

Chemistry Seminar Abstracts for the Year 2014

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N-acetylcysteine Amide, a Thiol Antioxidant that Prevents Bleomycin-induced Toxicity in Human Alveolar Basal Epithelial Cells

Maria Fan, Dept. of Chem., MS&T

Abstract: Bleomycin (BLM), a glycopeptide antibiotic from *Streptomyces verticillus*, is an effective antineoplastic drug. However, its clinical use is restricted due to the wide range of associated toxicities, especially pulmonary toxicity. Oxidative stress has been implicated as an important factor in the development of BLM-induced pulmonary toxicity. Previous studies have indicated disruption of thiol-redox status upon BLM treatment. Therefore, this study focused on (1) investigating the effects of BLM on A549 cells and (2) elucidating whether N-acetylcysteine amide (NACA) provides any protection against BLM-induced toxicity. Oxidative stress parameters, such as glutathione (GSH), malondialdehyde (MDA), and antioxidant enzyme activities were altered upon BLM treatment. Loss of mitochondrial membrane potential, as assessed by fluorescence microscopy, indicated that cytotoxicity is possibly mediated through mitochondrial dysfunction. Pretreatment with the thiol antioxidant NACA reversed the oxidative effects of BLM. NACA decreased the reactive oxygen species (ROS) and MDA levels and restored the intracellular GSH levels. Our data showed that BLM induced A549 cell death by a mechanism involving oxidative stress and mitochondrial dysfunction. NACA had a protective role against BLM-induced toxicity by inhibiting lipid peroxidation, scavenging ROS, and preserving intracellular GSH and mitochondrial membrane potential. NACA can potentially be developed into a promising adjunctive therapeutic option for patients undergoing chemotherapy with bleomycin.

Applications of Solid State NMR

Prof. Dewey Barich, Dept. of Chem., University of Kansas

Abstract: Solid State NMR (SSNMR) is a powerful analytical technique that offers multiple investigative avenues for studying a wide range of materials and properties. Materials as varied as fine organics, catalysts, soils, lignins, carbonaceous materials, minerals, and biological materials have been studied using SSNMR. This seminar will present several examples including quantitation of physical forms, structural information of complex materials, and conformational detail in crystalline materials.

Aerogels as Diverse Nanomaterials

Abhishek Bang, Dept. of Chem., MS&T

Abstract:

A. Polyurea-crosslinked dysprosia aerogels for drug delivery applications. Aerogels are promising materials as multifunctional drug delivery carriers. In this context, we investigated bio-compatible polymer-crosslinked dysprosia (X-DyOx) aerogels as drug delivery vehicles and demonstrated storage and release of paracetamol, indomethacin and insulin in phosphate buffer (pH = 7.4) or 0.1 N HCl (pH = 1) at 37 °C. As controls we used: (a) orderly-mesoporous silica (n-SiOx-MP4-T045), (b) macroporous polymer-crosslinked silica (X-SiOx-MP4-T045), and (c) randomly mesoporous polymer-crosslinked amine-modified silica (X-TMOS-co-APTES) aerogels. Drug uptake was significantly higher with X-DyOx (up to 35% w/w) relative to n-SiOx-MP4-T045 and X-SiOx-MP4-T045 (16-19% w/w), and was comparable to that of X-TMOS-co-APTES aerogels (up to 30% w/w). X-DyOx aerogels have shown much slower release rates (100% release in ~60 h) than their counterparts, whereas very fast to moderate drug release behavior was observed (100% release in 0.5 to 24 h). Considering that dysprosia is strongly paramagnetic, hence, can be focused magnetically, and can be also neutron-activated, X-DyOx-based materials have the potential of becoming multifunctional drug delivery vehicles.

B. Flexible polyurethane-acrylate aerogels for thermal insulation and environmental remediation. Flexible aerogels are particularly attractive materials for thermal insulation of sub-sea oil pipes, cryogenic tanks and oil-spill absorption, whereas a high degree of foldability is desirable. Herein, we report flexible aerogels via polyurethane-acrylate chemistry. For this, we designed a star shape monomer possessing urethane linkages of a triphenylmethane core with acrylate moieties. For comparison reasons, ethylene glycol dimethacrylate or 1,6-hexanediol diacrylate are used as variable length chain extenders, and their effect on the material properties of the resulting polyurethane-acrylate aerogels was investigated. Lower density polyurethane-acrylate aerogels (~0.14 g cm⁻³) were macroporous and flexible (by 3-point bending test), while higher density samples (0.66 g cm⁻³) were rigid and mechanically strong (by compression testing). Those properties were independent of the chain length of the extender, pointing to a nanoscopic origin for their flexibility, rather than to a molecular one.

C. Polydicyclopentadiene (pDCPD) aerogels: Nanostructure control via ring opening metathesis polymerization (ROMP) induced with Grubbs catalysts I and II. pDCPD polymers synthesized via ROMP are emerging as attractive materials for diverse applications ranging from separation media to body armor. They are synthesized from readily available dicyclopentadiene (DCPD), an inexpensive byproduct of petroleum refinery. Here, we developed pDCPD-based aerogels using two different Grubbs catalysts (GC-I and GC-II) with different catalytic activity towards ROMP. pDCPD based wet-gels synthesized from GC-II show excessive swelling in toluene (up to 200% v/v) followed by de-swelling and uneven shrinkage in acetone, resulting in severely deformed aerogels. However, wet-gels using GC-I retain their shape throughout processing. Percent crosslinking calculated via solid state ¹³C NMR shows that

GC-II-catalyzed pDCPD aerogels undergo only 4-5% crosslinking as compared to 17-23% when GC-I is used. Microscopically, pDCPD aerogels derived from GC-I and GC-II catalysts show different morphology (fibrous and particulate, respectively)

Polyacrylamide Microgels via Water-Free Inverse Emulsion Polymerization

Zun Chen, Dept. of Chem., MS&T

Abstract: Crude oil is an internationally important commodity raw material for energy and chemical industries. After primary, by natural pressure, and secondary, by water and gas driven, stages of oil recovery from a well field source, more than two thirds of the original oil remain in the reservoir. In these tertiary reservoirs, the directly water- or even polymer-flooding assisted recovery of reservoir resources are not efficient for displacing resource fluid due to severe heterogeneity of the geologic formations. The displacing agents, e.g., water, prefer low resistance wide pore channel flow of low pressure resistance compared to narrow pore, high pressure resistance flow. Therefore, excess water production becomes a major problem, which leads to early abandonment of otherwise unrecoverable hydrocarbon resources. To solve this problem, polymer gel treatments of the injection wells are being developed to preferentially limit flow through the ‘thief’ zones. Polymer gels can be cost-effective methods to improve sweep efficiency to reduce excess water production during oil recovery. We describe a novel polyacrylamide microgel synthesis by a pseudo-inverse emulsion polymerization in the absence of water. Two different crosslinkers are employed in this study to give the particle ‘smart’ properties, e.g., 2 stages of size expansion that are temperature sensitive. When put into water, the original dry particle can swell by as much as 25 times in size under low temperature (e.g., 40 °C). Exposure to a harsh reservoir environment, for instance, the stimuli of high temperature (e.g., 90 °C), can induce cleavage of one of the two crosslinking types to enable further expansion. The microgel access to targeted pore channels is thus controlled to realize changes in the reservoir flow profile within the geologic formation.

Accelerating Functional Genomics Using Mass Spectrometry

Dr. Trent R. Northen, Lawrence Berkeley National Laboratory, Berkely, CA

Abstract: Microorganisms exhibit complex metabolism and metabolic interactions with their environment, large parts of which remain unknown. Deficiencies in functional annotations of microbial genomes as well as incomplete knowledge of small molecule repertoires (metabolomes) of microorganisms limit the understanding of their metabolism. This talk will

introduce mass spectrometry based metabolomics and approaches to link these to microbial genomics. Including recent work connecting genes to the utilization of specific metabolites in bacteria by profiling metabolite utilization in libraries of mutant strains. Here, untargeted mass spectrometry-based metabolomics was used to identify metabolites utilized by soil microbes. Targeted high-throughput metabolite profiling of spent media of 8042 individual mutant strains was performed to link utilization to specific genes. Using this approach we identified genes of known function as well as those required for the metabolism of 'novel' metabolites. This work is being extended for the high throughput characterization of novel natural products using acoustic printing of nanoliter volumes coupled to nanostructure initiator mass spectrometry (NIMS).

Chromic Phenomena- Reversible Color Change Chemistry

Dr. Harlan J. Byker, Chief Executive Officer, Pleotint, LLC

Abstract: Electrochromic, thermochromic, and photochromic technologies have been used in many intensive and expensive attempts at commercial product development over the last 50 years. The chemistry and materials behind chromic technologies are described and a discussion of the commercialization attempts is given. A particular focus is given to the use of thermochromic materials for sunlight responsive, dynamic, energy saving windows which are now starting to be commercialized.

The Challenges and the Fun of Internal Rotation in Rotational Spectroscopy

Dr. Peter Groner, Dept. of Chem., UMKC

Abstract: Internal rotation and other large-amplitude motions (LAMs) in molecules affect rotational, vibrational and electronic energy levels and their respective spectra. Manifestations of the interactions between internal rotation and these other degrees of freedom are the appearance of spectra of conformers and shifts or splittings of spectral lines. A short review of the basics of rotational and vibrational spectroscopy is followed by explanations and illustrations of these effects. They become more interesting and more challenging in the presence of two or more LAMs. Significant progress has been made over the last two decades in instrumental and experimental techniques (sensitivity, resolution), data analysis and theoretical developments to study and understand the effects of internal rotation. For molecules with one or two methyl group internal rotors, it is now possible most of the time to assign and fit thousands of spectral lines to experimental precision and to high rotational quantum numbers. Thorough analysis of spectra may provide information about torsional potential functions, heights of barriers to internal

rotation, and conformational energy differences. Barriers determinable by rotational spectroscopy are lower than barriers determinable by NMR. The spectroscopy of molecules with internal rotation has found applications in radio-astronomy and the planetary sciences.

New Cathode Materials for Li-ion Batteries

Hooman Yaghoobnejad Asl, Dept. of Chem., MS&T

Abstract: Li-ion batteries play an essential role for powering-up a variety of equipment, from small portable electronic devices to heavy Electric vehicles (EVs). Research and development in this field is actively proposing new and alternative chemistries in cathode design from transition metal oxides in the first generation of these batteries to polyanion-based (PO_4 , SO_4 , SiO_4 , and BO_3/BO_4) compounds. In this context we are utilizing new synthesis routes to make novel compounds with combinations of different polyanions and transition metal compounds. The advantage of using polyanions rather than pure oxide in cathode composition is the added safety feature that comes from the strong covalency between the oxygen atom and the central main group element (P, S, B, or Si) in the polyanion. The presentation will focus on three new compositions $\text{Li}_3\text{Fe}_2(\text{HPO}_3)_3\text{Cl}$, $\text{LiFePO}_4\text{NO}_3$ and $\text{LiFeB}(\text{PO}_4)_2(\text{H}_2\text{O})_2$, recently discovered in our laboratory that show promising electrochemical activity for Li-ion battery. The details of synthesis, structure determination employing X-ray diffraction (single-crystal and powder) and results of electrochemical studies in Li-ion cells towards reductive lithiation and oxidative delithiation will be discussed. This presentation will also cover how fluoride substitution can tune the cell voltage in a particular structure type, namely tavorite, $\text{LiFePO}_4(\text{OH})_x\text{F}_{1-x}$ where $0 \leq x \leq 1$. In the conclusion a discussion relating the structure to the cell performance and also a comparison with some of other known cathode materials will be presented.

The Design and Application of a TPD Based Photorefractive Composite to Aberrated Image Restoration

Yichen Liang, Dept. of Chem., MS&T

Abstract: Organic photorefractive (PR) material has shown its considerable potential in practical applications due to its high figure of merits including low fabrication-cost, possibility of properties tuning by changing its composition and faster response time, etc [1]. In our approach, [1,1'-Biphenyl]-4,4'-diamine-*N,N'*-bis(3-methylphenyl)-*N,N'*-diphenyl (TPD) was used as the charge transfer matrix for the PR composite due to its high value of charge mobility among organic charge transporting materials. In addition, C_{60} and 4-azacycloheptylbenzylidene-

malononitrile were included in the composites as photo-sensitizer and nonlinear chromophore, respectively. To improve the performance of PR material, quantum dots (QDs) were doped inside the composites, which results in a dramatic improvement of response time. By surface modification process, a charge transfer ligands capped QDs were synthesized and it showed a significant enhancement of photoconductivity in the TPD based composites. The designed PR material has shown its ability in phase aberration elimination. This demonstrates the value of PR material in optical communication applications.