

# Chemistry Seminar Abstracts for the Year 2013

Nanostructure-initiator Mass Spectrometry with Acoustic Deposition: Multiplexed, High-throughput Pipeline for Metabolic and Enzymatic Activity Screening .....	3
By Xiaoliang Cheng, Life Science Division, Lawrence Berkeley National Laboratory	
Isocyanate Derived Organic Aerogels .....	3
By Chakkaravarthy Chidambareswarapattar, Dept. of Chem., MS&T	
Grabbing Scorpions: Fast, Functional Resin-Supported Chelates .....	4
By Prof. Patrick Desrochers, Dept. of Chem., University of Central Arkansas	
Chasing Trilobites: The Ordovician Period of the Anti-Atlas Mountains .....	5
By Dennis L. Whitney, Environmental Engineer, American Airlines, Retired	
Colloidal Unimolecular Particles .....	5
By Sager Gade, Dept. of Chem., MS&T	
Colloidal Semiconductor Quantum Belts, Platelets, and Magic-size Nanoclusters .....	6
By William E. Buhro, George E. Pake Professor of Arts & Sciences Chair, Dept. of Chem., Washington University, Saint Louis, MO	
Carbon Dioxide Capture and Hydrocarbon Separations in Metal-Organic Frameworks .....	7
By Jeffrey R. Long, Materials Sciences Division, Lawrence Berkeley National Laboratory and Dept. of Chem., University of California-Berkeley	
Formal Music Instruction in Grades 5 through 12 Improves Performance in Undergraduate Science and Engineering .....	7
By Robert Cesario, Dept. of Arts, Languages, and Philo, Director of Bands and Orchestras, MS&T	
Microwave Spectroscopy and the New Millennium: Advancing Technology in Two Directions....	8
By Garry S. Grubbs, Dept. of Chem., MS&T	
Cancer Biomarkers: From Large to Small Molecules .....	9
By Prof. Michael Wang, Dept. of Pathology, University of Missouri-Columbia	
Occurrence and Removal Study of Perchlorate Levels in Missouri Natural and Drinking Waters by Using Ion Exchange Chromatography- Tandem Mass Spectrometry .....	10
By Danielle West, Dept. of Chem., MS&T	
An Overview of Patent Law and What to Expect when Preparing and Submitting a Patent .....	10
By Rebecca Rich, Patent Attorney, Brewer Science Inc., Rolla, MO	
Strong Magnetic Coupling and Single-Molecule Magnet Behavior in Azophenine Radical-Bridged Dinuclear Complexes .....	11
By David Harris, Rang Jeon, & Jesse Park, Dept. of Chem., Northwestern University	

Molecular Models for the Study of Spin Relaxation and Magnetic Anisotropy.....	11
By Danna Freedman, Dept. of Chem., Northwestern University	
Investigation of Fluid Flow Behavior in Nano-scale Channels Using Single Molecule Imaging System.....	12
By Qihua Wu, Dept. of Chem., MS&T	
Structural, Electronic, and Catalytic Properties of Metal Complexes Bearing "P-N-P" Ligands	12
By Prof. Panayotis Kyritsis, Dept. of Chem., National and Kapodistrian University of Athens	
New Quantitative NMR Techniques for Determining Product Yield of Hydrothermal Biomass.	13
By Lingyu Chi, Dept. of Chem., MS&T	

## **Nanostructure-initiator Mass Spectrometry with Acoustic Deposition: Multiplexed, High-throughput Pipeline for Metabolic and Enzymatic Activity Screening**

Xiaoliang Cheng, Life Science Division, Lawrence Berkeley National Laboratory

**Abstract:** A major challenge in Synthetic Genomics is the disconnect between the rate of gene discovery and functional analysis. Determining the function of a gene now requires a disproportionate amount of effort relative to that required for gene identification. Similarly, construction of multigene pathways for biofuel production is relatively straightforward and results in enormous clone libraries, however, only a small fraction of clones can be tested due to analysis constraints inherent with traditional LC/GC-MS analysis. We are addressing this analytical bottleneck using acoustic printing to transfer nanoliter volumes onto nanostructure-initiator mass spectrometry surfaces, enabling us to perform 10,000's of assays/day, an increase in throughput of 1000-fold. This effort will serve as the foundation in the development of this new technology that will have several applications, including enzyme "cocktail" engineering for enhanced performance in industrially relevant biorefining operating environments for the production of sugars from biomass.

## **Isocyanate Derived Organic Aerogels**

Chakkaravarthy Chidambareswarapattar, Dept. of Chem., MS&T

**Abstract:** Aerogels are bulk monolithic materials, consisting of 3D assemblies of nanoparticles with high open porosity, high surface areas and are pursued for thermal insulation. After the synthesis of resorcinol-formaldehyde (RF) aerogels in 1989, for a number of years "organic aerogels" and "RF-aerogels" were almost synonymous terms. This is slowly changing as other classes of organic aerogels show up in the literature, including polyurethane, polyurea and more recently polystyrene, polybenzoxazine, polydicyclopentadiene and polyimide (PI) aerogels. The latter are pursued for the good chemical resistance, excellent mechanical properties and high thermal stability of their polyimide skeletal framework. Typically, polyimides are synthesized from a di-anhydride and a diamine with the classic DuPont two-step process via polyamic acids, which are converted to polyimides chemically with the use of dehydrating agents (e.g., acetic anhydride) along with base catalysts (e.g., pyridine). The first PI aerogels were described in 2006, and they were synthesized by that route. Here, we report polyimide aerogels via an alternative one-step room-temperature route that involves reaction of the same dianhydrides with the corresponding diisocyanates. The final aerogels are chemically indistinguishable (by IR and  $^{13}\text{C}$  CPMAS NMR) from those synthesized via the polyamic acid route. However, in terms of properties, the two materials are vastly different. Aerogels synthesized via the isocyanate route are nanofibrous as opposed to nanoparticulate morphology obtained from the amine route.

Following our successful synthesis of PI aerogels via the one-step isocyanate route [1], we have correlated bulk mechanical properties with the structure of the monomers. Thus, realizing the importance of multifunctional monomers in terms of imparting mechanical strength, we resort into a trifunctional isocyanate [tris(4-isocyanatophenylmethane): Desmodur RE; courtesy of Bayer, Corp. USA] with two different di-anhydrides, pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA). The resulting polyimide aerogels, PI-PMDA and PI-BTDA, are stable up to 400 °C (by TGA), as expected from polyimides. Despite relatively high bulk densities by aerogel standards (up to 0.6-0.7 g cm<sup>-3</sup>) and a decrease in porosity (down to ~50% v/v) PI-PMDA remain mesoporous and have high surface area (up to 435 m<sup>2</sup> g<sup>-1</sup>). On the other hand, with the same primary particle sizes, PI-BTDA shrink less, have lower bulk densities and higher porosities (up to 80%). Clearly, decreasing the molecular rigidity of the dianhydride (from PMDA to BTDA) has an immediate impact on the material properties of the resulting aerogels. Both kinds of PI aerogels are extremely robust materials with high energy absorption capabilities (e.g., PI-PMDA: 82±4 J g<sup>-1</sup> at 0.68 g cm<sup>-3</sup>; PI-BTDA: 47±1 J g<sup>-1</sup> at 0.37 g cm<sup>-3</sup>). Upon pyrolysis at 800 °C under Ar, PI aerogels are converted to carbon aerogels in high yields (52-59 % w/w). Along the way, design of other isocyanate derived organic aerogels is briefly discussed.

## Grabbing Scorpions: Fast, Functional Resin-Supported Chelates

Prof. Patrick Desrochers, Dept. of Chem., University of Central Arkansas

**Abstract:** The rapid one-pot synthesis of a functional scorpionate using microwave assisted methods will be described. Despite the 50+ year history and vitality of the scorpionate field (typically hydrotris(pyrazolyl)borate chelates used with every metal on the periodic table), the development of *heterogeneous* supported scorpionates is still in its infancy, with our own work (*Inorg. Chem.* 2011) representing one of only a handful of examples. The promise is great: couple the benefits of mature ligand development with the proven utility of heterogeneous systems. Immobilized metal affinity chromatography and high-throughput combinatorial methods are two such areas that could benefit from the use of versatile metal scorpionate chelates. The challenge is also great: supported scorpionates are generally difficult or expensive to make. Therefore, we demonstrate that such chelates can be reproducibly prepared inexpensively in a single step by MW irradiation of a mixture of pyrazole, NaH, and resin-supported phenylboronic acid. Results will demonstrate this supported-chelate is fully functional. Active coordination complexes of Cr(III), Cu(II), Co(II), and Rh(I) will be described. This area of research has great potential to significantly benefit the inorganic discipline and by association, the biochemical, material, and industrial applications it serves

## **Chasing Trilobites: The Ordovician Period of the Anti-Atlas Mountains**

Dennis L. Whitney, Environmental Engineer, American Airlines, Retired

**Abstract:** During the Ordovician period, which was approximately 490 to 445 million years ago, the Ozark Plateau, which contains Rolla, Jefferson City, and Springfield, was near the equator and on the eastern coast of the North American massif, whereas the Anti-Atlas Mountains of the Northwestern Sahara Desert were also near the equator and on the western shores of Gondwanaland. As a consequence, there is a very good chance that the paleoclimates of these two regions may have been very similar. However, the fossil record indicates that the paleoecology was perhaps dissimilar. Recently, fossil discoveries in the Atlas Mountains have revealed a new and diverse paleoecology. The discovery of this new fossil record has led to new insight into the nature of life in the Ordovician period.

On a recent trip to Morocco, the speaker investigated the quarries, where many of these fossils have been discovered. The new discoveries will be discussed along with their significance to the paleogeography and paleoecology of the Ordovician formations to both the Anti-Atlas Mountains and the Ozark Plateau. The significance of the different paleofaunas of the two regions will be discussed and fossil specimens will be displayed in order to support the discussion.

The comparison of these two paleoecologies indicates that the eastern shore of the North American massif possibly had a different paleoecology than the western shores of Gondwanaland. The fossil record in the Ozarks consists of mostly mollusks, whereas the fossils discovered in the Anti-Atlas Mountains reveal a rich diversity of living creatures, many of which are new to science. These ongoing discoveries are intriguing to scientists and have opened several new avenues of research into the evolution of life.

## **Colloidal Unimolecular Particles**

Sager Gade, Dept. of Chem., MS&T

**Abstract:**

### **Part I. Molecular Weight and Functionality Effects on Colloidal Unimolecular Polymer Formation and Stability**

The formation of anionic stabilized colloidal unimolecular polymer, CUP, particles from single polymer strands was investigated as a function of molecular weight. The CUP particle size was

correlated with the absolute molecular weight and its distribution. The characteristics of the particles were evaluated with respect to viscosity, acid number, size distribution and stability. The particle size varied from less than three nanometers to above eight nanometers representing polymers with molecular weight in the range of 4,000 to 153,000. Lower molecular weight polymers were found to be unstable due to insufficient ionic stabilization.

## **Part II. Synthesis of Amino Functional Colloidal Unimolecular Polymer Particles and their Use as Epoxy Curing Agents**

The synthesis and utilization of cationic stabilized CUP particles utilizing a low Tg acrylic polymer for the curing of epoxy resins. Copolymer of ethyl acrylate / acrylic acid were synthesized and reacted with aziridine to produce amino modified polymer and hence cationic stabilized CUP particles. This copolymer exhibits cold flow and produce a continuous film. Use of these CUP particles as epoxy curing agents was investigated.

## **Colloidal Semiconductor Quantum Belts, Platelets, and Magic-size Nanoclusters**

William E. Buhro, George E. Pake Professor of Arts & Sciences Chair, Dept. of Chem., Washington University, Saint Louis, MO

**Abstract:** Pseudo-1D nanocrystals such as quantum wires (QWs) and quantum belts (QBs, nanoribbons) are in principle capable of transporting energy (excitons) and charge over long distances, and thus may have applications in solar-energy conversion and other technologies. However, excitons and charge carriers in QWs and QBs sample extremely large surface areas and thus have a high probability of encountering surface trap sites, precluding efficient transport.

I will describe semiconductor QBs in which excitons are efficiently delocalized over the entire length of the nanostructures, and the photoluminescence efficiencies are as high as 40%, rivaling those of quantum rods. Crystalline, colloidal CdSe quantum platelets (QPs) are prepared at room temperature. The QBs and QPs are obtained from  $(\text{CdSe})_{13}$  nanoclusters entrained within lamellar-template structures. Their excellent optical properties result from the smooth facets and effective passivation afforded by the template synthesis, which minimize surface trap-site populations. The isolation and characterization of  $[(\text{CdSe})_{13}(n\text{-alkylamine})_{13}]$  derivatives will also be described.

## Carbon Dioxide Capture and Hydrocarbon Separations in Metal-Organic Frameworks

Jeffrey R. Long, Materials Sciences Division, Lawrence Berkeley National Laboratory and Dept. of Chem., University of California-Berkeley

**Abstract:** Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas storage and gas separation applications. In an effort to help curb greenhouse gas emissions from power plants, we are developing new MOFs for use as solid adsorbents in post- and pre-combustion CO<sub>2</sub> capture, and for the separation of O<sub>2</sub> from air, as required for oxy-fuel combustion. In particular, MOFs with open metal cation sites or alkylamine-functionalized surfaces are demonstrated to provide high selectivities and working capacities for the adsorption of CO<sub>2</sub> over N<sub>2</sub> under dry flue gas conditions. Breakthrough measurements further show compounds of the latter type to be effective in the presence of water, while calorimetry data reveal a low regeneration energy compared to aqueous amine solutions. MOFs with open metal cation sites, such as Mg<sub>2</sub>(dobdc) (dobdc<sup>4-</sup> = 2,5-dioxido-1,4-benzenedicarboxylate), are highly effective in the removal of CO<sub>2</sub> under conditions relevant to H<sub>2</sub> production, including in the presence of CH<sub>4</sub> impurities. Redox-active Fe<sup>2+</sup> sites in the isostructural compound Fe<sub>2</sub>(dobdc) allow the selective adsorption of O<sub>2</sub> over N<sub>2</sub> via an electron transfer mechanism. The same material is demonstrated to be effective at 45 °C for the fractionation of mixtures of C1 and C2 hydrocarbons, and for the high-purity separation of ethylene/ethane and propylene/propane mixtures. Finally, it will be shown that certain structural features possible within MOFs, but not in zeolites, can enable the fractionation of hexane isomers according to the degree of branching or octane number.

## Formal Music Instruction in Grades 5 through 12 Improves Performance in Undergraduate Science and Engineering

Robert Cesario, Dept. of Arts, Languages, and Philosophy, Director of Bands and Orchestras, MS&T

### Abstract:

**Introduction.** Universities have made efforts to increase capacity to alleviate the shortage of professional nurses, scientists, and engineers. While admission numbers have increased, attrition in undergraduate programs remains high. Stringent admission criteria exist, but educators strive to identify additional criteria that are better individual predictors of success. Filling a limited number of slots with students who are unlikely to succeed expends increasingly sparse resources of time, money, clinical, and laboratory space. Evidence suggests that participation in organized

music groups is associated with greater ability in math, reading, cognition, critical thinking, verbal skills, motivation, concentration, confidence, and teamwork. The purpose of this study was to determine if formal music instruction in grades 5 through 12 were associated with improved performance in undergraduate nursing programs and, by extension, presumably science and engineering programs.

**Methods.** The anonymous, online, survey examined the following hypotheses. Undergraduate students who participated in organized music instruction in grades 5 through 12 are more likely to (1) graduate from their chosen programs than students who have not had this experience, (2) have higher grade point averages upon finishing their degrees, and (3) do well on subsequent professional exams. In addition, it was hypothesized that there would be a positive relationship between duration of music instruction between grades 5 and 12 and the exit GPA of undergraduate students. For the survey all 78 accredited associate degree, diploma, and baccalaureate level nursing programs in Texas were invited to participate, yielding 306 completed surveys.

**Results.** The three hypotheses were supported ( $p < 0.001$ ). Of those who had graduated from a nursing program, a greater proportion, 64.8 %, had been in some type of organized music program. Graduates who had participated in music programs had average GPAs between 3.5 and 3.79 at graduation; whereas those who were not in music programs had GPAs between 3.0 and 3.19. A greater proportion of those who had been involved in an organized music group obtained their professional qualifications on their first attempt. The study also revealed that GPA correlated positively with number of years of music instruction ( $p < 0.01$ ).

**Conclusions.** Organized music participation data is objective, quantifiable, and can be collected quickly and inexpensively as it is readily available on the ACT and SAT student profiles. Music in public schools is available to almost all students in the state of Texas and thereby mediates potential bias of race, ethnicity, or socio-economic status. When selecting students for a limited number of nursing, science, and engineering schools, valid predictive criteria are essential and musical education seems to be a highly useful tool in this regard.

## **Microwave Spectroscopy and the New Millennium: Advancing Technology in Two Directions**

Garry S. Grubbs, Dept. of Chem., MS&T

**Abstract:** Microwave spectroscopy has long been a useful tool for studying and characterizing geometric and electronic structure of gas phase molecules and their interactions. This work describes the construction and implementation of two modern microwave instruments: the cavity Fourier transform microwave (FTMW) and chirped pulse Fourier transform microwave (CP-

FTMW) spectrometers. These spectrometers have been equipped with a laser ablation, pulsed supersonic nozzle which allows for the study of many species, both typical and exotic. This technology has also opened the door to spectroscopically study materials useful in creating transistors and microchips in the gas phase with exquisite precision. This can also be used as a tool to investigate typical processes utilized in the manufacturing of these technologies. Specific examples of study and characterization will be discussed.

## **Cancer Biomarkers: From Large to Small Molecules**

Prof. Michael Wang, Dept. of Pathology, University of Missouri-Columbia

**Abstract:** Life is a self-sustaining chemical process in a given organism. Cancer is the first killer of human life in medicine. Although there are great progresses in cancer research and clinical sciences in the past decades, cancer kills approximately 580,000 American citizens and 7.6 million people worldwide each year. From the medical perspective, prevention and early diagnosis of cancer are currently the most feasible solutions to reduce cancer mortality. In this presentation, I will use lung cancer as an example to discuss the current development of cancer biomarkers, an important tool for early diagnosis of cancer.

A cancer biomarker can be defined as the biological molecules found in blood or other biofluids or tissues as an indicator of the presence of cancer in the human body. These molecules may be the specific products of cancer cells or a specific response of the body to the presence of cancer. The molecules may be the mutated DNA fragments, abnormally elevated or reduced mRNA or microRNA, proteins or peptides, and even the small metabolites. In my lab, we utilize real-time PCRs as a basic methodology to detect DNA mutation, DNA methylation and microRNA levels as biomarkers in patient blood samples for early detection of lung cancer. We have identified several specific aberrant DNA methylation loci and abnormally elevated microRNA molecules in blood samples that could distinguish early stage of lung cancer patients from non-cancer controls. The test may be used for lung cancer screening or confirmation in the future. To further increase the sensitivity and accuracy of early cancer detection with an integrated strategy, identifying “oncometabolite” as a new type of cancer biomarker by cancer metabolomic study is a very promising direction. Scientists in chemistry will play a major role for this new discovery.

## **Occurrence and Removal Study of Perchlorate Levels in Missouri Natural and Drinking Waters by Using Ion Exchange Chromatography- Tandem Mass Spectrometry**

Danielle West, Dept. of Chem., MS&T

**Abstract:** Perchlorate ( $\text{ClO}_4^-$ ) has been utilized for a wide range of purposes: munitions, explosives, solid rocket propellant, pyrotechnics, fertilizers, airbag inflators, fireworks, and other industrial applications. Because perchlorate is highly soluble and chemically inert in water, it can be transported vast distances in groundwater or rivers. Therefore, perchlorate can exist in the natural water and drinking water due to its difficulty to be removed by the current water treatment processes. The US EPA has conducted perchlorate occurrence studies and found perchlorate contamination in both groundwater and surface waters serving as drinking water sources for more than 16 million people in at least 26 states nationwide in USA. Perchlorate has been detected in over 4% of public water systems nationally at the level of greater than or equal to 4  $\mu\text{g/L}$ . Missouri has large agricultural use of fertilizer, legal use of fireworks, and an U.S. army base, all of which could contribute to perchlorate contamination to our drinking water. For these reasons, Missouri University of Science and Technology and the Missouri Department of Natural Resources have collaborated in developing a sensitive ion exchange chromatography – tandem mass spectrometry (IC-MS/MS) method for direct analysis of perchlorate without any preconcentration procedures. The method has been applied to screen for the occurrence level of perchlorate in drinking water at 19 water facilities across the state of Missouri and the removal thereof.

## **An Overview of Patent Law and What to Expect when Preparing and Submitting a Patent**

Rebecca Rich, Patent Attorney, Brewer Science Inc., Rolla, MO

**Abstract:** The patent process can be confusing for scientists, both in industry and academia. This presentation is intended help familiarize you with patent terminology, patent law, and the patent process, and the implications for your research, publications, and potential commercialization. We will cover when filing a patent is appropriate, what to do before your patent is filed, the parts and filing of the patent application, the patent prosecution process, and patent issuance. Patent inventorship, ownership, and rights granted in a patent will be presented, with an emphasis on universities and government-funded research. Recent changes in US patent law will be discussed, as well as an overview of international patent filing. A brief discussion of careers in patent law will be included.

## Strong Magnetic COupling and Single-Molecule Magnet Behavior in Azophenine Radical-Bridged Dinuclear Complexes

David Harris, Rang Jeon, & Jesse Park, Dept. of Chem., Northwestern University

**Abstract:** This presentation will describe our efforts to synthesize single-molecule magnets with well-isolated spin ground states by employing radical bridging ligands. In particular, a series of dinuclear metal complexes of the bridging ligand azophenine has been synthesized. Chemical reduction of the iron congener affords a one-electron-reduced species. X-ray diffraction and Mössbauer spectroscopy confirm that the reduction occurs on azophenine to give an  $S = 1/2$  radical bridging ligand. Dc magnetic susceptibility measurements demonstrate the presence of extremely strong direct antiferromagnetic exchange between  $S = 2$  Fe(II) centers and azophenine radical in the reduced complex, giving an  $S = 7/2$  ground state with an estimated coupling constant magnitude of  $|J| \geq 900 \text{ cm}^{-1}$ . Mössbauer spectroscopy and ac magnetic susceptibility reveal that this complex behaves as a single-molecule magnet with a spin relaxation barrier of  $U_{\text{eff}} = 50(1) \text{ cm}^{-1}$ . To our knowledge, this complex exhibits by far the strongest magnetic exchange coupling ever to be observed in a single molecule magnet.

## Molecular Models for the Study of Spin Relaxation and Magnetic Anisotropy

Danna Freedman, Dept. of Chem., Northwestern University

**Abstract:** Quantum computation has the potential to break the most commonly employed encryption scheme and to accurately simulate quantum systems. For these reasons quantum computation is a highly active area of research with numerous qubit candidates proposed thus far. Intuitively, electronic spin can behave in a quantum fashion, therefore could serve as a candidate qubit. Yet thus far research in the area has been hampered by rapid spin decoherence. While synthetic chemists are adept at designing molecules with the ideal spin manifold the design principles for the synthesis of molecules with long coherence time have not been established. Research demonstrating progress towards the first set of unifying principles for quantum computation will be presented with future directions in employing these design principles to synthesize new candidate qubit molecules.

## Investigation of Fluid Flow Behavior in Nano-scale Channels Using Single Molecule Imaging System

Qihua Wu, Dept. of Chem., MS&T

**Abstract:** Many of unconventional tight gas reservoirs contain micro-scale or even nano-scale pores and channels, which are significantly different from conventional reservoirs. However, the fluid flow behavior in the nano-scale pores and channels is not well understood. In this study, a lab-on-chip approach for direct visualization of gas/water two phase flow behavior in nano-scale channels is presented. The nanofluidic-chips were designed and fabricated, and experiments of two phase flow in nano-scale channels with various depths were conducted. Images were captured by using epi-fluorescence microscopy method. The fluids velocities and pressure drop in the nano-scale channels were recorded and flow patterns were characterized. Three different flow patterns, single, annular and stratified flow were observed and their special features are described. Flow regime map was summarized and compared with results in conventional-size channels.

The drainage/imbibition processes in the nano-scale channels were also investigated. The residual saturations of gas or water in the nanochannels with different dimensions were compared. This work provides valuable information for better understanding the single and two phase flow behavior in the nano-scale channels. This study was financially supported by Research Partnership to Secure Energy for America (RPSEA).

## Structural, Electronic, and Catalytic Properties of Metal Complexes Bearing "P-N-P" Ligands

Prof. Panayotis Kyritsis, Dept. of Chem., National and Kapodistrian University of Athens, Athens, Greece

**Abstract:** A common theme in structural bioinorganic chemistry is the presence of sulfur-containing ligands in the active site of metalloenzymes, most commonly in the form of cysteine thiolate ( $RS^-$ ). Very rarely, Cys is replaced by selenocysteine, Se(Cys).

Synthesis of  $M^{(II)}L_2$  complexes ( $M = Mn, Fe, Co, Ni, Cu$ ), with "P-N-P"-type of bidentate LH ligands  $R_2P(E)NHP(E)R_2$  ( $E = S, Se; R = Ph, ^iPr$ ), affords  $M^{(II)}E_4$  metal sites with either tetrahedral or square-planar geometry.<sup>1-3</sup> That series of complexes was recently extended to include octahedral complexes of the general formula:  $[M\{(OPPh_2)(EPPh_2)N\}_2(sol)_2]$ ,  $M = Mn, Co, Ni; E = S, Se; sol = dmf, thf, dmsO$ .<sup>4</sup> All those tetrahedral and octahedral complexes are paramagnetic, and therefore amenable to physicochemical methods that directly probe the

magnetic centers. Recent investigations by Electron Paramagnetic Resonance spectroscopy, as well as their implications for the active sites of specific metalloproteins, will be discussed.<sup>5-7</sup>

“P-N-P”-type ligands have been also employed for the synthesis of Rh<sup>(I)</sup>, Ni<sup>(II)</sup> and Pd<sup>(II)</sup> complexes, showing activities towards hydroformylation,<sup>8</sup> polymerization<sup>9</sup> and C-C coupling reactions,<sup>10</sup> respectively. With proper design of the “P-N-P” ligand framework, such catalysts can be immobilized onto silica, mesoporous molecular sieves and clay solid supports, affording active heterogeneous catalytic systems.

## **New Quantitative NMR Techniques for Determining the Product Yield of Hydrothermal Biomass**

Lingyu Chi, Dept. of Chem., MS&T

**Abstract:** Hydrothermal biomass-to-fuel reactions are a viable pathway for generating liquid biofuels. Newly developed, quantitative HNMR techniques are employed to identify reaction intermediates, understand the mechanisms, and study the kinetics of hydrothermal biomass reactions. The investigations are carried out in a 5-mm NMR tube with a 1-mm capillary tube insert filled with an integration reference standard, so that the aqueous sample drawn from the reactive solution is isolated from the D<sub>2</sub>O lock and the external integration and chemical-shift reference. The external integration reference standard can be used to accurately report mass percentages of biomass reaction products. This presentation will identify some of the practical aspects pertaining to HNMR-based quantitative analysis and highlights some of the limitations, uncertainties, and applications of this particular approach to the analyses of biomass reaction products.