THE
PHILADELPHIA SECTION
OF THE
AMERICAN CHEMICAL
SOCIETY

Presents

THE ELEVENTH ANNUAL
STUDENT POSTER SESSIONS

ABSTRACTS

Thursday, February 10, 2010

Grand Court, Mitten Hall, Temple
University, Philadelphia PA
Welcome to the
THE ELEVENTH ANNUAL STUDENT POSTER SESSIONS

Once again this year the annual student poster sessions sponsored by the Philadelphia Section of the American Chemical Society are hosted by Temple University’s department of chemistry. Submissions have been accepted in the areas of graduate, undergraduate, and high school study.

This year brings excitement as The Dow Chemical Company has graciously sponsored the prizes to be awarded to the top presenters in each category. This is the first major event of the year hosted by the Philadelphia Section ACS during the International Year of Chemistry. We hope that you enjoy your evening at Temple, and that we will see you again at other ACS functions throughout the year!
The section chair, the poster planning committee, and everyone involved with the activities tonight would like to thank Dr. Catherine T. Hunt and The Dow Chemical Company for their assistance with sponsoring the presenter prizes for this event.
THE ELEVENTH ANNUAL STUDENT POSTER SESSIONS

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THE ELEVENTH ANNUAL STUDENT POSTER SESSIONS

GRADUATE AND POST-DOCTORAL POSTERS
1. Thioamides as Fluorescence Quenchers: Minimalist Chromophores to Monitor Protein Dynamics

Jacob M. Goldberg, Solongo Batjargal, E. James Petersson
University of Pennsylvania, Philadelphia, PA, USA.

Reducing the size of spectroscopic probes can increase the spatial resolution of fluorescence experiments on protein dynamics. We have shown p-cyanophenylalanine (Cnf) and backbone thioamides to be a distance-dependent fluorophore/quencher pair. We have used this pair to study the thermal denaturation of a Cnf/thioamide-labeled version of villin headpiece by fluorescence spectroscopy. We are currently exploring quenching interactions with other fluorophores and developing methodology to incorporate thioamides in large proteins. The small size of the thioamide probe opens the possibility of mapping conformational changes with a density far beyond what is currently possible.

2. Molecular dynamics studies of amphipathic peptides embedded within a lipid bilayer

Thuy Hien T Nguyen, Dr. Zhiwei Liu, Dr. Preston B Moore.
Department of Chemistry & Biochemistry, University of the Sciences, Philadelphia, PA, United States

Ion-channels embedded within the membrane play a crucial role in numerous cell processes such as signaling, energy conversion, and ion conductance. Homo-oligomeric ion-channels are a common class of ion-channels and are the main focus of many protein-membrane structure studies. The overall goal of this research is to quantify the structural, dynamical, and energetic properties of transmembrane amphipathic peptides which form homo-oligomeric ion-channels. In order to achieve this goal, we performed both all-atom (AA) and coarse grain (CG) molecular dynamics (MD) simulations on systems with different oligomeric states, specifically in the tetramer, pentamer and hexamer bundle. These simulations allowed us to determine which oligomeric state is more stable. In addition, we also analyzed the tilt angle, radial distribution, water hydration, area per lipid, and bilayer thickness from both AA and CG simulation data. In summary, our simulations can lead us to understand the assembly of peptides in membranes better, which is of great importance when designing antimicrobial, antiviral, and other pharmaceutical agents that will target ion-channels.
3. Nanostructured- POSS Electrolytes for Lithium Ion Batteries

Parameswara Rao Chinnam and Stephanie L. Wunder
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The motivation for the development of solid polymer electrolytes (SPEs) arises from its safety advantages over liquid electrolytes. In particular SPEs are non-flammable and avoid the problem of electrolyte leakage, both of which can result in fires/explosions. However, SPEs have lower conductivities at room temperature (RT) compared to those of liquid electrolytes, so there is a need to develop SPE with improved RT conductivities. In the current work, we have synthesized a new, novel lithium salt (POSS-Benzyl\textsubscript{7}(BF\textsubscript{3}Li)\textsubscript{3}) and prepared electrolytes from mixtures of this salt with another nanomaterial, namely polyoctahedral silsesquioxanes-ethylene glycol (POSS-PEG\textsubscript{8}). POSS-Benzyl\textsubscript{7}(BF\textsubscript{3}Li)\textsubscript{3} was synthesized from commercially available POSS-Benzyl\textsubscript{7}Li\textsubscript{3} in methylene chloride by addition of BF\textsubscript{3}-etherate under anhydrous conditions. The structures of these materials are shown in Figure 1. We have investigated the temperature dependent conductivities for mixtures of POSS-PEG\textsubscript{8} with POSS-Benzyl\textsubscript{7}(BF\textsubscript{3}Li)\textsubscript{3} as a function of oxygen/lithium ratio, and compared these with the precursor lithium salts, POSS-Benzyl\textsubscript{7}Li\textsubscript{3} and LiBF\textsubscript{4}. The conductivity of the POSS-PEG\textsubscript{8}/POSS-Benzyl\textsubscript{7}(BF\textsubscript{3}Li)\textsubscript{3} was 1.1 x 10\textsuperscript{-4} S/cm at 25\textdegree C and reached 2.6 x 10\textsuperscript{-3} at 90\textdegree C, an increase of ca 80 with respect to POSS-Benzyl\textsubscript{7}Li\textsubscript{3} and 20 with respect to LiBF\textsubscript{4}. This nanostructured electrolyte phase separates into conductive and structural microphase separated domains, so that the potential exists to incorporate it into a SPE.

Figure 1: Structures of POSS-Li\textsubscript{3} and POSS-(BF\textsubscript{3}Li)\textsubscript{3}; R=Phenyl
4. Dibutyl Phthalate and Other Pesticide Residues from Various Types of Tropical Fruits

Hoa Trinh, Dr. Kishore K. Bagga, Dr. Kevin Owens
Drexel University College of Medicine and Drexel University

Due to the potential health hazards of pesticides, the current investigation was performed. The work here reported involved the detection, identification using GC/MS, and comparison of the presence of pesticides in the peel and the pulp of some tropical fruits. Data from this work has shown the presence of dibutyl phthalate (pesticide) in most of the fruits tested, and that green mango had the largest number of pesticide residues present; whilst in the case of guava no pesticides were detected. Furthermore, there was a larger pesticide residue content in the peel versus the pulp of the fruits tested.

5. Prostaglandin and sex hormone determination in urine sample by high performance liquid chromatography

Guoxiu Wei, Susan Jansen Varnum
Department of Chemistry, Temple University, Philadelphia, PA, 19122

Prostaglandins (PGs) and sex hormones and their metabolites play an important role in many diseases such as hypertension, inflammation and breast cancer. By studying these compounds as biomarkers from urine or tissue, it is possible to predict or prevent diseases in a simple way. We have developed a method to successfully separate the combination of 9 prostaglandins and 8 sex hormones. In our study, this method is applied to urine sample from hypertension patients. Reverse phase liquid chromatography using a Waters symmetry C18 column was applied for the separation of PGs and sex hormones and their metabolites. Phosphoric acid was introduced to improve the separation. The results show that our method can work on biological samples and achieve good separation without complicated sample pretreatment.
6. Adsorption of Carbon Dioxide onto Aluminum Doped Ferrihydrite
Andro-Marc Pierre-Louis, Douglas B. Hausner, Narayan Bhandari, Wei Li, Richard Harrington, Jongsik Kim, Brian L. Phillips, Clare P. Grey, James D. Kubicki, and Daniel Strongin

Surface adsorption of carbon dioxide (CO\(_2\)) on soil minerals plays an important role in the properties of minerals, both in term of reactivity and stability. Limited work has been done on the CO\(_2\) adsorption of mixed Al and Fe (oxy)-hydroxides while CO\(_2\) sorption on their single-component Al and Fe counterparts have been widely studied. X-ray photoelectron spectroscopy (XPS), atomic adsorption (AA), transmission electron microscopy, X-ray diffraction, and attenuated total reflectance Fourier transform Infrared Spectroscopy (ATR-FTIR) combined with density functional theory (DFT) calculations were used to investigate the gas-phase adsorption of CO\(_2\) on Al-doped 2-line ferrihydrite. Al-substituted ferrihydrite samples were synthesized under atmospheric conditions (i.e. containing CO\(_2\)) as well as controlled CO\(_2\) free conditions. The Al content mixed in solution of ferrihydrite varied between 0 and 100 Al mol\%. Above Al substitutions of 10 mol\%, the results from XRD, XPS, and FTIR analysis indicated that the nanoparticles consisted at least in part of a mixed phase of ferrihydrite and bayerite/gibbsite. ATR-FTIR experiments showed that as the Al mol% increased beyond 10% the bicarbonate complex, formed by passing CO\(_2\) over the particles, exhibited shifts in its vibrational modes due to adsorption on Al-based phases. The presence of hydrogen bonded water on the surface of ferrihydrite and Al-doped ferrihydrite prevented the formation of bicarbonate complexes. While the bicarbonate complex was only found to be stable under dry-CO\(_2\) reactant conditions, carbonate was present whether the CO\(_2\) was dry or contained atmospheric amounts of water vapor.
7. Photo-Induced oxidation of Arsenite to Arsenate on ferrihydrite

Narayan Bhandari\textsuperscript{1}, Richard J. Reeder\textsuperscript{2} and Daniel R. Strongin\textsuperscript{1}

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Arsenic (As) is a Group I human carcinogen and over 137 million people in more than 70 countries are affected by a high level of arsenic in drinking water, including the United States. Although, As mainly exist in two redox forms As(III) and As(V), As(III) is believed to be 25-60 times more toxic than As(V). Therefore simple water treatment procedures that are capable of inducing As(III) oxidation and or adsorption are urgently needed. In this context, photochemistry of an aqueous suspension of the iron oxyhydroxide, ferrihydrite, in the presence of As(III) has been investigated in our laboratory using various techniques. Both IR spectroscopy and X-ray absorption spectroscopy results show that the exposure of ferrihydrite to As(III) in the dark leads to an adsorbed As(III)-bearing species, but the exposure of this As(III)-bearing surface to light leads to the conversion of adsorbed As(III) to As(V). Analysis of the solution phase shows that ferrous iron is released into solution during the oxidation of As(III) to As(V). The photochemical reaction, however, shows the characteristics of a self-terminating reaction which is likely due to the passivation of the ferrihydrite surface by the strongly bound As(V) product. Our results suggest that ferrihydrite could be potential candidate material for As removal, due to its dual functions as an oxidant (in presence of light) and sorbent.
8. Studies of Silyllithium Formation and Stability

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Silyl anions are usually prepared by treatment of chlorosilanes with lithium metal. Silyl anions can also be prepared under similar conditions from fluorosilanes, hydrosilanes and disilanes. The silyl anions generally require at least one phenyl substituent on the silicon. We have developed a simple $^1$H NMR method for monitoring and analyzing the progress of lithiation and have used this method to study reactions of Ph$_3$SiH, Ph$_2$MeSiH and PhMe$_2$SiH. This qualitative method has also been extended to a quantitative method for titration using BHT as an internal standard.

The accepted mechanism for silyl anion formation is more complicated than formation of organolithium reagents.

9. Micellar High Pressure Liquid Chromatography: Retention and Behavior of Estrogens

Jelena Drazenovic,¹ Susan Jansen-Varnum²
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Separation of seven estrogens (estrone, estradiol, estriol, 2-OH estrone, 4-OH estrone, 16α-OH estrone, and 2-methoxy estrone) was achieved using a single micellar high pressure liquid chromatography method and their retention behavior in the micellar mobile phase has been studied. A partitioning model incorporating the third partition created by addition of sodium dodecyl sulfate (SDS) in the mobile phase has been constructed. The application of micellar partitioning to achieve separation has been modeled, specifically evaluating the role of the micelle in the partitioning process.
10. Isolation of a high-valent and 4-coordinate manganese cubane cluster with a pendant manganese atom. Photosystem II inspired manganese-nitrogen clusters

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Hetero-dicubanes of manganese-imido bridged compounds with chemical formula $[\text{Mn}_2(\text{N})_2(\text{m}_3\text{NBu}^t)_6\text{Li}_6(\text{thf})_4(\text{m}_4\text{Cl}_2)]$ (1) and $[\text{Mn}_4(\mu_6-\text{N})(\text{m}_4\text{NBu}^t)_7\text{Li}_3\text{X}(\text{m}_4\text{NBu}^t)_3]$ (2) ($X=52\% \text{ Li, 48}\% \text{ Mn=N}$) have been subsequently obtained by one pot synthesis under anaerobic conditions. The compound 1 is an octa-nuclear di-cubane cluster in which half of the cluster consists of a MnLi$_3$(NR)$_4$ heterocubane. The two Mn ions have terminal nitride ligands and high oxidation states of (VII). The four metal sites in cubane 1 are bridged by three m$_4$-NBu$^t$ imides ligands and two m$_4$-chlordide ions acting as bridges between the dicultanes. The compound 2 is also a hetero-dicubane imido-bridged core, in which the manganese cubane moiety m$_4$-NBu$^t$ imide ligation on its seven corners and its eighth corner shared with adjacent cubane through $\mu_6$-Nitride bridge. The adjacent Lithium cubane has three m$_4$-tertiary butyl imide bridging in which the fourth corner is occupied by either Mn=N or Li. The compound 2 provides precedent for the future isolation of {Mn$_4$Ca} tetrameric clusters existing in the natural photosynthetic OEC (oxygen evolving complex) model.

11. Analysis into the functionality of metalloenzymes has led to a better understanding of the metal active-site through the use of model systems. These studies suggest reaction pathways that can be synthetically reproduced for research purposes and for applications in industry, environmental sciences, and pharmaceutical technology. One such example of a metalloenzyme active site incorporates metal-activated hydroxide ions acting as nucleophiles, typically bound to zinc, in hydrolytic reactions. Another example includes active sites that contain a copper center where electron transfer between the metal and substrate occur. Interest in the direct observation of these active sites and thus the development of improved solutions to synthetic hydrolytic and redox catalysis initiated this research project. Previously developed zinc enzyme mimics do not behave catalytically in organic solvents. It is suggested that water-solubility should provide catalytic properties with enhanced reaction rates by regeneration of the metal-hydroxide bond. In previously developed copper mimics, it was observed that the substrate-binding mode is dependent on the electronic properties of the ancillary ligand. By varying the electronic properties of the ancillary ligand, a better understanding of substrate binding could be deduced. Our endeavor in the development of novel zinc and copper model systems utilizes the newly developed tris(3,5-diisopropyl - 1,2,4-triazolyl)hydroborate ligand and tris(3,5-diisopropyl -1,2,4-triazolyl)methane ligand systems that could provide unique structural and electronic properties to the metal complex.
12. Vibrational Sum-Frequency Generation Spectroscopy of Mineral/Water Interfaces

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Understanding the chemistry at mineral/water interfaces is important because all environmentally relevant processes, e.g. dissolution, occurring in the presence of these minerals, are dominated by interfacial interactions. Frequency-resolved Vibrational Sum-Frequency Generation (VSFG) Spectroscopy provides interface-specific information, e.g. identity, concentration, and environment of chemical species at the interface. Time-resolved VSFG can give information on the dynamic behavior, e.g., how fast thermal energy is transferred, of interfacial molecules on the femtosecond timescale.

At an aqueous-mineral (M) interface there are many possible hydroxyl species, e.g., H-OH and M-OH. VSFG can distinguish between the different hydroxyl species by probing the “combination-band” region, the vibrational frequency region corresponding to the combination of the fundamental O-H stretch and the fundamental bending mode of M-O-H, which occurs at different frequencies depending on M. For example, the Flourite (CaF$_2$) /water interface under conditions of high pH shows a peak in the VSFG spectra at 3700 cm$^{-1}$, which has been attributed to “free-OH” vibrations. It is speculated that this free-OH belongs to the Ca(OH)$_2$ formed at high pH due to ion-exchange reaction and the high solubility of CaF$_2$. However, it could also belong to OH$^-$ or non-hydrogen-bonded H$_2$O. The results presented will shed light on this ambiguity.
13. Characterization of pre-blast and post-blast residues of improvised explosive devices (IEDs) using laser electrospray mass spectrometry (LEMS)

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Improvised explosive devices (IEDs) are often used by terrorists, in guerilla warfare, and in the wars in Afghanistan and Iraq. Since the invasion of Afghanistan in 2001, there have been 5,764 U.S. soldier casualties as a result of roadside bombs. Due to the increase in the use of IEDs, there is much more research going into IED detection. There are two types of IED detection, pre-blast, for prevention and safety, and post-blast, for forensics and the rapid identification of the explosive. IEDs can contain many types of explosives, including nitrated organic explosives (as seen in military grade explosives), compounds containing unstable peroxide groups, and inorganic salts. The principal focus of this experiment is the detection of post-blast residue from inorganic salt IEDs such as nitrates, chlorates, and perchlorates, as these are the easiest to procure by terrorists. Direct analysis of the material or pre/post-blast sample would be advantageous since sample would not be lost in the transfer step. LEMS allows for this by using a femtosecond laser pulse to non-resonantly vaporize neutrals from a surface followed by capture and ionization in the electrospray plume. A single electrospray solvent was used that composed of two cationic pairing agents to bind anions, which are not seen in positive mode, and a lipid to bind cations that are in the low m/z cutoff range. This solvent allows for a wide range of analytes, from inorganic salt IEDs to sugar and nitrated explosives, to be detected. Here, we present data from simulated inorganic salt IEDs, and pre- and post-blast fireworks using LEMS.
14. Preservation of the biological activity of the tobacco mosaic virus upon nonresonant femtosecond laser vaporization

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The tobacco mosaic virus (TMV) is one of the most widely studied viruses in genetics, biology and chemistry. However, the atmospheric pressure gas phase conformation of the intact virus has yet to be studied. Laser electrospray mass spectrometry (LEMS) is a newly developed atmospheric femtosecond (fs) laser vaporization technique that has shown to preserve the condensed phase conformation of proteins during vaporization as determined by electrospray post-ionization. Here, a healthy leaf is infected with vaporized TMV. The appearance of lesions three days after vaporization of the virus on to the leaf confirms that the fs laser vaporization not only maintains the native conformation but also preserves the virus’s biological function. In addition, the LEMS mass spectra of TMV within healthy and infected leaves is also presented.

15. Concise Enantioselective Synthesese of (-)-Strychnine, (-)-Norfluorocurarine and (-)-Akuammicine.

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Strychnos alkaloids such as akuammicine, Norfluorocurarine and strychnine are excellent targets for showcasing synthetic methodology due to their polycyclic, complex architectures. We have discovered a novel Sequential One-Pot Cyclizations: Concise Access to the ABCE Tetracyclic Framework of Strychnos. In this poster, we disclose the routes toward concise Enantioselective total synthesese of Akuammicine, Norfluorocurarine and Strychnine.
INVESTIGATING THE INSTRUMENTAL OPTIMIZATION AND SENSITIVITY OF LASERSPRAY IONIZATION FOR PROTEIN ANALYSIS.

Diana L. Sardelis\textsuperscript{1}, Charles N. McEwen\textsuperscript{1}, Kevin G. Owens\textsuperscript{2}, Catherine M. Bentzley\textsuperscript{1}. University of the Sciences Department of Chemistry & Biochemistry, 600 south 43\textsuperscript{rd} Street, Philadelphia, PA, 19104. \textsuperscript{1} Drexel University Chemistry Department, 3141 Chestnut Street, Philadelphia, PA, 19104.\textsuperscript{2}

Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) is a powerful technique to analyze biological molecules including proteins, peptides and nucleic acids. Unfortunately, it has limitations in quantitation, mass resolution and obtaining structural information related to fragmentation of singly charged ions. However, laserspray ionization (LSI) overcomes these issues. LSI differs instrumentally from vacuum MALDI in the positioning of the laser linearly through a glass plate, the use of atmospheric pressure and the absence of an electric field. These changes produce mass spectra similar to Electrospray (ESI) with multiple charges, whereas MALDI shows predominately singly-charged ions. Addition of FAB matrices in ESI enhances the multiple charges and improves the signal. Although LSI is currently not as sensitive as vacuum MALDI, it has the potential for improvements by (1) optimizing the ion current by adjusting different instrumental parameters, (2) improving sample preparation and (3) determining how the multiply charged ions are produced via supercharging studies.
17. Induced Fit Docking to generate a Binding Hypothesis for steroidal CYP17 inhibitors to the human Androgen Receptor

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In the initial stages of prostate cancer, cell survival and proliferation are regulated through the Androgen Receptor (AR), acting as activator of transcription upon binding to androgens, like Testosterone (T) and dihydrotestosterone (DHT). CYP17 is a key enzyme for androgen biosynthesis and several compounds have been reported so far as pharmacologically active against this target. Recently Njar and colleagues discovered a novel class of potent steroidal CYP17 inhibitors (C-17 benzoazole and pyrazine derivatives) that, interestingly, also possess AR modulating properties. The impressive multiple in vitro biological activities exhibited by the steroidal C-17 benzoazole and pyrazine derivatives (i.e. inhibition of CYP17, strong anti-proliferative prostate cancer cell and anti-androgenic activities) justify the need to elucidate, at a fine level, the molecular mechanism for their AR modulating activities. The main goal of the present research was to generate a binding hypothesis for the steroidal CYP17 inhibitors to the human Androgen Receptor using a structure based drug design approach. To do so, and in order to deal with the flexibility of several residues buried in the AR binding pocket (which is known to accommodate a variety of ligand structures), a flexible receptor docking protocol based on the Glide Induced-Fit methodology (www.schrodinger.com) has been successfully implemented. The binding hypotheses generated for the most active compounds (like the first in class, VN/124-1) are actually the ideal starting point to guide the rational design and synthesis of novel VN/124-1 analogs with improved AR modulating properties.
18. Discovery of Novel Macrolide Antibiotics: Synthesis and Biological Evaluation of 4,10-didesmethyl Telithromycin and 4-desmethyl Telithromycin

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The rapid emergence of antibiotic-resistant bacteria represents a serious health threat that shows no signs of abatement. A sharp decline in the number of pharmaceutical companies with active antimicrobial research programs underscores the need for new sources of antibiotics. As a part of a rational structure-based drug design program, we apply the paradigm of natural product structural simplification (i.e., desmethylation) to the 3rd-generation macrolide antibiotic telithromycin (2), which is an FDA-approved semisynthetic analogue of erythromycin (1) in clinical use since 2004. The rationale behind desmethylation comes from crystallographic studies of 1 and 2 bound to ribosomal subunits, which corroborate biochemical mechanisms of antibiotic resistance (e.g., ribosomal modification and mutation). From his original work co-crystalizing telithromycin with the ribosome of Haloarcula marismortui Steitz has put forth a ‘steric clash’ hypothesis to rationalize how A2058G ribosomal mutations confer bacterial resistance; namely, the change from an adenine to guanine results in the replacement of a proximal hydrogen in adenine to an amine group in guanine. As a consequence, a steric clash between the C4 methyl and the amino group of G would result. Recently, Mankin et. al. have published the crystal structure of Telithromycin bound to the Escherichia coli ribosome at ~3.3 Å–3.4 Å resolution (Figure 1A). A structural modification of this crystal structure has been created to show the steric clash between the C4 methyl and G2058 mutation (Figure 1B). The positioning of the bound telithromycin macrocycle core, in comparison to H. marismortui, is conserved in this more clinically relevant bacteria. In turn, we hypothesize that the replacement of the C4 methyl group of 2 with hydrogen should relieve this ‘steric clash’ and thus offer a means of addressing antibiotic resistance arising from mutation by desmethylation. We have recently accomplished the de novo synthesis of 4,10-didesmethyl telithromycin (3), which was found to be biologically active against both wild type and mutant bacterial strains and comparable to 2 in potency. We tested it against a range of bacterial strains of E. coli and S. aureus using telithromycin (2) as a control (Table 1). We are currently working on the total synthesis of 4-desmethyl Telithromycin (4).
19. The Functional Amino Acid Navigator

Jason Cargill and Peter M. Palenchar

The purpose of Functional Amino Acid Navigator (FAN) is to create a database that captures information about how enzymes function with respect to interacting with small molecules and critical amino acids involved in catalysis, and then use that database to address questions related to how enzymes function, genome annotation and evolutionary changes in allosteric sites. FAN will give a detailed picture of enzymes interact with small molecules at the atomic level where possible. The data in FAN is gathered from primary published literature about how specific enzymes function. The database itself will also contain direct quotes and references from the primary published material that can be accessed through a search function. Information can also be added to FAN by outside individuals after registration. Data is entered into FAN using the data entry form. The objective of the data entry form is to gather the relevant information with respect to the protein, reaction, and interactions so that it can be searched and used later. The search function in FAN is still growing. As of now, users can select data by enzyme commission number, molecule ID, protein sequence, interaction description ID, amino acids involved in interactions, atoms involved in interactions, and Pubmed ID. The relevant interactions are selected, and the data is output. When inputting data, FAN utilizes an ontology to describe how enzymes interact with small molecules (e.g. substrates and allosteric effectors). This is based on the existing biochemical language used to describe such interactions. FAN will also analyze BLAST protein sequence alignments to help ensure correct protein annotation by identifying amino acids for which FAN contains a function and determining if they are conserved based on the BLAST alignment. The data collected in FAN can be used to compare and contrast differences in allosteric sites from multiple species to gain information about evolutionary adaptations. As of now, FAN contains information covering over a dozen enzyme commission numbers and more than three hundred interactions already in place.
20. Catalytic Hydrogenation with Ru(II) N-Heterocyclic Carbene (NHC) Complexes

Joseph DePasquale¹, Mukesh Kumar¹, Matthias Zeller², Elizabeth T. Papish¹,*¹Drexel University and ²Youngstown State University

The complexes, [CH₂(ImEt₂)Ru(h⁶-cymene)Cl]PF₆ (1) and (Im₆CH₂CH₂OCH₂CH₃)(h⁶-p-cymene)RuCl₂ (2) have been synthesized and characterized by X-ray crystallography and spectroscopic methods. Complex (1) contains a bis-N-heterocyclic carbene (NHC) ligand with ethyl substituents while complex (2) contains a monodentate NHC with a dangling ether group. Complexes (1) and (2) have been shown to be active hydrogenation and transfer hydrogenation catalysts for the reduction of carbonyl and olefinic double bonds. The dangling ether group may increase the catalytic activity by serving as a proton shuttle and/or serving as a hemilabile group. Preliminary mechanistic studies have been attempted and the formation of a Ru-H ligand in complex (1) has been observed by ¹H NMR.

21. Investigation on sensitized chemiluminescence systems and their mechanism for naproxen and coumarin based on H₂O₂-Na₂SO₃ and Fenton’s reagent, respectively in aqueous medium

Patel, Mohit P.; Pesce, Vincent A.; Jones, Kristin R.; Kulick, Kimberly.; Martoff, Charles J. and Varnum, Susan J.

The aim of this work is to use a known simple and rapid method for the determination of naproxen (NAP) and coumarin that does not require sophisticated instruments but give results comparable to those obtained by existing optical methods. Specifically, a stop-flow injection method will be utilized to study the chemiluminescence (CL) properties of NAP and coumarin. The optical properties of NAP will be studied in the presence of hydrogen peroxide (H₂O₂) and sodium sulphite (Na₂SO₃) in an aqueous medium. The optical properties of coumarin will be studied in the presence of hydrogen peroxide, ethylenediaminetetraacetic acid (EDTA) and ferrous sulphate (FeSO₄) in aqueous medium as well. The experimental condition for both systems will also be investigated and optimized.
Carbon nanomaterials possess unique structural, electrical, and mechanical properties, which make them potentially useful for applications in biology and medicine. Graphitic carbon nanofibers (GCNFs) are novel nanoscale materials that can be prepared inexpensively, in gram quantities, via the catalytic decomposition of carbon monoxide or hydrocarbons over mono- or bi-metallic catalysts. Recent studies have described the use of functionalized GCNFs as nanoscale biosensors, biomimetic membranes, neuroelectrochemical electrodes, and gas sensors. Surface functionalization and characterization are essential steps to the further development of GNF applications. Our research has been directed at the identification and quantification of surface oxides on GNFs. Oxidation of the graphite nanofibers with mineral acids introduces oxygen functional groups to the surface. Identification and quantification of surface functional groups have been carried out using FLOSS (Fluorescent Labeling of Surface Species). The selective labeling of carboxyl, aldehyde/ketone, and hydroxyl groups has been carried out in solution phase with model compounds and on the fiber surface. With these procedures established, similar experiments are being performed to attach compounds with amino groups to the GCNF surface by reductive amination.
23. Investigation of Heterocyclic Sulfones as Medicinal Compounds

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Heterocyclic sulfones have been shown to have a high level of activity against human immunodeficiency virus type 1. In addition they have expressed a variety of other medicinal properties including activity against tuberculosis, pneumocystis carinii pneumonia, and as tranquillizers. Due to this wide spectrum of medicinal properties, heterocyclic sulfones were investigated for novel activity using computational methods. From these studies two new molecular targets for heterocyclic sulfones have been established: aldose reductase and phosphodiesterase 4b. Inhibitors of aldose reductase have been suggested for the treatment of a variety of diseases including diabetes and heart disease. Phosphodiesterase 4b inhibitors are used in the treatment for COPD and other asthma related diseases. Further screening was accomplished to optimize the binding affinity of the heterocyclic sulfones in their perspective target. The sulfones determined to have the most affinity for the target(s) are currently being synthesized using modified halide displacement and sulfide oxidation reactions. As a future part of this project these sulfones will be assayed to validate activity in the computationally determined targets. This poster will elaborate on the computational and synthetic work completed.

24. Investigation of hazardous, volatile hydrocarbons in commercial beverages

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In 1990, the Food and Drug Administration announced the presence of benzene in a number of commercial beverages. With the exception of Perrier water, it was proposed that the presence of benzene was due to the metal-catalyzed radical reaction between ascorbic acid and benzoic acid. This reaction is dependent on pH, presence of metal, and the ability of the hydroxyl radicals to react with benzoic acid. Although the presence of benzene can be explained by this reaction other volatile hydrocarbons (VOCs) may also be present such as toluene, xylene, petroleum bi-products, and common chlorination bi-products such as chloroform. Experiments on benzene formation and beverage analysis will be tested for VOCs using headspace trap gas chromatography mass spectrometry. Results will be compared to the VOCs maximum contaminants level established by the Environmental Protection Agency.
Carbohydrates are being increasingly appreciated for their critical roles in biological functions. Studies on the molecular basis of carbohydrate-mediated events in organisms are driven by the availability of those carbohydrates. It is essential to develop methods with which to synthesize diverse carbohydrates, and glycosylation is a key reaction. We have been investigating the synthesis of cyclopropyl glycosides and their use as donors in the synthesis of disaccharides and also glycosyl amino acids. We are investigating two routes for the synthesis of cyclopropyl glycosides. One route involves the glycosylation of substituted cyclopropyl alcohols. The other utilizes cyclopropanation of a vinyl glycoside. In this study, we will attempt to synthesize the core disaccharide of Lipid A through the use of cyclopropyl glycosides.
26. Ammonia Production on Prebiotic Mineral Surfaces Relevant to Enzyme Evolution on the Hadean Earth

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A hypothesis in this research is that there may have been a transition period on the Hadean (young) Earth where inorganic iron-sulfur clusters were adapted for use by the biological world. It has been proposed by others that prebiotic chemistry originated on the surface iron sulfides within the extreme environment of hydrothermal vents (i.e., the "iron-sulfur world") on the ocean floor (Wächtershäuser 1988). It is established that both FeS and Pyrite (FeS2) can accelerate ammonia production in simulated Hadean Earth environments (SingiReddy and others 2011; Summers and Chang 1993). This development is significant since ammonia is required for the production of amino acids, which are needed for the formation of enzymes such as nitrogenase, which also contains a Mo,W, Fe or V “doped” iron-sulfur (cubane) cofactor.

Under current study is the conversion of nitrite and nitrate to ammonia on pyrite doped with MoS42-. This technique has been shown to produce biologically relevant cubane structures on the pyrite surface (Bostick and others 2003). Current literature lacks studies that have investigated the surface chemistry and reactivity of these surfaces within the Hadean Earth context. This work will present present results from laboratory based experiments using in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) to investigate the reduction of nitrite and nitrate on a MoS42- doped pyrite surface. Using ATR-FTIR we will present data that helps to determine the nature of the surface intermediates involved in nitrite and nitrate reduction that occurs on the Mo doped pyrite surface.

References

27. The Characterization of an Unusual Beta-Hydroxybutyrate Dehydrogenase from the Parasite *Trypanosoma brucei*.

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There are many unique features to energy metabolism in African trypanosomes, the unicellular eukaryotic parasites responsible for African Sleeping Sickness. For example, several of the glycolytic enzymes are compartmentalized and are regulated uniquely. We have identified an unusual, putative trypanosomal β-hydroxybutyrate dehydrogenase (HBDH), an enzyme involved in the production of ketone bodies. We have cloned this gene from *Trypanosoma brucei* genomic DNA, overexpressed soluble protein in *E. coli*, and have purified the protein to approximate homogeneity. Kinetic studies were carried out to verify HBDH activity and to determine the parameters $K_M$, $V_{max}$, and $K_i$ values for substrates and inhibitors. Cofactor preference was examined for *Tb*βHBDH and it was found that *Tb*βHBDH utilizes both NAD(H) and NADP(H) equally well, distinguishing the parasite enzyme from other characterized βHBDHs. Uniquely, the trypanosome enzyme binds NAD(P)$^+$ in a cooperative fashion. The oligomeric state of the enzyme was determined through size exclusion chromatography. Finally, RNA interference studies, verified by Western blot analysis, were done to begin to study the *in vivo* role of βHBDH in *T. brucei*. This enzyme in trypanosomes is unusual in that most single-celled eukaryotes do not have an HBDH homolog. Furthermore, the parasite enzyme most closely resembles bacterial sources of the enzyme.

28. Magnetic studies of electron-doped europium sulfide

**Will Boncher**, Georgetown University  
Department of Chemistry, Stoll Research Group

Single source precursor routes to nanomaterials of lanthanide chalcogenides have been investigated; of particular interest are size dependent phenomena in the redox active lanthanides of sulfur and selenium. Here, results are presented on the effect of particle size and electron doping on magnetic properties of europium sulfide. Synthesis, and characterization of nanoparticles, bulk polycrystalline material as well as magnetic studies and effects of oxidation are shown.
29. In situ Observation of Morphological Changes of Pd Nanoparticles Under Hydrogen Exposure

Devika Sil\textsuperscript{1}, Douglas Hausner\textsuperscript{2} and Eric Borguet\textsuperscript{1}
\textsuperscript{1}Department of Chemistry, Temple University, 1901 N. 13\textsuperscript{th} St., Philadelphia, PA 19122.
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Thin films and wires of Pd nanoparticles have been used as hydrogen sensors. The response mechanism is based on hydrogen induced lattice expansion (HILE) of Pd. In order to better understand and observe HILE, Pd nanoparticles with diameters ranging between 5-10 nm were prepared via a novel inorganic route. The nanoparticles were characterized using Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) measurements. Thin films of these nanoparticles were prepared by drop casting a solution of Pd nanoparticles onto the thin native oxide coating of a silicon wafer and were then subjected to hydrogen exposure (90\% N\textsubscript{2} and 10\% H\textsubscript{2}). The AFM images recorded before and during H\textsubscript{2} exposure reveal an expansion of the nanoparticles. We interpret the morphological change to be due to the lattice expansion either as the formation of PdH\textsubscript{2} from Pd or due to the phase transition of PdH\textsubscript{2} from $\alpha$ to $\beta$. 
THE ELEVENTH ANNUAL STUDENT POSTER SESSIONS

UNDERGRADUATE POSTERS
30. CO$_2$ Catalyzed Reduction with a Nanostructured p-GaP Semiconductor Electrode

**Lena Hoober, Michael Kelly**  
Princeton University

There has been a rising interest to be able to trap the excess of atmospheric CO$_2$ and convert it to potentially useful fuels, such as methanol and other alcohols or organics. It has been shown that a p-GaP semiconductor electrode is able to photoelectrochemically convert CO$_2$ to methanol using light with a pyridine catalyst. Structuring this electrode would increase the already low current densities required for selective conversion to methanol. To obtain these nanostructured surfaces the electrode surface is anodically etched in 1 molar sulfuric acid. The electrochemical behavior of the electrodes was investigated by linear sweep voltammetry and bulk electrolysis. SEM measurements indicate that upon etching the electrode surface is polished and removes any impurities from the surface. The effect of surface morphology on product distribution is also discussed.

31. The Dynamics of the Acetylene-vinylidene Isomerization Mechanism Following the Computational Approach

**Nader Anz and Jonathan Smith**  
Department of Chemistry, Temple University

Vinylidene is a bi-radical that is very high in energy relative to acetylene with a 45.91 kcal/mole energy difference and a low barrier to isomerization. Thus, vinylidene isomerizes to acetylene. To develop a better understanding of the isomerization mechanism of vinylidene to acetylene, the dynamics were studied using computational methods. First, the formation of vinylidene was carried by subjecting vinylbromide to vacuum UV radiation of a wavelength of 193 nm as shown in the reaction presented in Figure 1.

Next, the experimental energy transfer amounts were obtained from the examination of the time-resolved IR emission and using the Lennard-Jones collision rate parameters obtained by our group. Analysis of the data showed a loss of energy resulting from the collisions of different inert gas atoms with acetylene. Acetylene showed tremendous enhancement of energy transfer per collision rate when its vibrational energy was higher than 1.5x $10^4$ cm$^{-1}$. This energy is near the barrier of its isomerization to vinylidene. In order to test the reproducibility of the results, a new set of parameters was developed in collaboration with Bill Hase and colleagues from Texas Tech University. The parameters were for the exponential form equation of the Lennard-Jones potential. The classical trajectories were only obtained for the non-bonding interactions of Ar with acetylene using the computational program Venus 961. The computations were performed using a 7.0 Å impact parameter and the following vibrational energies for acetylene: 30.0, 40.0, 50.0, 60.0, and 70.8 kcal/mole. The results showed that the amount of transferred energy increases as the vibrational energy of acetylene increases. Thus, the pre-exponential parameters are valid since they are in agreement with the experimental results.
32. Acetylene-vinylidene isomerization dynamics and influence on energetics and collisional energy transfer

Mark A. Fennimore and Jonathan M. Smith
Department of Chemistry, Temple University

Acetylene has proven an interesting case study, both for its ubiquity in nature as well as its implementation in industry. It is readily used in a variety of commercial applications and scientific inquiries, and as such, knowledge of its chemical and physical properties is indispensable. Furthermore, its prevalence as an intermediate in combustion reactions makes the study of highly vibrationally excited acetylene a potentially lucrative endeavor, and perhaps holds the promise of a new and exciting field of study.

This promise has compelled us—and other researchers—to probe the dynamics of energized acetylene, through its photodissociation with vinylhalides, primary vinylbromide. This photodissociation is accomplished via vacuum UV at 193nm, which results in rovibrationally excited hydrogen bromide (HBr) and vibrationally excited acetylene; this excited acetylene is subsequently tracked via time resolved Fourier transform infrared emission spectroscopy; the data obtained in this manner is used in conjunction with molecular dynamics in order to explore the underlying mechanisms that dictate vibrationally excited acetylene’s behavior.

With the use of Born-Oppenheimer molecular dynamics, we are attempting to explore the behavior of highly excited acetylene and perhaps more importantly, its unstable isomer counterpart, vinylidene. Vinylidene is the bi-radical transient of acetylene and exists only on the order of the pico-second. The highly anharmonic potential surface of the isomerization between acetylene and vinylidene, the high barrier height towards the transition state, and the shallow potential well of the transient make an equilibrium between acetylene and vinylidene seemingly unlikely, but in fact such an equilibrium is observed both theoretically and experimentally given the appropriate detection method. It has further been demonstrated that by neglecting the isomerization equilibrium described above, the kinetics fail and only by its inclusion does theory match observation.

We present computational results using Born-Oppenheimer-molecular-dynamics (BOMD) to explore the creation of vinylidene via photolysis of vinylbromide. Once created, vinylidene will invariably tend towards acetylene due to the great exothermicity of the isomerization potential surface. Also, because acetylene in a known intermediate in combustion reactions, we will explore various free-radical and noble-gas collision trajectories in order to determine the resulting vibrational, rotational, and translational energetics of acetylene and its isomer. We will also present the ground-state energies of all relevant species at a refined level of theory, while honing in on the optimum molecular geometry for the transition state.
33. The presence of metals in the dissolved and sedimentary fractions of the Susquehanna-Lackawanna River system of Pennsylvania

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Intensive mining of four high-grade Anthracite coal zones in Northeastern Pennsylvania during the Industrial age has resulted in the reduction of pH of surrounding water bodies, and subsequent mobilization of various metals in the watershed. We have assessed the presence of iron, zinc, copper, calcium and nickel in the water column and sediments of the Susquehanna and Lackawanna rivers and their tributaries. This watershed receives drainage from heavily mined terrain and in turn is one of the major contributors of industrial pollution to the Chesapeake Bay. The distribution of metals in the dissolved aqueous and sedimentary fractions shows that there is a marked preference for certain metals to be deposited in the sediments rather than the dissolved fraction, while other metals are predominantly sequestered in the water column. These and other results will be presented in the context of the biogeochemical cycling of metals in river waters.
In this study we measured the UV/Vis-spectroelectrochemical properties of the fluoride-bound myoglobin and compared it to those of myoglobin without fluoride. From pH 4.7 to 9.0, the midpoint potential of myoglobin shows a decrease of about 20 mV. The decrease in the midpoint potential can be attributed to the binding of the hydroxide ion (OH\(^-\)) at higher pH. The midpoint potential of the fluoride-bound myoglobin is maintained at about 0 mV (vs SHE) from pH 6.4 to 9.0. However, at lower pH, the midpoint potential starts to decrease up to a limiting value of -45 mV (vs SHE) at pH 4.7. The shifting of the midpoint potential of myoglobin in the presence of fluoride coincides with the pK\(_a\) of a distal histidine at pH 5.7. Thus, the decrease in the midpoint potential is due to the stabilization of the coordinated fluoride ion, through hydrogen bonding from the protonated distal histidine. Based on the midpoint potentials of myoglobin with fluoride ion, the calculated difference in free energies between the myoglobin with the unprotonated distal histidine (above pH 6.4) and that with the protonated histidine (pH 4.7) is about 4.8kJ, which is the typical energy of a hydrogen bond. This is a promising method that can be used to quantify interactions between distal residues and heme-bound ligands. Such interactions are key to O\(_2\) binding in hemoglobin and myoglobin and O-O bond cleavage in heme peroxidases.
35. Preparation and Characterization of Covalently Conjugated Polymer-Gold Nanocomposites Useful for Biomedical Diagnostics

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We synthesized a covalently conjugated polymer-gold nanocomposite which has a wide range of potential applications in the areas such as biosensing, biomedical diagnostics, and targeted therapeutics. The process involves the synthesis of carboxylic acid-terminated gold nanoparticles followed by covalent conjugation of the nanoparticles with an amine-functionalized polymer, polyethyleneimine. We first synthesized citrate-stabilized gold nanoparticles, which were functionalized with carboxylic acid groups through a ligand exchange reaction with thioctic acid. We established the optimum condition for the interaction between carboxylic acid-terminated gold nanoparticles and polyethyleneimine, which affords the formation of stable nanocomposites without significant aggregation. Subsequently, the electrostatically bound polymer-gold nanocomposites were covalently conjugated using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide. The resulting nanoparticles and nanocomposites were analyzed by transmission electron microscopy, UV-visible spectrophotometry, and attenuated total reflectance-infrared spectroscopy. In future, the research will be extended to the preparation of nanocomposite composed of biocompatible poly(amidoamine) (PAMAM) dendrimer. The covalently conjugated polymer-gold nanocomposite can find its use in targeted diagnostic imaging, when functionalized appropriately with a specific biomolecular binding moiety.
36. PRODUCTION, PURIFICATION, AND CHARACTERIZATION OF A DESIGNED 3-HIS DI-IRON CARBOXYLATE PROTEIN

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Nitro groups are important features in numerous biologically active compounds. To date, there are only two oxygenases known to catalyze their formation. One of these is AurF, which uses molecular oxygen and catalyzes the stepwise mono-oxygenation of p-aminobenzoate to form p-nitrobenzoate, a necessary component of the subsequent synthesis of aureothin, an antibiotic. AurF is a naturally-occurring di-iron carboxylate protein found in *Streptomyces thioluteus*. Its active site, while similar to that of many well-studied di-iron carboxylate proteins, contains an extra histidine residue and is therefore of great interest for scientific study.

As natural proteins are complex and can be difficult to study, a minimal, designed 3-His protein has been developed which mimics the core structure of the natural protein. This investigation seeks to determine whether this designed protein also mimics the functionality and spectroscopic properties of the natural protein. If so, studies of the designed protein would greatly aid our understanding of how the natural AurF protein functions.

At present, the designed 3-His protein has been over-expressed, produced, and purified. The presence of the correct protein was confirmed using gel electrophoresis, high-performance liquid chromatography (HPLC), and MALDI-TOF mass spectrometry. The metal binding and oxygen-activating capabilities of the 3-His protein were then observed by fluorescence and UV-visible absorption spectroscopy. The secondary structure and folding properties of the protein were analyzed using circular dichroism (CD) spectroscopy. In the future, electrochemical potential studies and Mössbauer spectroscopic studies will be conducted on the synthetic protein.
37. Bacterial Stress Response to Hydrogen Peroxide

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Bacteria demonstrate the ability to respond to stress at an observable level. Using an agar plating method, we have investigated the effects of hydrogen peroxide, an oxidative stress inducing molecule. The Carestream Molecular Imaging software system was used to take pictures of each plate and analyze the data with respect to the number and area of each colony. By plating increasing number of *Escherichia coli* on plates with different hydrogen peroxide concentrations, we have investigated the effects of hydrogen peroxide on the area of colony, including the distribution of the area of the colonies. Our results show low doses of the stressor affect the distribution of the area of the colonies, even though the area of the colonies is not significantly altered. Higher levels of hydrogen peroxide decrease the area of the colonies, but also affect the distribution of the area of the colonies. These results indicate that the bacterial responses are complex and not totally captured by analyses that are based only on the mean behavior of the bacteria.

38. PURIFICATION OF MULTIWALL CARBON NANOTUBES BY DYNAMIC OXIDATION IN AIR

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Multiwalled carbon nanotubes (MWCNTs) have shown promise in a variety of applications but are still produced as a complex mixture containing amorphous and graphitic carbon, MWCNTs in addition to catalyst that if used may be present at a weight of several . We report initial results on using dynamic oxidation, a method validated for single walled carbon nanotubes (SWCNTs). Dynamic oxidation is based on the selective oxidation of carbonaceous impurities during the heating of as-produced MWCNTs at a constantly increasing temperature in air. However, compared to SWCNTs there are fewer quantitative techniques to assess MWCNT purity. We have used Raman spectroscopy, X-ray diffraction and Transmission Electron Microscopy to assess the effects of dynamic oxidation on MWCNT morphology and purity and ultimately to determine the optimal temperature of final oxidation for MWCNTs with and without metal catalyst.
39. Synthesis of a methylenedioxy-substituted ribonuclease inhibitor

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Ribonuclease (RNase) catalyzes the degradation of RNA into smaller components. For instance, *E. coli* RNase III carries out the hydrolysis of an RNA phosphodiester,\(^1\) and HIV RNase H hydrolyzes an RNA bond in RNA-DNA hybrid molecules\(^2\). To carry out these processes, both ribonucleases require two divalent metal ions in their active site. In previous studies it has been reported that the specific arrangement of the three oxygen atoms in 2-hydroxyisoquinoline-1,3(2\(H\),4\(H\)) dione 1 mimics the metal ion-mediated protein interaction, making compound 1 an inhibitor of ribonucleases like *E. coli* RNase III and HIV RNase H. It may be possible to synthesize more potent inhibitory compounds and to build in selectivity, and for that reason our lab is exploring the effect of substitution on the parent structure 1. 2-Hydroxy-6,7-methylenedioxy-1,3(2\(H\),4\(H\))-isoquinolinedione 3 is one derivative of the parent compound and it is being prepared in the lab by using a six-step sequence beginning with piperonal 2.

\[ \text{1} \rightarrow \text{2} \rightarrow \text{3} \]

40. Comparison of peripheral blood cells and Bone Marrow Cells of Osteogenetic Imperfecta mice to Wildtype mice

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Osteogenetic Imperfecta (OI) is an inherited bone fragility disorder characterized by genetic defects in type 1 collagen expression. Mice models of OI mutations are currently being used to investigate means of applying gene therapy to cure the disorder. However no documentation demonstrates the process of hematopoiesis in the OI. Addressing this issue is important in understanding how osteoblasts (bone making cells) affect hematopoiesis in the disease.

In this experiment we examine the differences in peripheral blood cells and bone marrow cells (BMCs) of the osteogenesis imperfect murine (OIM) in comparison to wildtype (WT) mice.

A complete blood count (CBC) of the peripheral blood showed significantly low numbers of white blood cells (WBC), red blood cells (RBC) and hemoglobin. However, WBC subsets (B cells, T cells, monocytes and granulocytes) and platelets showed statistical similarities in numbers. An analysis of BMCs indicated similarities in B cells, monocytes and granulocytes. On the other hand, our data indicated a significantly low number of hematopoietic stem cells in the bone marrow of OI mice. Spleen analysis indicated a smaller spleen in OI. However, there was a significantly high number of hematopoietic stem cells in the spleen of OI. Out data indicates that even though OI has significantly low number of cells, the cells are normal but the microenvironment in which the cells exist in the bone marrow is abnormal. This is supported by a significantly high number of cells in the spleen which replenishes the hematopoietic stem cells in the bone marrow.

41. Synthesis of Low-Coordinate Manganese Clusters

Carol Lam, Michael Zdilla

Photosystem II uses a tetranuclear manganese structure to achieve the efficient oxidation of water. Current synthetic models feature 6-coordinate manganese with multidentate ligation, which stabilizes high oxidation states, and leaves no coordination site for water to bind. For a viable biomimetic chemistry, this project focuses on the synthesis of 4-coordinate manganese-oxo clusters with sterically bulky terminal ligands. The development of such low-coordinate clusters offer promise for better biomimetic models. Using oxidation reactions with Managanese compounds and bulky ligands, low coordinate clusters were attempted to be made in nitrogen-rich environment. Prepared clusters were characterized by NMR and single-crystal X-ray diffraction techniques.
42. Differentiating UV-VIS Spectra by Normalized Line Spectra Analysis
Kelsey Wilkinson, Thomas Pritchett
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A new method for differentiating ultraviolet-visible spectroscopy (UV-VIS) spectra has been developed. The absorbances from the spectrum are normalized. The first derivative of the spectrum is then used to determine the minima, maxima, and inflection points. The normalized absorbances are plotted against the wavelengths, at which the minima, maxima, and zero-intercepts occurred. These plots are called Normalized Line Spectra.

The discriminating variables between the derivatives of different compounds are the actual wavelengths selected for normalization using the first derivative spectra as well as the normalized absorbances at these wavelengths – similar to the use of fragment masses and relative intensities in mass spectrometry to identify different compounds. Examples will be given to show how similar spectra can be differentiated using the Normalized Line Spectra.

43. Pyrite Oxidation Suppression in Mining Waste through the Coating of a Two-tailed Phospholipid
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In recent years, acid mine drainage (AMD) has become one of the most pressing environmental issues. When left untreated, mining waste, which can contain toxins such as mercury, arsenic, and lead, will spontaneously oxidize to form a variety of acidic species, the chief constituent of which being, H₂SO₄, which forms from the oxidation of pyrite (FeS₂) (see reactions 1 and 2). A potential protocol for the remediation of AMD sites is the suppression of pyrite oxidation is to use a two-tailed phospholipid coating. Phospholipid added to the waste in solution forms a dense coating around the waste particles, protecting the pyrite from attack by Fe³⁺ ion, the initiator of the oxidation reaction.

Elemental analysis of the waste was performed using EDS and XRD. Fresh and aged waste samples (lipid coated and a control) were placed in fritted glass columns and left to react under the flow of pH controlled water. Oxidation rates and the solution pH were measured daily and the concentration of sulfate ions were measured using ion chromatography. The thermal stability of the coating was also assessed by repeating the flow experiment while subjecting the samples to freezing temperatures. Initial findings suggest that the lipid coating is effective in suppressing pyrite oxidation, the main contributor to acid production in mining waste.
44. Characterization of a Putative Trypanosome Transcription Factor

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Trypanosoma brucei, the parasite responsible for causing African Sleeping Sickness, has many unusual biochemical features and processes, including RNA Polymerase II (RNAPII)-dependent gene transcription. For example, protein coding gene promoters have yet to be identified and several known transcription factors appear absent from the genome. We have identified a trypanosome-specific protein that is associated with the RNAPII transcriptional machinery: TbTAF49 (TFIIB Associated Factor, 49kDa). While this protein contains motifs associated with known transcription factors, the protein is unique to trypanosomes. RNA interference studies have revealed that TbTAF49 is essential for parasite growth. We have also demonstrated that this protein tightly interacts with DNA. In these experiments, biotinylated DNA bound to magnetic streptavidin beads was mixed with trypanosome nuclear extract. Following several stringent washes containing either high salt (KCl) or nonionic detergent (TWEEN20) to challenge the protein-DNA interaction, interacting proteins were identified through Western blot. Five unique DNA sequences were queried for interaction with TbTAF49: The trypanosome U6 and Spliced Leader gene promoter sequences, an internal region from the TbTAF49 open reading frame, unrelated DNA from lambda phage, and the internal region of the bla gene. Despite the stringent challenge with either 1.0M KCl or 0.2% TWEEN20, TbTAF49 interacted with all DNA sequences tested. Thus, TbTAF49 appears to bind DNA in a non-specific fashion. Currently, work is underway to determine the role of this protein in the parasite.
Solid polymer electrolytes (SPEs) are safer than liquid electrolytes but have lower conductivities at room temperature (RT) compared to liquid electrolytes. We have previously shown that nanostructured electrolytes composed of POSS-PEG₈ (polyoctahedral silsesquioxanes-ethylene glycol) and POSS-Benzyl₇(BF₃Li)₃, whose structures are shown in Figure 1, have reasonable conductivities at RT (1 x 10⁻⁴ S/cm at 25 °C), which reach 2.6 x 10⁻³ S/cm at 90 °C. These materials are viscous liquids. As shown in Figure 1, one end of the Li salt is very hydrophilic (ionic), and the other is very hydrophobic (many phenyl groups). When mixed with POSS-PEG₈, the Li⁺ dissociates, and the nanomaterial appears to be microphase separated. In order to form a SPE, we have mixed POSS-Benzyl₇(BF₃Li)₃/POSS-PEG₈ with two polymers, polystyrene (PS) and a block copolymer of PS and polyethylene oxide (PEO), PS-b-PEO, in which the molecular weight of the PS block is 384,000 and the molecular weight of the PEO block is 8,000; We expected that the PS would preferentially separate into the hydrophobic (structural) phase. The PS-b-PEO was used as a surfactant to compatibilize the hydrophobic and hydrophilic microphase separated domains. We did form solids when the POSS-Benzyl₇(BF₃Li)₃/POSS-PEG₈ was mixed with PS or PS/PS-b-PEO. However, our goal was to minimize the amount the PS/PS-b-PEO that was needed to form a solid polymer electrolyte.

Figure 1: Structures of POSS-Li₃ and POSS-(BF₃ Li)₃; R=Phenyl
46. Chi Ngong Tang, Jhenny Galan, Shubhashis Chakrabarty, Zhiwei Liu, Guillermo Moyna
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Studies of the conformational flexibility of heterocyclic arylamide foldamers
Foldamers are synthetic polymers that adopt stable, secondary structures in solutions. The folding of foldamers is controlled through non-covalent interactions like hydrogen bonds (H-bond) and \( \pi-\pi \) stacking. Arylamides are an important class of foldamers that consists of aromatic rings and peptide bonds. Previous research showed changing various H-bond acceptors in different sites of the aromatic ring influences the conformational flexibility and often controls the overall geometry of the oligomers.

Using a combination of quantum mechanics, molecular dynamics simulations, and NMR NOE experiments, the conformational behavior of N-methylfuroylamide and N-methylthiophenecarbonylamide, foldamers building blocks, in various solvents is examined. The results are compared to non-heterocyclic arylamides with similar acceptors but different H-bonding geometry and electronic features. We have assessed quantitatively the outcome of varying structural features, solvent types, and H-bonding abilities of the acceptor on the conformational preference of arylamides. The quantitative evaluation of the backbone flexibility will contribute to a more efficient rational design of functional foldamers.

47. In Situ Vibrational Sum Frequency Spectroscopy of the Electrolyte/Electrode Interface for Modeling Structure, Dynamics and Reactivity of a Working Fuel Cell

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Vibrational Sum-frequency generation (VSFG) spectroscopy is a second-order nonlinear optical technique which is intrinsically sensitive to vibrations of molecules within only several molecular layers at the interface. We use SFG to study the electrochemistry occurring at the interface between a metal and an aqueous salt solution as a voltage is applied, thereby simulating a working fuel cell. Interfacial chemistry strongly influences the overall efficiency of the cell. The results obtained by studying the electrochemical interface at different salt concentrations may provide insight into the structure and orientation of water molecules in the Helmholtz layer, as well as the solvation and adsorption of the ions undergoing oxidation and reduction at the interface. We present the experimental setup in our laboratory that enables this study and provide preliminary VSFG data of the water structure at the water-gold interface, as a simplified model of an electrolyte/electrode interface.
48. Creation and Characterization of Mutated 2-His Diiron Carboxylate Model Proteins

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Diiron proteins represent a rapidly growing class of metalloenzymes that are involved in the binding and activation of oxygen in biological systems. Certain similarities are apparent between individual proteins within the diiron family, like an EXXH motif housed within a four-helical bundle. The arrangement of the active site of each individual enzyme and the overall scaffolding of the protein, however, vary from species to species. What becomes of great importance to scientific study, therefore, is how these natural proteins adjust their active site environments to exploit the chemical properties of their iron cofactors and thus obtain such a vast variety of reactions.

To better understand the matter, de novo design of synthetic models has been employed. By positioning ligands within minimal scaffolding to promote certain catalytic functions, these peptide-based models seek to better explain the chemistry of the natural systems. Like the natural proteins, the functions of the peptide models can be altered through slight adjustments of the active site environment. Our study centers around creating multiple mutants using a 2-histidine model to investigate how certain required residues interact within a 3-histidine model. The optimization of PCR conditions allowed the successful mutation of single amino acid residues at the 18th, 81st, and both 18th and 81st positions of the 2-His gene, as verified by genetic sequencing. Also confirmed by genetic sequencing was the 2-His mutant protein with mutations at all three of the desired sites.

The triple mutant, along with two single mutant proteins, were expressed successfully in E. coli. Both single mutant proteins were purified via high-performance liquid chromatography, with the molecular weight of each model confirmed by MALDI-TOF spectroscopy. Work has been done to express the triple mutant protein. Purification procedures are underway to isolate the protein from cell lysate for characterization studies, which include MALDI-TOF mass spectroscopy, circular dichroism, cobalt binding, and ferroxidase activity assays.
THE ELEVENTH ANNUAL STUDENT POSTER SESSIONS

HIGH SCHOOL POSTERS
49. Caffeine Concentration in Popular Brands of Coffee

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The purpose of this experiment was to compare the caffeine content of various popular brands of coffee. The coffees used were Folgers Medium Roast, Wegmans Exotic Day Break Roast, Starbucks Pike Place Roast, Eight O’Clock Medium Roast, Peet’s House Blend, Maxwell House Medium Roast, and Dunkin’ Donuts Medium Roast. Coffee of each brand was brewed then analyzed for caffeine content using high performance liquid chromatography. It was expected that the caffeine contents would be relatively close, but that the most popular brands – Folgers, Maxwell House, and Starbucks – would contain the most caffeine. However, this prediction was not entirely true. Of the brands tested, Folgers contained the most caffeine, followed by Peet’s, Maxwell House, Eight O’Clock, Dunkin’ Donuts, Starbucks, and finally Wegmans Exotic. Additionally, the caffeine contents varied widely, with Folgers Medium Roast producing 151% of the caffeine content of Wegmans Exotic, the brand which produced the least caffeine. These results show that, to maximize caffeine consumption, customers should purchase Folgers Medium Roast coffee over its competitors.

50. The Effect of Mass of Grounds Used on Caffeine Content in Coffee

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This paper examines the effect amount of coffee grounds on the caffeine concentration. LeChatelier’s principle predicts that a change in status quo prompts an opposing action in the responding system. Therefore, as more coffee is added, caffeine concentration should increase at a slower rate. To test this, both the mass of grounds used and darkness of coffee—as another check—were utilized. Samples at 50%, 75%, 100%, 125%, 150%, 200%, and 300% of the recommended amount of coffee were used. The resulting samples were run through an HPLC and UV Spectrometer to quantify both the darkness of the coffee as well as the concentration of caffeine. Instead of finding a plateau or hyperbolic relationship, both sets of data yielded a linear correlation. It would appear that a specific mass of coffee grounds yields a specific concentration of caffeine, irrespective of the molarity of caffeine already in solution.
51. Correlation between Brewing Temperature and Caffeine Concentration in a Typical Cup of Coffee

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This study was designed to investigate the correlation between caffeine concentration in brewed coffee and the brewing temperature. Basic principles of solubility dictate that as system temperature increases the solubility of solutes increases proportionally. Scaled cups of Folgers Medium Roast Coffee were brewed at various temperatures. Samples of each brew were then collected and analyzed for caffeine concentration using high performance liquid chromatography. The amount of dissolved caffeine was found to increase in a linear relationship in milligrams per degree Celsius with brewing temperature. As the brewing temperature approached the boiling point of pure water, there was no plateau effect observed in the amount of caffeine present. Additionally, the concentration of flavor causing compounds was found to similarly increase with temperature, thus yielding the possibility of a creating stronger tasting brew without wasting additional beans. Based on this study, it is possible to increase the caffeine content of a typical morning cup of coffee by approximately 11% by simply brewing at a higher temperature, something regular coffee drinkers can do in their own homes.
52. Using High Performance Liquid Chromatography to Determine How Brew Time Affects the Amount of Caffeine in Coffee

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In this experiment High Performance Liquid Chromatography (HPLC) was used to determine the amount of caffeine in coffee brewed for different lengths of time. The goal of this experiment was to uncover a correlation between brew time and the amount of caffeine in coffee. It was predicted that the relationship would be directly proportional, hypothesizing that given more time, more caffeine would dissolve into the coffee solution. However it was found that a power model more accurately describes this relationship. Coffee was brewed at varying amounts of time and then each sample was run through the HPLC. Next, the data was used to calculate the amount of caffeine in each sample and the results were graphed. Analysis showed a correlation between the two variables, but not a directly proportional relationship as predicted. The percentage of caffeine that comes out of the coffee during the first 10 seconds of brewing was also calculated. The results of this experiment could determine the ideal brew time for maximizing the amount of caffeine in coffee.
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