with caps at both ends and a disulfide bond in the middle. We anticipate applications of the beta cap motif to include protein folding dynamics studies, investigations of near-neighbor effects on tryptophan fluorescence, and rational design of hyperstable peptides and proteins for use as inhibitors of beta fibril formation or as scaffolds for pharmacophore display.

## 75. The $^{13}\text{C}_\alpha$ and $^{13}\text{C}_\beta$ Shifts Reveal Clear Pattern along Strands in Beta Hairpins

**Irene Shu**, James M. Stewart, Brandon L. Kier, Michele Scian and Niels H. Andersen, Dr., Department of Chemistry, University of Washington, Seattle, WA

It has long been recognized that  $^{13}\text{C}_\alpha$  and  $^{13}\text{C}_\beta$  chemical shift deviations (CSDs) from random coil values have different characteristics for residues in  $\alpha$ -helical versus  $\beta$ -sheet regions of proteins; CSDs of  $^{13}\text{C}_\alpha$  (and  $^{13}\text{C}'$ ) are positive and those of  $^{13}\text{C}_\beta$  are negative in  $\alpha$ -helices, while these are reversed in  $\beta$ -sheets. Although Rico and co-workers were early advocates of using the  $^{13}\text{C}_\alpha$  and  $^{13}\text{C}_\beta$  shifts qualitatively (and even quantitatively) as a means for assessing  $\beta$ -hairpin fold populations, unlike the case of  $\text{H}_\alpha$  and  $\text{H}_\text{N}$  shifts, the more detailed pattern of the  $^{13}\text{C}$  CSDs along the  $\beta$ -strands does not appear to have been recognized in literature yet. Many amide units have H-bonds with two strands and the range of  $^{13}\text{C}$  CSDs occurring in  $\beta$ -sheets overlaps with the narrower range for  $\alpha$ -helices. There also appears to be a discrepancy in the prediction of H-bonding effects on  $^{13}\text{C}$  shifts in helices versus hairpins. To answer these questions,  $^{13}\text{C}$  structuring shifts have been determined for a series of designed hairpins of varying fold stability. Our study reveals that the diagnostic  $^{13}\text{C}$  shifts for  $\beta$ -structuring are associated, almost exclusively, with the cross-strand H-bonded residues, and instances in which aromatic ring current effects on  $^{13}\text{C}$  CSDs can be as large as the secondary structure shifts. Results from a further search of  $^{13}\text{C}$  shifts in  $\beta$ -structures of proteins will also be reported as a test of the generality of the conclusions based on the model hairpins.

## 76. Characterization of Subunit E and G Interactions in a Yeast V-ATPase by Site-Directed Mutagenesis

**Sara Johnson**, Cameron Stroyan and Deanna Dahlke Ojennus, Ph.D., Department of Chemistry, Whitworth University, Spokane, WA

The yeast vacuolar ATPase (V-ATPase) is a multi-subunit enzyme that pumps protons across a membrane upon hydrolysis of ATP via a rotary mechanism. The peripheral stalk of the enzyme complex consists of several proteins, including subunits E and G. Subunits E and G have a high alpha-helical propensity and likely adopt an extended coiled-coil conformation which stabilizes the stator elements of the membrane-bound ( $V_0$ ) components to the peripheral ( $V_1$ ) components of the enzyme. Site-directed mutagenesis is used to determine the specific sites of interaction between subunits E and G in order to refine a structural model of the yeast V-ATPase.

## **77. Expression of Recombinant R-Body Proteins for Structural Studies**

**Michael Harms**<sup>1</sup>, Josiah Ward<sup>2</sup>, Deanna Dahlke Ojennus, Ph.D.<sup>1</sup> and Finn Pond, Ph.D.<sup>2</sup>,  
(1)Department of Chemistry, Whitworth University, Spokane, WA, (2)Department of Biology,  
Whitworth University, Spokane, WA

Bacteria of the genus *Caedibacter* are obligate endosymbionts found in certain strains of *Paramecium*. When released and taken up by a sensitive strain of paramecia, they can confer a killing trait. Killing is coincident with the appearance of R-bodies which are large proteinaceous ribbons. Type 51 ribbons from *C. taeniospiralis* are coiled into cylindrical structures, but unroll in a telescopic fashion upon a drop in pH. The genes needed for expression of R-body proteins (*rebA*, *rebB*, and *rebC*) have been amplified from *C. taeniospiralis* 116 by PCR and placed in *E. coli* high-yield protein expression vectors. Recombinant Reb proteins are expressed and purified for structural studies including characterization by solution NMR spectroscopy.

## **78. Mutagenesis Strategies to Improve Stability and Oxygen Affinity of Circularly Permuted Hemoglobin**

**Ngoc-An T. Huynh**, Haomin Ye and Spencer J. Anthony-Cahill, Department of Chemistry, Western Washington University, Bellingham, WA

The goal of our research is to engineer and characterize an innovative recombinant hemoglobin for use as a blood replacement. Our initial design,  $\alpha$ -cp $\beta$ , incorporates circularly permuted  $\beta$ -subunits coexpressed with wild-type  $\alpha$ -subunits. Characterization of  $\alpha$ -cp $\beta$  by analytical size exclusion chromatography, stopped-flow ligand-binding, and flash photolysis displays decreased stability and increased oxygen affinity. Our current work involves incorporating into the original  $\alpha$ -cp $\beta$  protein framework, two  $\beta$ -subunit mutations ( $\beta$  G16A and H116I), known to improve stability in hemoglobin, as well as the Providence mutation ( $\beta$  K82D), which is known to decrease oxygen affinity. We have successfully introduced these mutations into  $\alpha$ -cp $\beta$  and are working to express, purify and characterize these novel constructs. If the two mutant proteins show the expected improvements in stability and function, we will combine both sets of mutations to determine if the desirable effects are additive.

## **79. Protein Dynamics of Peroxiredoxins Studied by Hydrogen/Deuterium Exchange Mass Spectrometry**

**Sasidhar Naga Nirudodhi** and Claudia S. Maier, Department of Chemistry, Oregon State University, Corvallis, OR

### **Introduction**

Peroxiredoxins (Prxs) are important antioxidant enzyme that reduces H<sub>2</sub>O<sub>2</sub> in cells and removes alkylhydroperoxides by undergoing the catalytic cycle. Our goal is to study the impact of the conformational properties on the oxidative regulation of Prxs by correlating the H/D exchange dynamics of eukaryotic and bacterial Prxs with the susceptibility to hyperoxidation.

### **Method**

Protein samples were equilibrated under non-denaturing conditions for 30 mins and diluted 20-fold into D<sub>2</sub>O-phosphate buffer of (pH 7) and incubated for distinct time periods. Exchange will be quenched by acidifying with 0.1 M phosphate buffer (pH 2.5). Digestion using immobilized pepsin was performed for 1 min at 0 °C. Pepsin beads were removed by centrifugation and the remaining sample is subsequently flash-frozen in liquid nitrogen. Peptic peptides were separated by "cold" reverse phase LC using a Waters nanoAcquity system and peptide analysis was performed on a Waters LC-T ToF instrument. Data analysis was assisted by the use of HXMS software (Weis, Engen, Kass J. Am. Soc. Mass Spectrom. 2006, 17, 1700–1703).

## **Preliminary Data**

MS/MS analysis of the peptic peptide digests was used to identify peptides and after optimization of the digestion conditions complete sequence coverage was observed for both form, reduced and oxidized proteins. When the deuterium levels of peptic fragments from oxidized, reduced wild-type Prx and several mutants were compared some similarities and differences were observed. For instance, peptic fragments 51-60, 61-67, 96-110, 123-132, 148-156 of T77V Prx has greater exchange in the reduced than the oxidized form. The peptide 1-20 experienced less exchange than the peptide 36-43 in the oxidized Prxs. But, reverse trends for the latter two peptides were observed in reduced Prxs. In general, reduced proteins showed higher exchange rates than oxidized forms. This trend was also confirmed by comparing the global H/D exchange properties of the diverse disulfide-linked versus reduced proteins.

## **80. Magneto-hydrodynamics Enhancement of Electrochemical Processes**

**Robert Neville O'Brien, Professor Emeritus**, Chemistry, University of Victoria, Victoria, B.C. Canada, BC, Canada

In all electrochemical processes the conductance of the electrodes or current collectors is electronic, the conductance of the electrolyte electrolytic, that is the movement of charge particles from one electrode to the other. In general, electronic is a million to a thousand times faster than electrolytic. Electrolytic conduction is by migration, diffusion and convection. In the earth's gravimetric field and in liquid electrolytes the convection dominates. If convection can be enhanced, the rate of discharge of a battery can be increased, the loss of energy to the heating of the electrolyte avoided and more energy and power delivered to the useful load. In terms of portable energy reservoirs, the battery becomes more efficient, degrades less energy supplied to heat and on discharge again wastes less energy in the electrolyte resistance to heat.

Nickel metal hydride batteries contain only ferro-magnetic material and are easily magnetized with a magnetizing machine to give 32% better out-put. A 2007 Prius battery pack was magnetized and spiked with a highly para-magnetic ion which increase in-city driving mileage by 53.5%, and about 10% on the highway. Two Prius taxis damaged their transmissions, and one its inverter in two months presumably by using full power very frequently. Zn-air batteries have been magnetized and the electrolyte spiked and successfully cycled without fractals and with increased output. Li-ion camera batteries have been magnetized and showed much improved output.

## ***Chemistry, Energy, and Sustainability 2***

**Organizer:** Justin Lytle Pacific Lutheran University

**Presider:** Justin Lytle Pacific Lutheran University

## **81. A Realistic Energy Scenario**

**E. Gerald Meyer**, Arts and Sciences, University of Wyoming, Laramie, WY

Realistic scenarios must consider the various primary energy categories and the characteristics of their component types. The energy types considered are fossil fuels, nuclear fuels, solar-wind, and gravity (hydro). The pros and cons of these categories and types are reviewed. The secondary energy types, electricity and hydrogen, are discussed in terms of the requirements for substrate, primary energy, and the subsequent distribution and use. The conclusion is that electricity generated with a mix of coal and nuclear is optimum with the present use of hydro continued. The use of solar/wind energy for base load generation is discussed with the conclusion that without the development of large scale electricity storage it will not be feasible for the 20% to 30% penetration. The use of biofuels is discussed with the conclusion that for surface transportation plug-in electric vehicles make the most sense with biofuels for other applications. Ultimately a fusion primary energy system will probably supplant the other primary systems.

## 82. Climate Change Science: Update

**Richard H. Gammon, Professor**, Department of Chemistry and School of Oceanography, University of Washington, Seattle, WA

The most recent international summary of climate change science (IPCC '07) is now seriously out of date. This presentation will highlight the most important research findings and global observations since 2006, the cutoff date of the IPCC science synthesis. Most importantly, more recent research suggests that the climate sensitivity has been seriously underestimated, as has the prediction of likely sea-level rise in this century. The observed rate of global fossil fuel use and consequent atmospheric CO<sub>2</sub> increase in recent years exceed the highest previous forecasts (A1F1 scenario). Ocean and forest sinks for CO<sub>2</sub> are now observed to be slowing, saturating. Since 2006, global atmospheric methane is increasing rapidly, likely due to high-latitude release from peat/permafrost. Ocean acidification is now recognized as a very serious and long-term consequence of rising CO<sub>2</sub>, threatening marine ecosystems globally. Projections of changing climate going centuries ahead suggest irreversible damage to the planet (i.e. widespread desertification) lasting a thousand years or more.

## 83. Improving Centuries-Old Electrical Energy Storage Devices by Rethinking Multifunction On the Nanoscale and in 3D

**Debra R. Rolison**<sup>1</sup>, Jeffrey W. Long<sup>1</sup>, Justin C. Lytle<sup>1</sup>, Megan B. Sassin<sup>1</sup>, Jennifer L. Dysart<sup>1</sup>, Jean Marie Wallace<sup>2</sup>, Christopher N. Chervin<sup>1</sup> and Katherine M. Pettigrew<sup>1</sup>, (1)Code 6170, Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, DC, (2)Nova Research, Inc., Alexandria, VA

Electrical energy storage in batteries and electrochemical capacitors (ECs) girds any future success in the global effort to shift energy usage away from fossil fuels. A marked improvement in the performance of these power sources is critical for this effort, yet both are mature technologies experiencing incremental, not revolutionary improvements. Repeating the usual strategies to improve performance will not get the job done—what might is redesigning the reaction interphases in which the fundamental processes that store energy in batteries and ECs occur. Energy researchers are now rethinking the requisite multifunction—mass and charge transport, electronic and ionic conductivity, and electron-transfer kinetics—in light of nanoscience and architectural design in three dimensions. The design and fabrication of three-dimensional multifunctional architectures from the appropriate nanoscale building blocks for chemical, physical, and physicochemical charge storage will be highlighted [1,2], including the use of “nothing” (void space) and deliberate disorder as design components as well as the importance of reexamining in a nanoscopic form those materials that yielded poor energy-storage performance when used in a macroscopic form. [1] Long, J.W.; Rolison, D.R. *Acc. Chem. Res.* 2007, 40, 854. [2] Rolison, D.R.; Long, J.W.; Lytle, J.C.; Fischer, A.E.; Rhodes, C.P.; McEvoy, T.M.; Bourg, M.E.; Lubers, A.M. *Chem. Soc. Rev.* 2009, 38, 226–252.

## 84. A Stable Pt/C Electrocatalyst Modified with Poly(diallyldimethylammonium chloride) for Oxygen Reduction

**Sheng Zhang**<sup>1</sup>, Yuyan Shao<sup>2</sup>, Geping Yin<sup>1</sup> and Yuehe Lin<sup>2</sup>, (1)School of Chemical Engineering & Technology, Harbin Institute of Technology, Harbin, China, (2)Pacific Northwest National Laboratory, Richland, WA

One of the most challenging issues for polymer electrolyte membrane (PEM) fuel cell commercialization is its poor material durability. The degradation of electrocatalytic materials in PEM fuel cells results mainly from three aspects: Pt dissolution/redeposition, Pt migrating/agglomerating on carbon support, and Pt nanoparticle detaching from carbon support. Most of the studies on improving the durability of PEM fuel cell electrocatalytic materials only treat one or two aspects. Here we report an “all-in-one” strategy to improve the durability of Pt catalysts. A long-chain

polyelectrolyte, poly(diallyldimethylammonium chloride) (PDDA), is employed to stabilize platinum nanoparticles. Our PDDA-Pt/C electrocatalyst exhibited higher activity towards oxygen reduction reaction (ORR) than commercial Etek-Pt/C. The durability of PDDA-Pt/C was improved by a factor of 2 as compared with Etek-Pt/C. X-ray photoelectron spectroscopy (XPS) characterization of PDDA-Pt/C revealed the interaction between Pt nanoparticles and PDDA, which increased Pt oxidation potential (thus decrease the degradation of Pt from dissolution/redeposition) and prevents Pt nanoparticles from migrating/agglomerating on or detaching from carbon support. This provides a promising strategy to improve both the durability and activity of electrocatalysts for fuel cells. This work is widely interesting for scientists in the fields of nanomaterials, electrochemistry, electrocatalysis, and fuel cells.

## **85. Electrochemical Effects of Gold Nanoparticles On Electrodeposited Molybdenum Oxide Thin Films**

**Anne K. Bentley**, James M. Chatham and Eric A. Randall, Department of Chemistry, Lewis & Clark College, Portland, OR

Molybdenum oxide thin films co-electrodeposited with gold nanoparticles have been studied as cathode materials for lithium ion batteries. The incorporation of gold nanoparticles into the layered molybdenum oxide films could increase cathode performance by increasing available surface area for lithium ion insertion. Gold nanoparticles were synthesized and stabilized with citrate or cysteamine capping ligands. The colloidal stability of the cysteamine-capped nanoparticles was investigated using dynamic light scattering techniques as a function of both pH and cysteamine concentration. Excess salts were removed from the cysteamine-capped nanoparticle colloids using a straightforward dialysis method. The electrochemical behavior of the MoO<sub>3</sub>-gold nanoparticle composite films was characterized using cyclic voltammetry and compared to that of untreated MoO<sub>3</sub> films.

## **86. Clean Hydrogen: Prospects and Challenges**

**Walter V. Cicha, Ph.D.**, Institute for Fuel Cell Innovation, National Research Council Canada, Vancouver, BC, Canada

Worldwide, 45 – 50 megatons (Mt) of hydrogen are produced annually and is predominantly used in the chemical and petrochemical industry. The vast majority - 96 % - is produced from fossil fuels, typically natural gas. Thus, in the absence of carbon capture and sequestration (CCS), which holds some promise of industrial application but today still is at the demonstration stage, hydrogen production is a significant source of greenhouse gas CO<sub>2</sub>, and contributes to climate change. In an effort to reduce dependence on fossil fuels for stationary and motive power generation, and thus reducing GHG emissions, energy visionaries are pushing for large-scale development of renewable primary energy sources coupled with enhanced electricity and hydrogen energy carrier capacities. Some have envisioned a hydrogen economy of the future, where combustion engines will be replaced by fuel cells. However, any such visions will require an order of magnitude increase in hydrogen production capacity derived from clean (non-GHG emitting) energy sources over the next 20-30 years. This presentation will analyze the prospects and challenges of the most promising known sustainable energy driven pathways to hydrogen. The advantages and limitations of the routes will be compared and a few examples of latest research breakthroughs will be offered.

## **87. Ionic Liquids: A Shortcut to Thermochemical Hydrogen?**

**Nicholas AuYeung** and Alexandre Yokochi, Chemical, Biological, and Environmental Engineering, Oregon State University, Corvallis, OR

Thermochemical water splitting routes such as the Sulfur-Iodine cycle may be greatly improved via the use of ionic liquids as reaction media. In order to enable large scale implementation of this cycle, approaches that simplify product stream management following the initial Bunsen reaction are particularly important, especially with regards to the management of excess water and excess

iodine. Of special interest is the facile liberation of a concentrated, anhydrous stream of hydrogen iodide and sulfuric acid from the ionic liquid medium without resorting to the present methods, which include reactive distillation for the hydrogen iodide-water azeotrope. Beyond examining the kinetics of the Bunsen reaction itself and the evolution of hydrogen iodide and sulfuric acid from the reaction mixture, we identified conditions under which the reaction system may be biased to intentionally produce a stream of hydrogen sulfide based on a normally undesired side-reaction. The feasibility of this novel Sulfur-Sulfur cycle as well as the applicability of ionic liquids in the Hybrid Sulfur (also known as Westinghouse) Cycle will be discussed.

## **88. Leaching Characteristics of Hanford Ferrocyanide Wastes**

**Matthew Edwards**, Sandra Fiskum, Rick Shimskey and Reid Peterson, Radiochemical and Engineering, Pacific Northwest National Laboratory, Richland, WA

During defense weapons production from the 1940's through the 1980's millions of gallons of radioactive waste were put into underground storage tanks on the Hanford Site, Richland, Washington. Approximately 140 metric tons of ferrocyanide, in the form of  $\text{Fe}(\text{CN})_6^{-4}$  salts, were added to Hanford tank wastes (along with  $\text{NiSO}_4$ ) in an effort to scavenge  $^{137}\text{Cs}$  (e.g., as  $\text{Cs}_2\text{NiFe}[\text{CN}]_6$ ). This ferrocyanide waste form is now one of the many complex, radioactive, tank waste mixtures at the Hanford Site that is intended to be vitrified at the Waste Treatment and Immobilization Plant. Prototypic pretreatment operations (caustic leaching, washing, and filtration) were performed on the ferrocyanide waste to assess mobilization of phosphate-, oxalate-, and aluminum-bearing phases from the solid phase to the aqueous phase. Extensive solids phase characterization before and after caustic leaching and washing identified elemental, radioisotope, and crystal information. Other than complete gibbsite removal from the solid phase, virtually no other concentration or mineralogical changes were observed. However, between 50% and 70% of the  $^{137}\text{Cs}$  component was removed during caustic leaching and washing. This is antithetical to other Hanford waste types studied and will be discussed in more detail.

## ***General Session - Analytical 2***

**Organizer:** Gary Christian University of Washington

**Presider:** Ray von Wandruszka University of Idaho, Moscow, ID

## **89. The Clouding of Acidic Sodium Dodecyl Sulfate Solutions**

**Joey Charboneau** and Ray Von Wandruszka, Department of Chemistry, University of Idaho, Moscow, ID

The clouding of sodium dodecyl sulfate (SDS) in strongly acidic solutions has been used in separations, but its mechanism has generally been misinterpreted. Rather than being akin to nonionic clouding, the process involves the slow hydrolysis of SDS to dodecanol, passing through a series of compositions at which the aggregation of surfactant is promoted by nucleation onto traces of insoluble product. At the onset this lowers the critical micelle concentration of SDS, and later it results in mixed aggregates of macroscopic size that give the solution a cloudy appearance. The increasing dodecanol content eventually causes coalescence of a coacervate phase which evolves into a solid layer of dehydrated dodecanol. The process continues over an extended period and the initial stages can be monitored through the I1/I3 ratio of pyrene fluorescence and surface tension measurements. The mixed SDS/dodecanol systems formed in acid hydrolysis can be mimicked in neutral solution by combining the appropriate amounts of SDS, dodecanol, and NaCl.

## **90. The Role of Quinoid Moieties in the Redox Chemistry of Humic and Fulvic Acids**

**Noel Palmer** and Ray Von Wandruszka, Department of Chemistry, University of Idaho, Moscow, ID

Dissolved humic and fulvic acids reduce inorganic arsenic to varying degrees depending on solution pH, ionic strength, and type of humate used. Quinoid moieties are not the only functionalities

responsible for this, but they do play an important role. ESR spectroscopy showed a free radical content of bulk and size-fractionated aqueous humic acid samples that could not account for the entire charge transferred to arsenate during the reduction process. Separation of humates into hydrophobic and hydrophilic fractions indicated that the former had a higher initial rate constant for the reduction, but that the two became similar later in the process. Fluorescence excitation–emission matrices of the quinoid components of the humates exhibited shifts typical of their redox transformation. This gradual shift took place during the first 24 h of reduction process, after which the spectra no longer changed. The reduction of arsenate, however, still occurred after this period, indicating that species other than quinoids were involved. This was borne out by the fact that the rate constants for the later processes were smaller.

### **91. Kinetics of Reactions of Superoxide with Manganese in Simulated Natural Waters**

**Hillary D. Easter**, Bettina M. Voelker and Stuart Paul Hansard, Department of Chemistry, Colorado School of Mines, Golden, CO

Superoxide radical ( $O_2^-$ ) may play an important role in the oxidation of manganese (Mn) in natural waters. Using continuous flow analysis with the chemiluminescence reagent methyl *Cypridina* luciferin analogue (MCLA), we directly observed the reaction between  $O_2^-$  and Mn(II) in simulated natural water samples. Samples contained Suwannee River Fulvic Acid (SRFA) to simulate organic ligands that may be present in natural waters and were made at pH 8.2. Modeling the chemiluminescence data obtained for the reaction between  $O_2^-$  and Mn indicated  $MnO_2^+$  being formed as a transient species in a step-wise oxidation of Mn(II) to Mn(III). Results from our model suggest that the oxidation of Mn(II) by  $O_2^-$  takes place on a timescale of a few hours assuming  $[O_2^-]$  is on the order of  $10^{-10}$  M.

### **93. The Development of An in-Situ Instrument for Measurement of Seawater Alkalinity**

**Robert D. Hart**, Department of Chemistry, University of Montana, Missoula, MT

Total alkalinity ( $A_T$ ) plays a key role in the understanding of several fundamental marine processes such as the calcium carbonate budget, anthropogenic carbon dioxide uptake and the impacts of  $CO_2$  on sensitive ocean ecosystems. Our lab has set out to develop a high precision, fully autonomous instrument to better understand the role  $A_T$  plays in ocean carbon cycling.

This instrument utilizes a new titration method, tracer monitored titration (TMT), which quantifies titrant additions without volumetric or gravimetric measurements. With TMT measurements of  $A_T$ , an acid-base indicator (the tracer) is used to monitor titrant concentrations and solution pH through spectrophotometric absorbance data. Titration information is calculated throughout a titration from Beer's law and the indicator equilibrium expression.

In April 2008, an in-situ autonomous instrument was designed based on a laboratory prototype. In September 2008, underway field testing was done off the coast of Oregon on an NSF research vessel, the R/V *Wecoma*. A large data set was collected over this time yielding data with larger than desired noise which was attributed to particle fouling of the optical cell. Current research is focused on improvements to the instrument's protocol in hopes of better understanding sources of error before further field testing.

## **94. Incorporating Laser-Induced Breakdown Spectroscopy (LIBS) Into the Laser-Based Optical and Chemical Imager (LOCI)**

**Paul L. Tremblay**<sup>1</sup>, Timothy R. McJunkin<sup>2</sup> and Jill R. Scott<sup>1</sup>, (1)Department of Chemical Sciences, Idaho National Laboratory (INL), Idaho Falls, ID, (2)Industrial Technology, Idaho National Laboratory (INL), Idaho Falls, ID

Previously, a custom light collecting system was developed to allow surface laser-induced fluorescence (LIF) for speciation of uranium to be collected from samples inside an internal source Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) to form the laser-based optical and chemical imager (LOCI). LIF spectra are obtained using low laser irradiance prior to the high irradiance laser desorption/ionization event for acquiring FTICR-MS spectra. This light collecting system is being optimized for also acquiring laser-induced breakdown spectroscopy (LIBS) spectra because it is compatible with a laser scanning device to allow imaging or mapping of a sample. The light collecting setup uses a series of fiber optics and a ring-shaped mirror with special curvature to collect the light on and above the surface of the sample. In the current version, the fiber optics are coupled through a multiplexer before entering the spectrometer. Initial evaluation revealed that the light collecting system allows LIBS spectra to be easily acquired by altering the timing of the spectrometer without any changes in the collecting optics. Experiments to characterize the performance of the LIBS acquisition under various atmospheric conditions will be discussed.

## **95. Trace Explosive Characterization From Various Substrates**

**Carla Miller** and Timothy Yoder, Chemistry, Idaho National Laboratory, Idaho Falls, ID

The amount of time that an explosive is present on the surface of a material is dependent upon the original amount of explosive on the surface, temperature, humidity, rain, etc. This laboratory study focused on examining the similarities and differences of explosive fingerprints once they have been subjected to various temperatures and humidity over a period of time. TNT, RDX, and Semtex-H were deposited onto the surface of a material substrate by fingerprinting of the actual explosive. The substrate surfaces used during this study were: 50% cotton/50% polyester as found in T-shirts, 100% cotton with a smooth surface such as that found in a cotton dress shirt, 100% cotton on a rough surface such as that found on canvas or denim, suede leather such as might be found on jackets, purses, or shoes, and painted metal obtained from a car hood at a junk yard. The samples were not pre-cleaned prior to testing and contained sizing agents, and in the case of the metal, oil and dirt. The substrates were photographed using a Zeiss Discover V12 stereoscope with Axiocam ICc1 3 megapixel digital camera prior to being placed in an environmental chamber held at a constant temperature and humidity, then again at various set times after being in the environmental chambers. An optical comparison was made from sample to sample. In addition, atomic force microscopy and scanning electron microscopy images were obtained from some of the samples. Some of the samples were also analyzed on explosive trace detection equipment. The results are presented in this paper.

## **96. Consumer Chemistry with the FUN-SCIENCE Program**

**Jerry DeMenna, Dr.**, Chemistry, FUN-Science Academics / Chem-Chek Labs, Bronx, NY

All Scientific Technologies rely on *Analytical Chemistry*. Environmental Engineers need to "quantitate" the concentration of Pollutants. Petrochemists need to "identify" the compounds in Crude Oil. Pharmaceutical Chemists need to "evaluate" the Extracts of Natural Products. Nutritional Lab Technicians need to "measure" all the items on the "Label". Food Scientists need to "determine" the Flavors in a Meal. All these topics have meaning for the Students... so they can relate to them and appreciate the "analysis" of these things. Using common and economical Analytical Technology; from \$75 pH Pens to \$40,000 GC-MS Systems; the *FUN-SCIENCE Program* provides the Teacher / Lab Instructor a "library" of "real-World" applications: \* pH Titration of Vinegar, \* Conductivity of Salt in potato Chips, \* ORP of Antioxidants in Tea, \* Spectrophotometric determination of UV-SPF in

Sunscreen Lotions, \* Colorimetric analysis of Iron in Breakfast Cereals using Beers Law, \* Fluorescence of Quinine in Tonic Water, \* determination of Hydrogen Peroxide using the Phosphorescence of Luminol Light Sticks, \* "Latent Energy" in Snack Foods by Juice Can Calorimetry, \* Caffeine content of Soda Pop by Liquid Chromatography, \* concentration of Alcohol in Mouthwash by Gas Chromatography... and more! Come see, learn and be amazed (or shocked!)

### ***General Session - Computational Chemistry***

**Organizer:** Dean Waldow, Ph. D. Pacific Lutheran University, Tacoma, WA

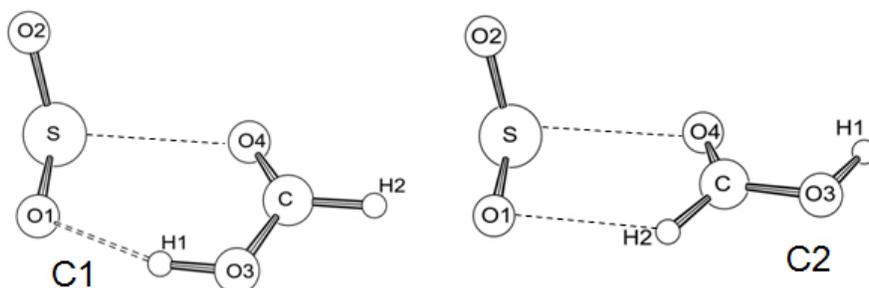
**President:** David L. Patrick Western Washington University, Bellingham, WA

#### **97. WITHDRAWN**

#### **98. SO<sub>2</sub>-Formic Acid Dimers. Computational Study of Hydrogen Bond and Donor-Acceptor Interactions**

**John W. Keller**, Sifat Chowdhury and Bronwyn L. Harrod, Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, AK

Computational and spectroscopic studies of formic acid have shown that in the gas phase this molecule often forms bidentate complexes, both homodimeric and heterodimeric, where formic acid donates one hydrogen bond and forms a donor-acceptor interaction using its carbonyl oxygen lone pair electrons. The cyclic dimers of formic acid and other carboxylic acids are well known examples. The complex of formic acid with SO<sub>2</sub> provides an opportunity to compare the strengths of these two types of interactions in isomeric complexes, and in the transition states between them. Using semi-empirical, ab initio, and density functional theory methods with basis sets up to aug-cc-pVTZ size, we identified six energy minima and six transition states on the SO<sub>2</sub>-formic acid potential energy surface. The syn conformation of formic acid is predicted to form the most stable bidentate complexes (C1 and C2), with C1 going on to formic-sulfurous anhydride, a covalent complex. The anti conformation forms three monodentate complexes (C3-C5). C1 can interconvert between mirror image isomers by breaking either the O-S donor-acceptor interaction (TS1) or the H-bond (TS2). Analysis of the energies and vibrational frequencies of these complexes sheds light on the relative importance of, and interplay between, the two attractive forces.



## ***Novel Polymer Science for Modern Applications 2***

**Sponsor:** ACS Division of Polymer Chemistry

**Organizer:** Mark Dadmun University of Tennessee, Knoxville, TN

**Organizer:** Dean Waldow Pacific Lutheran University, Tacoma, WA

**President:** Mark Dadmun University of Tennessee, Knoxville, TN

### **99. Polymer Semiconductors for Electronic and Solar Energy Applications**

**Samson A. Jenekhe**, Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, WA

Advances in the controlled synthesis, processing, and tuning of the properties of conjugated polymer semiconductors promise improvement in the performance of organic semiconductor devices and are accelerating the emerging era of plastic electronics. Our laboratory is exploring a molecular engineering approach to readily processable and robust, high charge carrier mobility materials needed for developing the next generation high-performance organic light-emitting diodes (OLEDs) for displays and solid-state lighting, field-effect transistors, logic circuits, and low-cost solar cells. In this talk, I will discuss recent work in these areas from our laboratory. New polymer semiconductors with donor-acceptor architectures have enabled achievement of enhanced light harvesting in solar cells and ambipolar charge transport in field effect transistors for logic circuits. At the nanoscale, we have investigated the self-assembly, nanoscale morphology, charge transport, and electronic and optical properties of various classes of polymer semiconductor nanostructures. Towards a better understanding of structure-property relationship in polymer semiconductors, we have investigated various macromolecular architectures, including homopolymers, alternating copolymers, and block copolymers, and diverse properties such as light emission, charge transport, and photovoltaic properties.

### **100. Diblock Conjugated Copolymers: Synthesis, Morphology, Thin Film Transistors, and Photovoltaic Cells**

**Pei-Tzu Wu**<sup>1</sup>, Guoqiang Ren<sup>2</sup>, Felix S. Kim<sup>2</sup>, Chaoxu Li<sup>3</sup>, Raffaele Mezzenga<sup>4</sup> and Samson A. Jenekhe<sup>2</sup>, (1)Department of Chemical Engineering, University of Washington, Seattle, WA, (2)Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, WA, (3)Department of Physics and Fribourg Center for Nanomaterials, Fribourg University, Fribourg, Switzerland, (4)University of Fribourg and Nesté Research Center, Lausanne 26, Switzerland

All-conjugated diblock copoly(3-alkylthiophene)s with different compositions have been synthesized and their field-effect carrier mobilities, photovoltaic properties, and unique phase behavior in the solution and in the melt were characterized. Diblock copoly(3-alkylthiophene)s were found to self-assemble into short nanowires with uniform dimensions by TEM imaging. Diblock copoly(3-alkylthiophene)s annealed above the homopolymer melt transitions (280 °C) were observed by small

and wide angle X-ray scattering (SAXS and WAXS) to be microphase-separated into a lamellar structure with two crystalline domains and two interlayer d-spacings. The two different interlayer stacking distances originate from two phase-separated domains in the lamellar structure. Interestingly, the field-effect charge transport and photovoltaic properties of the microphase-separated diblock copolymers are found to have similar properties before and after thermal annealing, unlike the dependence of carrier mobility and photovoltaic efficiency commonly seen in poly(3-alkylthiophene)s. Our results suggest that microphase-separated diblock copolythiophenes can be employed easily as good p-channel semiconductors in thin-film transistors and photovoltaic cells without rigorous annealing process.

### **101. High-Performance Organic Thin Film Transistors and Organic Solar Cells Based On Novel Donor-Acceptor Copolymer Semiconductors**

**Felix Sunjoo Kim**<sup>1</sup>, Hao Xin<sup>1</sup>, Guoqiang Ren<sup>1</sup>, Xugang Guo<sup>2</sup>, Mark D. Watson<sup>2</sup> and Samson A. Jenekhe<sup>1</sup>, (1)Department of Chemical Engineering and Department of Chemistry, University of Washington, Seattle, WA, (2)Department of Chemistry, University of Kentucky, Lexington, KY

Great efforts have been made in the last decade to develop high-performance organic thin film transistors (OTFTs) and efficient organic solar cells (OSCs) for applications in consumer electronics. In such low-cost and large area applications, organic semiconductors potentially have many advantages, such as inexpensive, high-throughput processability and materials compatibility. Here, we present high-performance OTFTs and OSCs based on a phthalimide-containing donor-acceptor copolymer semiconductors. Charge-carrier mobility as high as 0.28 cm<sup>2</sup>/Vs for holes was achieved in standard bottom-contact and bottom-gate OTFT devices under ambient conditions. Studies of the morphology revealed high interconnectivity of domains as well as short-range lamellar ordering of polymer backbones in the polymer semiconductor thin films. Investigation of the photovoltaic properties was naturally followed because of the high mobility and low band-gaps of the copolymer semiconductors. The power conversion efficiency of 2.0% was recorded in blends of the copolymer semiconductor donor and a fullerene derivative acceptor. Results of our present studies of the charge transport and photovoltaic properties of the novel donor-acceptor copolymer semiconductors demonstrate that the materials are promising for the development of high-performance OTFTs and OSCs.

### **102. Polymer Blend Compatibilization by in-Situ Multiblock Copolymer Formation**

**Mark Dadmun**, Earl Ashcraft, Haining Ji and Jimmy Mays, Department of Chemistry, University of Tennessee, Knoxville, TN

Difunctional reactive polymers, telechelics, were used to reactively form multiblock copolymers in-situ when melt blended with a blend of polystyrene and polyisoprene. To quantify the ability of the copolymer to compatibilize the blends, the time evolution of the domain size upon annealing was analyzed by SEM. It was found that the most effective parameter to quantify the ability of the copolymer to inhibit droplet coalescence is  $K_{rel} \cdot t_{stable}$ , the relative coarsening constant multiplied by the stabilization time. These results indicate that intermediate molecular weight telechelic pairs of both highly reactive Anhydride-PS/NH<sub>2</sub>-PI and slower reacting Epoxy-PS/COOH-PI both effectively suppress coalescence, with the optimal molecular weight being slightly above the critical molecular weight of the homopolymer,  $M_c$ . The effects of telechelic loading were also investigated, where the optimal loading concentration for this system was 0.5 wt.%, as higher concentrations exhibited a plasticizing effect due to the presence of unreacted low molecular weight telechelics present in the blend. The results of these experiments provide a clear understanding of the role of telechelic loading and molecular weight on its ability to reactively form interfacial modifiers in phase separated polymer blends, and provides guidelines for the development of similar reactive processing schemes that can use telechelic polymers to reactively compatibilize a broad range of polymer blends.

### **103. Probing Concentration Fluctuations of a Polybutadiene / Polystyrene Blend with Added Diblock Copolymer**

**Dean Waldow** and Christopher J. Hamre, Department of Chemistry, Pacific Lutheran University, Tacoma, WA

High temperature dynamic light scattering (DLS) and cloud point measurements were used to study polystyrene (PS) / polybutadiene (PB) blends with added PS-PB diblock copolymer. A diblock copolymer can lead to the formation of a bicontinuous microemulsion (BME) phase at certain concentrations. Correlation function measurements as a function of scattering angle were conducted over a large temperature range of 180°C to 75°C. The intensity autocorrelation functions for all polymer compositions were fit using a double exponential function. Zero-shear viscosities of the blends were also measured and were used in determining dynamic correlation lengths. Two concentration fluctuation modes were observed in most situations and were only previously seen in binary blend systems. The dynamic correlation lengths from the fast mode for diblock concentrations less than 8% diverge near their phase separation temperatures. The diblock blends with concentrations in the range of 8% - 12% have fast dynamic correlation lengths that peak and do not diverge when temperature is lowered suggesting the presence of a BME similar to research presented in the literature. The slow mode results were inconclusive though appeared to have some connection of the phase boundary.

### **104. Thickness Dependence of Low Molecular Weight Polystyrene / Polybutadiene Thin Film Polymer Blends Studied by Atomic Force Microscopy**

**Luke Latimer** and Dean Waldow, Department of Chemistry, Pacific Lutheran University, Tacoma, WA

Polystyrene (PS) and polybutadiene (PB) thin film polymer blends systems were studied using Atomic Force Microscopy. The surface morphology of spin-coated low molecular weight PS/PB thin film binary blends was explored as a function of film thickness and annealing time. This blend system is comparable to previously studied bulk systems. The thickness of PS/PB thin film blends ranged from 9 to 78 nm as generated from 0.5 to 5.0 % (w/w) polymer in toluene. Film dewetting and phase separation were characterized by surface roughness, lateral domain size, and contact angle. Pinhole formation and surface phase separation were observed at room temperature. Connections are made to the thickness dependence of the PS glass transition temperature as well as to scaling behavior.

### ***Chemical Education: General Interest***

**Organizer:** Dharshi Bopegedera The Evergreen State College

**Organizer:** Carole Berg Bellevue Community College, Bellevue, WA

### **105. New Tool for Teachers, National Historic Chemical Landmarks Website**

**Janan M. Hayes**, Merced College - retired, Sacramento, CA

One of the American Chemical Society's best kept secret teacher supplemental aids is the National Historic Chemical Landmarks (NHCL) program. But now with the introduction of a new interactive website, [www.acs.org/landmarks](http://www.acs.org/landmarks), teachers, students, and all inquiring minds have an opportunity to learn more about the chemically related achievements in the advancement of society. Learn more about Scotch Tape, Jamestown Colony, Tide detergent, and many other NHCL sites. Plus, now there are maps, a timeline, puzzles and games in addition to detailed descriptions of the various landmarks. Come, see, and go home with a new informative resource from ACS.

## **106. Making Interdisciplinary Connections – Where Chemistry Makes a Difference**

**A. M. R. P. Bopegedera, Dr.** , Department of Chemistry, The Evergreen State College, Olympia, WA

We all know that chemistry is the central science. We proclaim this in our classrooms. In today's world where interdisciplinary teaching is not only popular, but very much a necessity, can the central science help us make connections between disciplines? Having taught for 18 years at a college that prides itself on a curriculum that is primarily interdisciplinary in nature, I would like to share some of my successful "teaching and learning moments" where chemistry made all the difference in making connections between disciplines. These teaching moments include interdisciplinary programs at the introductory (majors and non-majors), intermediate, and upper level classes.

## **107. The New ACS Guidelines for Chemistry in Two-Year College Programs**

**George S. Kriz**, Chemistry, Western Washington University, Bellingham, WA

Community colleges play a vital role in training the 21st century workforce by providing access to higher education and fostering success for a diverse student body. The recently released "Guidelines for Chemistry in Two-Year College Programs" seeks to promote institutional excellence and increase communication between community college chemistry programs and their partners in education, industry, and government. This paper will provide an overview of the guidelines and how they can be used to support students, faculty, and programs at community colleges. Copies of the guidelines will be distributed.

## **108. A Different Approach: The Chemistry Open Laboratory at Pacific Lutheran University**

**Craig B. Fryhle** and Dean Waldow, Department of Chemistry, Pacific Lutheran University, Tacoma, WA

The Chemistry Open Laboratory at Pacific Lutheran University program is a novel, blended, stimulating, and efficient environment for students to conduct laboratory work during their chemistry studies. Non-majors, general, organic, and analytical chemistry laboratory courses are taught in the Open Laboratory, as well as some aspects of upper division laboratories. The Open Laboratory provides flexibility for students to accommodate other activities in their schedule, such as music or sports, it affords flexible faculty scheduling, and it allows excellent sharing of resources. It is simultaneously an open physical space and a philosophical approach to laboratory teaching. This presentation will describe the space, how it is used, and the infrastructure that supports it. Tours of the Open Laboratory and department facilities will be available through an on-site sign-up process at NORM.

### ***General Session - Analytical 3***

**Organizer:** Gary Christian University of Washington

**President:** Paul C.H. Li, Ph.D. Simon Fraser University, Burnaby, BC, Canada

## **109. Carbon Nanotube-Based Electrochemical Sensor for Assay of Salivary Cholinesterase Enzyme Activity: An Exposure Biomarker of Organophosphorus Pesticides**

**Dan Du**, Jun Wang, Chuck Timchalk and Yuehe Lin, Pacific Northwest National Laboratory, Richland, WA

Certain saliva enzymes may be useful biomarkers for detecting exposures to organophosphorus pesticides. Saliva biomonitoring offers a simple approach for rapidly evaluating those exposures in real time. In this regard, an electrochemical sensor coupled with a micro- flow injection system is

developed for rapid and sensitive characterization of cholinesterase enzyme (ChE) activities in rat saliva. The electrochemical sensor is based on a carbon nanotube (CNT)-modified screen printed carbon electrode (SPE), which is integrated into a flow cell. Because of the excellent electrocatalytic activity of the CNTs, the sensor can detect electroactive species that are produced from enzymatic reactions with extremely high sensitivity and at low potentials. The sensor is very sensitive to varied AChE concentrations with a detection limit down to 2 pM. Then, the inhibited ChE by organophosphorus agent can be completely reactivated by introducing nucleophiles such as pralidoxime iodide. This oxime-induced reactivation is the primary therapeutic approach to organophosphorus poisoning. Based on this double test of enzyme activity, a new rapid and reliable method for determination of trace organophosphorus exposure is proposed. This approach is very valuable and represents a new field for the improvement of diagnosis of exposure to organophosphorus pesticides.

### **110. Analysis of HSCCC Instrument Parameters for the Development of Universal Standards for Optimal HSCCC Performance**

**Brian J. Carroll, PhD<sup>1</sup>**, Clinton J. Dahlberg<sup>1</sup>, Andrew I. Mix<sup>1</sup>, Matthew L. Tripp, PhD<sup>2</sup> and Jeffrey S. Bland, PhD, FACN<sup>2</sup>, (1)Phytochemistry, Metagenics/MetaProteomics Nutrigenomics Research Center, Gig Harbor, WA, (2)Metagenics/MetaProteomics Nutrigenomics Research Center, Gig Harbor, WA

Since the seminal report by Ito et. al. describing the first design of high-speed counter current chromatography (HSCCC) instrumentation, a wide variety of unique HSCCC designs have been reported. Despite the lack of uniformity in instrument design, HSCCC has been successfully implemented in laboratories throughout the world enabling countless analyses and purifications of natural products. A survey of various reported HSCCC instrument parameters was conducted in order to determine which if any instrument parameters occur with greater frequency. The central premise motivating this survey is that frequently occurring parameters are associated with optimal or near optimal HSCCC performance. Guided by the experience and expertise of previous HSCCC design engineers, the data compiled herein is used as an aid in the construction of universal HSCCC design "rules-of-thumb". These "rules-of-thumb" will contribute to the standardization of HSCCC instrumentation. Universal HSCCC design standards allows for the standardization of HSCCC equipment thus enabling even more widespread use of this powerful technology.

### **111. Cyclodextrin-Enhanced Fluorescence Detection of Ribose-Modified Meisenheimer Complexes of Adenosine and Inosine by Capillary Electrophoresis**

**Thomas K. Green**, Department of Chemistry & Biochemistry, Institute of Arctic Biology,, University of Alaska Fairbanks, Fairbanks, AK, Luc Denoroy, CNRS, FRE 3006, Laboratoire de Neuropharmacologie, Faculté de Pharmacie, Université Claude Bernard Lyon 1, F-69373 Lyon Cedex 08, France and Sandrine Parrot, ISPB and IFNL, Plate-forme NeuroChem, Université Claude Bernard Lyon 1, F-69373 Lyon, France

Ribose-modified Meisenheimer complexes of adenosine and inosine were synthesized by reaction with trinitrobenzenesulfonic acid under basic conditions (Figure 1). The derivatives were separated and detected by capillary electrophoresis (CE) with laser induced detection (LIF). Excitation was at 410 nm using a diode laser. Injection of 50  $\mu$ M of each analyte yielded peaks with S/N  $\sim$  10 using a 20 mM borate buffer at pH 9.2. Addition of 10 mM hydroxypropyl- $\gamma$ -cyclodextrin (HP-  $\gamma$ -CD) to the buffer enhanced the S/N by a factor of 40-45 for each analyte, with decreased migration times. Fluorescent enhancement is attributed to inclusion of the Meisenheimer complex into the hydrophobic cavity of the HP- $\gamma$ -CD. The signal of Meisenheimer complex of ATP is also enhanced, although less dramatically. The technique holds promise for submicromolar fluorescence detection of ribose-containing substrates such as ATP, GTP, etc. Future work will include an investigation of the absorption/emission properties of the derivatives in the presence of various cyclodextrins, as well as NMR studies of the inclusion complexes.

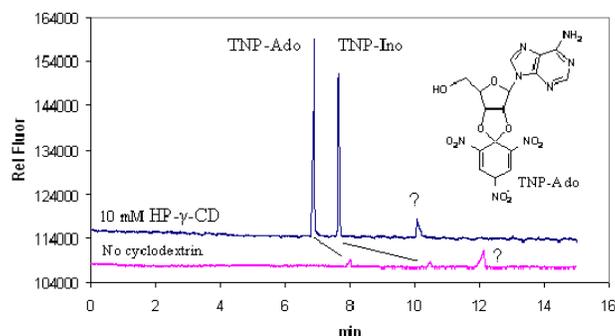


Figure 1. Separation and detection of Ribose-modified Meisenheimer complexes of Adenosine (TNP-Ado) and Inosine (TNP-Ino). Capillary: 50  $\mu$ m, 60 cm, 30 kV, 50  $\mu$ M injected each, 1.5 psi-s, 20 mM borate, pH 9.2.

## 112. Influence of Nucleation and Grain Growth On Contaminant Localization in Electroformed Ultra-High Purity Copper

**Esther E. Mintzer**, Daniel J. Edwards, O. Thomas Farmer III, David C. Gerlach, Martin Liezers and Eric W. Hoppe, National Security Directorate, Pacific Northwest National Laboratory, Richland, WA

The next generation of fundamental physics experiments probing the mass of the neutrino or searching for dark matter will require components of unprecedented purity. Copper has become the material of choice for these and other applications requiring low-activity materials, such as low-fault integrated circuits, because of its lack of naturally occurring radioisotopes, its excellent physical properties, and the ability to purify it to a high degree via electrodeposition. Of concern in the production of ultra-high purity copper is determining the mechanisms of contaminant deposition, especially considering evidence for non-homogeneous distribution of impurities in the bulk material. Contaminant localization and its relationship to nucleation and grain growth were investigated in electroformed copper via scanning electron microscopy (SEM) with electron backscatter diffraction (EBSD), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and secondary ionization mass spectrometry (SIMS).

## 113. Analysis On a Single Biological Cell Selected Using a Microfluidic Chip

**Paul C.H. Li, Ph.D.** and Yuchun Chen, Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada

Multidrug resistance (MDR) has become an obstacle of cancer chemotherapy because the membrane proteins of the MDR cancer cells will pump the chemotherapeutic drug out of the cells. In this work, a single leukemia CEM MDR cell was isolated and captured by a glass microfluidic single-cell biochip for drug transport and retention study. The experiments were then repeated on other single cells. Daunorubicin (DNR), an anti-cancer drug with intrinsic fluorescent emission at 575 nm, was used in the study. Simultaneous optical imaging and fluorescent measurement were achieved on the captured single cancer cell. Intracellular drug concentration variation from the change of the cellular fluorescence intensity was monitored, with real-time background correction. The cell sample suspended in cell culture medium was introduced into the chip from one reservoir. By adjusting the liquid pressure from the reservoirs, we could select one cell and move it to the cell retention structure. After a cell was captured inside the single-cell chip, we first introduced DNR to the cell via the central reagent microchannel. Then, the cellular fluorescent signal increased, which indicated DNR was transported into the cell. Thereafter, the cellular fluorescent signal reached a steady level in about 10 minutes, indicating a balance of drug accumulation and drug efflux rates. Then a DNR solution with cyclosporine (CsA) was introduced to the cell. In the presence of CsA, which was an MDR inhibitor used to reverse the MDR effect, the cellular fluorescence further

increased and reached a higher level. This indicated that the drug efflux was partially inhibited and the DNR retention inside the cell was higher when CsA was present. The accompanied cell imaging data allow us to determine how the anticancer drug and the inhibitor affect the cellular shape.

#### **114. Optimized On-Line Alignment of Gas Chromatograms for Real-Time Decision Making**

**Jeremy S. Nadeau**<sup>1</sup>, Thomas I. Dearing, Ph. D.<sup>1</sup>, Brian G. Rohrback, Ph. D.<sup>2</sup>, L. Scott Ramos, Ph. D.<sup>2</sup> and Robert E. Synovec, Ph. D.<sup>1</sup>, (1)Department of Chemistry, University of Washington, Seattle, WA, (2)Infometrix, Inc., Bothell, WA

Retention time alignment is often required to improve the precision of gas chromatographic data. Metrics for evaluating alignment performance include the correlation coefficient and the correlation coefficient with the Wallis Filter [J. Chromatogr. A, 1998, 805, 17-35]. Filtering the data before evaluating the correlation coefficient removes much of the chemical differences and improves the relationship between retention time uncertainty (peak shifting) and the correlation coefficient. The metric only requires inputs for the target and the sample to be aligned to the target. Therefore, this metric can be used to optimize parameters for on-line analysis. Targets and alignment parameters are optimized in real-time using the optimized metrics. Improvements to metric and target selection and parameter optimization are shown to improve classification with Principal Component Analysis (PCA) and a windowed version of PCA, Windowed Factor Analysis (WFA) [Anal. Chim. Acta, 2007, 584, 370-378]. WFA shows local variation to identify local changes, while PCA shows how well a new sample fits within the calculated model. These analyses show when the sample types change over time and when a new sample type is introduced into the sample stream. The improvements to classification make real-time decision making possible in an on-line system. With this real-time alignment methodology, maximum shift limits and maximum confidence limits for the PCA model and for WFA are set. When any limits are exceeded, the user receives a warning message to re-optimize the parameters, throw out the sample, or add the data to an on-line model. If the user does not give the requested feedback, the parameters are re-optimized and the data are re-aligned. This methodology improves classification for all chemical classes of the on-line re-optimized data over the initially optimized data as shown in PCA results with the Degree of Class Separation (DCS) [J. Chromatogr. A, 2005, 1096, 101-110].

#### **115. Bifunctionalization of Graphene for Biosensing**

**Hong Wu**<sup>1</sup>, Xinhuan Kang<sup>1</sup>, Jun Wang<sup>1</sup>, Dan Du<sup>1</sup>, Jun Liu<sup>1</sup>, Ilhan A. Aksay<sup>2</sup> and Yuehe Lin<sup>1</sup>, (1)Pacific Northwest National Laboratory, Richland, WA, (2)Department of Chemical Engineering, Princeton University, Princeton, NJ

Graphene, a basic material of carbon nanotubes (CNTs), is an unusually simple material with startling physical and chemical properties, such as an ultimately large surface-to-volume ratio, high electrical conductivity and electron mobility at room temperature, good mechanical strength and flexibility. Along with the surface functional groups, such as epoxy, hydroxyl, and carboxyl groups, the surface lattice defects on graphene sheet facilitated the preparation of graphene-based electrocatalysts and biosensors. Glucose oxidase immobilized on the graphene modified glassy carbon electrode with a layer of chitosan film has achieved its favorable micro-environment for direct electrochemistry and sensitive detection of glucose. Graphene-based bionanocomposite film was also prepared by electrodepositing platinum nanoparticles onto graphene/chitosan modified glassy carbon electrode with further enzyme immobilization. With the electrocatalytic synergy of graphene and platinum nanoparticles to hydrogen peroxide, a sensitive biosensor with detection limit of 0.6  $\mu\text{M}$  glucose was achieved. The large surface area and good conductivity of graphene suggests that graphene is a potential candidate for sensor material. The hybrid nanocomposite sensor provides new opportunity for clinical diagnosis and point-of-care applications.

## General Session - Inorganic 1

**Organizer:** Mark Wicholas Western Washington University, Bellingham, WA

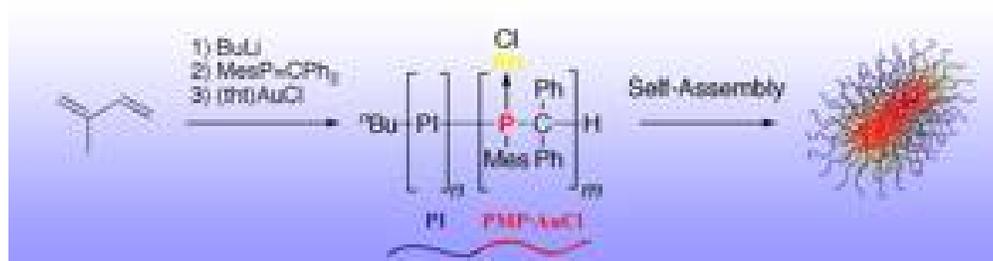
**President:** John D. Gilbertson Western Washington University, Bellingham, WA

### 116. Low Coordinate Phosphorus Chemistry: From Molecules to Polymers to Controlled Nanostructures

**Derek P. Gates**, Department of Chemistry, University of British Columbia, Vancouver, BC, Canada

The systematic development of the chemistry of carbon forms the basis of organic chemistry and has made possible the construction of increasingly complex structures. By analogy to the well-established principles of carbon chemistry, there is a desire to develop a predictable and rational synthetic chemistry for phosphorus. Although at a much more primitive stage of development, numerous parallels exist in molecular chemistry between C=C and P=C bonds.<sup>1</sup> Addition polymerization, perhaps the most important reaction of a C=C bond, has only recently been extended to the P=C bond in a phosphalkene.

This presentation will survey our recent work on the radical and anionic polymerization of P=C bonds, including mechanistic aspects. Living anionic polymerization methods provide a novel method to prepare controlled microstructure phosphorus polymers and block copolymers.<sup>2</sup> Recent work will be highlighted, in which functional isoprene-phosphalkene block copolymers are employed as macromolecular templates for the self-assembly of gold nanostructures (Fig. 1).<sup>3</sup>



**Figure 1.** Synthesis of isoprene-phosphalkene block copolymers and use in the self-assembly of gold nanostructures.

References:

<sup>1</sup> Mathey, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 1578.

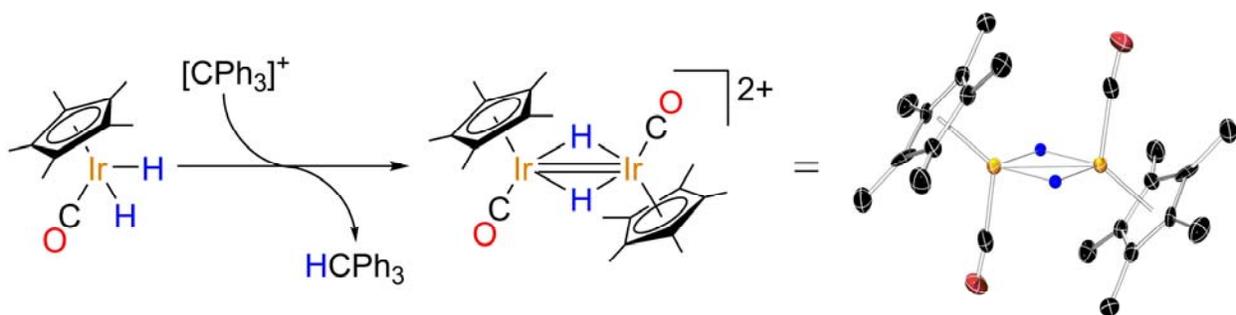
<sup>2</sup> Noonan, K. J. T.; Gates, D. P. *Angew. Chem. Int. Ed.* **2006**, *45*, 7271.

<sup>3</sup> Noonan, K. J. T.; Gillon, B. H.; Cappello, V.; Gates, D. P. *J. Am. Chem. Soc.* **2008**, *130*, 12876.

## 117. Syntheses of Dinuclear Iridium Complexes Containing Cp\* and Carbonyl Ligands

**Joseph M. Meredith**, Karen I. Goldberg, Werner Kaminsky and D. Michael Heinekey, Department of Chemistry, University of Washington, Seattle, WA

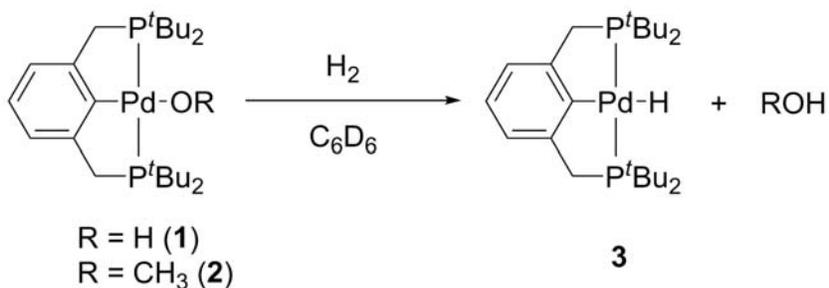
The syntheses of the monomeric cationic complexes  $[\text{Cp}^*(\text{CO})\text{Ir}(\text{R})(\text{CH}_2\text{Cl}_2)]^+$  were attempted ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{R} = \text{Me}, \text{H}$ ). The target complexes were not obtained; instead, dimeric products were isolated in high yields. The reaction between  $\text{Cp}^*(\text{CO})\text{Ir}(\text{Me})(\text{Cl})$  and  $[\text{Li}(\text{Et}_2\text{O})_{2.5}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  afforded the cationic complex  $[\{\text{Cp}^*(\text{CO})\text{Ir}(\text{Me})\}_2(\mu\text{-Cl})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  in high yield as a mixture of diastereomers. The mono-chloro bridged complex  $[\{\text{Cp}^*(\text{CO})\text{Ir}(\text{Me})\}_2(\mu\text{-Cl})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}\{^1\text{H}\}$  NMR, and IR spectroscopies. Reaction of  $\text{Cp}^*(\text{CO})\text{Ir}(\text{H})_2$  with  $[\text{CPh}_3]^+[\text{BAR}^{\text{F}}_4]^-$  produced the dicationic complex  $[\{\text{Cp}^*(\text{CO})\text{Ir}(\mu\text{-H})\}_2]^{2+}[2\{\text{B}(\text{C}_6\text{F}_5)_4\}]^{2-}$  in excellent yield. The dimeric iridium dihydride  $[\{\text{Cp}^*(\text{CO})\text{Ir}(\mu\text{-H})\}_2]^{2+}[2\{\text{B}(\text{C}_6\text{F}_5)_4\}]^{2-}$  has been characterized by  $^1\text{H}$  NMR and IR spectroscopies as well as elemental analysis and single crystal X-Ray diffraction.



## 118. Hydrogenolysis of Palladium(II) Hydroxide and Methoxide Pincer Complexes

**Gregory R. Fulmer**<sup>1</sup>, Richard P. Muller<sup>2</sup>, Richard A. Kemp<sup>3</sup> and Karen I. Goldberg<sup>1</sup>, (1)Department of Chemistry, University of Washington, Seattle, WA, (2)Multiscale Dynamic Materials Modeling, Sandia National Laboratories, Albuquerque, NM, (3)Department of Chemistry, University of New Mexico, Albuquerque, NM

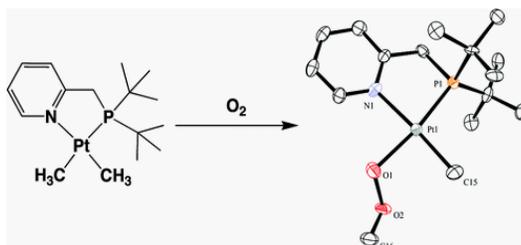
Hydrogenolysis of metal hydroxides or alkoxides, resulting in release of water or alcohol and production of a metal hydride, could be a highly valuable combination step of product release and catalyst regeneration within a catalytic cycle. Hydrogenolysis reactions of the palladium(II) complexes  $(\text{PCP})\text{Pd}\text{-OH}$  (**1**) and  $(\text{PCP})\text{Pd}\text{-OCH}_3$  (**2**) ( $\text{PCP} = 2,6\text{-bis}(\text{CH}_2\text{P}^t\text{Bu}_2)\text{C}_6\text{H}_3$ ) to form water and methanol, respectively, and the corresponding palladium(II) hydride (**3**) were performed. In the presence of water, the palladium(II) hydroxide was found to be in equilibrium with a water-bridged dimer complex. Kinetic studies indicate that the reaction of the palladium(II) hydroxide and  $\text{H}_2$  proceeds exclusively through the hydroxide monomer to form the palladium(II) hydride and water. Computational studies suggest a four-center intramolecular proton transfer as opposed to an oxidative addition/reductive elimination pathway.



## 119. Insertion of Dioxygen Into a Platinum(II)-Methyl Bond to Form a Platinum(II) Methylperoxo Complex

**Kyle A. Grice** and Karen I. Goldberg, Department of Chemistry, University of Washington, Seattle, WA

Platinum complexes are known to perform catalytic C-H functionalization of alkanes. Particularly desirable in catalytic alkane functionalization and other oxidations would be the use of molecular oxygen as an oxidant, since molecular oxygen is inexpensive, abundant, and environmentally benign. We have synthesized a platinum(II) complex (PN)PtMe<sub>2</sub> (PN = 2-((di-tert-butylphosphino)methyl)pyridine) which reacts with molecular oxygen to form (PN)PtMe(OOMe), a platinum(II) methylperoxo complex. This is a highly unusual reaction for platinum alkyls and is promising for the development of alkane oxidation reactions using oxygen as the oxidant. The structure of (PN)PtMe(OOMe) has been confirmed by X-ray crystallography.



## 120. Investigation of a New Class of Ligands with Hydrogen Bond Donors/Acceptors in the Secondary Coordination Sphere

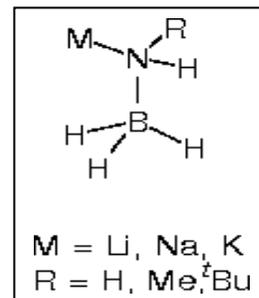
**John D. Gilbertson**, Department of Chemistry, Western Washington University, Bellingham, WA

This research focuses on new complexes that contain biologically relevant metal ions bound to pyridinediimine (PDI) ligands that contain hydrogen bond donors/acceptors proximal to the central metal ion(s). These ligands mimic specific chemical environments of the secondary coordination sphere of relevant metalloproteins. The synthesis and characterization of these ligands and relevant metal complexes were investigated. These results and the potential to tune complex reactivities towards biologically relevant substrates will be discussed.

## 121. Mechanistic Studies of Hydrogen Release From Alkaline Metal Amidoboranes

**Avery T. Luedtke** and Tom Autrey, Pacific Northwest National Laboratory, Richland, WA

The fixation of hydrogen in the form of a solid hydride containing lightweight elements is a promising approach to energy storage, and an extensive effort by numerous research groups is currently being made in this area. One such hydride that has a high hydrogen content is NH<sub>3</sub>BH<sub>3</sub> (AB) and derivative compounds MNH<sub>2</sub>BH<sub>3</sub> [M = Li (LAB), Na (SAB), K (PAB)]. These compounds, unlike most solid hydrides, thermally release hydrogen at moderate temperatures (*ca.* 90 °C). LAB, SAB, NaNH(Me)BH<sub>3</sub> (SMAB), KNH(Me)BH<sub>3</sub> (PMAB), and KNH(<sup>t</sup>Bu)BH<sub>3</sub> (PBAB) were synthesized by addition of excess LiH, NaH, or KH to a THF solution of AB or alkyl aminoborane followed by filtration and removal of the volatiles and were characterized by <sup>1</sup>H NMR spectroscopy, <sup>11</sup>B NMR spectroscopy, and powder X-ray diffraction. The kinetics of H<sub>2</sub> release during the thermolysis of these solid metal amidoboranes was investigated by volumetric analysis of the gas released. Based on the relative rate of H<sub>2</sub> release, solid and solution NMR spectroscopic characterization of the products of thermolysis, and TG/DSC plots, a mechanism for H<sub>2</sub> release will be discussed.



## ***Bioanalytical Mass Spectrometry 1***

**Organizer:** Frantisek Turecek University of Washington, Seattle, WA

### **122. Membrane Proteome Quantification Using Membrane-Impermeable Chemical Probe and Stable Isotopic Labeling**

**Haizhen Zhang**, Roslyn N. Brown, Weijun Qian, Matthew E. Monroe, Samuel O. Purvine, Ronald J. Moore, Marina A. Gritsenko, Athena A. Schepmoes, Ljiljana Pasa-Tolic, Richard D. Smith and Mary S. Lipton, Pacific Northwest National Laboratory, Richland, WA

In this study, we have developed a large scale membrane proteome quantification strategy by combining membrane protein enrichment using a membrane-impermeable chemical probe and quantifications using high-performance mass spectrometry and stable isotopic labeling. Membrane-impermeable chemical probe has been applied for the enrichment of membrane proteins expressed by *Shewanella oneidensis* MR-1, a gram-negative bacterium with known metal-reduction capability via extracellular electron transfer between outer membrane proteins and environmental electron receptors. LC/MS/MS analysis resulted in identifying 2,780 unique peptides from 321 membrane proteins which corresponded to 87% and 79% of all the identified unique peptides and proteins in the experiment, respectively. To demonstrate that the proposed strategy was specific and sensitive to protein abundance change in cell membranes, quantifications of enriched membrane proteins by stable isotopic labeling were further carried out for both wild-type and mutant cells which were generated from deletion of a type II secretion protein, *gspD*. The quantification data resulted in reduced expression in abundance of some outer membrane cytochromes such as *OmCA* and *MtrC* in *gspD* mutant cells, which agreed with the previously published studies.

### **123. Phosphoserine-Arginine Interactions in Phosphopeptide Ions in the Gas Phase**

**Thomas W. Chung** and Frantisek Turecek, Department of Chemistry, University of Washington, Seattle, WA

Intramolecular interactions between protonated arginine and phosphate groups in peptide ions are of intense current interest. We investigated such interactions in four model pentapeptides, pSAAAR, ApSAAAR, AApSAR, and AAAPSR, using electron capture and transfer in the gas phase. Experimental studies of dissociations of doubly protonated peptides were performed using ETD-LTQ-MS for electron transfer dissociation and ECD-LTQ-FT-ICR-MS for electron capture dissociation. Large differences between ECD- and ETD-MS spectra were found that pointed to fundamentally different types of dissociations in the charge-reduced ions. Alongside mass spectrometric experiments, interactions between the phosphate group in phosphoserine and the protonated arginine residue were studied by *ab initio* and DFT calculations to elucidate hidden rearrangements in gas-phase peptide ions. Gas-phase secondary structures of the four model pentapeptides were studied to elucidate the ion dissociations and rationalize the observed differences.

### **124. WITHDRAWN:**

## **125. qPACIFIC: How to Quantify Deeper Into the Proteomics Ocean**

**Alexandre Panchaud**, Scott A. Shaffer and David R. Goodlett, Department of Medicinal Chemistry, University of Washington, Seattle, WA

The vast majority of shotgun proteomics experiments are conducted using data-dependent precursor ion selection; i.e. ions are selected for MS2 fragmentation based on: 1) presence of a signal, and 2) intensity. While very popular and successful, this approach suffers from limited dynamic range. Recently, we presented a data-independent acquisition method showing superior performance on serum analysis (eight orders of magnitude dynamic range) that we named Precursor Acquisition Independent From Ion Count (PACIFIC). Here, we present a novel quantitative, multiplexed PACIFIC workflow. Protein samples are labelled using isobaric tagging approaches, e.g. TMT (ThermoFisher). A collision induced dissociation (CID) spectrum is acquired every 1.5 m/z value whether a precursor ion is observed or not followed by a pulse-Q dissociation (PQD) spectrum in the low m/z range where TMT reporter ions are expected. Thus, in a single LC-MS/MS experiment 30 such scans are acquired (i.e. 15 pairs of CID/PQD) across a range of 22.5 m/z. Repeated injections are performed in an identical fashion until the desired m/z mass range is achieved. CID and PQD spectra are merged into a single composite spectrum using in-house software, searched with Sequest, validated using FDR < 1% and quantified using Libra (TPP, ISB, Seattle). Two reference sets were designed with 14 protein standards. Theoretical ratios spanned from 0.1 to 10 (reporter 126 over 127). All 14 proteins were identified in average with >80% sequence coverage and the expected ratios for the 14 proteins matched to less than 20% deviation. A similar experiment was conducted on a whole cell lysate of *Pseudomonas aeruginosa*. Twice the same amount of digest was tagged to mimic a 1:1 ratio distribution. A total of 1400 proteins were identified at FDR<0.5% of which 800 were quantified. The average/median ratio distribution was 1.01/1.00 with a standard deviation of 0.15.

## **126. Structure to Function: High-Throughput Multi-Stage Tandem Mass Spectrometry Platform for the Characterization of Lipid A Extracts From Gram-Negative Bacteria**

**Jace W. Jones, Ph.D.**<sup>1</sup>, Ying Sonia Ting<sup>1</sup>, David R. Goodlett, Ph.D.<sup>1</sup> and Robert Ernst, PhD<sup>2</sup>, (1)Department of Medicinal Chemistry, University of Washington, Seattle, WA, (2)Microbial Pathogenesis, Dental School, University of Maryland - Baltimore, Baltimore, MD

Lipopolysaccharide (LPS) constitutes the majority of the outer layer of the outside membrane of Gram-negative bacteria and represents one of the microbial molecular signals responsible for activation of the mammalian innate immune system. Recognition of LPS, in particular its bioactive component lipid A, has provided mammalian immune systems with a key strategy for defense against many Gram-negative pathogens. Previous studies have shown that alteration of lipid A structure greatly affects bacterial virulence serving as a survival strategy. Structural diversity in lipid A is often exhibited in the fatty-acid position and composition, phosphorylation and terminal monosaccharide modifications. A high-throughput multi-stage tandem mass spectrometry platform has been developed with the emphasis on characterizing diagnostic product ions from the dissociation of gas-phase lipid A anions. These diagnostic product ions provide routine and comprehensive structure determination for a variety of lipid A extracts from numerous Gram-negative bacteria. Furthermore, we devised a computational method that we refer to as Structural

Analysis of Lipid A (STALA) to guide manual interpretation of lipid A tandem mass spectra. Ultimately, our goal is to relate specific lipid A structure to biological function. To this end, we will highlight an example where we assessed the pro-inflammatory response of LPS towards human and murine simulated cells.

### **127. High-Sensitivity Planar FAIMS Analyzers Using New Front and Rear Interfaces**

**Alexandre A. Shvartsburg, Ph.D**, Ridha Mabrouki, Keqi Tang, Ryan Kelly, David C. Prior and Richard D. Smith, Biological Sciences Division, Pacific Northwest National Laboratory, Richland, WA

Field asymmetric waveform ion mobility spectrometry (FAIMS) is gaining acceptance for rapid separations of complex biological and environmental samples prior to mass spectrometry (MS). FAIMS filters ions passing through a gap between two electrodes that may be planar or curved. Despite inherent advantages of the planar geometry and its universal adoption in stand-alone FAIMS devices, commercial FAIMS/MS systems have employed curved FAIMS configurations that could be interfaced to MS more effectively. We present a new planar (p-) FAIMS design with slit-shaped entrance and exit apertures that substantially increase ion transmission in and out of the analyzer. Coupling of p-FAIMS to multi-emitter electrospray ionization (ESI) sources using a matching multi-inlet aperture raises the ion current entering the device by up to 5 times and allows ESI liquid flow rates reaching  $\sim 50 \mu\text{L}/\text{min}$ . A rectangular back interface increases the transmission of ribbon-shaped ion beams output by the p-FAIMS to downstream stages such as MS or conventional (drift tube) IMS by up to 20 times, compared to the standard circular aperture. Overall, the ion signal in ESI/FAIMS analyses increases by over an order of magnitude without compromising the high FAIMS resolution provided by the homogeneous electric field in planar geometries.

### ***Chemistry, Energy, and Sustainability 3***

**Organizer:** Justin Lytle Pacific Lutheran University

**Presider:** Justin Lytle Pacific Lutheran University

### **128. Selective Oxidation with Oxygen in Supercritical Water; Bringing Green Chemistry to Bulk Chemicals**

**Walt Partenheimer**, Consultant. DuPont (retired), Portland, OR and John L. Fulton, Pacific Northwest Laboratory, Richland, WA

Terephthalic acid is currently manufactured in multi-ton quantities by the reaction of dioxygen with p-xylene in acetic acid using a Co/Mn/Br catalyst. Terephthalic acid is used to make polyethylene(terephthalate), commonly called 'polyester' or 'PET' by its reaction with ethylene glycol. Although the terephthalic acid is obtained very selectively and in high yield, the use of the organic solvent, acetic acid, is problematic for two reasons 1) it is co-oxidized to undesirable by-products and 2) the terephthalic acid must be further purified before it can be used in PET manufacture.

We have now shown that terephthalic acid can be obtained from p-xylene in *supercritical water* in 92% yield at 400°C with a residence time of 18 s using a  $\text{MnBr}_2$  catalyst. Equally important is that the by-product, 4-carboxybenzaldehyde, is absent in the terephthalic acid. In the current process, in acetic acid, the product contains 0.2% of 4-carboxybenzaldehyde which requires a separate plant to remove this impurity. The remainder of the discussion will be on why non- $\text{scH}_2\text{O}$  is not an active oxidation solvent while  $\text{scH}_2\text{O}$  is, and the similarity in chemistry of  $\text{scH}_2\text{O}$  to that of acetic acid. The structure of the  $\text{MnBr}_2$  catalyst has been determined in  $\text{scH}_2\text{O}$  using EXAFS and XANES and is shown to be tetrahedral  $[\text{Mn}(\text{H}_2\text{O})_2\text{Br}_2]$ . The mechanism will be briefly discussed.

## **129. On-Road, in-Use Gaseous Emission Measurements by Remote Sensing of School Buses Equipped with Diesel Oxidation Catalysts and Diesel Particulate Filters**

**Daniel A. Burgard** and Melissa Provinsal, Department of Chemistry, University of Puget Sound, Tacoma, WA

A remote sensing device was used to obtain on-road and in-use gaseous emission measurements from three fleets of schools buses at two locations in Washington State. This paper reports each fleet's carbon monoxide (CO), hydrocarbons (HC), nitric oxide (NO), and nitrogen dioxide (NO<sub>2</sub>) mean data. The fleets represent current emission retrofit technologies such as diesel particulate filters, diesel oxidation catalysts and a control fleet. This study shows that CO and HC emissions decrease with the use of either retrofit technology when compared to control buses of the same initial emission standards. The CO and HC emission reductions are consistent with published U.S. EPA verified values. The total oxides of nitrogen (NO<sub>x</sub>), NO, and the NO<sub>2</sub>/NO<sub>x</sub> ratio all increase with each retrofit technology when compared to control buses. Most prior research suggests that NO<sub>x</sub> emissions are unaffected by the retrofits, however, these previous studies have not included measurements from retrofit devices on-road and after nearly five years of use. This study suggests that the vast introduction of these devices on diesel fleets across the country could have negative impacts.

## **130. Remote Sensing Measurements of Gaseous Emissions From Marine Vessels**

**Daniel A. Burgard** and Jacob A. Berenbeim, Department of Chemistry, University of Puget Sound, Tacoma, WA

Marine vessels remain one of the last mobile emission sources with few regulations. In the summer of 2008 the gaseous emissions from both recreational and commercial marine vessels passing through the Hiram H. Chittenden locks in Seattle, WA were collected using a Remote Sensing Device (RSD). This instrument can measure carbon monoxide (CO), hydrocarbons (HC), the NO<sub>x</sub> components nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>). Boat identification numbers were recorded and many vessels were matched to state records. These records were used to compare Make, Model Year and Fuel Type to their emission measurements. Measurements from nearly 200 vessels (75 matched) will be presented. This is the first in-use study of individually measured boats and provides baseline data in this maneuvering operating mode. Mean emissions from this fleet suggest that boats are one of the dirtiest mobile emission sources in the US.

### ***High School Chemistry***

**Organizer:** Steve Ufer Washington High School

**President:** Steve Ufer Washington High School, Tacoma, WA

## **131. CRISTAL Labs for High School Chemistry**

**Steve Ufer**, Washington High School, Tacoma, WA

CRISTAL (Chemistry Resources and Instructional Strategies for Motivating All Learners) labs were developed and revised in the early 1990's to provide students with quality labs which challenge them to do their own reasoning and to apply the concepts to solving problems. Each lab is labeled as exploratory, concept development or application and the learning cycles are organized around common chemistry topics. Experienced teachers will be familiar with many of the experiments, but they are well organized and rewritten to be more engaging. In using these labs for the past twelve years, I have found that they are easily adapted to match the grade level expectations for Washington State.

### **132. High School Research Course**

**Norman A. Nielsen**, Science Department, Northwest Christian High School, Lacey, WA

A research based chemistry laboratory course was introduced at Northwest Christian High School two years ago. The goals for the course were several: to provide a genuine research atmosphere in a high school class room, to afford a broader background in laboratory chemistry which would assist student transition into college work, to introduce methods research scientists use in their laboratories, to develop problem solving skills and experience using them, and to afford hands-on experience to help hone good laboratory technique. The course was designed to be multi-disciplined, as most scientific projects in today's world, involving aspects from biology, chemistry, physics, and computers. Another goal was for students to solve problems and conduct experiments for which neither students nor instructor would know the results in advance. Lastly, the course problems were designed to be challenging, but enjoyable enough to cause students to consider science as a career. This paper will describe the requirements for the course, how these were met, how funding was obtained, some of the difficulties encountered, response by the students, and research results obtained.

### **133. Fuel Cells in High School Chemistry**

**Laura K. Baumgartner, M. Eng. NBCT**, Bellevue School District, Robinswood High School, Bellevue, WA

This session will showcase activities and equipment developed at University of California Berkeley in partnership with the Schatz Energy Research Center and AC Transit, and used in the Bellevue School district to instruct high school chemistry and environmental science students about the use of hydrogen fuel cells in transportation applications. Links to a free online simulation and video will be distributed, as well as information about how hydrogen can be compared to more traditional fuels, sources of hydrogen through electrolysis and reformation, and how a fuel cell works. Participants will engage in data analysis comparing fuel cell buses to other commercially available bus technologies and they will simulate the function of a hydrogen fuel cell. These activities address NSES standards related to the structure of matter, atoms, and chemical reactions.

### **134. High School Chemistry Students' Representation of a Chemical Reaction at the Particulate Level**

**Anne L. Kern, Ph.D.**, Curriculum and Instruction, University of Idaho-Coeur d'Alene, Coeur d'Alene, ID, **Nathan B. Wood, Ph.D.**, School of Education, North Dakota State University, Fargo, ND and **Gillian Roehrig**, Curriculum and Instruction, University of Minnesota, Minneapolis, MN

According to Johnstone (1991), a major challenge in learning chemistry is students' abilities to simultaneously negotiate three different "worlds" or representational levels:

1. The macroscopic world, where matter, and changes in its properties, can be described in terms of characteristics that can be observed directly (i.e. senses, observations).
2. The submicroscopic/particulate world, where matter is represented as its constituent atoms and molecules (i.e. molecular models or particulate diagrams).
3. The symbolic world, where matter and interactions are represented symbolically (i.e. molecular formulae and chemical equations).

He emphasizes that chemists navigate these three worlds fluidly, often referring to all three "worlds" in the space of one sentence. However, students are often unable to make sense of how the symbolic representations in a chemical equation are related to observable changes in matter or how molecular formulae are related to bonding in molecules. This presentation reports on the

qualitatively different ways in which high school chemistry students attempt to represent a chemical reaction at the atomic/molecular level.

### **135. Chemistry Education within An Academy Model**

**Dewey J. Moody, Ph.D.**, Science Department, Ballard High School, Seattle, WA

For the last few years, the education area has been struggling with the success and/or appropriateness of the "academy" model and how best to implement such programs. The Ballard High School Biotechnology Career Academy (BCA) is one example of a three year academy program that begins in the 9<sup>th</sup> grade and is focused upon science. The sequence of science classes begins with Biology, followed by General Chemistry and finishing with Genetics. There are three key issues facing the successful application of this particular academy model. The first is the selection criteria for entry. Only 32 positions are available for a potential 9<sup>th</sup> grade pool of approximately 450. Data will be presented to justify our program entry screening criterion that requires the successful completion of Integrated II mathematics. The second issue is whether or not 10<sup>th</sup> graders, as part of the second year of the three year program, are prepared for the level of mathematic rigor demanded for successful completion of General Chemistry. The third and last issues is whether or not this model can address the needs of high-potential low-performing students that might need one additional year of preparation prior to entry into an academy oriented program.

### ***Chemistry of the Bioregion***

**Organizer:** Brian Naasz Pacific Lutheran University

**President:** Brian Naasz Pacific Lutheran University

### **136. Direct Monitoring of the Formation Kinetics of Volatile Dis-Infection by-Products in Complex Aqueous Samples Using Membrane Introduction Mass Spectrometry**

Owen O.D. Stechishin, Cameron C. Newhook, Chris C. Gill and **Erik T. Krogh**, Department of Chemistry, Applied Environmental Research Laboratories, Vancouver Island University, Nanaimo, BC, Canada

Halogenated methanes and acetonitriles are associated with the treatment of natural waters with active chlorine dis-infecting agents in some municipal drinking water systems. We report quantitative data on the simultaneous production of several trihalomethanes and/or dihaloacetonitriles by passing a reaction mixture in a re-circulated closed loop over a semi-permeable membrane interface coupled to an ion-trap mass spectrometer. Aqueous solutions containing natural organic matter or model compounds were treated with active chlorine under conditions that mimic drinking and/or wastewater disinfection. The formation of trace quantities of volatile dis-infection by-products (DBPs) was monitored in 'real-time' directly in harsh and complex reaction media at low parts per billion levels. Detection is achieved by selected ion monitoring and/or tandem MS techniques. Several quantification strategies will be compared including the use of isotopic dilution using an in-line permeation tube for continuous monitoring in flow-through applications. Trichloromethane yields and initial production rates from several model DBP precursors and some common pharmaceutical compounds. We report initial results on the formation kinetics of trihalomethanes produced upon chlorination of natural surface waters on Vancouver Island.

### **137. Contaminant Residues in Demersal Fish and Invertebrates From Areas of the Puget Sound, WA**

**Robert K. Johnston, PhD**, Marine Environmental Support Office - NW, US Navy, Bremerton, WA and Jill M. Brandenberger, Battelle Marine Science Laboratory, Pacific Northwest National Laboratory, Sequim, WA

Cooperative sampling between the Puget Sound Naval Shipyard Project ENVironmental INVESTment (ENVVEST) and Puget Sound Ambient Monitoring Program (PSAMP) was conducted for the 2003,

2005 and 2007 trawl sampling in Puget Sound. Samples of English sole, rock sole, sand sole, ratfish, surfperch, staghorn sculpin, graceful crab, and sea cucumber were collected and analyzed for residues of polychlorinated biphenyls (PCBs) and metals. Data from mussel watch stations monitored in the Puget Sound from 2002, 2004, and 2006 and from caged mussels deployed within Sinclair and Dyes Inlets from June – September 2005 (84 days) were evaluated to assess contaminant accumulation and effects on growth. The biota samples from 2007 also included the analysis of dogfish tissues collected from Admiralty Inlet and stable isotope ratios of  $d^{15}N$  and  $d^{13}C$  in all species. The tissue residue levels were compared to ecological and human health risk benchmarks. The whole body (wet weight) concentrations of PCBs, As, and Ag were highest in ratfish; dogfish had the highest levels of total Hg; crabs were elevated for Cd, Cu, Ni, and Zn; and sea cucumbers had the highest concentrations of Cr and Pb. In general, the urban bays (Elliott Bay, Commencement Bay, Duwamish, and Sinclair Inlet) had higher concentrations of contaminants than the other areas. The ratfish, dogfish, and staghorn sculpin had the highest  $d^{15}N$  ratios suggesting that these species occupied higher trophic levels. The wide range of stable isotope and contaminant concentrations within species among the various locations indicates different exposure gradients, feeding preferences, and trophic relationships for different areas of the Puget Sound.

## ***Plenary Session 2***

**Presider:** Frantisek Turecek University of Washington, Seattle, WA

**Session Overview:** Professor Neil Kelleher (University of Illinois, Urbana-Champaign) will describe a variety of world records and applications using the highest performance type of mass spectrometry (i.e., Fourier-Transform MS), with special emphasis on natural products research (biosynthesis and discovery) and MS-based proteomics.

### **138. Frontiers in Mass Spectrometry**

**Neil Kelleher**, Department of Chemistry, University of Illinois, Urbana, IL

Modern mass spectrometry can be loosely divided into the two realms of interrogating small molecule or large molecules. Incredibly complicated mixtures of either are now processed at high rates to capture the molecular details of everything from wine to crude oil to the entire protein complement of whole cell extracts. A variety of world records and applications using the highest performance type of mass spectrometry (i.e., Fourier-Transform MS) will be described, with special emphasis on natural products research (biosynthesis and discovery) and MS-based proteomics. For the latter, a revolutionary "Top Down" approach to protein and proteome analysis will be described. It combines new technologies for protein fractionation, with new advances in MS-hardware and tailored bioinformatic approaches. Top Down Mass Spectrometry holds promise for improved diagnostics and a deeper understanding of the signaling and regulatory "codes" eukaryotic cells use that are written in the language of post-translational modification.

## ***General Poster Session 2***

**Organizer:** Kerry W. Fowler, Ph.D. Past-Chair, Puget Sound Local Section, Seattle, WA

**Session Overview:** Tuesday Poster Session: Presenters for odd numbered posters should be by their posters during the first half of the session and even numbered posters during the second half.

### **139. Quantification of Oxycodone and Its Major Metabolites in Human Plasma by HPLC-MS/MS**

**Mary E. Leonard**, Vance Cooper and Lori D. Payne, BASi Northwest Laboratory, BASi, McMinnville, OR

Oxycodone is an opioid analgesic widely used to treat moderate to severe pain. It is metabolized on cytochrome P450, where it undergoes *N*-demethylation to noroxycodone and *O*-demethylation to oxymorphone. Oxymorphone, a minor metabolite, is itself a potent opioid, and noroxycodone, a major metabolite, may be a source of active metabolites that contribute to analgesia. Conversion via *N*-demethylation is 2-14 times that of *O*-demethylation; hence, the circulating concentration of oxymorphone following oral administration of oxycodone is low relative to the circulating concentrations of oxycodone and noroxycodone. Simultaneous quantitation of oxycodone and its metabolites is desirable to account for differences in individual metabolism of the drug. Since naltrexone is often pre-administered to prevent dependence, a highly selective assay is also required. BASi has developed a sensitive and robust method for accurate quantitation of oxycodone, oxymorphone and noroxycodone in human plasma using SPE cleanup and LC-MS/MS. The range of the assay is 0.1-100 ng/mL for oxycodone and oxymorphone and 0.5-100 ng/mL for noroxycodone. The method has been validated according to FDA guidance and has been used successfully to measure oxycodone and metabolite concentrations in clinical samples.

### **140. Virtual Screening Used to Find Potential Allosteric Inhibitors of Beta-Carbonic Anhydrase**

**Nathan Knapp**, Jeff D. Cronk and Stephen D. Warren, Department of Chemistry, Gonzaga University, Spokane, WA

Carbonic anhydrases catalyze the interconversion of carbon dioxide and bicarbonate ion, an essential process for growth and propagation of many organisms. A noncatalytic allosteric bicarbonate binding site was discovered in *Escherichia coli* carbonic anhydrase (ECCA) and is also found in *Haemophilus influenzae*  $\beta$ -carbonic anhydrase (HICA). The binding site in these proteins contains a ligand that consists of a bicarbonate molecule and two water molecules. Online databases of commercially available compounds were virtually screened using both shape-fitting and molecular docking programs from OpenEye software to find potential inhibitors to replace this ligand in ECCA and HICA. The top virtual screening results for each protein have been collected and can now be purchased for *in vitro* testing of inhibitory activity.

### **141. Iridium: A Curated Database of Protein-Ligand Complexes and Binding Data**

**Thanh D. Do**<sup>1</sup>, Gregory L. Warren<sup>2</sup> and Stephen D. Warren<sup>1</sup>, (1)Department of Chemistry, Gonzaga University, Spokane, WA, (2)OpenEye Scientific Software, Santa Fe, NM

Computational chemistry, like any other predictive science, uses models of physical phenomenon to make predictions. The Achilles heel of every model is the quality of the experimental data upon which it is built or validated. Unfortunately, in protein-ligand modeling too little time and attention has been paid to this important detail. We present here a protein-ligand structure database called Iridium, so called to reflect the scarcity of reliable information. The data in Iridium is from published sources, *e.g.* structures and electron density can be found in the RCSB, however enormous time and effort has been taken in annotation and curation. We found that 20% of the ligands in this data set contained errors, *i.e.* incorrect bond orders, element types and/or stereochemistry and missing functional groups. Binding data in terms of  $K_i$ ,  $K_d$  or  $IC_{50}$  of 86% of the total complexes in the database were also reported. These data were collected from primary and other relevant journal articles. The database will be made freely available with the hope it will reduce the prevalence of coprolite in modeling theory.

## 142. Synthesis of Microspheres

David Drohman, Caleb Fritz, Sarah Gabel, Janaye Lockett, Joseph Schuh and **Norman Nielsen**, Northwest Christian High School, Lacey, WA

Microspheres are used as carriers of drugs, biological and chemical sensors, and fluorescent dyes in fluorimetry. This lab has previously prepared polystyrene microspheres by batch-wise radical dispersion/precipitation polymerization. Since these polymerizations produced spheres with unpredictable diameters, it was of interest to develop a formulation model capable of predicting product sphere diameter. In the current work it was found that a 25 ml. reaction batch yielded microspheres with incrementally increasing diameters of 4-40 microns when the monomer concentration in the batch was correspondingly increased from 3-26 percent. Batch size was kept at 25 ml. and the ratios of cross linking monomer, stabilizing polymer, and radical initiator to styrene monomer were maintained. As monomer concentration increased, product sphere diameters increased exponentially. Lower diameter batches (4-21 microns) gave nearly mono-disperse sphere diameter product. Larger diameter batches gave increasingly poly-disperse mixtures of sphere sizes. Product isolation involved steps of suspending reaction mixtures in alcohol, allowing larger spheres to settle, and removing the supernatant liquid containing the still-suspended smaller spheres. The sphere diameter to monomer concentration data best fit the exponential equation:

$$D = 0.127 e^{-0.224C} + 5.56$$

where D is microsphere diameter and C is monomer concentration.

## 143. Novel Cascade Reactions and Pilot Scale Library Design for the NIH Compound Repository

Justin Dietrich, PhD<sup>1</sup>, **Christopher Hulme, Associate Professor**<sup>1</sup>, Gerry Maggiora<sup>1</sup>, Nathalie Meurice, PhD<sup>2</sup> and Joachim Petit<sup>2</sup>, (1)College of Pharmacy, University of Arizona, Tucson, AZ, (2)Chemogenomics and Drug Discovery, The Translational Genomics Research Institute (TGen), Scottsdale, AZ

**Abstract:** This poster details the discovery of several novel cascade reactions enabling the generation of arrays of pharmacologically relevant small molecules. As such, the synthetic routes are high in molecular complexity generating power and operationally friendly producing attractive compounds for inclusion in file enhancement strategies. Compound libraries and core chemotypes have been designed utilizing the 'Chemtech' portfolio of technologies and occupied scaffold space compared to existing nearest neighbors in the NIH molecular repository. Cascade sequences are launched from a common multi-component reaction precursor. Combined, this collaborative effort is navigating chemical space, delivering libraries and member molecules possessing 'high iterative efficiency potential' for expedited value chain progression. Bench to bedside case studies demonstrating the value of such approaches to file enhancement will be briefly discussed.

**Iterative Efficiency = f (Iterative Speed, accessible chemical diversity)**

## 144. Determination of Phenolic Content, Antioxidant Activity and Mineral Content of Popolo (*Solanum americanum*) Leaves

Leticia U. Colmenares, PhD and **Jon Lai**, Natural Science, UH-Windward Community College, Kaneohe, HI

This research studies the phenolic content (determined by GAE, Gallic Acid Equivalent using Folin-Ciocalteu reagent and HPLC), antioxidant activity (determined by TEAC, Trolox Equivalent Antioxidant Capacity using the ABTS Assay) and the mineral (Cu, Fe and Zn) content using AAS of

leaf extracts of Popolo (*Solanum americanum*), an indigenous Hawaiian plant. This plant has been known for its medicinal value by ancient Hawaiians and is used in other countries as medicine and vegetable. The measured antioxidant activity of 7.93 mg TEAC and 20.14 mg GAE per gram dry weight of popolo is higher than many medicinal herbs and common vegetables in the literature. Currently under-utilized, the plant's potential use as an agricultural, nutritional and herbal product is enhanced by these data.

#### **145. Synthesis of 1,3-Azaborines as Potential Inhibitors of HIV-1 Protease**

**Jesse Lee Nye**, Pei-Mien Chen, Elizabeth Nicolaeva, Tajinder Heer, Amanda Blackmore and Levente Fabry-Asztalos, PhD, Chemistry, Central Washington University, Ellensburg, WA

HIV/AIDS has affected about 40 million people. One type of drug that is used to treat HIV/AIDS is a protease inhibitor. HIV-1 protease is one enzyme responsible for the propagation of mature viral particles. By inhibiting HIV-1 protease it is possible to slow the replication of the virus and delay the onset of AIDS. Often, HIV-1 protease becomes resistant to inhibitors; therefore, new drugs are needed. Here, we propose the synthesis of novel protease inhibitors using known and new synthetic methodologies. The proposed structures are borinic acids containing a heterocyclic ring with a nitrogen beta to the boron. Similar non-heterocyclic compounds have shown good inhibitory values and we hope that these inhibitors will possess better inhibitory properties, have increased bioavailability, have less toxicity, and potentially be more stable than their non-heterocyclic counterparts and the protease inhibitors currently in use. Important intermediates have been synthesized and are being used in the final reactions of the proposed synthetic scheme. We hope that these compounds will become lead compounds for further drug discovery for HIV/AIDS.

#### **146. Taxanes: From Yew Tree Bark and Needles and Soil!**

**Alex Samuels**, Department of Chemistry, University of Portland, Portland, OR and Angela Hoffman, Chemistry, University of Portland, Portland, OR

Paclitaxel (Taxol®) is a cytotoxic compound that was originally found in the bark of the Pacific yew tree, *Taxus brevifolia*. Today paclitaxel is an important chemotherapy agent used to treat lung, ovarian, breast, and other cancers. The most common technique for obtaining the drug is to extract the paclitaxel from *Taxus* species plant material or to extract taxanes such as baccatin III from the plant and produce paclitaxel by semisynthesis. We have already shown that paclitaxel can be extracted from soil in which yew trees have grown. Our goal was to increase the yield of paclitaxel per tree, rooting medium and water runoff from trees grown in a green house. These studies have shown promising results. By utilizing two simple extractions, it is possible to get more paclitaxel out of every yew tree. Support was provided by The University of Portland and NSF grant no. 0521648.

#### **147. Natural Products From Forest Resources for Use as Arthropod and Fungal Biocides**

**Joe Karchesy**<sup>1</sup>, Marc C. Dolan<sup>2</sup>, Daniel K. Manter<sup>3</sup>, Nicholas A. Panella<sup>4</sup>, Yvette Karchesy<sup>1</sup>, Gabrielle Dietrich<sup>4</sup>, Rick G. Kelsey<sup>5</sup>, Javier Peralta-Cruz<sup>6</sup> and Joseph Piesman<sup>2</sup>, (1)College of Forestry, Oregon State University, Corvallis, OR, (2)Division of Vector-Borne Infectious Diseases, Centers for Disease Control and Prevention, Fort Collins, CO, (3)USDA Agricultural Research Service, Ft. Collins, CO, (4)Arboviral Diseases Branch, Centers for Disease Control and Prevention, Fort Collins, CO, (5)PNW Research Station, USDA Forest Service, Corvallis, OR, (6)Organic Chemistry, Escuela Nacional de Ciencias Biologicas del Instituto Politecnico Nacional, Mexico City, Mexico

Natural products from Pacific Northwest forest resources can offer alternatives to the use of synthetic pesticides for control of arthropods of public health concern and forest microbial pathogens. Tree heartwoods whose extracts showed high toxicity (LC<sub>50</sub> <100 ppm) in preliminary brine shrimp bioassays, also were found to be good sources for biocide and repellent compounds. Comparisons were made for the activities of the isolated compounds, derivatives, and extracts from

yellow, incense, Port-Orford, and western red cedars, and western juniper against mosquitoes (*Aedes aegypti*), ticks (*Ixodes scapularis*), fleas (*Xenopsylla cheopis*) and the microbe responsible for Sudden Oak Death (*Phytophthora ramorum*).

For example, laboratory bioassays show that hinokitiol from western redcedar, thymoquinone from incense-cedar, and nootkatin from yellow-cedar all exhibit strong antimicrobial activity toward *P. ramorum* (EC<sub>50</sub> = 2.0 to 10.0 ppm). The mode of action for nootkatin is disruption of the membranes surrounding zoospores and sporangia.

Biocidal assays against arthropods showed that carvacrol, nootkatone, and valencene 13-ol were the most effective. Repellency against ticks showed that nootkatone and valencene-13-ol had repellent concentration (RC<sub>50</sub>) values of 0.0458 and 0.0712% (wt:vol) respectively compared to DEET (RC<sub>50</sub> = 0.0728%).

#### **148. REVERSED CHLOROQUINE COMPOUNDS THAT OVERCOME *P. Falciparum* RESISTANCE to QUINOLINE-BASED DRUGS**

**Bornface Gunsaru**<sup>1</sup>, David. H. Peyton<sup>1</sup>, Cheryl Hodson<sup>1</sup>, Katherine Liebman<sup>1</sup>, Steven Burgess<sup>2</sup>, Westin Morrill<sup>2</sup>, Shawheen Shomloo<sup>2</sup> and Jane Xu Kelly<sup>1</sup>, (1)Department of Chemistry, Portland State University, Portland, OR, (2)DesignMedix, Inc, Portland

Malaria infects about 350 million people each year, of which nearly one million people die, many of them in Africa south of the Sahara. Chloroquine (CQ) was the drug of choice to treat malaria for nearly half a century, but widespread resistance has severely reduced its effectiveness. Reversal agents (chemosensitizers) can reinstate the activity of chloroquine, but high dosages of the reversal agent (RA) in a cocktail raise questions about the clinical viability of this approach. We hypothesized that covalently attaching a RA moiety to a chloroquine-like moiety would give a "reversed chloroquine" (RCQ) able to overcome the effects of resistance with a much reduced RA dose, as the RA is now part of the drug. A library of compounds was thus generated based on this design. From this library, RCQs were identified that exhibit lower IC<sub>50</sub> values than CQ against even D6, a "chloroquine-sensitive" strain of *P. falciparum* malaria, and reduced the IC<sub>50</sub> against various "chloroquine-resistant" strains typically by 2- to 3- orders-of-magnitude relative to CQ. Thus, the RCQ-approach may be viable in the struggle against malaria, as well as open a route toward new therapies for other diseases that have drug resistance mechanisms similar to malaria.

#### **149. Antibacterial Potential and GC-MS Studies of Select Medicinal Plants of Mojave Desert**

**Kaveh Zarrabi**<sup>1</sup>, Noppawen Nitrosesatien<sup>1</sup>, Jung Jae Koh<sup>1</sup>, Suheir Naserddin<sup>1</sup>, Eva Abanyan<sup>1</sup>, Maxym Myroshnychenko<sup>2</sup>, James Estevez<sup>2</sup>, Deborah Harber<sup>2</sup> and Heidi Porter<sup>2</sup>, (1)Physical Sciences, College of Southern Nevada, Las Vegas, NV, (2)Biological Sciences, College of Southern Nevada, Las Vegas, NV

Six medicinal plants collected from Mojave Desert, *Krameria erecta* (Little leaf Rhatany), *Eriodictyon cliforicum* (Yerba Santa), *Gutierrezia sarothrae* (Snakeweed), *Oenothera biennis* (Evening Primrose), *Encelia farinosa* (Brittle Bush), and *Eriodictyon glutinosum* (Yerba Santa). The plants were processed and extracted with water-methanol, methylene chloride, and hexane. 18 plant extracts were tested for their antibacterial activity against *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Bacillus subtilis*, *Escherichia coli*, *Klebsiella pneumoniae*, *Enterobacter aerogenes*. Water-methanol extracts of *Oenothera Biennis* and *Krameria erecta* have shown significant antibacterial activities. The minimum inhibitory concentration (MIC) of these two plants was 31.25 and 62.5 µg/ml respectively. GC-MS analyses of the plant extracts exhibiting antibacterial activities are presented.

## 150. The Synthesis of CDCA (Chenodeoxycholic acid) Derivates and Their Transition Complexes

**Murat Turkyilmaz** and Fatma Genc, Department of Chemistry, Trakya University, Edirne, Turkey

Bile acids have played important role in several area of chemistry in recent years. There is a vast amount of potential pharmacological applications of bile acids and their derivatives which includes analgesics, radiopharmaceuticals and antibiotics. These compounds are useful for development of supramolecular and nanomolecular systems.

Between the two hydroxyl groups, the most reactive one is the hydroxyl at the C-3 position. We prepared the beta mesylate from methyl cholate using triphenylphosphine and diisopropyl azodicarboxylate (DIAD). Sodium azide attacks the mesylate by an SN2 reaction to afford azide ester, which is reduced by triphenylphosphine in aqueous THF to give our ligand. Therefore we converted C-3 hydroxyl group of CDCA (chenodeoxycholic acid) to amino group and then we binded some transition metals to amino and hydroxyl groups. All compounds was confirmed.

## 151. Esterification of Lithocholic Acid with Some Analgesics

**H.R. Ferhat Karabulut**<sup>1</sup>, Murat Donmez<sup>1</sup> and Hasan Ozyildirim<sup>2</sup>, (1)Department of Chemistry, Trakya University, Edirne, Turkey, (2)Trakya University, Edirne, Turkey

Bile acids and their derivatives have been used in the treatment of bile acid deficiency which is one of the major predisposing factors of dissolution of cholesterol gallstones. Also they can be used as carriers for liver-specific drugs. In literature the medicinal applications of bile acids, their conjugates and non-opiate analgesic complexes have been discussed. In our study, we planned to get some analgesic derivatives with bile acid. We used lithocholic acid as a bile acid and first of all we converted lithocholic acid to methyl ester and then it was reacted with naproxen, diclofenac and flurobiprofen using DCC (dicyclohexylcarbodiimide) or Yamaguchi methods. We had better results by Yamaguchi method than DCC method. These compounds were confirmed by IR spectrum, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum.

## 152. Recent Work Toward a Total Synthesis of the GABA Antagonist, (-)-Anisatin

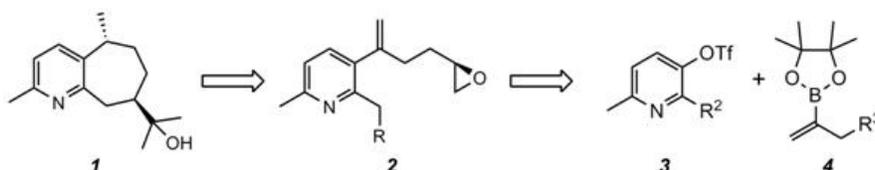
**Jeffrey A. Charonnat**, Nobuko Nishimura, Yvonne Nguyen and Donna Manglona, Department of Chemistry and Biochemistry, CSU Northridge, Northridge, CA

(-)-Anisatin is an extremely potent, non-competitive GABA antagonist that acts irreversibly at the presynapse but reversibly at the postsynapse. This poster presents recent work toward a total synthesis of (-)-anisatin.

## 153. Recent Progress Toward the Synthesis of Cananodine

**Toby J. Ligon** and James R. Vyvyan, Department of Chemistry, Western Washington University, Bellingham, WA

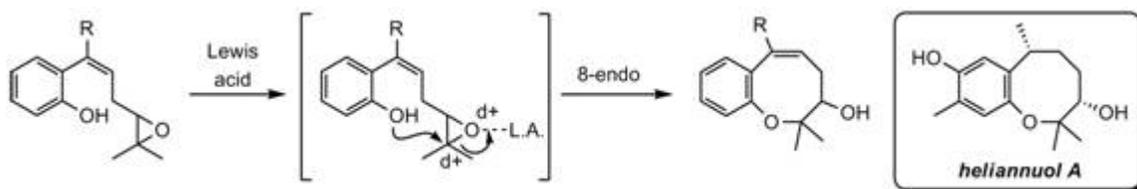
A synthetic approach to the synthesis of cananodine (**1**), a guaipyridine alkaloid isolated from the fruits of *Cananga odorata*, is described. Cananodine (**1**) is a valuable synthetic target because it exhibits significant activity against two human hepatocellular carcinoma cell lines. Key steps in the synthetic route to **1** include a Suzuki-Miyaura-type cross coupling of pyridine triflate (**3**) with alkenylboronate (**4**), and an intramolecular epoxide alkylation of **2** to form the 7-membered ring of the natural product. Model studies and current progress toward the synthesis of **1** will be presented.



## 154. Progress Toward the Synthesis of Heliannuol A Using 8-Endo Epoxide Cyclizations

**Katie R. Tallman**, Erik W. Werner and James R. Vyvyan, Department of Chemistry, Western Washington University, Bellingham, WA

Heliannuol A is part of family of allelochemicals that have been isolated in small quantities from the sunflower, *Helianthus annuus*, and has been shown to selectively inhibit the germination and growth of other plants. A heliannuol A analogue was synthesized via an 8-endo phenol epoxide strategy utilizing a conformational constraint and Lewis acid catalysis. The synthesis of the epoxide and cyclization results will be presented.



## 155. Microwave-Assisted Organic Synthesis of 2,5-Disubstitutedbenzofuran-3-Carboxylic Acids

**Jared Rigoli**, Joe Rigoli and Aaron Mills, Assistant Professor, Department of Chemistry, University of Idaho, Moscow, ID

Microwave-assisted organic synthesis (MAOS) has proven its utility in the synthesis of heterocycles. Previously, 2,5-disubstitutedbenzofuran-3-carboxylic acids have shown to have antiinflammatory, antiviral, and muscle relaxant properties. We report a new method for the rapid and efficient synthesis of 2,5-disubstitutedbenzofurans by the reaction of  $\beta$ -ketoesters, *p*-quinone, and a metal halide catalyst under microwave irradiation. Previously the synthesis of 2,5-disubstitutedbenzofuran-3-carboxylic acids was plagued by low yields (~20-30%) and long reaction times (1-2 days). Using microwave irradiation, we studied the effect of varying solvent, metal catalyst, reaction times, and reaction temperature on benzofuran yields. Through the methodical optimization of the benzofuran cyclization reaction we obtained the products in > 70% yield and reduced the reaction time to 45 minutes. All the products were characterized by  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR and GC/MS.

## 156. Synthesis of 2,3-Dibenzyl-1,1-Difluoroglycerol

**Elizabeth A. Goossen**, Daniel Tt. Yee, Timothy Rhoads, Kylie Vadnais, Austin Wisecup and Stephen D. Warren, Department of Chemistry, Gonzaga University, Spokane, WA

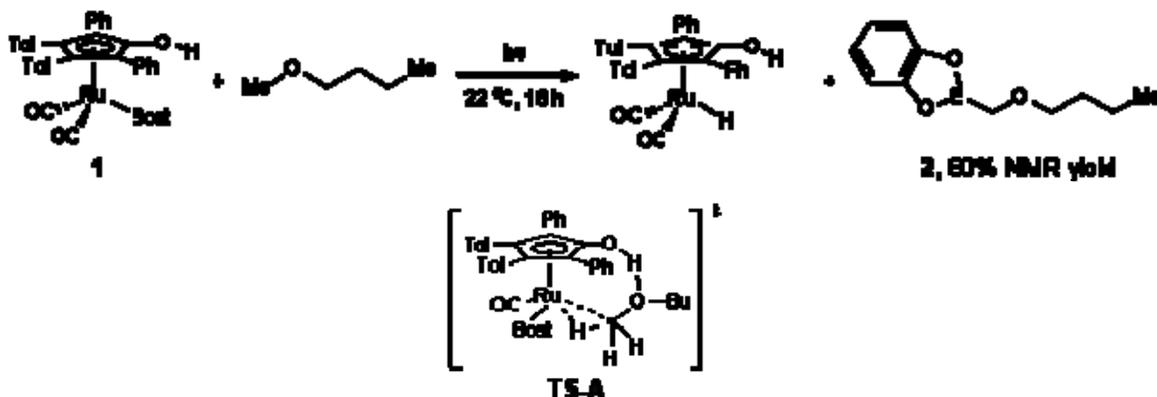
Metabolic pathways frequently include 3-carbon unit intermediates. Fluorinated 3-carbon unit molecules can function as mimetics of metabolic intermediates and as biological probes of those pathways. D-mannitol is an inexpensive starting material that can serve as a common synthetic precursor for a variety of 3-carbon molecules. We optimized methods for the complete protection of D-mannitol's hydroxy groups followed by selective deprotection of the terminal protecting groups. The 3,4-monoisopropylidene-D-mannitol product was selectively reprotected and cleaved to produce a variety of 3-carbon unit precursors. The 3-carbon units were fluorinated using the nucleophilic fluorination agent deoxofluor. These fluorinated mimetics could potentially be used as probes in biological systems.

## 157. Boron-Substituted Analogs of the Shvo Hydrogenation Catalyst: Applications in Directed C-H Borylation

**Liza Koren-Selfridge**, Joel A. Hanson and Timothy B. Clark, Department of Chemistry, Western Washington University, Bellingham, WA

Directed C-H functionalization reactions have received considerable attention recently due to the desire to incorporate functional groups into inexpensive unfunctionalized organic substrates. One such example of a C-H functionalization reaction uses metal boryl complexes to convert C-H bonds into C-B bonds. The incorporation of a boron functional group into organic substrates through C-H functionalization reactions is ideal due to the ability to convert C-B bonds into C-C, C-O, or C-N bonds. Our work has focused on the use of boron-substituted analogues of the Shvo hydrogenation catalyst. The desired ruthenium boryl complex **1** was expected to result in directed C-H functionalization through hydrogen bonding of the hydroxy group with the substrate.

Synthesis of complex **1** involved the activation of bis(catecholato)diboron reagent in the presence of 4-methoxyphenol to generate the desired complex. This complex was then combined with butyl methyl ether under photolysis conditions, resulting in C-H functionalization product **2**. Known complexes without the directing hydroxy group are also being synthesized in order to compare the selectivity of these complexes with complex **1**. These results will verify that our product results from directed C-H functionalization (via the transition state **TS-A**) rather than resulting from the preferred reactivity of the methoxy methyl group.



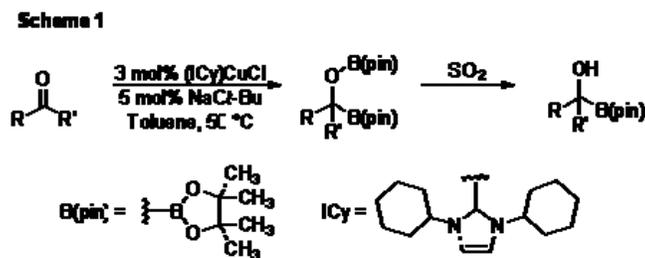
## 158. Copper-Catalyzed Diboration of Ketones: Facile Synthesis of Tertiary Alpha-Hydroxy Boronate Esters

**Melissa L. McIntosh**, Cameron M. Moore and Timothy B. Clark, Department of Chemistry, Western Washington University, Bellingham, WA

The synthetic versatility of carbon-boron bonds makes organoboronate esters and acids valuable intermediates in organic synthesis. Alpha-heteroatom-substituted boronate esters have emerged over the past two decades as synthetically valuable intermediates in asymmetric homologation reactions. The synthesis of complex and highly functionalized versions of these boronate esters has been limited due to the required reaction conditions. Several recent reports have begun to highlight the ability to generate alpha-heteroatom-substituted boronate esters by the diboration of polarized double bonds (C=X).

Our group has explored the diboration of various ketones using the (ICy)CuOt-Bu catalyst developed by Sadighi and co-workers in the diboration of aldehydes. We found that (ICy)CuOt-Bu could be generated in situ using 3 mol % (ICy)CuCl and 5 mol% NaOt-Bu (Scheme 1). This catalyst system was shown to cleanly afford the diboration of various ketones in toluene at 50 °C over 2–22 hours. Products derived from aryl ketones are prone to decomposition during isolation via silica gel chromatography. Products derived from alkyl ketones result in hydrolysis of the O-B bond providing

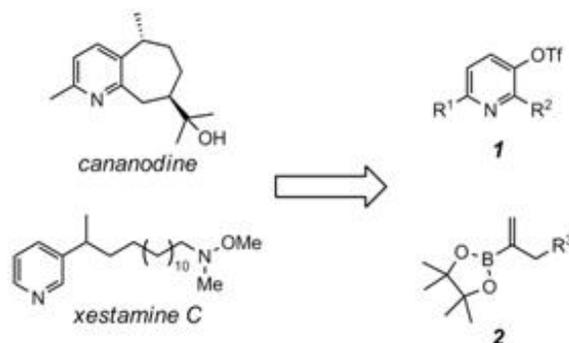
the desired alcohol. The diboration of alpha, beta-unsaturated ketones results in the 1,4-addition products, which can be utilized in an Aldol reaction, providing three contiguous stereocenters in high selectivity.



## 159. Suzuki-Miyaura Cross Coupling of Pyridyl 3-Triflates with Alkenyl Boronates

**Kelsey K. Motanic**, James R. Vyvyan, Toby J. Ligon and Hayley S. Wall, Department of Chemistry, Western Washington University, Bellingham, WA

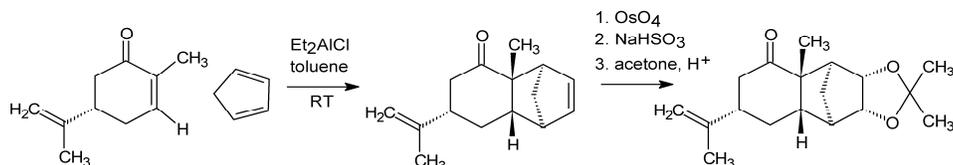
Suzuki-Miyaura coupling of pyridyl 3-triflates (**1**) with alkenylboronates (**2**) proceeds in good yield. Application of this reaction to the synthesis of the natural product skeletons of cananodine and xestamine C will be presented. Cananodine is a guaipyridine natural product derived from the fruits of the evergreen tree *Cananga odorata*. Xestamine C is a novel pyridine lipid isolated from the sponge *Xestospongia wiedenmayeri*.



## 160. Syn-Exo Selective Lewis Acid Catalyzed Diels-Alder Reaction of Carvone with Cyclopentadiene

**Carey R. Fristoe** and John W. Keller, Department of Chemistry and Biochemistry, University of Alaska Fairbanks, Fairbanks, AK

Cyclic enones commonly undergo endo Diels-Alder addition to cyclic dienes, with or without a Lewis acid catalyst. We hypothesized that in case of carvone, the steric bulk of the 5-isopropenyl group would force exo addition of the dienophile, and reaction anti to the 5-substituent. Carvone reacted with cyclopentadiene in toluene solvent and 20 mol% diethylaluminum chloride catalyst. After 48 h at RT, aqueous workup, extraction with ethyl acetate, and flash chromatography, a moderate yield of the syn-exo product was obtained. Oxidation with osmium tetroxide gave a cis diol that was converted to the acetonide. 1D and 2D NMR spectra were consistent with proposed structures. Computational studies showed that the carvone ring adopts a half-chair conformation with the isopropenyl group occupying the equatorial position; in this conformation the diene prefers to approach anti to the puckered C rather than anti to the substituent.



## 161. Synthesis of a Series of Amphiphilic 2,3-Di-O-Sulfoalkyl-6-O-Alkyl Cyclodextrins for Use as Mass Transfer Promoters in Biphasic Catalytic Systems

**Michael Jaramillo**, Daniel L. Kirschner and Thomas K. Green, Department of Chemistry and Biochemistry, University of Alaska, Fairbanks, AK

Modern industrial reactions use large quantities of harmful solvents and reagents that have raised much concern in recent years. As a result, the use of biphasic catalytic processes has become of great interest because they use reduced amounts of organic solvents and harmful reagents. In these systems, organic reactants are converted to products using a water soluble catalyst. However, the interaction of the reactant and the catalyst is often limited by the water solubility of the reactant. We recently synthesized a series of amphiphilic cyclodextrins (CD) which were applied to the hydroformylation process as mass transfer promoters. The 2,3-Di-O-Alkyl-6-O-Sulfoalkyl CD's proved to be effective in the conversion of 1-decene to undecanal. These cyclodextrins have the less open, primary face of the CD towards the aqueous phase. We hypothesize that having the more open, secondary face orientated towards the aqueous phase will result in better interaction between the alkene and the water soluble catalyst, and will increase the rate of conversion. Thus, a synthetic route has been proposed for a new series of 2,3-Di-O-Sulfoalkyl-6-O-Alkyl CD's. Synthesis and characterization of these molecules is in progress. Their application in the hydroformylation process will be compared to those previously studied.

## 162. Sterically Hindered Diketones

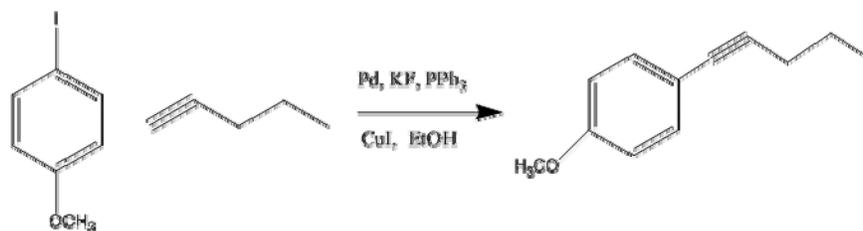
**Kaitlyn Miller**<sup>1</sup>, Richard E. Sykora<sup>2</sup> and Greg T. Spyridis<sup>1</sup>, (1)Department of Chemistry and Biochemistry, Seattle Pacific University, Seattle, WA, (2)Department of Chemistry, University of South Alabama, Mobile, AL

Acetylacetone (2,4-pentanedione) and other  $\beta$ -diketones are molecules in dynamic equilibrium with both tautomers present in measurable concentration at equilibrium. The keto-enol ratio in these systems is modulated by solvent polarity, hydrogen bonding capacity and the concentration of dissolved salts. This ratio is also exquisitely sensitive to the size of the substituent attached to the carbon between the carbonyls, with the keto concentration increasing as the steric bulk rises. We wish to report our progress in preparing  $\beta$ -diketones possessing a trityl,  $(C_6H_5)_2HC$ , 9-fluorenyl or 9-phenylfluorenyl group on the carbon between the carbonyls for X-ray analysis in an effort to observe the effect large groups have on the carbon-carbon bond linking the diketo moiety and the ligand.

## 163. Microwave Accelerated Sonogashira Reactions

**Heather Brogan, B.S.** and Gary M Lampman, Department of Chemistry, Western Washington University, Bellingham, WA

The reaction of various iodosubstituted aromatic compounds with 1-pentyne was performed using microwave technology. Traditionally, this reaction is carried out with refluxing. Iodosubstituted aromatic compounds with electron releasing groups attached to the aromatic ring are slow to react under reflux. Implementation of microwave technology gave the desired products in 30 minutes for starting compounds with both electron withdrawing and electron releasing groups attached to the ring.



#### **164. Comparison of Solvent and Terminal Diene Substitution On Relative Reaction Rates of the Diels-Alder Reaction with N-Phenylmaleimide**

**Adrienne Hollister**, Patrick Kunkel, Sam Whedon and Neal Yakelis, Pacific Lutheran University, Tacoma, WA

The effects of solvent and diene functional groups on the relative reaction rates of the Diels-Alder reaction of N-phenylmaleimide with *trans,trans*-2,4-hexadienal and *trans,trans*-2,4-hexadien-1-ol were examined. Of the solvents tested, water was determined to be the most effective due to a hydrophobic effect. *trans,trans*-2,4-hexadienal reacted at a considerably slower rate than *trans,trans*-2,4-hexadien-1-ol, which was explained by resonance and molecular orbital theory.

#### **165. Chemical Vapour Deposition of Titanium Silicide : Equilibrium Ti-Si-H-Cl-Ar System**

**Y. K. Rao**, Department of Materials Science and Engineering, University of Washington, Seattle, WA

The chemical vapour deposition of titanium silicide from feed-gas-mixtures composed of halides and silane is investigated by the equilibrium model in the temperature range of 700K to 1100K at a total pressure of 101.325 kPa (1.0 atm): at constant atom-ratios H/Cl and Ar/H, search is made for the phase-boundary limits using an iterative equilibrium constant method in combination with De Donder's extent of reaction formalism. The feed-gas composition is characterized by the parameter  $r = [\text{Ti}/(\text{Ti} + \text{Si})]$ ; large  $r$  signifies a titanium-rich mixture and small  $r$  corresponds to a silicon-rich feed. The present work is concerned with the establishment of  $r$ -limits which ensure that pure silicide is deposited from the vapor-phase uncontaminated by the silicon-phase. The respective influences of temperature and H/Cl atom-ratios on the phase-boundaries are determined. The results are of value in thin-film deposition (for VLSI electronic circuit manufacturing) and in silicide-coated structural materials for high-temperature applications.

#### **166. Low-Temperature Electronic Absorption and Luminescence Spectroscopy of Magnesium Tetrabenzoporphyrin in Polystyrene Matrices**

**Kelly A. Carman**, Jamie C. Cooper and John W. Kenney III, Chemical Physics Laboratory, Concordia University, Irvine, CA

Magnesium tetrabenzoporphyrin (MgTBP), has been studied extensively by many spectroscopic methods in a wide variety of environments (solvents, solvent systems, and rigid opaque and transparent matrices) over a wide range of temperatures (room temperature to liquid helium temperature). In this investigation, MgTBP is dispersed in thin films of polystyrene (PS) to facilitate spectroscopic measurements at cryogenic temperatures. The resulting transparent PS matrices containing MgTBP maintain structural and optical integrity when cycled repeatedly between room temperature and cryogenic temperatures. Moreover, molecules of MgTBP to which pyridine is axially coordinated can be imbedded in PS matrices. Comparative spectroscopic investigations of MgTBP dispersed in liquid solvents and in PS matrices clearly show that the PS matrix environment minimally perturbs the electronic states of MgTBP. This contrasts markedly with polymethylmethacrylate (PMM) matrices of MgTBP in which dramatic spectral perturbations are observed. Low-temperature electronic absorption and luminescence spectroscopy of MgTBP/PS systems will be reported.

#### **167. Synthesis and Characterization of p-Type ZnO From Single Source Precursors**

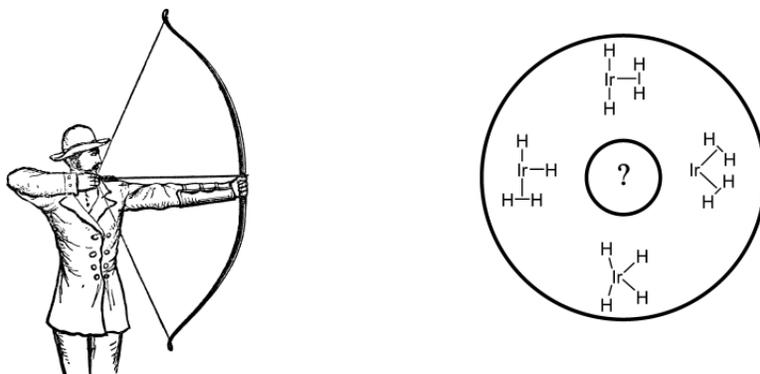
Jesse S. Hyslop<sup>1</sup>, Jennifer L. Young<sup>1</sup>, **Jerry D. Harris**<sup>1</sup>, Brian J. Frost<sup>2</sup>, Alex Punnoose<sup>3</sup> and Seth M. Hubbard<sup>4</sup>, (1)Department of Chemistry, Northwest Nazarene University, Nampa, ID, (2)Department of Chemistry, University of Nevada, Reno, Reno, NV, (3)Department of Physics, Boise State University, Boise, ID, (4)Department of Physics, Rochester Institute of Technology, Rochester, NY

Many new zinc(acetate)<sub>2</sub>(amine)<sub>y</sub> compounds have been synthesized and characterized. Zn(acetate)<sub>2</sub>(ethylenediamine) has been characterized by X-ray crystallography, and the other compounds were characterized by NMR spectroscopy. Many compounds were also characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine their thermal stability and to gage their potential usefulness as precursors to nitrogen-doped zinc oxide films prepared by spray pyrolysis and nitrogen-doped zinc oxide powders by a sol-gel synthesis route. Both films and powders of zinc oxide have been characterized by X-ray diffraction. The electronic properties of the films have been probed by Hall measurements. Detailed results of the project will be presented. The work was supported by NASA Idaho Space Grant Consortium, NASA Idaho EPSCoR, NASA John H. Glenn Research Center, the M.J. Murdock Charitable Trust, and the National Science Foundation, NSF DMR-0840265.

### 168. Where Are the H Atoms? Experimental and Computational Studies of the Structure of An Iridium Polyhydride

**Travis J. Hebden**<sup>1</sup>, Paula M. B. Piccoli<sup>2</sup>, Thomas F. Koetzle<sup>2</sup>, Arthur J. Schultz<sup>2</sup>, Karsten Krogh-Jespersen<sup>3</sup>, Alan S. Goldman<sup>3</sup>, Thomas J. Emge<sup>3</sup>, Karen I. Goldberg<sup>1</sup> and D. Michael Heinekey<sup>1</sup>, (1)Department of Chemistry, University of Washington, Seattle, WA, (2)Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL, (3)Department of Chemistry, Rutgers University, Piscataway, NJ

The complex (POCOP)IrH<sub>2</sub> (POCOP =  $\eta^3$ -(1,3-OP<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) has been shown to be an efficient catalyst for H<sub>2</sub> release from ammonia borane (AB). During the course of AB dehydrogenation, the predominant Ir-containing species present in solution is (POCOP)IrH<sub>4</sub>. The structure of this complex has been investigated using NMR techniques and IR spectroscopy. We have also studied the structure of the closely related complex (PCP)IrH<sub>4</sub> (PCP =  $\eta^3$ -(1,3-CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in solution. The resulting solution data reveal a different arrangement of H atoms around the Ir than a solid-state structure obtained by neutron diffraction analysis.



### 169. Metal-Organic Frameworks Supported by Mixed Carboxylic and Nitrogenous Ligands

**Xiaotai Wang**, Department of Chemistry, University of Colorado Denver, Denver, CO

Three-component reactions involving d-block ions and carboxylic and nitrogenous ligands under hydrothermal conditions generate three novel metal-organic frameworks (MOFs) formulated empirically as Ni<sub>2</sub>(PDA)<sub>2</sub>(BPP)(H<sub>2</sub>O) · 2.5H<sub>2</sub>O (**1**), Ni(PDA)(BPE) (**2**), and Cd(PDA)(BPY)·H<sub>2</sub>O (**3**), where PDA = 1,4-phenylenediacetate, BPP = 1,3-bis(4-pyridyl)propane, BPE = 1,2-bis(4-pyridyl)ethane, and BPY = 4,4-bipyridine. The synthesis, characterization, and properties of these MOFs will be discussed.

## **170. Plasma Enhanced Chemical Vapor Deposition of Germanium Sulfide Thin Films**

**Patrick J. Whitham**, Rene Rodriguez and Lisa Lau, Dept. of Chemistry, Idaho State University, Pocatello, ID

Studies on the properties of chalcogenide materials have indicated the possibility of using germanium sulfide materials in phase memory applications. Phase change memory devices store information by altering resistances within the phase material through changes in microstructure. The deposition of  $\text{Ge}_x\text{Se}_y$  by plasma enhanced chemical vapor deposition (PECVD) has been reported in the literature.

Our previous work focused on controlling the PECVD conditions to deposit thin films of  $\text{Ge}_x\text{S}_y$  with a desired stoichiometry from germanium tetrachloride and hydrogen sulfide, a fairly poisonous gas.

Films deposited in this way were of good quality and were largely  $\text{GeS}_2$ . Extension of this method to the formation of  $\text{Ge}_x\text{Se}_y$  involves the use of hydrogen selenide, which is much more toxic than hydrogen sulfide.

We are currently exploring the use of alkylsulfides and alkylselenides such as dimethyl or diethylsulfide and dimethyl or diethylselenide as novel, less toxic replacements for hydrogen sulfide and hydrogen selenide in the formation of germanium sulfide thin films. The relative mass flow rates, reactor pressure, substrate temperature and deposition power conditions may all affect germanium sulfide and germanium selenide deposition stoichiometry, and the effects of each of these parameters are being explored. Results of the morphology, spectroscopy, and electronic properties of thin films deposited using these alkyl substitutes will be reported.

## **171. Determination of Synthetically Made $\text{CuInS}_2$ Nanoparticle Passivating Groups Using Various Polar Solvents**

**Cyril Bajracharya**, Lisa Lau, Chivin Sun and Rene Rodriguez, Department of Chemistry, Idaho State University, Pocatello, ID

When synthesizing  $\text{CuInS}_2$  nanoparticles, species related to the starting materials may physisorb or chemisorb onto the product. One nanoparticle characteristic that was confirmed with CHNS combustion analysis showed that as the size of the nanoparticle decreases, more starting material-related species are likely to be attached to nanocrystalline structures of the nanoparticle. Some of these starting material species are useful and necessary through their action as passivating groups. The passivating groups can be solvents or thiol additives used to help make the  $\text{CuInS}_2$  nanoparticles. Other physisorbed groups are related to solvent or Cu or In salts present as reactants. Although the passivating groups of the nanoparticles are necessary, they likely also lead to a decrease in the usefulness of these particles as semiconductor materials in electronic circuits like solar cells. Too much passivation per  $\text{CuInS}_2$  formula unit likely corresponds to a decrease in cell device efficiency.

Attempts to eliminate excess starting material-related species in the purification of nanoparticle samples of  $\text{CuInS}_2$  that were produced from a single source precursor will be discussed. The first step is modified washing of the nanoparticles, with solvents such as benzene and methanol. This concept is similar to column separations which use solvents of different polarities. Species physisorbed to the passivated nanoparticles are separated through this process and may be identified through spectroscopic and spectrometric techniques.

Other starting material-related species that are chemisorbed to the surface are much more difficult to identify. Synthetic cleavage has been attempted to remove and characterize these chemisorbed species. Results of attempts to quantify both the physisorbed and chemisorbed species attached to the nanoparticles using chemical methods and instrumental methods including FT-IR and NMR will be presented.

## 172. The Synthesis of 1-Phospha-[2.2.2]-Bicyclooctane, and Its Application in Metal Complexes

**Michael A. Rak** and D. Michael Heinekey, Department of Chemistry, University of Washington, Seattle, WA



Phosphines are very useful ligands for transition metal catalysis. They are sterically and electronically tunable and generally unreactive. In some low-valent metal complexes, activation of ligand C-H bonds is an undesirable side reaction. The title compound has been synthesized in a short and direct route from inexpensive starting materials. In this phosphine, the alkyl substituents are bound in a rigid framework to prevent C-H bond activation. The synthesis of this versatile ligand will be presented and its properties explored with an emphasis on applications in coordination chemistry.

## 173. Incorporation of Quantum Dots in Polymer Light-Emitting Electrochemical Cells

**Amanda J. Norell Bader**<sup>1</sup>, Shawn Divitt<sup>2</sup> and Janelle M. Leger<sup>2</sup>, (1)Department of Chemistry, Western Washington University, Bellingham, WA, (2)Department of Physics, Western Washington University, Bellingham, WA

Semiconducting polymers have enormous potential to expand the applications of electronic and optoelectronic technologies. Current inorganic semiconductors are expensive and limited, whereas polymer semiconductors are solution-processable and can be deposited *via* screen printing or ink-jet printing, allowing inexpensive fabrication at low temperatures over large areas and on flexible substrates. Polymer optoelectronic devices, such as LEDs and solar cells, have been successful, but suffer from poor performance and stability. To circumvent this difficulty, a novel hybrid structure based on a polymer light-emitting electrochemical cell (LEC) incorporating colloidal quantum dots (semiconductor nanocrystals) is being pursued. Devices with quantum dots have been inefficient due to an insulating surface ligand layer, but the LEC structure limits the active layer thickness, reducing the charge tunneling barrier. Quantum dots were synthesized and included in polymer LEC structure with promising results. Current-voltage measurements and emission spectra of these devices were collected, showing better color purity in devices which incorporate quantum dots. This method has the potential for low cost and efficient hybrid LEDs and solar cells.

## 174. A Green Process for Perchlorate Removal From Wastewater Based On Nanocomposite Carbon Nanotubes and Polypyrrole

**Xinhuang Kang**, Jun Wang, Hong Wu, Jagan Bontha, Michael A. Lilga and Yuehe Lin, Pacific northwest national laboratory, Richland, WA

**Abstract:** Perchlorate, which is used as an oxidizer in jet and rocket fuels, missiles, flares and explosives, is an extensive contaminant in surface water and groundwater in many countries. It is well known that perchlorate can lead to concerns regarding iodine deficiency and thereby affect the production of thyroid hormones. In this study, a green and highly effective process for perchlorate removal based on electrically switched ion exchange (ESIX) was developed with electrodeposition of polypyrrole (PPy) on the high surface area of carbon nanotubes (CNTs). The supporting material is carbon fleece (CF), which is porous with high surface area. The anion-exchange behavior, ion-exchange capacity, removal efficiency of perchlorate and selectivity of CF-CNTs-PPy nanocomposite film are characterized with cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS). The results show that perchlorate is more selective than other anions including nitrate and chloride when the CF-CNTs-PPY film is exposed to the mix solution containing NaClO<sub>4</sub>, NaNO<sub>3</sub> and NaCl, suggesting that the CF-CNTs-PPY film has a higher affinity for perchlorate. After a

perchlorate exchange experiment, electrodes were regenerated in situ with a controlled potential. The removal efficiency of perchlorate can retain about 80% for thirty times regeneration.

### **175. Immunoassays of Phosphorylated Cholinesterase as Biomarkers for Rapid Diagnosis of Exposure to Organophosphorous Agents**

Yoyu Zhang, Chiantso Lin, Jun Wang, Hong Wu, Kulwadee Pinwattana, Zhiwen Tang, Chuck Timchalk and **Yuehe Lin**, Pacific Northwest National Laboratory, Richland, WA

Numerous analysis methods for effectively monitoring neurotoxic organophosphates (OPs) have been developed to assess OP exposures. Biomonitoring of OP exposures is recognized to be one of the best approaches. Among these, enzyme linked immunosorbent assay (ELISA) and Western blot (WB) methods are simple, rapid detection methods for biomarkers. In this work, we used ELISA and WB methods to find specific antibodies for phosphorylated acetylcholinesterase (OP-AChE) and butyrylcholinesterase (OP-BchE) and evaluate their specificity and sensitivity for rapid diagnosing the exposure to OP agents. Our results indicate that anti-phosphoserine antibody can specifically bind to OP moiety of phosphorylated ChE and don't bind to unmodified ChE. Furthermore, couples the AChE or BchE antibody with anti-phosphoserine antibody can be used for direct detecting OP-AChE or OP-BchE that prepared with paraoxon as an OP model agent with sandwich immunoassay method. Low detection limit were obtained. Such immunoassay holds great promise as a simple, selective and sensitive for the effective biomonitoring and diagnosis of potential exposures to OP agents.

Reference:

[1] Hua Wang, Jun Wang, Charles Timchalk, and Yuehe Lin. Magnetic Electrochemical Immunoassays with Quantum Dot Labels for Detection of Phosphorylated Acetylcholinesterase in Plasma. *Anal. Chem.* 2008, 80, 8477–8484.

### **176. Mobile On-Line Air Quality Monitoring in the Seattle-Tacoma Airshed Using Portable Membrane Introduction Tandem Mass Spectrometry**

Nicholas G. Davey<sup>1</sup>, Jacob M. Etzkorn<sup>1</sup>, Ji Hyun Park<sup>2</sup>, Robert S. Crampton<sup>2</sup>, Cole T.E. Fitzpatrick<sup>2</sup>, Timothy V. Larson<sup>2</sup>, Christopher D. Simpson<sup>2</sup>, Michael G. Yost<sup>3</sup>, Chris C. Gill<sup>1</sup> and **Erik T. Krogh**<sup>1</sup>, (1)Department of Chemistry, Applied Environmental Research Laboratories, Vancouver Island University, Nanaimo, BC, Canada, (2)University of Washington, Seattle, WA, (3)PNASH Center, Seattle, WA

We have modified a quadrupole ion trap GC-MS/MS system for use as an on-line air monitoring platform for volatile and semi-volatile (VOC and SVOC) molecules using a capillary hollow fibre semi-permeable membrane introduction interface. Continuous on-line quantitation of target analytes is achieved using an in-line permeation tube for the continuous infusion of a deuterated internal standard. VOC/SVOCs derived from vehicle exhaust (BTEX, naphthalene) and tracer molecules for woodsmoke (2-methoxyphenol) were monitored over a multi-day excursion in Tacoma, WA during a large-scale air mass inversion in January, 2009. Measurements were made from moving vehicle(s) that drove prescribed routes around fixed locations and a central monitoring site. Concurrent measurements of PM<sub>2.5</sub> (nephelometry) and particle soot absorption photometry were collected adjacent to various fixed sites in an effort to better understand the extent to which fixed site regulatory monitors reflect concentrations of air toxics in the surrounding community. Interim results of spatially and temporally resolved data will be presented that indicate influences from both specific and diffuse sources, including wood burning and major traffic events.

## ***ACS Puget Sound Section Centennial Symposium***

**Organizer:** Craig Fryhle Pacific Lutheran University, Tacoma, WA

**Session Overview:** The Puget Sound Section is celebrating its 100th anniversary this year. This symposium will spotlight the only national ACS meeting ever hosted in Seattle, the section's efforts to digitally archive aspects of its history, and recognize the efforts of volunteers such as the many people who have chaired the section since 1909. Certificates will be presented to all Past-Chairs in attendance, and the section's centennial will be celebrated with an anniversary cake at the afternoon break.

### **177. The Space Needle in a Test Tube**

**Harriet Wasserman**, IT Services, Seattle Central Community College, Seattle, WA

The 1983 National ACS meeting in Seattle was the first since about 1920. An excited team of Puget Sound Section members worked for over two years. The weather cooperated. In addition to the usual outstanding array of technical papers, participants enjoyed wine tastings, tours of points of interest and coordination with the Pauling Award. We'll share some materials and remembrances of the meeting and related events.

### **178. Bites of History-Digitizing the Puget Sound Chemist**

**Susanne Redalje**, UW Libraries, University of Washington, Seattle, WA

Bites of History: Digitizing the Puget Sound Chemist

The Puget Sound Chemist put out its first issue October 1939. In its first 'non' editorial (it was pointed out that they didn't really have departments yet so this couldn't really be an editorial), the editor states "...members of the American Chemical Society in the Puget Sound Section are a group of men and women, as well as chemists; that they have business and social, as well as scientific interests in common; and, that there are happenings other than meetings in the section of interest to all." Bulletins record the history of an organization, sometimes serious, often light hearted. They tell of the travels of their members, who received grants, the hot topics of the day, that you could get a deluxe banquet dinner for 85 cents in 1939. As members, we receive these bulletins, hopefully read them, but then what? Libraries bind them and put them on their shelves for all to see but it is hard to really gain much without reading from start to finish. The UW Chemistry Library is digitizing the Puget Sound Chemist to preserve the information found in them but also to help bring that information to life again.

### **179. Local Sections Are the Bloodlines of the ACS**

**Attila E. Pavlath**, Western Regional Research Center, Albany, CA

The ACS was founded in 1876 with 38 members. It was stagnant until 1891 until a group of chemists in Rhode Island decided to create a local section. Within ten years local sections were formed everywhere and the membership increased exponentially. Today we have 189 local sections and 155,000 members. Without local Sections we would have a publishing company, but not the world's largest scientific organization. The lecture will elaborate on the necessity and importance of the local sections, and the thousands of the unselfish volunteer workers who maintain the nationwide activities of the ACS. It will recognize the diligent effort of countless of ACS members of the Puget Sound Section through honoring its still living Chairs by a certificate.

## ***Bioanalytical Mass Spectrometry 2***

**Organizer:** Frantisek Turecek University of Washington, Seattle, WA

### **180. A Heterotrifunctional Modular Crosslinker for Chemical Proteomics**

**Toni Kline, Ph.D.**<sup>1</sup>, Kathleen Christina Barry<sup>1</sup>, Ivanka Karadzik<sup>2</sup>, Pragma Singh<sup>2</sup>, David Robinson Goodlett<sup>2</sup> and Samuel I. Miller<sup>1</sup>, (1)Immunology, University of Washington, Seattle, WA, (2)Medicinal Chemistry, University of Washington, Seattle, WA



Chemical crosslinking combined with mass spectrometry can be applied to the study of low-abundance, membrane-bound, and multimeric proteins that have otherwise proven difficult to isolate and characterize. Crosslinking between protein domains or between two distinct interacting proteins in a protein complex provides direct structural and mechanistic information. We prepared a heterotrifunctional modular photoaffinity linker: The modules of the crosslinker are the two orthogonal functional

groups necessary for sequential protein capture, and the acetylene, which remains functionally silent during the crosslinking and is engaged in a post-modification step for connection to a reagent moiety such as biotin, a fluorophore, or a mass tag.

We demonstrate the ability of our compound to crosslink both cytosolic and membrane-associated proteins, and subsequent 'click' chemistry to bond the crosslinked proteins to different reagent moieties. One of these moieties, an azido phosphoester that we synthesized as part of this project, illustrates the use of infrared multiphoton dissociation (IRMPD) mass spectrometry, an emerging technique for rapid identification of *bone fide* crosslinked peptides within a complex mixture. These novel reagents may overcome the liabilities of low specificity and overwhelming complexity that can hamper chemical crosslinking/mass spectrometry, enabling this technology to exert its full potential in chemical proteomics.

### **181. Mapping and Quantification of Oxidative Post-Translational Protein Modifications with Mass Spectrometry**

**Claudia S. Maier**, Department of Chemistry, Oregon State University, Corvallis, OR

Covalent protein adducts of reactive lipid peroxidation products are considered as hallmarks in many oxidative stress-related diseases and aging. Mass spectrometry is a central technology that enables site mapping and quantification of oxidative stress-related post translational protein modifications. We develop chemical approaches for the identification, characterization and quantitation of aldehyde-mediated modifications to proteins associated with oxidative stress. Using a combination of aldehyde-specific chemical probes, affinity enrichment techniques and advanced mass spectrometric techniques we identify and determine the site of modification of major protein targets of Michael-type addition reactions caused by aldehydic lipid peroxidation products in cellular systems and animal models of oxidative stress and aging. We have also developed a targeted proteomics approach for the quantification of distinct oxidative modifications using LC-multiple reaction monitoring which allows us to establish aldehyde-modified proteins as *in vivo* markers of oxidative stress.

## General Session - Inorganic 2

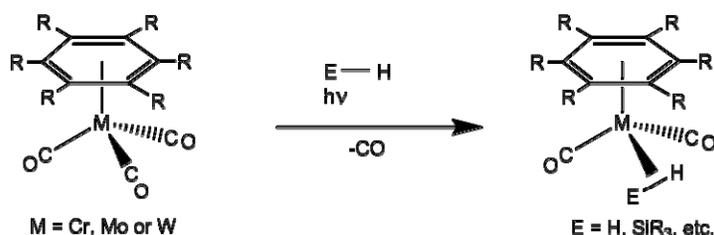
**Organizer:** Mark Wicholas Western Washington University, Bellingham, WA

**President:** John D. Gilbertson Western Washington University, Bellingham, WA

### 182. Observation of Group VI ( $\eta^6$ -arene) $M(CO)_2(E-H)$ Type Sigma Complexes Using NMR Spectroscopy

**Jonathan D. Egbert** and D. Michael Heinekey, Department of Chemistry, University of Washington, Seattle, WA

Complexes of the general formulation ( $\eta^6$ -arene) $M(CO)_3$  ( $M = Cr, Mo, \text{ or } W$ ) were exposed to ultraviolet radiation in alkane solvents with added sigma bond donors to afford thermally labile species. The activation of sigma bonds by a series of ( $\eta^6$ -arene) $M(CO)_2$  fragments has been studied both as a function of the chosen arene and the metal. We present the spectroscopic detection and characterization of the resulting species. One bond coupling constants  $J_{EH}$  ( $E = D \text{ or } Si$ ) were measured by NMR spectroscopy and used to gauge the degree of sigma bond activation upon coordination to the metal. These complexes represent a simple, soluble and tunable system for the study of sigma bond activation.



### 183. Investigation of a Cobalt-Phosphate Electrochemical Oxidation Catalyst for Reactivity with Organic Substrates

**Lisa S. Park-Gehrke** and James M. Mayer, Department of Chemistry, University of Washington, Seattle, WA

Fuel cells are expected to be important energy sources in the future, on large and small scales, so cheap materials are needed to develop practical systems. A novel anode for water oxidation has recently been reported by Nocera et al., involving an electrodeposited cobalt-phosphate ( $Co-PO_4$ ) layer on indium tin oxide (ITO). We have investigated the potential for this anode to oxidize organic substrates, including methanol, hydroquinone, the tosylate ion, benzyl alcohol, and propylamine. One would expect the electrochemical oxidation of organic complexes to be more favorable than that of water, but we have found that these potential substrates are not catalytically oxidized by the  $Co-PO_4$  system, as evidenced by cyclic voltammetry and controlled potential electrolysis experiments. The presence of most of these substrates had no effect on the water oxidation reaction, and no electrochemical response due to the substrates was observed from 0 - 1400 mV potential. Amines were oxidized in the presence of the  $Co-PO_4$  electrode but the reactions resulted in decomposition of the  $Co-PO_4$  coating on the indium tin oxide (ITO) electrode. Therefore, this  $Co-PO_4$  anode is not a potential lead in the development of novel anodes for fuel cells using organic fuels.

#### **184. X-Ray Structures and Spectroscopic Properties of $\text{Na}_2[(\text{VO})_2(\text{ttha})](\text{H}_2\text{O})_8$ and $[\text{Zn}(\text{H}_2\text{O})_6][\{\text{Zn}(\text{H}_2\text{O})\}_2(\text{ttha})](\text{H}_2\text{O})_4$**

**William A. Howard**<sup>1</sup>, Zachary N. Pickett<sup>1</sup>, Z. A. Carlson<sup>1</sup>, Bronwyn L. Harrod<sup>1</sup>, Daniel Widener<sup>1</sup> and Keliang Pang<sup>2</sup>, (1)Department of Chemistry & Biochemistry, University of Alaska Fairbanks, Fairbanks, AK, (2)Department of Chemistry, Columbia University, New York, NY

$\text{Na}_2[(\text{V}^{\text{IV}}\text{O})_2(\text{ttha})] \cdot 8 \text{H}_2\text{O}$  (ttha = triethylenetetramine-N, N', N'', N''', N''''-hexaacetate ion), prepared by treating  $[\text{VO}(\text{H}_2\text{O})_5][(\text{VO})_2(\text{ttha})] \cdot 4 \text{H}_2\text{O}$  with  $\text{Na}_6(\text{ttha})$ , has been spectroscopically characterized and structurally characterized by single crystal X-ray diffraction, and modeled by density functional theory (DFT). Furthermore,  $[\text{Zn}(\text{H}_2\text{O})_6][\{\text{Zn}(\text{H}_2\text{O})\}_2(\text{ttha})] \cdot 4 \text{H}_2\text{O}$  was also spectroscopically and structurally characterized. The X-ray structure revealed distorted octahedral geometries around the vanadium and the zinc centers in both complexes. The electronic absorption spectrum of  $[(\text{VO})_2(\text{ttha})]^{2-}$  (aq) features absorptions at ca. 200 nm ( $\epsilon > 13900 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 255 nm ( $\epsilon = 3480 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), 586 ( $\epsilon = 33 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), and 770 nm ( $\epsilon = 38 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). Time-dependent density functional theory (TDDFT) predicts absorption peaks at 297, 330, 458, 656, and 798 nm in the electronic absorption spectrum of  $[(\text{VO})_2(\text{ttha})]^{2-}$ . TDDFT assigned the peak at 798 nm to be the  $\alpha$  spin HOMO→LUMO transition, which corresponds to the peak at 770 nm in the actual spectrum. The  $\alpha$  spin HOMO and LUMO are partly comprised of d orbitals on both vanadium centers, and the first derivative electron spin resonance spectrum suggests that the two unpaired electrons in  $[(\text{VO})_2(\text{ttha})]^{2-}$  are localized near the vanadium centers.

#### **185. Preparation of Superhydrophobic Surface On Gauze of Stainless Steel in Supercritical Carbon Dioxide**

**Youichi Enokida**, Kazuyuki Hayashida and Kayo Sawada, Ecotopia Science Institute, Nagoya University, Nagoya, Japan

A method of preparing a superhydrophobic surface on gauze of stainless steel in supercritical carbon dioxide at 250 bar and 40 degrees C has been developed. Sol-gel reactions using tetraethyl orthosilicate (Wako Pure Chemical Industries, Ltd., Japan) and water as well as tetraethyl orthotitanate (Wako Pure Chemical Industries, Ltd., Japan) and water in a microemulsion system of water in supercritical carbon dioxide were employed to form roughness in submicron onto the gauze of stainless steel being followed by coating of 1H,1H,2H,2H-perfluorooctyl triethoxysilane (Aldrich Japan, Japan) as hydrophobic reagent also in supercritical carbon dioxide. As a result of a series of the treatments in supercritical carbon dioxide, a superhydrophobic surface was successfully prepared, and the contact angle of water droplet was more than 140 degrees. We studied effects of surfactant chemicals, molecular ratio of water to surfactant, treatment temperature, and molecular ratio of water to alcoxides on size distribution of the roughness, and the roughness formed by the sol-gel reaction ranged from 0.27 to 1.56 micrometers. The most effective parameter that influences size of the roughness was surfactant chemical; Tergitol TMN-3 of 95% in purity (Dow Chemical Japan, Japan) formed smaller deposits rather than a well-known surfactant system of sodium bis(2-ethylhexyl) sulphosuccinate (AOT) and f-pentanol. As an example of an application of using the superhydrophobic surface layer on the steel gauze, platinum (Pt) nanoparticles were deposited through capillary condensation of Pt precursor, 1,5-cyclooctadien dimethyl platinum(II), dissolved in supercritical carbon dioxide, and then this composite materials showed isotopic exchange ability for hydrogen atoms that deuteriated or tritiated hydrogen atom in diatomic hydrogen molecules transferred into water molecule.

## **Medicinal Chemistry**

**Organizer:** Kerry W. Fowler, Ph.D. Past-Chair, Puget Sound Local Section, Seattle, WA

**President:** Kerry Fowler, Ph.D. Past-Chair, Puget Sound Local Section, Seattle, WA

### **188. Pt(II) Complexes of 4,4'-Disubstituted-2,2'-Bipyridine: Structure and Cytotoxicity**

**Byron L. Bennett**<sup>1</sup>, R. David Grigg<sup>1</sup>, James Lai<sup>2</sup>, Alok Bhushan<sup>2</sup>, Vikas Sehdev<sup>2</sup>, Sara Gilmore<sup>2</sup>, Van Vo<sup>3</sup> and Zeynep Kabuloglu-Karayusuf, MS<sup>3</sup>, (1)Department of Chemistry, Idaho State University, Pocatello, ID, (2)Department of Biomedical and Pharmaceutical Sciences, Idaho State University, Pocatello, ID, (3)Department of Chemistry, University of Nevada - Las Vegas, Las Vegas, NV

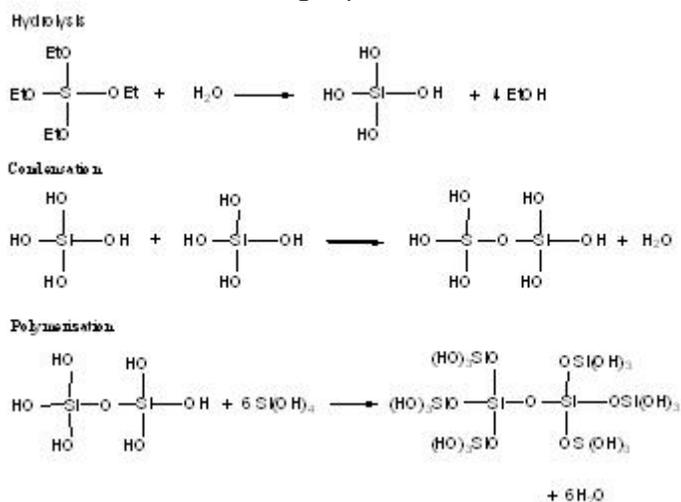
The preparation and characterization of dichloro [4,4'-di(R)-2,2'-bipyridinyl] Platinum(II) complexes; where R =  $-(\text{CH}_2)_3\text{CF}_3$  (**1**),  $-\text{O}(\text{CH}_2)_2\text{CH}_3$  (**2**),  $-(\text{CH}_2)_3\text{CH}_3$  (**3**) are reported. NMR spectroscopy confirms both the constitution of the complexes and their stability in DMSO via observation of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{195}\text{Pt}$ . Solid state XRD data has been obtained for **1** (P2(1)/c; a = 14.3055, b = 9.3301, c = 17.9611,  $\alpha = 90.000^\circ$ ,  $\beta = 91.314^\circ$ ,  $\gamma = 90.000^\circ$ ; d = 1.204,  $wR^2 = 0.0557$ ). In-vitro cologenic viability assay studies support the role of **1**, **2**, and **3** as cytotoxins for L1210 cells as IC50s of less than 10  $\mu\text{M}$  have been observed for all three complexes. In the context of literature and other complexes generated by the authors a preliminary structure activity relationship is proposed with respect to impact of substituent position on the pyridyl ring, isomerism within the substituent, and elemental composition.

### **187. Bioactive Glasses for Restoring Tooth and Bone Tissue**

**Harry B. Davis, Research Chemist**, Jack L. Ferracane and John C. Mitchell, School of Dentistry, Oregon Health and Sciences University, Portland, OR

Composed primarily of amorphous silicates that contain metal oxides and phosphate, bioactive glass refers to a class of inorganic materials that is not simply biocompatible in living tissues, but has the ability to promote beneficial biological activity. The inorganic structure is much like that of natural tooth and bone tissue, and their use in dental applications for tooth and bone repair is well-established. We have used the sol-gel method to make new materials which have surface areas on the order of hundreds of square meters per gram; these serve as reservoirs for ions such as  $\text{Ca}^{2+}$ ,  $\text{PO}_4^{3-}$ , and  $\text{F}^-$  which are necessary for restoration of damaged tooth tissue and prevention of caries. The surface of the bioactive glass also serves as a substrate upon which beneficial hydroxylapatite forms when exposed to body fluids, and as a substrate for the growth of proteins that eventually allow osteoblasts to form new bone. We have observed quantitative relationships between the mole-percent composition, the surface area, and the ability of our bioactive glasses to release beneficial ions and form apatite upon exposure to simulated body fluid. With the use of these relationships we can tailor the properties of the bioactive glass to suit specific applications.

## Sol-gel process



### 186. Discovery and SAR of Antiproliferative N6,5'-Bisureidoadenosine Derivatives

**Matt A. Peterson**, Marcelo Oliveira and Chris Cutler, Chemistry and Biochemistry, Brigham Young University, Provo, UT

Recently we discovered a new class of bisureidoadenosine derivatives that showed promising activities (GI50 = 1–6  $\mu\text{M}$ ) against roughly half of the human cancer cell lines in the NCI 60 panel. The results of such screening along with protein kinase binding activities and preliminary SAR studies of these compounds will be presented.

### 189. Diverse Isoxazole Glutamate Analogs Arise From a Common Intermediate

**Nicholas R. Natale**, Kevin C. Rider, Ph.D., Philippe Diaz, Richard J. Bridges, Sarjubhai A. Patel, John M. Gerdes, C. Sean Esslinger and Charles M. Thompson, Core Laboratory for Neuromolecular Production, The University of Montana, Missoula, MT

Since Krogsgaard-Larsen's pioneering development of AMPA in 1980, isoxazoles have played a useful role in delineating selectivity among proteins that bind glutamate in the CNS. We previously reported an improved preparation of AMPA analogs, including a catalytic asymmetric route. Subsequent binding studies indicate that there exists a distinct SAR distinguishing Receptors and Transporters, specifically the AMPA receptor from the System Xc- transporter, which relates to the size and distance of a lipophilic group in the C-5 position from the functionalized isoxazole. Further investigation of this observation has lead us to examine routes to C-3 carboxy analogs of ibotenate, homo-ibotenate, and homo-AMPA, as well as investigate bioisosteres which are not limited to amino acids, all originating from a common intermediate. Our recent progress on this endeavor from both chemistry and biology perspectives will be described.

## Chemical Education: Upper Division Labs

**Organizer:** Carole Berg Bellevue Community College, Bellevue, WA

**Organizer:** Dharshi Bopegedera The Evergreen State College

### 190. A Microchip Capillary Electrophoresis Experiment for Undergraduate Instrumental Analysis Courses

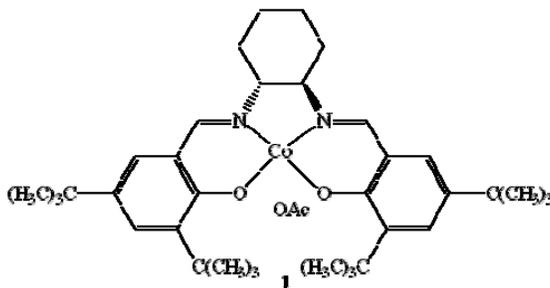
**Adam T. Woolley**, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT

A new microchip capillary electrophoresis (CE) laboratory experiment for undergraduate students has been developed and implemented in the instrumental analysis laboratory course (Chemistry 523) at Brigham Young University. In the experiment, students compare poly(methyl methacrylate) and polydimethylsiloxane microchips, fill microchannels with liquids, learn to align microdevices in a microscope designed for laser-induced fluorescence detection, and carry out microchip CE of fluorescently tagged amino acids. The students also explore the influence on separation of the injection time duration and distance to detection in a CE microchip. This experiment gives students the opportunity to learn to use a number of important research tools including optical microscopy, microfluidics, laser-induced fluorescence, and microchip electrophoresis. Importantly, multiple groups of students were successful in carrying out microchip CE separations on their own as part of this laboratory. Results from these student groups will be reported, as well as ongoing planned revisions and improvements to the experiment. This laboratory provides students with valuable training in various pertinent techniques in the field of microfluidics and should help the next generation of chemists learn to use new microscale methods.

### 191. Preparation and Use of a Chiral (salen)Co<sup>III</sup> Catalyst: Hydrolytic Kinetic Resolution of Epoxides in the Introductory Organic Laboratory

**John E. Hanson**, Bill Dasher, Tim Hoyt and Eric Scharrer, Department of Chemistry, University of Puget Sound, Tacoma, WA

Jacobsen and coworkers reported that the chiral (salen)Co<sup>III</sup> complex **1** is an effective catalyst for the hydrolytic kinetic resolution of epoxides. Introductory organic students can successfully prepare this catalyst in 4 steps: (1*R*,2*R*)-1,2-diaminocyclohexane L-tartrate is prepared by selective crystallization from a mixture of 1,2-diaminocyclohexane isomers; the diimine salen ligand is formed by reaction of the resolved *trans*-1,2-diaminocyclohexane with 2 equivalents of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde; the (salen)Co<sup>II</sup> complex is prepared by treatment of the salen ligand with Co(OAc)<sub>2</sub>; and the desired catalyst is obtained by aerobic oxidation in the presence of acetic acid. Students then use their catalyst to resolve one of three racemic epoxides: styrene oxide, phenyl glycidyl ether, or benzyl glycidyl ether. After separating the resulting diol and unreacted epoxide by flash chromatography the products are characterized by H-NMR and chiral GC or chiral HPLC. Nearly all students are able to successfully prepare the catalyst **1** and obtain highly enantioenriched epoxides using it. This series of experiments introduces students to a variety of important laboratory techniques and reinforces many important concepts related to chirality, stereochemistry, and optical activity.



## 192. An Undergraduate Laboratory Course Using Very Low-Field NMR to Demonstrate the Overhauser Effect

**Mark D. Lingwood** and Songi Han, Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA

We are developing portable, very low-field NMR equipment for use in an undergraduate instructional laboratory, with the specific aim to demonstrate the Overhauser effect. The Overhauser effect involves saturating the populations of nuclear or electron spins to cause the transfer of polarization to other nearby nuclear spins through dipolar interactions. The nuclear Overhauser effect is commonly used in NMR spectroscopy, primarily for distance measurements between proximal spins. In our case we saturate the electron spin of a stable radical species, which is known as Overhauser dynamic nuclear polarization (DNP), and can result in dramatically increased NMR signal of the solvent nuclei.

The students were provided with a home built 1.5 mT electromagnet, a commercially available NMR spectrometer, and the equipment to perform Overhauser DNP experiments. They then built and characterized their own NMR probes and began acquiring spectra. In continuing lab periods, students investigated the longitudinal relaxation properties ( $T_1$ ) of various solutions, then quantified the amount of signal enhancement from DNP. The laboratory was coupled to a weekly discussion section where the theory behind NMR and MRI was presented along with current areas of research in the field. Student response to the first offering of this class was overwhelmingly positive.



## 193. A Research-Based Approach to Learning Pseudo-Rate Reactions

**Timothy L. Sorey** and Anthony Diaz, PhD, Department of Chemistry, Central Washington University, Ellensburg, WA

A laboratory experiment was designed for upper division chemistry majors to solve a pseudo-rate constant by incorporating mathematical modeling, technological measuring, and analytical calculating. During this six hour lab, a lab instructor plays the role of a principal investigator as students fill the role of a lab researcher who constructs theoretical mathematical models of metal-ligand chemistry to solve for pseudo first order reactions, applies previous knowledge of Beer-Lambert Law and kinetic spectroscopy to explore the reaction of Nickel II/Pyridine-2-azo-p-dimethylaniline complex ( $Ni^{2+}$ /PADA) with  $NH_3$ , and proposes a plausible quantitative value for a pseudo-rate constant for this reaction. This approach applies multiple supporting teaching strategies that chemist recognize as a research-based problem solving approach. Results within **CHEM 383: Physical Inorganic Chemistry Laboratory** will be reported from the 2008 and 2009 Spring Quarters, along with student use of Excel Software and MicroLab FS522 software and hardware systems.

## ***Chemistry of Chocolate***

**Organizer:** Rob Synovec University of Washington

**President:** Andrew McShea Theo Chocolates, Seattle, WA

**Session Overview:** Scientists from the University of Washington and Theo Chocolates (organic, fair trade, bean-to-bar) in Seattle, WA will tackle the science of those fermented and roasted seeds of *Theobroma cacao*.

### **194. Development of a GC x GC - TOFMS Method Using SPME to Determine Volatile Compounds in Cacao Beans**

**Elizabeth Humston**<sup>1</sup>, Yan Zhang<sup>1</sup>, Gregory Brabeck<sup>1</sup>, Andrew McShea<sup>2</sup> and Rob Synovec<sup>1</sup>,  
(1)University of Washington, Seattle, WA, (2)Theo Chocolates, Seattle, WA

A method to analyze volatile compounds in the head space above cacao beans has been developed and evaluated. The method utilizes solid phase micro extraction (SPME) sampling followed by comprehensive two-dimensional gas chromatography (GC x GC) coupled with time-of-flight mass spectrometry (TOFMS). For the SPME procedure, a polydimethyl siloxane/divinyl benzene (PDMS/DVB) fiber was implemented. Cacao beans from four geographical origins (Ivory Coast, Ghana, Ecuador, and Costa Rica) were studied under two storage conditions, either dry (no surface mold on the beans) or high moisture (surface mold present on beans). A given cacao bean sample was sealed in a SPME vial and the vial heated in a water bath to a given extraction temperature. Extraction temperatures of 45, 60, 80, and 100 °C were analyzed. The fiber was then exposed to the headspace at the desired extraction temperature for 10 min. An optimal extraction temperature of 60 °C was determined. Many peaks were found to either increase or decrease as a function of the two storage conditions (dry or high moisture). Four representative compounds were identified and quantified (on a relative basis): acetic acid, nonanal, tetramethyl pyrazine, and trimethyl pyrazine. Acetic acid and nonanal were found to be substantially elevated in the dry storage conditions, while the two pyrazines were substantially elevated in the high moisture storage conditions. The results for the bean storage conditions (i.e., dry vs. high moisture), indicate that bean surface chemistry metabolism plays a role in the concentration of analytes, and this information can be readily determined using this analytical technology and methodology.

### **195. The Chemistry and Physiological Effects of Bio-Active Moieties in Dark Chocolate: Molecular Composition, Manufacturing Techniques and Clinical Data**

**Andrew McShea**, Theo Chocolates, Seattle, WA

The consumption of high-cacao-content chocolate has been associated with positive health benefits ascribed to flavanol antioxidants derived from the ground, fermented cocoa seeds of *Theobroma cacao*. However, flavanols impart a bitter, astringent flavor to foodstuffs, frequently masked in chocolates and confections by aggressive processing and adulteration with other flavors. Recent reports have implied that not all varieties of dark chocolate are created equally, and significant caveats exist regarding its potential health benefits. It is perhaps not surprising that extensive processing, dilution, and the addition of flavor modifiers may improve the palatability of chocolate, but could have negative nutritional and clinical benefits. We describe the chemical composition of chocolate and the clinical data associated with the consumption of flavonoid-rich comestibles. We review the steps in chocolate manufacturing that directly affect the antioxidant levels in chocolate products, and the caveats associated with claims of health benefits from the consumption of dark chocolate.

## General Session - Organic

**Organizer:** Kerry Fowler, Ph.D. Past-Chair, Puget Sound Local Section, Seattle, WA

**President:** Kerry Fowler, Ph.D. Past-Chair, Puget Sound Local Section, Seattle, WA

### 196. A Concise Synthesis of Capuramycin

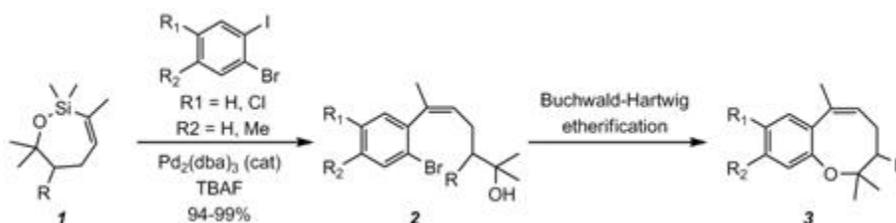
**Michio Kurosu**, Microbiology, Immunology, and Pathology College of Veterinary Medicine and Biomedical Sciences, Colorado State University, Fort Collins, CO

A concise total synthesis of capuramycin, a promising preclinical TB drug lead, is achieved by high-yield formations of the cyanohydrin and 4'',5''-glycal derivative. Each step is operationally very simple and a high-yielding conversion. Moreover, the building blocks utilized in this synthesis can readily be synthesized from the commercially available uridine derivative and D-mannose. We have synthesized capuramycin analogs by 1) modifying the structures of building blocks, 2) reductive amination of the synthetic intermediate with a variety of primary amines, and 3) coupling of the carboxylic acid with pharmacologically interesting primary and secondary amines. A detailed synthesis of capuramycin and its analogs will be discussed.

### 197. 1-Benzoxocanes Via Intramolecular Buchwald-Hartwig Etherification

**James R. Vyvyan**, Scott L. Bray, Erik W. Wold and Courtney A. Engles, Department of Chemistry, Western Washington University, Bellingham, WA

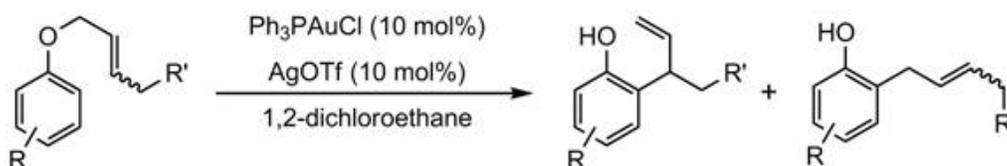
The 1-benzoxocane skeleton, present in the helianane natural products, presents a significant synthetic challenge. Intramolecular hydrosilylation of 2-methyl-5-heptyn-2-ol using Trost's conditions produces cyclic vinyl silane **1**. Palladium-catalyzed coupling of **1** with aryl iodides proceeds in high yields to produce tertiary alcohols **2** that contain a Z-olefin. The presence of the olefin facilitates an intramolecular Buchwald-Hartwig etherification reaction to produce the 1-benzoxocane skeleton **3**. Hydrogenation of the olefin produced helianane. Effects of different R groups, bases, and ligands on the cyclization will be presented.



### 198. Development of a Gold(I)-Catalyzed Aromatic Claisen Rearrangement

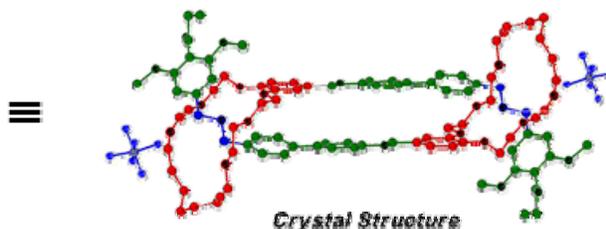
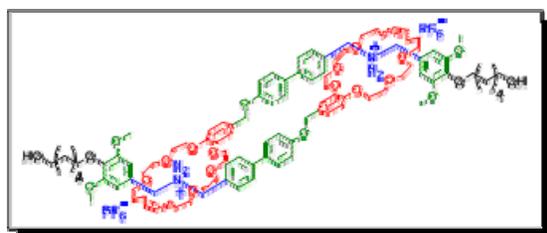
**James R. Vyvyan**, Jennifer Bennett, Heidi E. Dimmitt, Jennifer K. Griffith, Laura D. Steffens and Rebecca A. Swanson, Department of Chemistry, Western Washington University, Bellingham, WA

Triphenylphosphinegold(I) triflate catalyzes the conversion of aryl allyl ethers to the corresponding [3,3]- (Claisen) and [1,3]-rearrangement products. The product distribution depends on the stereochemistry of the olefin in the allylic ether as well as the position and electronic properties of the aryl substituent(s). Results supporting an ion pair mechanism will be discussed.

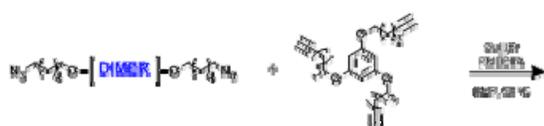


## 199. Toward Molecular Muscles: [c2]Daisy-Chain Dimer Synthesis and Incorporation Into Materials

Paul G. Clark and Robert H. Grubbs, Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA



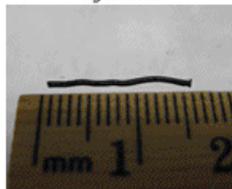
Materials Synthesis



Gel in Glass  
Capillary Tube



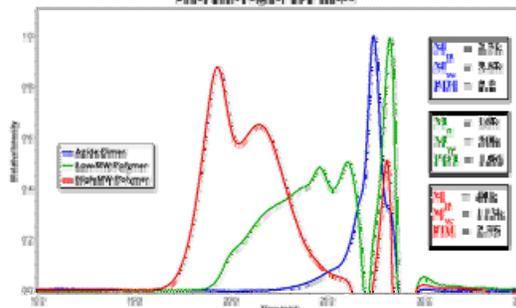
Free Gel  
Cylinder



LINEAR DIMER CLICK POLYMER



Linear Dimer Click Polymer GPC Traces



We report the synthesis of a [c2]daisy-chain dimer (DCD) whose interlocked architecture permits dimer extension and contraction, mimicking the motion of a biological muscle. Dimerization via ring-closing metathesis of a self-complementary macromer containing both a recognition moiety (diolefinic crown-type structure) and a guest moiety (dibenzylammonium ion) was readily achieved upon addition of Grubbs 2<sup>nd</sup> generation ruthenium olefin metathesis catalyst. Addition of a small excess of strong base to a solution of the dimer rapidly induced quantitative deprotonation of the ammonium, and addition of excess acid restored the dimer to its original "bound" conformation. The separation of the ammonium and crown species within the structure of the macromer produced a DCD whose "bound" state is contracted, with restoration of the strong ammonium-crown interactions effecting the dimensional change. Post-dimerization azide functionalization of the DCD facilitated incorporation of the dimer within materials. The  $\alpha,\omega$ -diazide DCD and a dialkyne were subjected to copper-catalyzed 'click' reaction conditions, generating linear polymer. Reaction of the azide-functionalized dimer with a trialkyne produced a macroscopic gel, which, prior to gelation, was intercalated within glass tubes to yield uniform gel cylinders.

## ***Chemical Education: Lower Division Labs***

**Organizer:** Carole Berg Bellevue Community College, Bellevue, WA

**Organizer:** Dharshi Bopegedera The Evergreen State College

### **200. Teaching LIMS In Your Lab for Real-World Analyses**

**Jerry DeMenna, Dr**, Chemistry, MeasureNet Technology / FUN-Science Academics, Bronx, NY

The protocol for making Analytical measurements in Real-world Laboratories requires Data entry into a networked LIMS... or Laboratory Information Management System. Commercial LIMS keep track of ALL Data from ANY Analytical device... from a \$100 pH Meter to a \$1,000,000 LC-MSMS... and provides a universal format for processing, transferring and presentation. Pharmaceutical companies, Clinical labs & Hospitals, Environmental firms and Gov't organizations rely on the throughput, integrity and accuracy of a LIMS. A true LIMS allows multiple Instrument outputs to be controlled regardless of the Instrument (Electrochemical, Spectrophotometer, Chromatograph, Physical) and Format (Spectrum, Beers Law Calibration Plot, Thermometric Curve). Our undergrad Labs use a true LIMS from MeasureNet Technology, which allows us to interface up to thirty (30) "Universal Workstations" to Instruments through their high-resolution A/D Controller into a single (1) Network Computer and Color Printer. All the Student Data is fully ID'd and stored simultaneously on our school Server and off-site on the MeasureNet Server. Depending on the level of the Lab Class, you can use their series of EXCEL Macros and Templates for post-run processing of the Data. Sit back and get "informed" about the new way to truly Network in your Laboratory!

### **201. A General Chemistry Hybrid Laboratory Program**

**Richard Nafshun**, Department of Chemistry, Oregon State University, Corvallis, OR

Oregon State University offers five General Chemistry sequences (non-science majors, science majors, engineers, honors, and nursing); the largest being the non-science majors sequence with an enrollment of 900 students. A test group from the non-science majors sequence participated in a program which involved both traditional on-campus laboratory activities and online virtual laboratory activities (a "hybrid" program).

Survey, interview, and evaluation programs were facilitated. Data and results will be discussed.

### **202. Attitudes of Pre-Service Elementary Teachers towards Chemistry**

**Erin N. Wilson**, Frackson Mumba, Vivien Mweene Chabalengula and Kevin C. Wise, Department of Curriculum and Instruction, Southern Illinois University Carbondale, Carbondale, IL

This study explored the attitudes of pre-service elementary education teachers toward chemistry as a science and chemistry in courses. Attitudes were broken into image, cognitive, and affective domains. A sample comprised 94 pre-service teachers from four different classes at a Midwestern university. Attitudes were assessed using a questionnaire developed by Shwartz, et. al, [2006]. Preliminary data analysis showed an overall positive attitude toward chemistry as a science and in courses. A significant difference was found between those with a science concentration and those in other fields in the cognitive domain. One-way ANOVA revealed a significant difference in the affective domain between those who had taken one or fewer college chemistry courses and those who had taken four or more college chemistry courses. Implications of these findings on chemistry teaching and learning and teacher education will be discussed.

### **203. Using Oral Rehydration Solutions in the General Chemistry Laboratory**

**James J. Neitzel, Ph.D.**, Chemistry, The Evergreen State College, Olympia, WA

Diarrheal diseases are one of the most common causes of childhood death on a global scale. One of the most cost-effective treatments for these diseases is the use of oral rehydration solutions (ORS). This treatment was used as the basis for teaching chemistry in a biomedical context.

For students in a general-organic-biochemistry sequence a laboratory was developed that had students prepare various oral rehydration solutions. Students measured the density, pH, osmotic strength, and salinity of their solutions. They were able to compare these physical properties of their solutions made using standard formulas (such as that of the World Health Organization), as well as solutions made from recipes for improvised solutions using common household ingredients and measuring devices. In a linked biology component students learned the physiological basis for the effectiveness of these solutions.

This laboratory exercise gave students practice in making solutions, density, concentration units, pH and buffers, and the colligative properties of water. Typical student data will be presented.

#### ***Lab Safety Workshop: Rehab the Lab – Enhancing Chemical Consciousness***

**Organizer:** Douglas Mandt Pacific Lutheran University

**Workshop Leader:** Dave Waddell, Lead Investigator KING COUNTY METRO, Seattle, WA

**Session Overview:** This presentation will provide attendees with information from the award-winning Rehab the Lab Program. King County (Washington) has partnered with secondary schools to create positive, lasting environmental change and has removed over 40 tons of hazardous chemicals from their schools.

### **204. Rehab the Lab – Enhancing Chemical Consciousness in Secondary Schools**

**Dave Waddell, Lead Investigator**, Chemical Waste Management, King County Metro, Seattle, WA

This presentation will provide attendees with information from the award-winning Rehab the Lab Program in Washington State's King County that has partnered with secondary schools to create positive, lasting environmental change and remove over 40 tons of hazardous chemicals from their schools. Hazardous materials are commonly found in middle and high schools, including explosives, radioactive materials, corrosives, poisons, restricted pesticides, ignitable liquids, reactives, PCBs, oxidizers, carcinogens and numerous unknowns. As a result, the bomb squad was brought into over 50% of our high schools.

This presentation will provide attendees with:

- Visual and technical information on chemical mismanagement issues found at schools.
- Barriers to changing improper behaviors, improving environmental compliance and incorporating pollution prevention practices.
- Tools and techniques to successfully overcome those barriers to engage science and art teachers in proper chemical hygiene practices including an on-line School Chemical Hazards Database
- Copies of alternative labs that use less chemicals and less hazardous chemicals.

The Rehab the Lab Program works with schools to:

- Eliminate stockpiles of old hazardous chemicals from science stockrooms. Deactivate potentially explosive compounds.

- Educate teachers on ways to reduce waste, manage their chemicals properly and minimize future chemical-related liabilities.
- Provide alternative laboratory practices that will reduce the need to purchase high-risk chemicals.
- Help non-lab programs (e.g., shop classes, photo labs and art classes, etc.) incorporate pollution prevention strategies and proper waste management concepts into their practices.
- Encourage use of less hazardous alternatives in grounds management, teaching and custodial work.

### ***Strategies to Promote Active Learning***

**Organizer:** A. M. R. P. Bopegedera, Dr. The Evergreen State College, Olympia, WA

**Organizer:** Carole Berg Bellevue Community College, Bellevue, WA

**Session Overview:** This session will include presentations on guided-inquiry learning in the laboratory, Peer-Led Team Learning (PLTL), and a mini-workshop on Process-Oriented Guided Inquiry Learning (POGIL).

### **205. Designing a Guided Inquiry Laboratory Curriculum for Qualitative Analysis**

**Stephanie B. Austin**, Department of Chemistry, Seattle University, Seattle, WA

The study of qualitative analysis is intended to foster an understanding of the fundamental chemical principles of solubility, pH and equilibrium systems. The common teaching paradigm directs students to follow proscribed separation schemes; students report feeling bored, frustrated by unexpected results, and that they don't understand the purpose/learning goal of the lab. Our goals for the student, which we achieve by adopting a guided inquiry (GI) approach, are expanded knowledge of the chemical principles underlying qualitative analysis, practice in experimental design, and application of the scientific method. The GI lab operates on the premise that students learn better when they are actively engaged in the construction of their own knowledge within a social/cooperative setting. Under our curriculum model students collect and organize observations of precipitation reactions between an array of single cations and various reagents. Based primarily on this information, they design and verify schemes to separate a solution containing five cations; they then test their schemes in the analysis of a solution of unknown composition. Analysis of student learning survey results conducted on a pilot class (Spring 2009) will be used to modify the final curriculum, scheduled for formal introduction in Spring 2010.

### **206. Peer-Led Team Learning (PLTL)**

**Morton Z. Hoffman**, Department of Chemistry, Boston University, Boston, MA

PLTL was created in the early 1990's at the City College of New York (CCNY) in response to the observation that the students who were entering colleges and universities were becoming increasingly more poorly prepared in chemistry and mathematics with the resultant dramatic increase in the percent of poor grades in general and organic chemistry and the dropout rate of students from the sciences. PLTL is a partnership of faculty, learning specialists, and peer leaders who have worked together to help students build conceptual understanding and problem-solving skills in their science and mathematics courses. The PLTL model introduces a new structure, the peer-led workshop, where students work together in groups to solve challenging problems that have been designed by the faculty in order to engage them with the subject material and with each other. The team is guided by an experienced student, perhaps one who had taken the course earlier and who is trained to lead the workshop. In short, PLTL provides an active learning experience for

the students, a leadership role for the undergraduate peer leader, and a creative new dimension to faculty teaching. See <[www.pltl.org](http://www.pltl.org)>.

### **207. Student-Active Learning (POGIL) at the University of Washington**

**Andrei Straumanis, Ph.D.**, Chemistry, University of Washington, Seattle, WA

POGIL is a lecture-less teaching method that seeks to increase student engagement in the classroom by having students work in self-managed teams to analyze data and draw conclusions, modeling the way a team of scientists function in the research laboratory. The method has been successfully adopted in sections of organic chemistry at the University of Washington, and this talk will include an interactive demonstration, as well as comparison of POGIL versus lecture student achievement data from the past two years at UW.

### **208. More Effective Group Work: Using Process-Oriented Guided Inquiry Learning (POGIL) to Increase Student Interaction**

**Stacey Fiddler**, Portland Community College, Portland, OR and **Jennie K. Mayer**, Chemistry Department, Bellevue College, Bellevue, WA

Do you have groups that are quiet? Is there little or no interaction within groups? Do you feel overwhelmed when lots of students need help at the same time?

Students learn the most when they teach others. How do we get our students to teach each other? Using inquiry-based activities can be a good starting point for encouraging discussions in groups. But it must also be accompanied by a structure that allows the silence to be broken. Assigning student roles gives students some responsibilities that prevent independent work. Certain techniques and instructions can be given to keep everyone in the group on the same page. Self-assessments can track improvements in group performance and prompt students to reflect on their own learning.

This session will focus on the use of guided inquiry materials and the facilitation of group work to keep students engaged during class. We will also discuss the recent formation of a Northwest network of teachers using guided inquiry(<http://www.pogilnw.org>) can serve as an ongoing resource for classroom observations, other workshops, and a national network of peers.

In no time, your problem will be to keep the students quiet!