Abstract Submission LIst

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Session 1:

Kyralyssa Hauger, Robert H. Neilson*

Title: *Synthesis and Characterization of Silylanilino Derivatives Containing Boron*

Abstract: Boron compounds containing silicon-nitrogen functional groups have a wide variety of derivative chemistry. In current research, we are investigating compounds containing Si-N groups attached to a 4-substituted Ph group to afford silylanilino derivatives. Due to the variety of reactions that can occur on the boron, these compounds hold the potential to be precursors to new inorganic-organic hybrid polymers and/or novel ring system. We report here the synthesis, characterization, and reactivity of some representative examples of (silylanilino)boranes.

Natalie Trinh, Kenneth J. Balkus Jr.*

Title: *Synthesis and Characterization of PIM-1/Cobalt SALEN as a Controlled and Site Specific NO Delivery Agent*

Abstract: Nitric oxide (NO) plays a significant role in many physiological functions including neutrotransmission, immunological responses, blood pressure control as well as antioxidant action. Recently, it has been shown that external applications of NO can promote the process of healing infected wounds . The importance of NO as a signaling molecule suggests potential applications for controlled and site specific NO delivery agent for wound healing. Transition metal complexes have been reported to modulate the concentration of NO in cellular environment. The incorporation of transition metal of NO complexes onto a support matrix will generate a suitable NO storage and delivery agent for wound healing. In this work, Polymer of intrinsic microporosity (PIM-1) complexed with N,N'-Bis(salicylidene)ethylenediamino cobalt (II) (CoSALEN) was synthesized using a simple precipitation method. Complexation was confirmed by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Solid state UV-Visible and Fluorescence Spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

J.P. Nimmo II, Peter Kroll*

Title: *First-principles studies of Amorphous Silicon Oxycarbide: Relating Structure to ^{29}Si NMR Data*

Abstract: Silicon oxycarbide ceramics, a phase composition of SiO_2, SiC, and C, exhibits a hierarchical structure with distinct structural elements at various length scales. Experimental data reveals nm-segregations of graphite-like carbon incorporated in a glassy matrix. However, the exact inclusion of the so-called “free” carbon, whether through interfacial bonds or via non-bonding van-der-Waals interactions, is unsolved.

In this study we show that it is possible to quantify interfacial bonding of carbon to the SiCO glass host via ^{29}Si nuclear mass resonance (NMR). We generate a variety of different SiCO models, optimize them and compute ^{29}Si chemical shifts with accurate electronic structure calculations. Based on results computed for thousands of Si sites we develop angular correlation functions that predict ^{29}Si chemical shifts using the Si-O-Si angles surrounding a Si nucleus for SiO_4-, SiO_3C-, and SiO_2C_2-tetrahedra. We find a large difference for correlation functions of SiO3C-tetrahedra depending on whether the bonding C atoms are four-fold (sp^3) or three-fold (sp^2) connected. This unique difference is used to analyze experimental ^{29}Si NMR spectra. While the angular correlation for SiO_4-tetrahedra provides the distribution of Si-O-Si angles in a material, the two different correlations for SiO_3C-tetrahedra allows quantification of sp^2-C bonding to Si.

Rebecca Weber, Chris Jeffrey, Zijun Yu, George Schoendorff, Angela K. Wilson*

Title: *The Effects of DFT Functionals on the Structures of Lanthanide Trifluorides*

Abstract: Main group species have been the primary focus of computational chemistry for decades, enabling a well-developed hierarchy of methods to evolve. However, for the lanthanides, there has been much less focus, and a hierarchy of methods has not evolved. In the work, density functional theory was utilized to study the series of LnF_3 (Ln = La-Lu). Optimized geometries and vibrational frequencies were calculated and compared to experiment. Five different functionals (B3LYP, PBE0, BP86, SVWN, and M06) were used in conjunction with effective core potentials (ECPs) and all-electron basis sets to determine the most accurate method for structural determination.

Eugenia Narh, Frederick M. MacDonnell*

Title: *Structure-activity Relationships and Redox Activity of Bioreducible Ruthenium(II) Polypyridyl Complexes*

Abstract: The bioreducible ruthenium(II) polypyridyl complexes $[(phen)_2Ru(tatpp)]Cl_2$ (**MP**) and $[(phen)_2Ru(tatpp)Ru(phen)_2]Cl_4$ (**P**) (where tatpp is 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-1:2''',3''']-pentacene) have been shown to cause DNA cleavage under aerobic and anaerobic conditions, have selective cytotoxicity and promising anti-tumor activity in mice. Their DNA cleavage activity is attributed to the redox activity of the tatpp ligand at modest (biologically accessible) reduction potentials. Structural variation of the redox-active ligand was performed, and the relationship of the redox activity of the modified complexes and their effectiveness to cleave DNA was investigated. This paper will present the development of novel related ruthenium(II) polypyridyl complexes consisting of varying aromatic bridging ligands and their structure-activity relationships as compared to the parent complexes **MP** and **P**.

Chris Jeffrey, Rebecca Weber, George Schoendorff, Angela Wilson*

Title: *Gauging Performance of Density Functionals for Determination of the Structure of Lanthanide Trifluorides*

Abstract: Of the lanthanide trihalidies, the trifluorides have the largest wealth of data (i.e., structures, frequencies) from experiment available and so are ideal candidates for gauging computational methods. In the present study, density functional (DFT) methods are evaluated for their ability to predict the structure and vibrational frequencies of the lanthanide trifluorides relative to experimental data. DFT functionals used include B3LYP, M06, BP86, PBE0, and SVWN, and the calculations have been done using the Stuttgart segmented effective core potential (ECP).

Zainab H. Alsunaidi, Thomas R. Cundari*, and Angela K. Wilson*

Title: *Amination of Benzene on the Ni (111) Surface: A Computational Study*

Abstract: Aniline plays a significant role as an intermediate in industrial applications. The most widely used production method of aniline is comprised of multiple reactions and it is inconsistent with the greening trend in chemical production. Thus, production of aniline by direct amination of benzene has long been a subject of interest. Here, an alternative route of producing aniline by a direct amination of benzene on the Ni (111) surface has been studied using spin-polarized slab model calculations with the PBE density functional. Possible reaction pathways of the interaction between ammonia and benzene were examined on the Ni (111) surface. Bond dissociation energies of the isolated reactants and products, adsorption sites and energies, structural analysis, and electronic density of states were also determined and will be discussed.

Anne Marti, Kenneth J. Balkus Jr.*

Title: *The Fabrication of a Zeolite Imidazolate Framework (ZIF) Membrane for the Separation of Ethanol from Water*

Abstract: Substituted Imidazolate Material-1 (SIM-1) is a zeolitic imidazolate framework (ZIF) that crystallizes in the SOD topology and is an interesting material for the separation of water/ethanol as it has pore size of 8 Å and a pore aperture < 3.4 Å. Herein, we report the synthesis of nano SIM-1 using an *in-situ* and linker exchange method. SIM-1 membranes were then fabricated by post synthetic modification (PSM) of a pressed wafer. Nanocrystals of SIM-1 wafer were crosslinked by a Schiff base condensation reaction with ethylenediamine. The SIM-1 membranes were then tested for the separation of ethanol from water at room temperature. The selectivity was 100 % over the course of many cycles for both membranes whereas membranes prepared without PSM degrade after only 1 separation cycle.

Kevin J. Bruemmer, Sara Merrikhihaghi, Christina Lollar, and Alexander R. Lippert*

Title: *^{19}F Magnetic Resonance Oxidative Decarbonylation Reaction-based Probes for the Specific Detection of Peroxynitrite*

Abstract: Peroxynitrite ($ONOO^-$) is a highly reactive species that is associated with aging, cardiovascular disease, and cancer. The cause and effects of $ONOO^-$ production in biological systems is not well understood due to a lack of direct and specific detection of $ONOO^-$. We report a novel reaction-based probe for the specific detection of $ONOO^-$ using ^{19}F magnetic resonance spectroscopy. We report a newly discovered oxidative decarbonylation reaction of ^{19}F-labeled isatins which, when treated with $ONOO^-$, provide anthranilic acid derivatives. ^{19}F magnetic resonance detection of these species provides a convenient and low-background readout of $ONOO^-$ formation.

Matt Sherman, Youngha Ryu *

Title: *Synthetic Caffeine Riboswitches as Genetic and Analytical Tools*

Abstract: The goal of this project was to identify a synthetic riboswitch for caffeine. The caffeine synthetic riboswitch will be useful to regulate gene expression in response to caffeine and detect caffeine in complex biological samples such as urine and blood. A riboswitch is a sequence of non-coding RNA that can specifically binds a ligand and thereby controls expression of genes associated with the biosynthesis, transport, or degradation of the specific ligand. In order to develop the caffeine synthetic riboswitch, we modified the theophylline-binding domain of a synthetic theophylline riboswitch. Caffeine is structurally similar to theophylline differing only by one N-methyl group. A total of 11 bases that showed significant interactions with theophylline in the theophylline riboswitch were randomized in the library design. The library was constructed by overlapping extension polymerase chain reaction and inserted into pTrp-TheoRS-CatUpp, a plasmid that encodes the upp-cat fusion gene under control of pTrp promoter. GH371 E. coli cells were transformed with the library and subject to a few rounds of the positive selection on chloramphenicol in the presence of caffeine and the negative election on 5-fluorouracil in the absence of caffeine. From the genetic screening, 192 individual single colonies were selected and tested for chloramphenicol resistance in the presence and absence of caffeine. Two clones clearly showed chloramphenicol resistance only in the presence of caffeine. These two caffeine riboswitch variants were sequence and will be further tested for colorimetric and fluorescence assays using beta-galatosidase (LacZ) and green fluorescence protein respectively as reporter genes.

Cindy Nguyen, Nimanka P. Panapitiya, Kenneth J. Balkus, Jr., Inga H. Musselman, and John P. Ferraris*

Title: *Use of Colloidal Metal-Organic Frameworks (MOFs) as Multifunctional Compatibilizers for Immiscible Polimide/Polybenzimidazole Blend Membranes*

Abstract: Fabrication of membranes comprising polymer blends, can combine the high gas permeability of one polymer with the high gas selectivity of another. However, due to the inherent immiscibility of polymers, blending can result in uncontrollable phase separation. Since the gas separation properties depend on the morphology of the membranes, the phase separation must be controlled. Here in, as synthesized colloidal zeolitic framework-8 (ZIF-8) was used as a multifunctional compatibilizer, for immiscible polyimide (PI)/ polybenzimidazole (PBI) blend membranes. The use of ZIF-8 is advantageous, since it helps to control phase separation while contributing to improve gas separation properties. PI: PBI (50:50) blend membranes were fabricated first and the membrane microstructure was examined with SEM imaging. Extensive phase separation was evident as indicated with large and non uniform distribution of the dispersed phase. Upon the incorporation of 5 wt% colloidal ZIF-8 the dispersed domain sizes became smaller and uniform suggesting a better compatibility between the polymers. As the ZIF-8 loading was further increased, the membrane morphology became even more uniform. Synthesis of both colloidal ZIF-8 and polyimide, characterization of fabricated membranes and the gas separation properties determined with the blend membranes will be presented.

Dalton Kim, Nicolay V. Tsarevsky, and Patty Wisian-Neilson*

Title: *Modification of Polyphosphazenes by Copper-catalyzed Reactions*

Abstract: *Polyphosphazenes* are a class of inorganic polymers characterized by alternating phosphorus and nitrogen atoms. While there are two general synthetic routes to polyphosphazene scaffolds, we describe the modification of P-alkyl and P-aryl polyphosphazenes that are synthesized exclusively through condensation polymerizations.

This study describes the synthesis and characterization of antimicrobial polyphosphazenes by the post-polymerization modification of poly(methylphenylphosphazene) **2**. Discussion will focus on the synthesis of azido-derivatives and the subsequent synthesis of 1,2,3-triazoles *via* Huisgen-type azide-alkyne cycloadditions.

Session 2:

Tejaswi Bhavanam, Ben Jang *

Title: *Synthesis, Modification, and Characterization of Supported Gold Catalysts for Selective Hydrogenation of Acetylene in the Presence of Ethylene*

Abstract: The selective hydrogenation of acetylene is an industrial process to remove traces of acetylene in ethylene stream for polyethylene production. Titania supported gold catalysts are prepared by impregnation (IM) and deposition precipitation with urea (DPU). 5% Au/TiO_2 catalysts are prepared by IM post washed with 1M NH_3, DPU(water washing) and DPU(Na_2CO_3 washing) are tested for selective hydrogenation of ~1% acetylene in excess of ethylene. The performance of 5%Au/TiO_2 catalysts depends on the method of preparation and the procedures afterward. Non- thermal RF plasma is an effective way to modify and enhance the activity of the catalysts. Catalysts prepared IM, DPU(water washing) and DPU(Na_2CO_3) has shown increase in activity after the H_2 plasma treatment. In addition, catalysts prepared by IM followed by post wash with NH_3 and then subjected to a non-thermal RF plasma for 15 min have shown higher acetylene conversion, selectivity and yield when compared to catalysts prepared by DPU.

Volumetric CO chemisorption measurements are performed on gold catalysts at different pretreatment conditions which are prepared by IM and DPU methods. The results of CO chemisorption of the catalysts will be related to the activity of the catalysts.

Matthew J. Carlson, Nathan J. DeYonker, Angela K. Wilson*

Title: *Exploration of Weighted Core-valence Basis Sets for the Correlation Consistent Composite Approach for Transition Metals*

Abstract: The correlation consistent Composite Approach for transition metals (ccCA-TM) has been shown to predict thermochemical properties for transition metal species to within 3 kcal/mol from experiment, on average, and at a reduced computational cost compared to CCSD(T) with a large basis set. Traditionally, core-valence correlation is described in this methodology using core-valence correlation consistent basis sets (cc-pCV*n*Z). The effect of using weighted core-valence basis sets (cc-p*w*CV*n*Z) in this step for the calculation of enthalpies of formation of a variety of first row transition metal compounds is investigated.

Do Nguyen, Kenneth J. Balkus, Jr., Inga H. Musselman and John P. Ferraris *

Title: *A Fast and Facile Synthetic Route for Zeolitic Imidazolate Framework 11 Nanoparticles*

Abstract: A rapid and easy procedure for synthesis of zeolitic imidazolate framework (ZIF) 11 nanoparticles was developed that included adding triethylamine and elevating the synthesis temperature. Using this method, the synthesis time was shortened from 3 days, as reported in the literature, to 30 minutes. The product was characterized to validate its crystallinity, particle size, and thermal stability. X-ray diffraction results showed that the correct crystallinity for ZIF-11 was obtained. The average size of ZIF-11 particles was determined from scanning electron microscopy images as 40nm. In addition, the ZIF-11 material exhibited high thermal stability up to 550^{o}C. Nanoparticles ZIF-11 will be incorporated into polymer blend systems for morphology control as well as gas separation purposes.

Dani Setiawan, Rob Kalescky, Elfi Kraka, and Dieter Cremer*

Title: *A New Approach for a Quantitative Description of Aromatic and Antiaromatic Molecules Based on Vibrational Spectroscopy*

Abstract: Aromaticity is an important concept in chemistry explaining the stability of a molecule on the basis of its □-electron delocalization. Many approaches have been developed to define and measure the degree of aromaticity using, *e.g.,* NMR chemical shifts, resonance energy analysis, electron densities, or molecular geometry parameters. In this work, a different approach is presented, which is exclusively based on vibrational spectroscopy. From experimental or calculated vibrational frequencies, local CC stretching force constants can be derived, which provide a reliable measure of the relative bond strength orders and reflect in this way the degree of □delocalization in a conjugated system. We can derive an aromaticity or antiaromaticity index directly from measured (calculated) vibrational frequencies. Results for a set of aromatic, non-aromatic, or anti-aromatic systems will be shown. It is demonstrated that especially in multicyclic systems, □-delocalization preferentially uses that path (peripheral or ring specific) that leads to the highest (lowest) degree of (anti)aromaticity. The method presented offers the possibility of a simple, quick, and direct measurement of the degree of aromaticity of a molecule utilizing vibrational spectroscopy.

Michael R. Jones, Angela K. Wilson*

Title: *Tyrosine-Phosphorylation in the Activity of Inhibitor of κB Kinase-β*

Abstract: Dimerization of the inhibitor of κB kinase subunit β (IKKβ) is required for its activation in aberrant regulation of the nuclear factor-κB (NF-κB) pathway that is involved in inflammatory diseases. Molecular dynamics simulations were used to investigate the impact of serine and tyrosine phosphorylation on IKKβ dimer. Intermolecular interactions, thermodynamic properties, and conformational changes were compared among a monomer and two different dimers and suggest that there is selectivity in the activation of IKKβ.

Jiaqi Wang, Angela K. Wilson*

Title: *Computational Study of the Oxidative Cleavage of C-H, C-C, C-O Bonds by Late First-Row and Second-Row Transition Metal Atoms*

Abstract: Small organic species methane, ethane, and methanol were utilized as the model molecules to study the oxidative insertion of C-H, C-C, and C-O sigma bond by late first-row and second-row transition metal atoms (Fe, Co, Ni, Cu, Ru, Rh, Pd, and Ag) to investigate the intrinsic catalytic properties of metals for bond activation reactions. Enthalpies of reactions (ΔH°_{298}) and activation energies were considered to study the thermodynamic and kinetic feasibilities of the model reactions. Density functionals (PBE, B97D, BLYP, TPSS, M06L, B971, B3LYP, PBE0, TPSSh, M06, and B2PLYP) and aug-cc-pVTZ (PP) basis set have been applied for equilibrium states and transition states. The results were compared to the corresponding values from CCSD(T)/CBS calculations.

Alan Humason, Wenli Zou, and Dieter Cremer*

Title: *What id the Longest Carbon-Carbon Bond in Chemistry? Investigation of 11,11-Dimethyl-1,6-methano[10]annulene*

Abstract: There are many examples with long CC interactions. However most of these involve stacking interactions such as the ‘pancake bonds’ and do not correspond to real covalent CC bonds. Among the molecules theorized to exhibit the longest CC bond in chemistry is the valence tautomer **1b** of 11,11-dimethyl-1,6-methano[10]annulene **(1a)**. For this molecule, the central C1,C6 interatomic distance has been determined by x-ray crystallography to be 1.808 A.[1] The nature of the equilibrium **1a-1b** and this bonding interaction was investigated by MP2, MP4, CCSD, CCSD(T), BD, BD(T), CASSCF, CASPT2, NEVPT2, MR-AQCC, and DIP-EOM-CCSD. Apart from this, various DFT functionals and REKS were used. All methods but those including both dynamic and non-dynamic electron correlation failed. A (14,14) active space was needed to get sufficient accuracy to determine the PES in the C1,C6 direction.

The molecule rapidly interconverts from **1a** to **1b** via a low barrier and executes in this way a large amplitude C1,C6 vibration.[3] Electron density, energy density, local mode force constant, and chemical shift calculations clarify the nature of the C1C6 interaction.

Sajani A. Basnayake, Kenneth J. Balkus Jr.*

Title: *Synthesis of a Novel Metal Organic Framework (MOF) Using a Novel Linker*

Abstract: Metal Organic Frameworks (MOFs) are porous crystalline materials consisting metal ions/clusters bridged by organic ligands. They have high surface areas (>1000 m^2/g) and thermal stability (~400^{o}C). In this study, we have created a new organic linker by reacting p-phenylenediamine with 2-imidazolecarboxaldehyde to form N^1,N^4-bis((1H-imidazol-2-yl)methylene)benzene-1,4-diamine. This linker has shown potential for forming MOFs when reacted with Zn^{2+} under mild solvothermal synthesis conditions. It was found that if the reaction was carried out at lower temperature with slow conditions, a dense and less thermally stable framework is formed. However, when the reaction was performed at slightly higher temperature, a different crystalline phase with high porosity and high thermal stability was formed. The two phases were characterized using X-Ray diffraction, Thermogravimetirc analysis, IR spectroscopy and N_2 adsorption.

Zahra Bassampour, David Y. Son

Title: *Selective Nucleophilic Replacement Reactions of Substituted Silanes*

Abstract: Several fundamental studies were conducted to check the preference of silicon to bind to amines, alcohols, and thiols. High yield, clean and rapid conversion from both $R_3Si\text{-}NHR'$ and $R_3Si\text{-}NR'_2$ to $R_3\text{-}Si\text{-}SR'$, and also from $R_3Si\text{-}SR'$ to $R_3Si\text{-}OR'$ were observed. Also, the rapid conversion of $R_3Si\text{-}NR_2$ to $R_3Si\text{-}NHR$ was realized. The ability to exploit this selectivity for the synthesis of new materials was investigated. In order to exploit the observed selectivity, several attempts were made to synthesize the monosubstituted compound, $Me_3SiSCH_2CH_2NH_2$. All of the reactions resulted in the formation of the disubstituted compound, $Me_3Si\text{-}SCH_2CH_2NH\text{-}SiMe_3$, instead of the monosubstituted compound. In additional experiments, the corresponding dithiocarbamate, $Me_3Si\text{-}SCH_2CH_2NHSCS\text{-}SiMe_{3,}$ was made from the disubstituted compound in high yield. In the second part of study, the selective syntheses of monosubstituted compounds by the reaction of Me_nSiCl_{4-n} , n=0-3, and ethanolamine were attempted. The compounds $Me_nSi(OCH_2CH_2NH_2)_{4-n}$ are potential cores for dendrimer synthesis, and can be incorporated into degradable epoxy networks.

My-Linh Van, Anne M. Marti, Kenneth J. Balkus Jr*

Title: *Enzyme Immobilization in a Metal-Organic Framework*

Abstract: Metal Organic Frameworks (MOFs) are porous crystalline structures constructed by metal centers and organic linkers. MOFs have large surface areas, high porosity, tunability, and chemical and thermal stability. They are typically used for gas storage/separations, chemical sensing and catalysis. Our focus is enzyme immobilization. Enzymes are useful in catalytic reactions because they show high selectivity; however they exhibit low thermal stability and low solubility stability in organic solvents. By using MOFs as a matrix for the enzyme, stability issues can be overcome. Through immobilization, the enzyme is expected to thrive at higher temperatures, and in a wider range of solvent systems.

STU-1, a gyroidal MOF, is an ideal matrix because it has high surface area (1225 m^2/g), large pores (27.3 x 15.4 Å) and exceptional thermal stability (420˚C). STU-1 is constructed using zinc nitrate hexahydrate and BIm (1,2-bis((5H-imidazol-4-yl)methylene)hydrazine)3. The enzyme of interest is Microperoxidase-11 (MP-11). Its size is 17.5 Å. The presence of the iron-heme group in MP-11 allows for the oxidation of organic molecules such as AmplexUltraRed to Resorufin.

MP-11 was successfully immobilized in STU-1 crystals and will be used in catalytic reactions in comparison to MP-11 by itself to determine the effectiveness of the immobilized enzyme.

Margaret J. Risher, Chen L. Yeow, William L. Whaley*, Rajani Srinivasan, Peter Bell

Title: *Isolation and Characterization of Isoflavones from Osage Orange: Project-based Laboratory Exercises for Introductory Organic Chemsitry*

Abstract: A series of project-based laboratory exercises involving the isolation and structural characterization of two isoflavones from the fruit of Osage orange was previously published (The Chemical Educator, 2007). These exercises were found to be appropriate for advanced undergraduate courses. After extensive testing, they were found to be too demanding with respect to time and effort for the typical class of Introductory Organic Chemistry that is taught at non-selective regional universities. A new series of extraction and separation protocols has now been developed that is much more time efficient and easier to perform for the average student. Previously, the extraction of isoflavones from the dried plant material was achieved with a solvent extractor of the Soxhlet type. A new protocol, that involves a stoppered flask and a Buchner funnel, has been found to adequately remove latex in a hexane fraction and also extract the isoflavones in an ethyl acetate fraction. After concentrating the ethyl acetate fraction, it was loaded onto a commercial chromatography cartridge containing basic alumina (Sep-Pak, Alumina-B, Waters, Corp.). Remaining traces of latex were eluted with pure hexane and then osajin was eluted with a mixture of 80% hexane and 20% ethyl acetate. Pomiferin was then eluted with pure methanol. The protocol provided approximately 3 to 5 milligrams of each compound. This amount is sufficient for structural verification using UV-Vis and FT-IR spectroscopy (ATR probe). The antioxidant activities of osajin and pomiferin were also compared by a reaction with diphenyl-picryl-hydrazyl (DPPH) radical monitored by absorbance at 515 nm.

Daniel Galles, Alysia Lowe, Samsuddin Mahmood, Dennis W. Smith Jr. and Kenneth J. Balkus Jr.*

Title: *Coated Acrylonitrile-based Terpolymer Prolongs Release of NO for Wound Healing Applications*

Abstract: Nitric oxide (NO) is an important molecule used in physiological processes, and is naturally synthesized by the body. Binding of this molecule to a solid storage material provides an effective means to introduce an increased concentration of NO in a wound area, increasing the rate of healing of a wound. The terpolymer acrylonitrile-co-1-vinylimidazole-co-isoprene (AN/VIM/IP) has been shown to bind NO and form the diazeniumdiolate donor group (NONOate). NONOates are desirable because they release 2 molar equivalents of NO at physiological temperature and pH. A solution of the terpolymer was made by dissolving solution-spun fibers in DMF. A fiber mat was then made by electrospinning the solution. The fiber mat was coated with a biodegradable polymer in order to slow the release of NO from the mat and improve the wound healing process over time. The results for bonding NO to the terpolymer and its release over a seven day period, as well as degradation of the polymer coating will be presented. After the fiber mat has been loaded with NO, the mat can be applied as a bandage to a wound area in order to improve healing of the wound.

<u>Mai Khong</u>, *Nimali Abeykoon, Shashwat Chaturvedi , John P. Ferraris**

Title: *Fabrication of Porous Carbon Nanofibers for Supercapacitors using Polybenzimidazole Incorporating Colloidal ZIF-8 Nanocrystals*

Abstract: Supercapacitors store energy in electric fields, which are created by the interaction between the capacitor's two conducting surfaces. The advantages of supercapcitors are the high power density and the stable cycle life comparing to batteries. However, in supercapacitors, the application area is limited because of the lower energy density. Porous carbon materials with large surface areas and suitable pore structures as active materials are important for supercapacitors to achieve high energy density. In this study, porous carbon nanofibers were fabricated by using electrospun polybenzimidazole (PBI) and zeolitic imidazolate framework 8 (ZIF-8) with varying weight loadings of colloidal ZIF-8 (10,20 and 50 wt%). The electrospun mats were stabilized at 450℃ to prevent premature decomposition. Afterwards, the mats were carbonized at varying temperatures for one hour and then placed under CO_2 activation for an additional hour. The combination of PBI and ZIF-8 leads to carbon nanofibers that have high porosity. Coin cell devices using the aforementioned porous carbon electrodes were fabricated, and cyclic voltammetry and charge-discharge tests were conducted. Characterization and the electrochemical performance of resulted carbon fibers will be presented.

<u>Michael Tshisekedi</u>, Giang Vu, Meisa Keivani, Phillip Duong, Ivone Menchaca, Phillip M. Pelphrey*

Title: *Synthesis and Evaluation of Novel DHFR Inhibitors*

Abstract: The synthesis of pharmaceutically active compounds is of great importance due to limitations of current medicinal agents currently on the market. The bacteria *Cryptosporidium hominus* and *Bacillus anthracis* have been labeled as highly pathogenic organisms and can be used as potential bioterror threats. One key method of research in the fight against these bacteria lies in the inhibition of dihydrofolate reductase (DHFR), an essential enzyme responsible for the reduction of dihydrofolate to tetrahydrofolate which, in turn, is used for thymidylate synthesis and, ultimately, cell growth. Inhibition of DHFR has found utility in the treatment of cancer, bacterial infections and parasitic diseases such as malaria. Primary DHFR inhibitors that have found clinical application include methotrexate (cancer chemotherapy), pyrimethamine (anti-protozoal) and trimethoprim (antibiotic). Herein, the synthesis of a new class of potential DHFR inhibitors will be presented.

Session 3:

Christopher South, Angela K. Wilson*

Title: *Analysis of the Electronic Structure of NdF^+ in Low Oxidation States*

Abstract: Potential energy curves for multiple electronic states of neodymium monofluoride cation (NdF^+) were calculated using the multi-reference complete active space self-consistent field method. Excited state potential energy curves were also calculated using the time-dependent equation of motion coupled cluster method and compared with the multi-reference curves. The dissociation energies, diatomic constants, transition energies and the electronic structure of the molecule were compared to experiment and previous theoretical calculations on similar molecular systems.

Imalka Munaweera, Yi Shi, Bhuvaneswari Koneru, Ruben Saez, Ali Aliev, W. Russell Coyle, Anthony J. Di Pasqua, Kenneth J. Balkus Jr.*

Title: *Novel Chemoradiotherapuetic Magnetic Nanoparticles for the Targeted Treatment of Non-small Cell Lung Cancer*

Abstract: Lung cancer is the leading cause of cancer-related death in the United States and 85% of all lung cancers are classified as non-small cell (NSCLC). Unfortunately, NSCLC is extremely difficult to treat and the survival rates are low; in 2012, the five year survival rate was only 17%. An innovative approach that may ultimately allow for the clinician to target and aggressively reduce tumor burden in patients with NSCLC will be presented. Platinum (Pt)-based radiosensitizers; cisplatin, carboplatin, oxaliplatin and holmium-166 radionuclide (166Ho; $E_{\beta\text{-max}} = 1.84$ MeV; $t½= 26.8$ h) have been incorporated in a garnet magnetic nanoparticle (Pt-HoIG) for selective delivery to tumors using an external magnet. The Pt anticancer drugs can be used as radiosensitizers, and the ^{166}Ho emits beta particles and gamma photons, which can be used for therapy and imaging, respectively. A major obstacle in therapy is the non-specificity of current treatments. Nonspecific anticancer drugs administered via intravenous injection are distributed throughout the entire body and are harmful to healthy tissues as well as tumor sites, leading to significant side effects. The nanoparticles reported here could potentially deliver their chemoradiotherapeutic 'cargo' directly to tumors in a patient, guided by a magnet. The HoIG and Pt-HoIG nanoparticles were characterized using PXRD, SEM, EDX, TEM, ICP-MS, and Zeta potential measurements. Neutron activated cisplatin-HoIG and oxaliplatin-HoIG showed greater toxicity than HoIG, free cisplatin and oxaliplatin toward NSCLC A549 cells. Thus, cisplatin and oxaliplatin act synergistically with the radioactive Ho making nontoxic doses of radiation extremely effective.

Atreyi Dasmahapatra, Peter Kroll*

Title: *Structure and Thermochemistry of Hafnia-Silica Glasses*

Abstract: Metal-oxide glasses are integral components of advanced electronic devices (CMOS technology). They also appear as oxidation products of metal-bearing ceramics. In this study we model HfO_2-SiO_2 glasses using ab-initio molecular dynamic simulations and analyze their structural, vibrational, and thermodynamic properties. The structures comprise Si connected tetrahedrally to O. Hf prefers four-fold coordination, but also appears five- and six-fold coordinated. The enthalpy of mixing HfO_2 into SiO_2 is 0.823 kJ/mol, indicating a solubility limit of 1.6 mol-% at the melting temperature of the glass (500 K).

The phonon densities of states (PHDOS) of hafnium-silicate glasses show gradual changes upon mixing HfO_2 into SiO_2. Computed infrared spectra are comparable to experimental data. We observe a rule of mixing of the heat capacity of the mixed glasses.

A non-linear effect is observed in the low-frequency range of vibrational modes, below 150 cm^{-1}. Upon mixing HfO_2 into SiO_2 these modes are depleted in comparison to pure silica glass, contrary to expectations driven by the higher mass of Hf in comparison to Si. The effect may be due to pinning of floppy modes persistent in the silica glass by heavy Hf atom. We speculate that the depletion may affect the thermal conductivity of HfO_2-SiO_2 glasses.

Michele S. McAfee, Onofrio Annunziata*

Title: *Polymer Diffusiophoresis and Salt Osmotic Diffusion in Aqueous Salt Solutions*

Abstract: Diffusion of a solute can be induced by the concentration gradient of another solute in solution. This transport mechanism, known as cross-diffusion, has been found to play an important role in many industrial and biological processes. This presentation describes the experimental determination of cross-diffusion coefficients for ternary systems containing poly(ethylene-glycol) (PEG) and sulfate, chloride or thiocyanate salts by Rayleigh interferometry at 25ºC. One cross-diffusion coefficient, denoted as salt osmotic diffusion, describes salt diffusion induced by a PEG concentration gradient, and is related to PEG-salt thermodynamic interactions. The second cross-diffusion coefficient, denoted as PEG diffusiophoresis, describes PEG diffusion induced by a salt concentration gradient, and is described as the difference between a thermodynamic and a transport parameter. Interestingly, the behavior of cross-diffusion coefficients follows the Hofmeister series, and large PEG diffusiophoresis occurs in the presence of sulfates.

We have developed a theoretical model describing the observed behavior of cross-diffusion coefficients in salting-out conditions based on parameters such as water thermodynamic excess and hydration. We have also developed another model based on ion binding describing cross-diffusion in salting-in conditions. This work is potentially of value for understanding transport of macromolecules in the presence of concentration gradients relevant to industrial and biological systems.

Wijayantha A. Perera, *Kenneth J. Balkus Jr*

Title: *Sodium Niobate Nanorods and Nanotubes – Graphene Binder Free Nanocomposite Flexible Paper Electrode for Supercapacitors*

Abstract: Supercapacitors have captured attention in the energy storage field due to high energy density and high power density. In this project it is manly study that how sodium niobate nanorods and nanotubes can be used as a supercapacitor electrode material. In order to prepare electrodes graphene was used as a platform. Graphene can be used to make binder free flexible paper electrodes. Sodium niobate nanorods were grown on the graphene sheets by wet chemical method. Graphen serves as a good substrate to grow nanorods. And also there are many advantages of graphene such as graphen is highly conductive, it has high surface area, it can form free standing papers, it can be functionalized and also it has been proven as a good electric double layer capacitance material. Sodium niobate has high faradic activity and also it has ability to intercalate Li^+ ions. Due to these properties electric double layer capacitance and pseudo capacitance can be increased.

Nathanael Mayo, Ali Aliev*

Title: *Flexible Transparent Loudspeakers*

Abstract: Since 2008, study of carbon nanotube (CNT) based thermophones has demonstrated the ability to produce thin, highly flexible, transparent loudspeakers. Contrary to conventional magnet based speakers, these loudspeakers operate by what is known as the thermoacoustic effect in which a modulated change in temperature in an active element induces a pressure wave in the surrounding medium. Thermal management in thermoacoustic devices is one of the primary concerns for improving device performance. We explore the effect of the device design and dimensions on sound generation and the cooling capabilities of the device. We experimentally verify the optimum spacing between the active nanotube element and the substrate. Potential applications of our devices include speaker elements for flexible electronics, an alternative for acoustic wave therapy for skin treatments, as well as cheap ingestible ultrasound devices.

Blake Wilson, Steven Nielsen*

Title: *Calculation of the Isothermal – Isobaric Partition Function using Nested Sampling*

Abstract: Nested Sampling is a powerful athermal statistical mechanical sampling technique that directly calculates the partition function, and hence gives access to all thermodynamic quantities in absolute terms, including absolute free energies and absolute entropies. Nested Sampling was first developed for atomic simulation in 2010 by Pártay et. al. However, their method only allowed for calculation of the canonical (NVT) partition function. We have extended Nesting Sampling to the isothermal-isobaric (NPT) partition function. This is important because it most closely represents the conditions under which many condensed phase experiments are performed, and allows for calculation of the Gibbs free energy and chemical potential.

Andrew Mahler, Angela K. Wilson*

Title: *Correlation Consistent Basis Sets for In–Xe*

Abstract: The correlation consistent basis sets have become widespread throughout a variety of computational methodologies by providing systematic descriptions of electron correlation through their layered application of correlation functions. Our research group has recently developed correlation consistent basis sets that are appropriate for describing the all-electron frozen-core electronic correlation for the atoms In-Xe. We describe the methodology for creating these basis sets as well as the systematic accuracy achieved by these basis sets in describing molecular properties.

David M. Marolf, Gregory L. Powell*

Title: *New Triosmium Clusters with Multidentate Phosphine Ligands*

Abstract: Although reactions between osmium carbonyl clusters and phosphine ligands have been studied extensively, none of them have been conducted at the elevated temperatures afforded by microwave heating. Recently, we have explored the reactivity of $Os_3(CO)_{12}$ with multidentate phosphine ligands such as bis(diphenylphosphino)methane (or dppm) and 1,1,1-tris(diphenylphosphinomethyl)ethane (or triphos) at high temperatures through the use of a microwave reactor. We have isolated four new triosmium clusters and characterized them via X-ray crystallography. These complexes result from orthometallation of a phenyl group to an osmium atom, C-H activation of a methylene group, or a combination of these two processes. We will present the details of the reaction parameters and the molecular structures of all new complexes.

Rawan Muhanna, Sajani Basnayake, and Kenneth Balkus Jr.*

Title: *Synthesis of Novel Imidazole Linkers to Create Novel ZIF Structures*

Abstract: Metal Organic Frameworks (MOFs) are crystalline compounds consisting of metal ions bridged by organic linkers. These crystals are highly porous and have a high surface area. These unique properties along with chemical and thermal stability make MOFs a promising alternative in fields including gas storage, catalysis, and drug delivery. There is a great variety of linker and metal combinations, and these differences yield MOFs with significantly different properties. Zeolitic Imidazolate Frameworks (ZIFs) are a sub-class of MOFs characterized by their tetrahedrally coordinated transition metal nodes connected by organic imidazole linkers. In this work we have synthesized a new bridged imidazole linker by employing Schiff base type reaction. 2-Imidazolecarbozaldehyde was reacted with o-Phenylenediamine to form a new crystalline linker. Results for the synthesis of a new ZIF prepared by reacting this linker with Zn^{2+} will be presented. The linker and the ZIF were characterized using powder XRD, SEM, and IR spectroscopy.

Minh Hoa Nguyen, Nhi Trinh, Alysia Lowe, Ken J. Balkus*

Title: *Transition Metal Complexes for Storage and Delivery of Nitric Oxide*

Abstract: Nitric Oxide (NO) is a signaling molecule that is found in many biological processes that have the ability to aid in wound healing process. However, delivery of NO to a wound can be difficult. A possible approach is to bind a NO releasing compound, a transition metal complex, to a PIM-1 polymer for creating nanofibers bandage.

PIM-1 is an ideal polymer to bind the transition metal complex because of its unusual high microporosity due to its rigid structure, combined with its loose chain packing. This creates a high free volume, therefore making it possible for the NO to pass through the bandage and reach the wound during the NO releasing process. The nanofibers bandage will be generate through a process called electrospinning. Electrospinning is a process in which a high voltage is used to create an electrically charged jet of polymer solution. The solution then dries or solidifies to leave a continuous polymer fiber. PIM-1 contains a cyano group, which makes it possible to form a bond with the nitrogen on the cyano group to the metal center of the metal complex. The transition metal complex will be releasing NO by photolysis.

Our goal is to bind the NO releasing compound, a transition metal complex: specifically RuSALEN-nitrosyl (RuSALEN-NO) and CoSALEN-nitrosyl (CoSALEN-NO), to a PIM-1 polymer for creating nanofibers bandage. The result of our recently work will be discuss, including the characteristic of synthesized PIM-1 Polymer, SEM image of the PIM-1 fiber, and release of NO from transition metal complexes.

Susana Aguirre-Medel, Munuve Mwania and Peter Kroll*

Title: *Surface Functionalization of β-SiC Quantum Dots*

Abstract: Silicon carbide (SiC) is a chemically inert, stable and biocompatible semi-conducting material. At the nanoscale SiC reveals photoluminescence, while bulk SiC is an indirect bandgap semiconductor without usable optical activity. Modifying the surface of SiC QDs with different chemical groups introduces functionalization and opens the venue for further applications of SiC QDs. We demonstrate a strategy that yields functionalized Silicon Carbide (SiC) quantum dots (QDs) in an aqueous environment in just one day. Hydroxyl terminated β-SiC QDs were prepared through photo-assisted electrochemical corrosion of bulk slurries. The SiC QDs were then chemically modified to yield an amine surface group ($-NH_2$). Aminated SiC QDs underwent further modification to yield thiol groups (-SH). Fluorescamine assay for primary amine groups confirmed success of amination while characterization of thiolated SiC QDs was attained through Ellmans assay. Further, taking advantage of Au's affinity to sulfur, composite Au-SiC nanohybrids (NHs) were fabricated. Transmission electron microscopy (TEM) results show successful fabrication of the Au-SiC NHs. Au-SiC NHs have enhanced optical properties that could be used for photo-catalytic activity, energy harvesting as well as for as environmental/analytical sensors.

Kenneth J. MacKenzie, Anne M. Marti, and Kenneth J. Balkus Jr.*

Title: *Adsorption of Nucleotides by bio-MOF-1*

Abstract: A subclass of MOF's known as bio-metal-organic-frameworks (bio-MOFs) use a zinc-adeninate building unit (ZABU), rather than the typical zinc-carboxylate cluster found in MOFs. These ZABU's can then be conjoined by organic linkers to form stable hybrid crystalline materials. Bio-MOFs have shown large pore sizes, and low crystalline densities, when compared to other MOFs. One bio-MOF in particular, known as bio-MOF-1, utilizes ZABU's connected by the 4,4-biphenyldicarboxylic acid (BPDC), forming a 3D, luminescent crystalline structure. With this work, we hope to demonstrate bio-MOF-1's potential ability to bind nucleotides, such as uracil and thymine, through the free amine functional moieties on the ZABU. Changes to bio-MOF-1's structure will be monitored using fluorescence and UV-Vis spectroscopy.

Zijun Yu, Rebecca Weber, George Schoendorff, Angela K. Wilson*

Title: *Comparison of Density Functional Methods for Lanthanide Compounds*

Abstract: The geometric structures and vibrational frequencies of fifteen LnF_3 (Ln = La-Lu) are determined. Calculations were performed with DFT using the B3LYP, the PBE0, the BP86, the SVWN, and M06 functionals and a triple-zeta basis set. The equilibrium bond length and symmetric and asymmetric stretching frequencies were obtained for each molecule and compared to experiment. The results exhibited high similarity to experimental data and showed that these functionals are effective methods for the structure determination for lanthanide trifluorides.

Prajay Patel, Peter Kroll*

Title: *Investigations of the Rhombohedral-to-cubic Transformation Path in Boron Nitride*

Abstract: We study the transformation mechanism for the phase transformation from rhombohedral boron nitride (r-BN) to cubic boron nitride (c-BN) using density functional theory methods within the local density approximation (LDA). The transformation mechanism is approximated by two independent parameters: one defining the compressional mode that brings layers in r-BN closer together, the other describing the buckling mode, relating to pyramidalization of atoms and formation of new bonds. The complete mechanism is mapped to a two-dimensional energy profile, providing the transformation path together with activation energy and reaction enthalpy. For pure BN, we find 0.175 eV/atom for the activation energy of the collective transformation. Aliovalent substitution of 8.33 mol-% AlN in BN yields a lower activation energy than for pure BN. The impact of substituting BN by C severely depends on the distribution of C atoms: while C_2-pairs within BN layers increase the activation barrier, other substitution patterns lead to a decrease. High pressure decreases the activation energy for the r-BN to c-BN transition, for pure and alloyed systems alike. The relevance of our study for the synthesis of c-BN at high pressures as well as for the thermal stability of c-BN compounds at high temperatures will be discussed.

Soo Hun Yoon, Gregory L. Powell*

Title: *New diosmium(I) complexes with dicarboxylate ligands*

Abstract: Complexes containing two osmium(I) atoms bonded to carbonyl and carboxylate ligands are relatively rare. We have been exploring the reactions of osmium carbonyl, $Os_3(CO)_{12}$, with carboxylic acids in a microwave reactor, and we have been able to prepare several new examples of these diosmium compounds. They include carboxylate ligands derived from suberic, sebacic, dodecanedioic, tetradecanedioic, and 1,3-adamantanediacetic acids. These are the first cases in which dicarboxylate ligands form intramolecular loops around the Os_2 units.

Houliang Tang, Nicolay V. Tsarevsky*

Title: *Synthesis and Functionalization of Disulfide-containing Polycyanoacrylates*

Abstract: Copolymers consisting of ethyl cyanoacrylates and chloroethyl methylacrylates have been prepared by free radical polymerization with small amounts of trifluoroacetic acid as anionic polymerization inhibitors. In the presence of excess carbon tetrabromides as efficient chain transfer agents, reductively degradable branched polymers were obtained with the disulfide-containing crosslinker bis(2-methacryloyloxyethyl) disulfides. Kinetics of both polymerization and reduction degradation were fully studied in our work. The polymers contained multiple alkyl bromide peripheral groups, which, along with the alkyl chloride pendant groups originating from 2-chloroethyl methacrylate, were into azide groups. The latter were used to attach various alkyne-functionalized molecules via copper catalyzed click chemistry.

Diego A. Lopez, Sumit Bhawal, and Frank W. Foss Jr *

Title: *Vitamin B1 Pathway: A Distinct Source for Novel Antibacterial Development*

Abstract: The current state of our antibiotic invention and development is dour. The always-increasing economic pressures have obliged pharmaceutical companies to market high revenue drugs; meanwhile, bacteria have gained resistance to all of our current chemotherapeutics. Our health care system is losing a billion dollar battle unless novel targets can be properly defined. Vitamin B1 pathway offers a rich and unexplored source for drug discovery; its biosynthetic pathway is ubiquitous and specific for many bacterial pathogens. HMP kinase, a major enzyme in thiamine's pathway, has been successfully overexpressed, purified, and assayed for enzyme inhibition. Efforts towards the synthesis of HMP analogs and their evaluation via high throughput screening have provided a better understanding of the enzyme's active site. Further utilization of computational and analytical tools will confirm the integration of the analogs into the catalytic process, resulting in the synthesis of a lead pharmacophore.

Sara Merrikhihaghi, Alexander R. Lippert*

Title: *Fluorescent Probes for Imaging Reactive Nitrogen and Sulfur Species*

Abstract: Fluorescent probes were designed for the specific detection and imaging of biologically generated reactive nitrogen and sulfur species. These probes offer the unmatched ability to help to understand their roles biological pathways using fluorescence microscopy and other tools. Our lab has been applying these probes in cell culture models of healthy physiology and disease states and this presentation will summarize our recent findings.

Nimali Abeykoon, John P. Ferraris*

Title: *Supercapacitor Performance of Carbon Nanofibers Derived from PAN/PMMA Polymer Blends*

Abstract: Supercapacitors are among the most promising electrochemical energy devices today, as they are fast charging and have long cycle life. However, supercapacitors currently are not able to replace batteries because of their lower energy storage capability. High surface area and porosity of the electrode material are essential to enhance the performance of supercapacitors. A supercapacitor electrode material containing a polymer blend, consisting of polyacrylonitrile (PAN) as the carbonizing polymer and polymethyl methacrylate (PMMA) as a sacrificial polymer is investigated. The polymer blend solution in DMF was electrospun to obtain a freestanding nanofiber mat. Porous carbon nanofibers were obtained from electrospining of PAN and PMMA with varying ratios (95:5, 90:10, 75:25). The mat was carbonized and activated by CO_2 at 1000 ^{o}C to obtain porous carbon nanofibers as PAN converts to carbon and the sacrificial polymer decomposes creating pores. Electrochemical performance of the supercapacitor was investigated by cyclic voltammetry and constant current charge-discharge. The introduction of PMMA into the PAN increase the surface area of PAN nanofibers and it enhance electrochemical performance of the carbon nanofibers. Characterization and the electrochemical performance of the resultant carbon nanofibers from different blend compositions will be presented.

Hongzhang Han, Nicolay V. Tsarevsky *

Title: *Functional Polymer Materials with Complex Architectures Produced by Using Exchange Reactions at Hypervalent Iodine Center*

Abstract: Hypervalent iodine compounds has been discovered for more than a century and been used in organic synthesis. Hypervalent iodine (HVI) bonds in (diacyloxyiodo)arenes $ArI(O_2CR)_2$ could conduct the exchange reactions with a number of external nucleophiles. The liability of the HVI bonds enables facile homolytic bond cleavage both thermally and photochemically which leads to a convenient access to a broad variety of radicals. Hyperbranched polymer could be made by self-condensing vinyl polymerization technique in which the inimers were conveniently generated in situ from the exchange reactions with vinyl carboxylic acid and HVI compounds. Additional polymeric materials with complex architectures such as star polymers and graft/brush polymers were synthesized when applying multi-carboxylic acids or polyacrylic acids in the exchange reactions with HVI reagents. Furthermore, HIV exchange reaction enables the introduction of chemical groups like ATRP initiating and "click chemistry" functionalities into various small or macromolecules which provides another synthetic route to functional polymeric materials.

Pradeep Budhathoki, Youngha Ryu*

Title: *Reversible Modification of the N-terminal CysteineResidue of Proteins using Pyruvic Acid Analogs*

Abstract: The N-terminal cysteine residue of proteins can selectively react with pyruvate analogs at pH 7 to form their corresponding 2-methyl-2,4-thiazolidinedicarboxylic acid derivatives. Aminoxy-containing reagents such as methoxylamine can easily reverse this reaction to regenerate the free cysteine residue. Novel pyruvate analogs were prepared with affinity (biotin) and fluorescent (pyrene) labels, which should be useful for the protein purification and detection, respectively. Also synthesized were pyruvate analogs with unique chemical handles such as azide and propargyl groups. These functional groups can be used to further modify proteins using bioorthogonal reactions without interfering with native biochemical reactions. All of the prepared pyruvate analogs were successfully tested for the selective and efficient N-terminal modification of the Z-domain as a model protein. The modification can be easily removed to regenerate the intact unmodified proteins.

Jameela Lokhandwala, Hilary Hopkins, Brian Zoltowski[*]

Title: *Structural Characterization of Fungal Photoreceptor-Envoy*

Abstract: Organisms contain elaborate mechanisms to sense and adapt to environmental stimuli. In particular, circadian clocks sense external cues to coordinate metabolism, growth, and sexual development to the diurnal light cycle. In organisms such as plants, fungi and animals, these clocks consist of complex networks of feedback loops integrated into a central circadian oscillator. We have a reasonable understanding of how the central oscillator operates, however, how multiple stimuli are integrated into the core clock to generate a coherent cellular response is poorly understood. In the filamentous fungi *Hypocrea jecorina* (anamorph *T. reesei*) cellulase gene expression, carbon catabolite repression, sulfur metabolism and adaptive stress responses are all under control of blue-light. A Light-Oxygen-Voltage (LOV) domain containing photoreceptor, ENVOY (ENV1) acts as a central node to integrate multiple input pathways into transcriptional machinery. This is achieved by two primary mechanisms: 1) As a direct photoreceptor, ENV1 acts in conjunction with another LOV domain containing photoreceptor Blue-Light-Receptor-1 (BLR1) to regulate clock controlled gene transcription by the BLR1/BLR2 complex. 2) ENV1 acts in a light-dependent and light-independent mechanism to regulate cellulase gene expression, stress responses and sexual development through intersection of G-protein coupled receptor (GPCR) signaling. Using a combination of solution biophysics and structural characterization we have demonstrated that ENV1 employs a divergent mechanism to incorporate oxidative stress and blue-light signaling into regulation of gene expression. Interestingly, although the core circadian machinery in T. reesei is conserved with N. crassa (VVD=ENV1, Blr1=WC1, Blr2=WC2), they differ on the level of fundamental chemistry and signaling mechanisms. Thus, even closely related species adapt integration of environmental variables into circadian regulation.

Jian Cao, Sara Merrikhihaghi, and Alexander R. Lippert*

Title: *1,2-Dioxetane Chemiluminescent Probes for Imaging H_2S in Living Cells*

Abstract: Chemiluminescent probes have significant advantages compared with fluorescent probes, such as no background interference, no need for light excitation and more convenience for tracking and detecting. Thus, chemiluminescent probes are attractive candidates to develop new types of reaction-based probes for various analytes. Recently, our lab has focused on designing reaction-based chemiluminescent probes for imaging hydrogen sulfide (H_2S). H_2S is a ubiquitous endogenous mediator, which plays a number of biological signaling functions and exhibits significant effects in numerous physiological systems, but understanding the precise mechanisms of its production and function demands new technological tools for its detection in living systems. We have developed a 1,2-dioxetane chemiluminescent H_2S probe for chemiluminescent imaging of H_2S generated in living cells. What's more, this probe can detect H_2S instantly, offering an advantage versus most available H_2S probes. Considering these advantages, we believe chemiluminescent probes will offer us a new tool to tracking reactive species in vivo.

David C. McLeod, Nicolay V. Tsarevsky*

Title: *Controlled Radical Polymerization of 4-Vinylphenyloxirane to Produce Highly Functionalized, Well-defined Homopolymers and Block Copolymers of Various Architectures*

Abstract: Abstract: Polymeric materials with numerous epoxide moieties pendant to the polymer backbone have the potential to serve as universal precursors for a plethora of novel materials due to the well-known ability of the epoxide functionality to undergo modification with a wide range of nucleophiles. Controlled radical polymerization techniques such as reversible addition-fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP) are routinely used to synthesize well-defined materials, but often exhibit unusually poor control with epoxide-containing monomers due to impurities in the monomer or side reactions between the mixture components and the epoxide functionality, leading to crosslinking or branching events. In this work we present a facile method for the synthesis of highly pure 4-vinylphenyloxirane (4VPO), an epoxide functionalized styrenic monomer. We then show that 4VPO can be homopolymerized with good control from a variety of alkyl-bromide initiators utilizing low copper catalyst concentration ATRP to create well-defined linear, star, and block copolymers. We further show that the well-controlled homopolymerization of 4VPO can also be accomplished using the RAFT technique with several different thiocarbonate chain transfer agents.

Zhaoxu Wang, *Nicolay V. Tsarevsky* *

Title: *Well-defined Redox-active and Fluorescent PolymerPrepared by Atom Transfer Radical Polymerization and Viologen-containing Intiator*

Abstract: Difunctional (2-bromoisobutyrate) viologen-containing atom transfer radical polymerization (ATRP) initiator was synthesized. Via ATRP with that initiator, well-defined polymers with a single viologen group with two arms of polymer chains were prepared. Polymers arms include poly(methyl methacrylate) which is hydrophobic, poly(oligomer(ethylene glycol) methyl ether methacrylate) which is hydrophilic and poly(di(ethylene glycol) methyl ether methacrylate) which is temperature-responsive due to the presence of lower critical solution temperature (LCST). The obtained polymers are redox-active and chemochromic, i.e. the polymers turn blue on introducing reducing agent and come back to yellow on introducing oxidizing agent, as proved by UV-vis spectroscopy. Surprisingly, the polymer is also fluorescent with a maxim emission at ca. 410nm and maxim excitation at ca. 350nm, as given by fluorescence spectroscopy. Upon further study, it was found that the fluorescence intensity is solvent-dependent, which make the viologen-containing polymers potential fluorescent sensors.

Sahila Perananthan, Jeliza Bonso, and John P. Ferraris*

Title: *Supercapacitor Electrode Material from Immiscible Polymer Blends*

Abstract: Electrochemical double layer capacitors utilize the electrode-electrolyte interface to store energy. High surface area that is accessible to the electrolyte could lead to an increase in the energy density. In this study, we prepared porous carbon nanofiber electrodes from polyacrylonitrile (PAN) and polystyrene (PS) polymer blends. Incorporation of pyrolyzing polymer, polystyrene, produce pores when it decomposes during the thermal treatments. The electrode material was prepared by electrospinning the blend solution followed by thermal stabilization, carbonization and CO_2 activation. The ratio of PAN to PS was varied to obtain the optimum performance. Electrochemical behavior of the material was characterized by cyclic voltammetry (CV) and galvanostatic charge/discharge. The preparation of the electrode material and the study of the morphology and electrochemistry will be presented.

Rangana Jayawickramage, Nimali Abeykoon, Sahila Perananthan, Jeliza Bonso, John Ferraris*

Title: *Enhanced Conductivity of 1-Butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)imide as an Electrolyte Double Layer Capacitor*

Abstract: 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr$_{14}$TFSI) is a commonly used ionic liquid electrolyte in supercapacitors. Even though Pyr$_{14}$TFSI is having a high ionic strength, flexible anion and asymmetric cation its conductivity is relatively low due to its high viscosity. Because of the high viscosity ions are not easily movable. To overcome this draw back organic solvents with a lower viscosity can be used with Pyr$_{14}$ TFSI as a mixture. It is reported that mixture of Pyr$_{14}$ TFSI with Propylene carbonate (PC) was able to achieve higher conductivities. In this study a mixture of PC and Ethylene Carbonate (EC) was used with Pyr$_{14}$ TFSI into different volume ratios and conductivity was measured. When compared with the systems of pure Pyr$_{14}$ TFSI, Pyr$_{14}$ TFSI +PC and Pyr$_{14}$ TFSI+EC, system of Pyr$_{14}$ TFSI+PC+EC showed higher conductivity. Furthermore this Pyr$_{14}$ TFSI+PC+EC system was used as the electrolyte with PAN-ABC electrodes and energy density and power density were investigated.