Conference Schedule

9:00 AM  Conference Opens: ESB 1001

9:00 – 9:30 AM  Welcome Statements
Kalju Kahn, UC Santa Barbara
David Mann, CEO of Vascular Biosciences

9:30 – 11:45 AM  Talks, first session

9:40 AM  Anthony Montenegro, CSU Fullerton
Kinetics Study of Reaction of Pinenes with Hydroxyl Radical at 1–8 Torr and 240-340 K Using the Relative Rate/Discharge Flow/Mass Spectrometry Method

10:00 AM  Crisand Anderson, Chapman University
Electron Shuttling by Humic Substances in Wetland Soils: Exploring a Novel Control on Anaerobic Decomposition

10:20 AM  Stephanie Moffitt, UC Santa Barbara
The Synthesis of an Exchange Bias Material Through Solid State Mixtures of Co and YFeO₃

Coffee Break

11:00 AM  Lucy Darago, UC Santa Barbara
Ca₂₋ₓEuₓMgSi₂O₇: Development of New Yellow Phosphors for Solid-State White Lighting

11:20 AM  Daniel Hernandez, CSU Long Beach
Synthesis and Characterization of Titanium Dioxide Composites with Applications in Dye-Sensitized Solar Cells

11:40 AM  Ludmila Youchkovets, Mount St. Mary’s College
Induced Monitoring–Flash–Quench-Induced Oxidative Damage to Guanine via HPLC: Dependence on Quencher

12:00 PM  Granton Jindal, Caltech
Using the H-tag to Standardize Purification of Azide-labeled Proteins

12:20 – 1:00 PM  Lunch Break and Poster Setup
1:00 – 2:40 PM  Talks, second session

1:00 PM  Daniel Bahr, CSU Long Beach
Chemical and Mechanical Analysis of Green Composites Made from Natural Fibers of Hemp, Flax and Hay

1:20 PM  Darin Khumsupan, CSU Long Beach
Reconstituted High Density Lipoprotein: a Nanovehicle to Transport and Delivery of the Antioxidant Piperine

1:40 PM  Maia Kinnebrew, UC Santa Barbara
Magnetic Resonance Spectroscopy Probes the Structural Assembly of a Solar Powered Membrane Protein

2:00 PM  Tuyen Tran, CSU Long Beach
Acrolein, a Tobacco Smoke Component Impairs Function of Apolipoprotein E, an Anti-atherogenic Protein

2:20 PM  Bianca M. Rivas, CSU Northridge
Diastereoselectivity of Radical Carbon–Carbon Bond Formation in Naphthalene-Stabilized Propargyl Cations

2:40 – 3:40 PM  Poster Session

3:40 – 4:00 PM  Talks, third session

3:40 PM  Megan Jackson, Caltech
Electrocatalytic Carbon–Halogen Bond Formation Using Halide Ions

4:00 PM  Amanda Young, Vanguard University
Mechanism of Didebromination by Zinc in Styrenedibromides

4:20 PM  Alex Bajaj, UC Los Angeles
Cloning, Expression, Purification and Crystallization of Rv2224c, a Putative Carboxylesterase, from Mycobacterium tuberculosis

4:40 PM  Cara Magnabosco, University of Southern California
A Characterization of the Biology and Nutrient Cycling of Two Glacial Lakes in Isfjord Radio, Svalbard

5:00 PM  Conference Closes
Kinetics Study of Reaction of Pinenes with Hydroxyl Radical at 1–8 Torr and 240-340 K Using the Relative Rate/Discharge Flow/Mass Spectrometry Method

Anthony Montenegro, Jacob S.A. Ishibashi, Phuong Lam, Zhuangjie Li

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Dr. Zhuangjie Li, Associate Professor

Abstract

A kinetic study was conducted on the reactions of α- and β-pinene with hydroxyl radicals at 1-8 torr and from 240K-340K using the relative rate/discharge flow/mass spectrometry (RR/DF/MS) technique to facilitate a better understanding of the role of pinene in the air pollution system. With isoprene as the reference compound our kinetic results indicate that at 298 K the reaction of α- and β-pinene with hydroxyl radicals has little pressure dependence at 1-3 Torr and their rate constants were determined to be $k_{\alpha\text{-pinene}} = (5.51\pm0.129)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{\beta\text{-pinene}} = (8.03\pm0.133)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ respectively, which are in good agreement with literature values within experimental uncertainty. At 240-340K the rate constant was found to negatively depend on temperature. The Arrhenius equation for α-pinene and β-pinene with hydroxyl radical was determined to be $k_{\alpha\text{-pinene}} = (1.34\pm0.22)\times10^{-11}\exp[(420\pm46)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{\beta\text{-pinene}} = (1.65\pm0.10)\times10^{-11}\exp[(470\pm17)/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. Using the rate constant determined at 277 K in this work and the average global hydroxyl radical concentration, the lifetime of α- and β-pinene was estimated to be 5.8 hours and 4.7 hours, respectively.
Electron shuttling by humic substances in wetland soils: exploring a novel control on anaerobic decomposition

Crisand Anderson, Chapman University
Jason K. Keller, Chapman University

Peatlands store one-third of the earth’s soil carbon and are responsible for almost 10% of the global methane flux. Despite their importance in the global carbon cycle, much of the decomposition in these wetland ecosystems cannot be explained by any known microbial process. Additionally, methane production is suppressed for extended periods by an unknown mechanism in many peat soils. We explored the potential for humic substances to act as organic electron acceptors (thereby suppressing methane production) in peatland soils. Humic reduction was quantified by comparing the electron shuttling capacities of oxidized peat soil and peat soil that was chemically reduced with H\(_2\) and a Pd catalyst. Measurements of electron shuttling capacities were compared to the rates of methane and carbon dioxide production during a two month laboratory incubation. Results suggest that the reduction of soil humics can be an important microbial process in anaerobic peatland soils, especially in ombrotrophic bog-like soils. However, the data also suggests that additional factors (pH, soil quality, microbial community, etc…) play a role in regulating CH4 production in peatland soils.
The synthesis of an exchange bias material through solid state mixtures of Co and YFeO₃

Stephanie Moffitt, University of California at Santa Barbara
Daniel Shoemaker, Ram Seshadri, Materials Research Laboratory

Exchange bias materials allow magnetic fields to be pinned in a certain direction. This pinning effect has the potential for being used as a spin valve in magnetoresistive random access memory (MRAM). It has been shown that by reducing out metallic, ferromagnetic nanoparticles within a lattice structure of an antiferromagnetic compound an exchange bias effect can be seen in the resulting material. This project attempts to create a new exchange bias material based on the above findings. Ferromagnetic cobalt nanoparticles will be reduced from a yttrium iron oxide (YFeO₃) anti-ferromagnetic matrix. This system has a Neel temperature of 654 K which makes it superior to previously published exchange bias systems because the exchange bias effect can be seen at room temperature. The material is made by first dissolving metal nitrates in water and then adding oxalic acid to create a homogeneous mixture of oxalates. Decomposed oxalates are heated at 1350 Celsius for 72 hours to make the single phase precursor. Thermogravimetric analysis is used to determine the ideal temperature required to reduce out the cobalt without reducing out the iron. The exchange bias material produced will be analyzed using temperature and field dependent susceptibility measurements. In response to this analysis the percent of cobalt will be adjusted to maximize the exchange bias property of the material. This project is funded by the RISE program at the University of California, Santa Barbara.
Ca$_{2-x}$Eu$_x$MgSi$_2$O$_7$: Development of new yellow phosphors for solid-state white lighting

Lucy Darago

College of Creative Studies, Chemistry and Biochemistry

University of California, Santa Barbara

Mentor: Nathan George, Department of Chemical Engineering
P.I.: Professor Ram Seshadri, Materials Department and Materials Research Laboratory

Phosphors consist of a host lattice doped with an activator ion, typically Ce$^{3+}$ or Eu$^{2+}$. Phosphors are used in solid-state white lighting to convert some of the blue light from an (In,Ga)N light emitting diode (LED), to yellow/orange: the combination appears white. Their usage depends on the fact that phosphors emit longer wavelengths than they absorb, ideally in the orange/red, as the system relaxes from an excited state to a ground state. The ideal phosphor is excited at 460 nm (the emission wavelength of conventional blue LEDs), has an emission wavelength in the yellow to red range of the color spectrum, and is efficient. In this study, the phosphor Ca$_{2-x}$Eu$_x$MgSi$_2$O$_7$ was investigated. The system was prepared by solid-state reactions, and the purity was confirmed by X-ray diffraction. First, heating temperature was optimized (to 1200 °C) to obtain a phase-pure compound and to maximize emission and excitation intensity, which were measured by fluorimetry. Next, Eu$^{2+}$ concentration was optimized (to 2.5 %), again to obtain maximum emission and excitation intensity. Ca$_{2-x}$Eu$_x$MgSi$_2$O$_7$ was found to emit light at a wavelength of 536 nm (green). Quantum yield measurements indicated that the compound's efficiency was about 14%. Future work will include co-doping with manganese and incorporation of aluminum into the system to try to red-shift the compound by disrupting the europium coordination or increasing crystal field splitting. Further characterization of the compound by temperature-dependent quantum yield measurements will also be performed.
Synthesis and Characterization of Titanium Dioxide Composites with Applications in Dye-Sensitized Solar Cells

Author: Daniel Hernandez, California State University, Long Beach

Mentors: Sergio Mendez, Department of Chemical Engineering, California State University, Long Beach; Shahab Derakhshan, Department of Chemistry & Biochemistry, California State University, Long Beach; Winny Dong, Tanya Faltens, Department of Chemical & Materials Engineering, California State Polytechnic University, Pomona

Dye-sensitized solar cells (DSSCs) are a class of relatively new, low cost, thin film solar cells based on a semiconductor formed by an electrolyte and photo-sensitized anode. One of the main components of the anode is a titanium dioxide thin layer, which absorbs the photo-catalytic molecular dye. In our study we focused on increasing the photo-catalytic performance of TiO$_2$ layer by modifying the surface chemistry of the titanium nanoparticles. This was accomplished using sol-gel synthesis methods and thermal treatments to manipulate the porosity, shape, and crystal structure of the particles. In addition, we performed a second set of synthesis reactions in which we doped the nanoparticles with carbon nanotubes. The TiO$_2$ particles and composites were then analyzed and characterized using electron microscopy (SEM), infrared spectroscopy (FTIR), x-ray diffraction (XRD), and BET nitrogen adsorption. Furthermore, their performance was tested using chemical degradation under UV-light. Our studies found the TiO$_2$/CNT composite to perform best. We believe this photo-catalytic synergy between TiO$_2$ and CNTs is due to their combined excellent UV and visible light absorption properties.
Induced Monitoring - Flash-Quench-Induced Oxidative Damage to Guanine via HPLC: Dependence on Quencher

Ludmila Youchkovets, Mount St. Mary’s College
Mentor: Dr. Eric Stemp, Department of Physical Sciences, Mount St. Mary’s College

Oxidative damage is important because it contributes to aging, cancer, and various types of diseases. Here oxidative damage to guanine was monitored by HPLC. The oligonucleotide strand, 5’-ATATGATATGGATATGATAT-3’ and its complement were made and purified. The duplex DNA was subjected to flash-quench treatment using Ru(phen)$_2$dpdz$^{2+}$ as the photosensitive intercalator and using Ru(NH$_3$)$_6^{3+}$ or Co(NH$_3$)$_5$Cl$^{2+}$ as the quencher. The DNA was digested with phosphatase to the nucleotide level and the mixture was then analyzed by reversed-phase HPLC. The nucleotides were observed by UV absorbance. With Ru(NH$_3$)$_6^{3+}$ as the quencher, 8-oxo-G was detected. With Co(NH$_3$)$_5$Cl$^{2+}$ as the quencher, no peak for 8-oxo-guanine was observed. When Lysine-Lysine-Lysine is also present during the flash quench treatment, two extra peaks were observed, consistent with formation of a crosslinked product. Attempts to isolate this product are underway.
Using the H-tag to Standardize Purification of Azide-labeled Proteins

Author: Granton Jindal, Caltech
Co-Mentor: Alborz Mahdavi, Caltech
Mentor: David Tirrell, Chemical Engineering, Caltech

Understanding protein expression levels and dynamics is critical to determining how cells function. Various methods have been developed to quantify proteomic changes in cells. The Tirrell laboratory has previously developed a method for tagging newly synthesized proteins, named bio-orthogonal non-canonical amino acid tagging (BONCAT). BONCAT involves metabolic labeling of proteins with the artificial amino acid azidonorleucine (ANL). We have developed a tag that can react with ANL and be used for enrichment of labeled proteins. It is demonstrated that the click reaction between the alkyne functionality of the tag and azide in ANL forms a stable triazole link. Azide-labeled GFP protein with an N-terminal FLAG tag was used as the test protein, and was enriched from a pool of Hela cell proteins. This strategy can be used in a variety of contexts to enrich for proteins that are labeled with artificial amino acids with azide side chains.
Chemical and Mechanical Analysis of Green Composites Made from Natural Fibers of Hemp, Flax and Hay

Author: Daniel Bahr, Kevin Cheng and Jay Chiang, Department of Chemical Engineering, California State University, Long Beach
Mentors: Sergio Mendez, Roger C. Lo, Yu-Fu (Paul) Ko, and Behnam Bahr, National Center for Green Technologies and Education, California State University, Long Beach

The goal of this project was to develop green composites that could potentially serve as an alternative to materials derived from non-renewable sources. The two systems that were investigated are woven fabrics and chopped fibers imbedded in a resin. Flax and hemp woven fabrics were chosen because of their lightweight and exceptional mechanical properties. To make these woven composites withstand moist environments, a commercially available marine resin was utilized as the matrix. A hand lay-up process was utilized to make multi-layers of fabric imbedded in the resin. The chemical properties were measured with FTIR spectroscopy, and the morphology was imaged with scanning electron microscopy. The tensile, three-point bending, and edgewise compression strengths of these green textile/woven composites were measured using ASTM protocols. We also studied composites made from hay straw fibers. Various chemical treatments of the raw hay were investigated to enhance the moisture resistance and mechanical strength. Our vision for this work is to minimize deforestation by using sustainable agricultural resources to fabricate new green composites for the construction building industry.
Reconstituted High Density Lipoprotein: a Nanovehicle to Transport and Delivery of the Antioxidant Piperine

Darin Khumsupan and Vasanthy Narayanaswami

Department of Chemistry & Biochemistry, California State University, Long Beach, Long Beach, CA 90840

The objective of this study is to employ reconstituted high-density lipoproteins (HDL) containing the N-terminal (NT) domain of human apolipoprotein E3 (apoE3) as a vehicle to transport and deliver an antioxidant called piperine to target sites. HDL are lipid-protein complexes that play a role in plasma cholesterol transportation in the body. A sub-fraction of HDL contains apoE, which plays a significant role in plasma cholesterol homeostasis. The NT domain of apoE has the ability to bind lipoprotein receptors, which allows it to mediate binding and uptake of lipoprotein complexes at the cell surface. Recombinant human apoE3-NT domain was over-expressed, isolated, and purified using a bacterial expression system. HDL was prepared by reconstituting dimyristoylphosphatidylcholine with human apoE3-NT in the presence and the absence of piperine. HDL was separated from protein-free lipid vesicles and lipid-free protein by size-exclusion chromatography. Fluorescence spectral analysis of the reconstituted HDL was carried out by taking advantage of the innate fluorescence properties of piperine. Our observations indicate that piperine has partitioned into the hydrophobic milieu of the phospholipid bilayer of HDL. This was confirmed by the blue-shift in the wavelength of maximal fluorescence emission. We propose that HDL containing apoE-NT may serve as a potential ‘nanovehicle’ for transporting and delivering piperine to target sites.
Magnetic Resonance Spectroscopy Probes the Structural Assembly of a Solar Powered Membrane Protein

Maia Kinnebrew

UCSB Department of Chemistry and Biochemistry

Katherine Stone

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Proteorhodopsin (PR) is a solar powered membrane protein that has significant technological implications for alternative energy. The high yield of proton pumping by PR together with its potential for mass production presents realistic opportunities for incorporation in bio-inspired energy-harvesting devices. In order to maximize the energy output of such devices, it is necessary to obtain the structure of PR in the membrane. However, obtaining structures of membrane proteins, especially those in oligomeric assemblies, is very challenging as a result of the oligomers’ large size, disordered nature, and ability to resist crystallization. Past work in the Han laboratory reveals the previously unknown oligomer interface, and here we focus on a region of the protein, residue 58, where unique contacts take place. We seek to probe this interfacial region of the protein as we vary both the membrane environment and the oligomeric state. By employing site-directed spin labeling and electron spin resonance, we were able to obtain structural details of the protein. We found that site 58 is sensitive to changes in the detergent concentration, indicating that it is either exposed to the detergent or it lies on the membrane interface. We also observe significant broadening of the continuous wave line-shape as the oligomeric state changes; this suggests that residue 58 is interacting with a neighboring PR on the oligomer interface. Through increasing knowledge of the structure of PR, plans to implement PR as a light-harvesting device become both more efficient and practical.
Acrolein, a Tobacco Smoke Component Impairs Function of Apolipoprotein E, an Anti-atherogenic Protein

Tuyen N. Tran, Tien Vu, California State University, Long Beach

Vasanthy Narayanaswami, Department of Chemistry & Biochemistry, California State University, Long Beach, Long Beach, CA 90840

The objective of the study is to examine the effect of oxidative modification on the structure and function of apolipoprotein E (apoE). ApoE is an exchangeable apolipoprotein that plays a crucial role in cholesterol transport in the blood and central nervous system. Considered an anti-atherogenic protein, apoE lowers plasma lipid levels by acting as a ligand for low-density lipoprotein receptors. Our goal is to understand the effect of environmental tobacco smoke exposure on plasma apoE and whether second hand smoke exposure predisposes people to developing heart disease. We hypothesize that chemical modification of essential lysines by acrolein, a highly reactive aldehyde present in tobacco smoke, alters the structure and function of apoE. To test our hypothesis, we employed recombinant rat apoE to perform in vitro modification. ApoE was over expressed, isolated, and purified by nickel affinity column chromatography. Sodium dodecyl sulfate polyacrylamide gel electrophoresis indicated the presence of a single band corresponding to about 34 kDa. Western blot analysis confirmed the identity of apoE, while high-performance liquid chromatography analysis confirmed the purity of the preparation. Secondary and tertiary structural analysis of apoE by circular dichroism and fluorescence spectroscopy, respectively, confirmed that the recombinant protein was folded. ApoE was treated with 10-fold molar excess of acrolein, followed by extensive dialysis to remove excess acrolein. Acrolein-modified apoE displayed a significantly decreased ability to interact with lipids. In addition, the affinity of acrolein-modified apoE for heparin was significantly lowered. The data suggest that acrolein causes significant structural and functional alterations in apoE.
Diastereoselectivity of Radical Carbon-Carbon Bond Formation in Naphthalene-Stabilized Propargyl Cations

Bianca M. Rivas, California State University, Northridge Department of Chemistry and Biochemistry, Stepan Harutyunyan

Gagik G. Melikyan (Faculty Advisor), California State University, Northridge Department of Chemistry and Biochemistry

The stereoelectronic parameters of alpha-substituents play an important role in radical C-C bond forming reactions mediated by transition metals. The main objective of this project was to probe an impact of alpha-naphthalene ring upon generation and intermolecular dimerization of cobalt-complexed propargyl radicals. The alternative experimental protocols included (a) treatment of cobalt-complexed methyl propargyl ethers with triflic anhydride, followed by in situ reduction of propargyl triflates with cobaltocene, and (b) generation of propargyl cations with tetrafluoroboric acid, followed by reduction with zinc. Radical C-C bond formation occurred in a highly regio-, chemo-, and stereoselective manner, affording d,l-1,5-alkadiynes as major diastereomers (up to 92%). An oxidative decomplexation with ceric ammonium nitrate yielded 1-naphthyl- and 2-naphthyl substituted d,l-1,5-alkadiynes in good yields (69-80%). Both d,l- and meso-stereoisomers were characterized by a totality of analytical methods, including X-ray crystallography. The novel methodology greatly enhances the potential of metal-mediated radical processes, allowing for the synthesis of polycyclic, multifunctional molecular ensembles otherwise hardly accessible.
Electrocatalytic Carbon-Halogen Bond Formation Using Halide Ions

*Megan Jackson, California Institute of Technology*

Mentor: Professor Harry Gray, California Institute of Technology,
Co-Mentor: Alec Durrell

Previous research in chemical synthesis has shown that the binuclear palladium complex, \([\text{Pd}(\mu-\text{OAc})\text{bzq}]_2\), successfully catalyzes carbon-halogen bond-forming reactions. This Pd\textsuperscript{II}-Pd\textsuperscript{II} species undergoes rapid bimetallic oxidative addition of chloride to a Cl-Pd\textsuperscript{III}-Pd\textsuperscript{III}-Cl by addition of the oxidant iodosobenzenedichloride (PhICl\textsubscript{2}). In the presence of excess benzoquinoline, the Cl-Pd\textsuperscript{III}-Pd\textsuperscript{III}-Cl species will undergo reductive elimination, regenerating the initial Pd\textsuperscript{II}-Pd\textsuperscript{II} complex. While PhICl\textsubscript{2} is a common oxidant in Pd-catalyzed C-H functionalization reactions, it is synthesized using large amounts of chlorine gas, a compound that is both physically and environmentally harmful. We have found the reaction can be run electrochemically, replacing chlorine gas with chloride salt and an electrode. Additionally, replacing the acetate bridge in \([\text{Pd}(\mu-\text{OAc})\text{bzq}]_2\) with trifluoroacetate may improve the rate and scope of the reaction by creating a less stable Pd\textsuperscript{III}-Pd\textsuperscript{III} intermediate, leading to faster reductive elimination and improving the overall rate of reaction. \([\text{Pd}(\mu-\text{TFA})\text{bzq}]_2\) was synthesized and characterized using NMR, and it was used to catalyze the chlorination of benzoquinoline. GC-MS and NMR show that the reaction produces chlorobenzoquinoline at lower temperatures and in a shorter time frame than the corresponding chemical synthesis.
Mechanism of didebromination by Zinc in styrenedibromides

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Dibromination-didebromination could be a very useful reaction sequence in the protection of alkenes in multistep syntheses. To investigate this mechanism, a Hammett study comparing the rates of didebromination for 1,2-dibromo-1-phenylethanones with differing para-substituents was conducted. The kinetic studies were carried out by time resolved UV-visible absorption, conductivity monitoring, and GC-MS. The results and implications of this mechanism will be discussed.
Cloning, Expression, Purification and Crystallization of Rv2224c, a Putative Carboxylesterase, from Mycobacterium tuberculosis

R. Alex Bajaj‡¶, Sum Chan‡, Duilio Cascio‡, James U. Bowie‡, David Eisenberg‡, and Mark A. Arbing‡

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Student(s): R. Alex Bajaj
Mentors: Mark A. Arbing, Duilio Cascio, James U. Bowie

Mycobacterium tuberculosis (MTB) has infected 2.2 billion people, with 8 million active cases and 2 million deaths each year. Mycobacterium tuberculosis is classified as neither Gram-positive nor Gram-negative bacteria, although its cell envelope resembles those of Gram-negative bacteria, containing a “pseudoperiplasmic space” between the cytoplasmic membrane and cell wall. Mycobacterial lipoproteins are analogous in location to Gram-negative periplasmic proteins and contain a “lipobox” sequence with a conserved cysteine residue subject to lipid modifications anchoring them in the membrane. Lipoproteins are involved in many cellular processes, such as cell envelope synthesis and interactions with host cells. The present research involved cloning and expression of eight MTB lipoproteins (Rv1244, Rv2905, Rv3593, Rv2224c, Rv2672, Rv3006, Rv0344c, and Rv0381c). Three of the proteins (Rv3593, Rv3006, Rv2224c) were successfully expressed and purified using affinity, size exclusion, and ion exchange chromatography. All three proteins were subjected to crystallization screening and Rv2224c was successfully crystallized. X-ray data collected from a single crystal at the Advanced Photon Source (beam line NE-CAT 24-ID-C) shows that the crystal diffracted to 3.3 Å resolution and belongs to space group P222₁ (a=61.33, b=62.04, and c=294.24 Å; α=β=γ=90°). To obtain phases and solve the structure, molecular replacement using an appropriate template is in progress. Further work will require high resolution data collection including Se-Met labeling and/or heavy atom derivative soaking to obtain phases. Rv2224c is required for MTB virulence and knowledge of the molecular structure should aid in the design of inhibitors of this protein which may be a new treatment for TB.
A Characterization of the Biology and Nutrient Cycling of Two Glacial Lakes in Isfjord Radio, Svalbard

Cara Magnabosco
B.S. Biochemistry, 2011
University of Southern California

ABSTRACT

Due to the fact that lakes in the high arctic are only exposed for two to three months out of the year, very little is known about the microbiology and nutrient cycling that occur in this region. Of greatest interest in these high arctic regions are the primary producers that control the majority of the biogeochemical cycling and carbon dioxide sequestration of the region. Therefore, it is important to understand how industrialization of the 20th and 21st centuries is affecting these delicate and vital ecosystems. This study explores two glacial lakes in the high arctic region of Svalbard. In order to gain insight on the nitrate and phosphate supply ratios driving primary production in the region, a series of nutrient enrichment experiments (mesocosms) on eleven locations throughout Isfjord Radio, Svalbard were performed. The results of these experiments reveal that the primary producers of this region are highly responsive to the increased nitrogen deposition from the burning of fossil fuels in North America and Europe. In particular, this study shows that, the past decade alone, diatom diversity within these two lakes has significantly decreased in response to the increased nitrogen loading of these freshwater systems.
Facile Fabrication of Microfluidic Chips for UV Absorbance-Based Detection

Author: Aaron Joffe, *California State University, Long Beach*
Mentor: Roger C. Lo, *Department of Chemical Engineering, California State University, Long Beach*

Advances in microfluidics technology have allowed for the miniaturization and improvement of many chemical and biological assays, such as determination of the nitrite concentration in wastewater and DNA/protein gel electrophoresis. Most microfluidics-based assays utilize fluorescence-based detection to determine the presence and abundance of a target molecule. Fluorescence-based detection of biological molecules, however, has limitations due to the fact that in many cases it requires the addition of fluorescent tags. These tags can disrupt the structure and function of many biological molecules, such as enzymes. Tag-free detection can be achieved with UV absorbance-based detection. However, to utilize this detection scheme reliably, microfluidic chips must be completely UV transparent and possess channel depths much greater than common soft lithography techniques allow. These specifications can be met by employing expensive microfabrication processes of UV transparent materials such as quartz or fused silica, which can end up costing hundreds of dollars per chip. In this work, we present a simple, inexpensive technique for the fabrication of customizable microfluidic chips that can be integrated with tag-free UV detection. These chips can be fabricated using commercially available quartz slides and a thiolene based optical adhesive. In addition to being UV transparent and cost-friendly, these chips are able to carry out reactions involving organic solvents, which can not be handled by other popular and inexpensive microfluidic chip materials, such as poly(dimethylsiloxane) (PDMS).
Analysis of chromophoric dissolved organic matter (CDOM) in a Southern California salt marsh with relationship to sediment depth

Paige Aiona, Chapman University
Catherine D. Clark, Warren J. De Bruyn, Chapman University

Colored dissolved organic matter (CDOM) affects many properties of water chemistry and the cycling of carbon in oceans, marshes, and lakes. This study examined the optical properties of CDOM in salt marsh sediments as a function of depth. The data was used to investigate the hypothesis that CDOM from sediments is dominating outputs from coastal salt marshes in Southern California. Pore water equilibrators ("Peepers") were used to collect samples from different depths of the sediments of a salt marsh that discharges into the Santa Ana River outlet in Huntington Beach, Orange County, Southern California, USA. After a two week period, the Peepers were retrieved and samples were extracted for optical analyses. Ultraviolet-visible absorption and scanning fluorescence spectrometers were utilized to determine what components were present in the CDOM as a function of depth.
Determination of Methylamine, Ethylamine and Triethylamine N-oxide Salts in Particulate Matter by Non-Suppressed Ion Chromatography

Authors: Eva Pearlstone, Scripps College, Eric Praske, Pitzer College, and Morgan Shattuck, Claremont McKenna College

Mentors: Kathleen L. Purvis-Roberts, Joint Science Department, Claremont Colleges; Philip J. Silva, Department of Chemistry, University of Utah; Bob Brown, Department of Chemistry, University of Utah; David R. Cocker III, Chemical Engineering, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside

Amines are hazardous organic compounds known to form salts in airborne particulate matter, but quantitative studies of amines are uncommon. This poster presents a simultaneous separation of methylammonium, dimethylammonium, trimethylammonium, ethylammonium, diethylammonium, triethylammonium, butylammonium, and N-hydroxy-triethylammonium performed by non-suppressed ion chromatography (IC) using 3 mM nitric acid/ 3.5 % acetonitrile (v/v) eluent solution and a Metrosep C2 250 (250 mm x 4 mm i.d.) column. The calibration of amine salts was used to determine concentrations of salts produced in smog chamber reactions of butylamine + N₂O₅ which were coupled to a Particle Into Liquid Sampler (PILS) at University of California-Riverside and analyzed via IC at the Claremont Colleges. The IC was also used to analyze cation content on filter samples from Logan, Utah. In the butylamine chamber reactions, the second samples taken in each experiment (at 16:30 minutes in the first and 13:28 minutes in the second) contained the highest concentrations of amine salts (3000 ± 120 and 2600 ± 590 ppb, respectively). The final sample from each experiment (taken at 20:14 and 19.15 minutes, respectively) showed lower concentrations of salts (440 ± 14 and 520 ± 50 ppb, respectively). Although no amine salts were found on the filter samples, inorganic cations were present, particularly Ca²⁺ which was quantified in two filter samples by Atomic Absorption Spectroscopy.
Exploring the Solar Energy Harvesting Capability of Proteorhodopsin Through Studies of Function and Dynamics

Aye Aye, Department of Chemistry, University of California, Santa Barbara
Mentor: Sunyia Hussain, Department of Chemical Engineering, University of California, Santa Barbara

Proteorhodopsin (PR) is a transmembrane protein abundantly found in several species of marine proteobacteria. PR binds to a light-absorbing retinal molecule and functions as a light-driven proton pump, similarly to the bacteriorhodopsin (BR) protein found in extremophilic archaea. PR-expressing bacteria power themselves with the aid of sunlight by creating a proton motive force across the cell membrane that drives the synthesis of ATP, the cell's unit of chemical energy. The energy-generating function of PR could be applied towards a wide variety of technologies ranging from photoresponsive biomimetic devices to solar-powered materials. The focus of my research is to measure the proton pumping ability of PR to provide a basis for developing and optimizing PR function in synthetic systems. Our experimental approach, adapted from a recent study (Glaubitz, et. al, BBA, 2009), includes making PR-incorporating lipid vesicles containing the pH-sensitive HPTS fluorescent dye. This requires the efficient expression and purification of PR from E. coli membranes. By measuring changes in the fluorescence properties of HPTS inside the vesicles, we can detect pH changes due to proton pumping since the quantum yield of HPTS will change accordingly. We expect that protons will be transferred out of or into the vesicles depending on the buffer pH, since PR has been hypothesized to be capable of bidirectional transport. We seek to relate our functional study to prior studies of PR dynamics from light absorption spectroscopy and electron paramagnetic resonance (EPR), and to work towards quantifying proton pumping by possibly using pH-sensitive EPR-active molecules inside the vesicles.
Development of High-Throughput Microfluidics to Study Enzyme Catalyzed Reactions

Author: Kevin Cheng, Jay Chiang and Aydin Nazmi, Department of Chemical Engineering, California State University, Long Beach
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Microfluidics involves the manipulation and interrogation of miniscule amounts of fluid within hand-sized devices. There is much interest in this technology from biotech companies, universities and national laboratories situated in California. Water-in-oil emulsions were flowed through microfluidic channels to generate steady streams of aqueous droplets. The novelty of our newly developed microfluidic system is that, in a short period of time and with small volumes, it can generate thousands of nanoliter size droplets where each drop has an incrementally different concentration of aqueous solution. This involves coupling the microfluidics with an external small mixing tank where the concentration of the aqueous solution can be controlled. So far we have demonstrated that we can generate an array of droplets with a concentration gradient of a fluorescent dye. Our aims for this proposed research project are to make an array of droplets where each has a slightly different, but controlled, concentration of substrate. Having such a complete set of nano-sized “test tubes” will allow us to perform enzyme-catalyzed reaction kinetic studies in a single experimental run, and thus reduce the time and amounts of fluid while collecting a large amount of data. The ultimate goal is to be able to provide a microfluidic platform that can be used to perform high-throughput studies of important biochemical reactions.
Investigating the Influence of Bound Drugs on Endogenous Ligand Binding
Through Site-Directed Mutagenesis of Human Serum Albumin

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Abstract:

Human serum albumin (HSA) is the most prominent plasma transport protein with two main ligand-binding sites and demonstrates an affinity for multiple endogenous and exogenous compounds. Literature regarding the competitive binding between endogenous and exogenous ligand binding to HSA mutations is limited. Site-directed mutagenesis of arginine-218 to histidine/proline, found in patients diagnosed with familial dysalbuminemic hyperthyroxinemia (FDH), will be analyzed to determine the effects these residues have on drug-ligand interactions. R218H and R218P mutations present in FDH disrupt bilirubin binding and increase affinity to thyroxine (T4)1. Once purified the two mutants HSA sequences will be confirmed through genetic sequencing. Next, the correct folding of mutant HSA and biological activity can be accomplished using circular dichroism and fluorescence binding assays. Finally, binding constants of heme between wild type and mutant HSA will be compared using isothermal calorimetry to determine the effect these mutations have on competitive binding. The long-term goal is to test the importance of local structural changes and the affects of mutations present within the human population on the overall protein function. Understanding how mutations to HSA influence elevations of hormone levels can help in the development of new diagnostic techniques/tests.

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Selective Small-Molecule Membrane Transport via Synthetic Molecular Receptors

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Chemists continue to have a problem with the delivery of small molecules across biological membranes. An impenetrable membrane often thwarts potential drugs that show promising in vitro activity. A possible solution to delivering these drugs could be to design synthetic receptors, capable of selectively transporting drug like molecules across a membrane. We aim to characterize the localization of fluorescently labeled cavitands in giant unilamellar vesicles by microscopy, evaluate fluorescent guest binding to giant unilamellar vesicles bound cavitands, in an effort to develop small molecule membrane transport using synthetic receptors.
Siderophore production by the ubiquitous *Marinobacter* species

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*Marinobacter* are opportunistic heterotrophic bacteria found throughout the ocean. They are moderately halophilic and euryhaline species that have been isolated from habitats as diverse as petroleum-field brines, ballast water from the Arctic, saline soils, surface seawater, marine snow, coastal hot springs, hydrothermal plumes, volcanic basalts and deep seawater. In addition, they produce high affinity, low molecular weight Fe$^{3+}$ organic ligands, called siderophores. Siderophore production has been previously demonstrated by two of the *Marinobacter* species, *M. aquaeolei* and *M. hydrocarbonoclasticus*. In this study, we investigated the production of siderophores by three additional *Marinobacter* spp. *M. salsuginis*, *M. algicola* and *M. sodiniaum*.

Initial investigations were carried out using a traditional colorimetric assay on active, iron replete cultures. This resulted in the detection of siderophores from *M. algicola* but not from *M. salsuginis*. The siderophores produced by *M. algicola* were isolated and identified by electrospray ionization mass spectrometry. A parent ion at 719 and 799 m/z gave fragmentation patterns consistent with petrobactin and petrobactin sulfonate. Since the *Marinobacter* genus are widely dispersed throughout the ocean, understanding their role in regulating iron chemistry may lead to further understanding of iron chemical cycle as an essential micronutrient.
Microbial Community of Terrestrial Mud Volcanoes Near the Salton Sea, California

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At the southeast edge of the Salton Sea, near the town of Niland, California, there is a small field of active geothermic mud volcanoes that continuously discharge anaerobic mud containing CO$_2$-rich gasses, hydrocarbons, and sulfur compounds at approximately 65°C. Terrestrial mud volcanoes host populations of unique microorganisms that may be involved in the sulfur cycle and hydrocarbon metabolism, but the microbial communities of mud volcanoes have not been well characterized. In this study, DNA was extracted from mud collected from the Salton Sea mud volcanoes, followed by amplification and cloning of bacterial and archaeal 16S ribosomal RNA gene sequences. Phylogenetic analysis reveals that approximately 44% of the bacterial species detected are affiliated with the family of anaerobic sulfate reducers, Desulfobacteraceae. Bacteria associated with the green sulfur bacteria, Chlorobi, were also detected. 38% of the bacterial taxa could not be unambiguously classified taxonomically, but are related to microbes identified from a marine mud volcano offshore Egypt and from marine methane seep sediments. Among archaeal clones, 6% are closely related to the thermophilic, sulfur respiring euryarchaeote, Thermococcus sibericus. The remaining 94% of archaea grouped with crenarchaea that have been detected in other geothermal environments, but have not yet been successfully cultured or characterized. Culture-based techniques are currently being employed to isolate microbes living in this environment. Overall, the microbes identified from the Salton Sea mud volcanoes reveal a strong link with sulfur respiration, many of which may represent novel species.
Characterization of SXR and RXRα Proteins

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The ligand binding domains of nuclear receptor proteins SXR and RXRα were expressed and purified using plasmid DNA technology in *E. coli* cells to begin the process of characterizing the structure of the SXR/RXRα complex. Plasmid DNA pET15b containing the ligand binding domains of the SXR/RXRα genes and pET15b only containing the gene for that of RXRα were transformed into BL21(DE3)pLysS *E. coli*. Protein expression tests were performed using varying concentrations of IPTG to determine optimum protein expression conditions. Since the recombinant proteins have an N-terminal histidine tag, a TALON column was used to purify the proteins, followed by SDS-PAGE analysis to determine the sample fractions that contained the desired protein. The proteins did not appear highly overexpressed and the molecular weights do not confirm that they are in fact the desired proteins. In order to confirm the identity of the plasmid DNA, restriction enzyme digests were performed using BamHI and XhoI restriction enzymes to determine the size of DNA fragments. The size of the largest DNA fragment reflecting protein cDNA in the pET15b/RXRα:SXR was determined to be 1.7 kilobases when cut with XhoI. This size was consistent with the cDNA of SXR/RXRα. In order to obtain reliable data on the protein expression, better controls need to be implemented as well as a Western Blot analysis to confirm protein identity.
Variation of Hypericin Production in Several Cultivars of St. John’s Wort

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Hypericum perforatum L. is an invasive weed that has been naturalized in the western part of the United States including California. H. perforatum, known commonly as St. John’s Wort, is a popular phytomedicinal remedy for depression. Hypericin and its family of related compounds are classified as naphthodianthrones, which are thought to be synthesized via a polyketide pathway. Variation of secondary metabolites can be affected by both abiotic and biotic factors. In this study, environmental factors were held constant to understand the degree of genetic variation present in hypericin production. Five H. perforatum cultivars were included in this study: New Stem, Helos, Elixer, wild type, and Topas. Total hypericin levels varied among cultivars from 0.01 – 0.28 μg/mg. Intra-cultivar variation in total hypericins was observed to be as high as 117%. Individual hypericin levels: pseudohypericin, protopseudohypericin, hypericin and protohypericin are reported for each cultivar.
Effects of Metal Ion Chelators on Gamma-Hydroxybutyrate Dehydrogenase Activity

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The alcohol dehydrogenase gamma-hydroxybutyrate dehydrogenase (GHB-DH) from Ralstonia eutropha contains tightly bound Fe(II). It catalyzes the oxidation of gamma-hydroxybutyrate (GHB) coupled to the reduction of nicotinamide adenine dinucleotide (NAD\(^+\)). When a person consumes GHB, he or she enters a trance-like state and is defenseless against sexual assault. Thus, GHB has been nicknamed the “date-rape” drug. To enhance personal safety, a rapid GHB-DH based assay is available to test for the presence of dosed GHB in food or drink. However, the ability of Fe(II) chelators to prevent GHB-DH from detecting GHB has not been characterized. The time-dependant effects of the chelators ortho-phenanthroline and ethylenediaminetetraacetic acid (EDTA) on the activity of GHB-DH was investigated. The enzyme was incubated in the presence of EDTA or ortho-phenanthroline for time periods ranging from 30 seconds to 30 minutes. Ortho-phenanthroline, but not EDTA, inactivated GHB-DH in a time-dependant fashion. These differing behaviors likely are due to the different molecular characteristics of the chelators. EDTA, a very common food additive, contains six chelation sites, but it adopts many different molecular conformations. Because of this entropic unfavorability, EDTA cannot pry ions out of proteins. In contrast, ortho-phenanthroline contains two chelation sites in a planar and rigid molecule. After the first chelation site binds the Fe(II), the second chelation site is held in a position facilitating attack. Ironically, the weaker equilibrium chelator ortho-phenanthroline is a much better inactivator of GHB-DH than is the stronger equilibrium chelator EDTA. It is fortunate that ortho-phenanthroline is not a food additive.
Effects of DNA Mismatches on DNA-Protein Crosslinking from Guanine Oxidation

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Oxidative DNA damage contributes to aging, cancer, and disease. Guanine is particularly vulnerable to oxidation, forming radicals which can form DNA-protein crosslinks. Here, we investigate the guanine radical reactivity dependence on its base pairing partner in DNA mismatches for the oligonucleotide 5’-ATATGATATGGATATGATAT-3’. DNA duplexes containing mismatches across from the 5’-G of the GG doublet were synthesized and fluorescently tagged. Radicals were created via flash-quench, and crosslinking was detected using agarose and polyacrylamide gel shift assays. Under native and denaturing conditions, crosslinking decreased as follows: G:G > G:A > G:T ≈ G:C ≈ G:U. Emission quenching studies indicated slight quenching efficiency variations, and thermal denaturation studies revealed a destabilization of ~15°C for all mismatches relative to well-matched DNA. However, neither duplex quenching nor stability explained the observed trend. The enhanced reactivity for guanine-purine mismatches was attributed to the formation of a lower oxidation potential sink. Analogous experiments with 8-oxo-G across from the mismatch observed a similar trend with less pronounced differences. Therefore, in DNA mismatches, guanine reactivity in oxidative DNA-protein crosslinking reactions depends on its base pairing partner.
Synthesis of α-Helical Peptidomimetics

Author: Monica Royer, California State University Long Beach
Mentor: Dr. Michael P Schramm, Department of Chemistry, California State University Long Beach

Cancer is propagated by certain protein-protein interactions that stop the cycle of natural cell death – apoptosis. Two of the most relevant protein-protein interactions are p53-MDM2 and Bak-Bcl. It has been determined that the key structural features needed to disrupt these highly specific protein-protein interactions and reinstate natural cell death is that of an α-helical structure. Recent additions to peptidomimetic synthesis techniques utilize literature procedure in which a 4-substituted pyrrole product is prepared via a regiospecific Friedel-Crafts acylation. The acylation utilizes commercially available acid chlorides to give α-helical peptidomimetic scaffolds. On large scale, these products can be reduced with p-Toluenesulfonylhydrazine followed by reduction with NaBH₄ to give a variety of hydrophobic “amino acid-like” side chains in excellent yield. The α-helical peptidomimetic scaffold is then constructed after condensation with an aldehyde. Upon completion of a small molecule library of more than 1000 peptidomimetic compounds, with varying substitutions, we hope to find multiple molecules that will be valuable in disrupting a variety of α-helical protein-protein interactions, including those relevant to cancer.
Site-Directed Mutagenesis of a Cysteine Motif Proposed to Ligate a 4Fe-4S Cluster in a Putative Dihydromethanopterin Reductase of *Methanosarcina mazei*

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The biological production of methane, a greenhouse gas, contributes to global warming. *Methanosarcina mazei* possesses a gene that codes for dihydromethanopterin reductase X (DmrX), which may proposed to catalyze the reduction of dihydromethanopterin (H$_2$MPT) to the methanogenesis cofactor tetrahydromethanopterin (H$_4$MPT). DmrX, a homolog of archael flavoprotein A (AfpA), contains two 4Fe-4S clusters bound to cysteines in the amino acid motif CxxCxxCx$_3$-7C. To gain insight into the structure and function of these iron-sulfur clusters, the DmrX gene was genetically altered by site-directed mutatgenesis, changing the cysteine at position 159 to a serine (DmrX:C159S). Since 4Fe-4S clusters are typically crucial for electron transfer within the enzyme, it was anticipated that altering a cysteine that ligates 4Fe-4S cluster might affect the incorporation of the cluster or its midpoint potential. The wildtype and mutant proteins were produced in similar amounts with His$_6$ tag in *Escherichia coli*; comparison of the UV-visible spectra of the two purified proteins were consistent with an effect of the altered residue on 4Fe-4S ligation. Both proteins exhibited the spectrum of a flavin, and dithionite eliminated the spectrum, indicating that dithionite was able to reduce DmrX and DmrX:C159S. The reduced wildtype enzyme was used to develop an enzymatic assay, which was consistent with the proposed role of DmrX in the reducing dihydromethanopterin to tetrahydromethanopterin. The wild-type and altered proteins were produced in sufficient quantities for electron paramagnetic resonance (EPR) spectrometry. Further analysis of this sample could reveal if the C159S mutation alters the midpoint potential of an iron-sulfur cluster.
The Synthesis of Novel Single and Homobivalent Phosphate Compounds as Cholinestarase Inhibitors

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It is generally accepted that the cholinergic deficit caused by the hydrolysis of acetylcholine by acetylcholinesterase (AChE) and butyrylcholinesterase (BChE) is correlated with the dementia known as Alzheimer’s disease (AD). Thus, cholinesterase inhibition is the main treatment for AD and significant attention has been devoted to the synthesis of AChE and BChE inhibitors. All drugs currently used to treat cognitive loss associated with AD are AChE and (to a lesser extent) BChE inhibitors. Recently we achieved highly selective BChE inhibition with compounds containing phosphate groups with aromatic and alkyl groups. To further explore the potential of these compounds as inhibitors, we synthesized both monovalent (single site) and bivalent (dual site) inhibitors. We hypothesized that the bivalent inhibitor could interact with multiple sites of the enzyme and may be a highly selective and potent BChE inhibitor. Preliminary studies showed the bivalent inhibitor to be a much more potent inhibitor than the most potent monovalent inhibitor, supporting our hypothesis.
Vitamin E Binding to Human Afamin—Automated Docking Studies

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Afamin, a member of the alpha-fetoprotein, Albumin and vitamin D binding protein gene family, is a novel glycosylated human carrier transport protein for vitamin E, an antioxidant proven to alleviate cellular oxidative stress. Radio ligand-binding assays suggest that Afamin has multiple binding sites for vitamin E, while Albumin, known to bind and transport many molecules, has been shown not to bind vitamin E. To understand this difference in vitamin E binding, simulated docking of vitamin E to Afamin and Albumin was conducted with ICM-Pro. In the absence of an Afamin crystal structure, a homology model was determined using the structure of Albumin as a template. Potential binding sites were identified using ICMPocketFinder. Results suggest that Afamin has two vitamin E binding sites, in domain IB and IIA, using the Albumin domain classification. These binding sites are hydrophobic. Bilirubin, a byproduct of heme catabolism, is known to bind Albumin in domains IB and IIA, and it has been shown in vitro to have limited affinity for Afamin. Simulated docking suggests that Afamin can indeed accommodate bilirubin in domain IB, and with lower binding affinity than Albumin. Crystallization trials with recombinant deglycosylated Afamin are in progress. This research project is funded by NSF (Grant number, NSF:HRD 0331537).
Zeoliticimidazolate frameworks (ZIF’s) are crystals that have a cage like structure. These crystals have a high affinity for the capture of the greenhouse gas, carbon dioxide. With the push to become more “green”, ZIF’s could potentially play an important role in the selectivity of capturing carbon dioxide. ZIF’s are more economical options, less toxic, and more efficient ways to capture carbon dioxide than other readily available methods. The successful synthesis of ZIF-8 in our lab has been confirmed by XRD and FTIR techniques. The behavior of this material in a real diesel engine is currently under investigation in our lab.
“Eximer Formation in 1-Methylnaphthalene with Pentadecane Bilayers on Al$_2$O$_3$ (001)”

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Bilayers of 1-methylnaphthalene fluorophore and pentadecane were deposited in a vacuum onto a cryogenically cooled Al$_2$O$_3$ crystal. While the crystal was heated through desorption to 400 K in a temperature programmed desorption (TPD) procedure, the adlayer molecules mixed and fluorescence of 1-methylnaphthalene was plotted as a function of temperature. Pentadecane layers desorb at a temperature of 275 K and do not emit while 1-methylnaphthalene layers desorb at 265 K. With increasing coverage of pentadecane in the bilayer, a new peak appears in the excimer fluorescence.
Bulk metallic glasses (BMG) are thermodynamically unstable amorphous alloys that possess desirable mechanical, electrical and chemical properties. One example is Vitreloy 101 (Cu_{47}Ti_{34}Zr_{11}Ni_{8}). Joining BMGs by welding is problematic because the high temperatures needed to form the weld may cause crystallization and a loss of their unique attributes. We have used a very useful tool for chemical engineering, the COMSOL Multiphysics program, to explore aspects of the welding process by modeling heat generation, transfer and cooling transport in Vitreloy 101. Our goal was to analyze the temperature behavior of the BMG ribbons. The model consisted of two copper electrodes and two ribbons of BMG. First, the 3D model was built with appropriate materials. Then the physics was added to this model as Joule heating and heat flux in a time-dependent way. Once the voltage was applied to the two electrodes, the weld was formed. A visual result of the heat generated in the ribbons and the cooling transport was produced.
Effects of Non-Luminescent Compounds on MethylNaphthalenes
Excimer Formation on Al$_2$O$_3$ (0001)

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When volatile aromatic molecules such as methyl or ethyl substituted
naphthalenes are vacuum deposited on surfaces, the arrangement of molecules
is random and amorphous. The electronic excitation of a molecular adlayer that
has been deposited this way results in excimer, or excited state dimers, and trap
fluorescence. By depositing a second layer of molecules whose excited state is
not in resonance with the impinging electromagnetic field and desorbs at a lower
temperature, the excimer and trap formation of the first layer can be altered. This
is done through resistive heating by a temperature programmed desorption
(TPD) procedure. By collisional energy transfer, the upper inert layer changes the
morphology of the luminescent lower layer so that the percentage of eximer
decreases, while the overall intensity increases.
Electrophilic opening of 1-arylbicyclo[4.1.0]hexanes
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Mentor: Eric J. Kantorowski, California Polytechnic State University, San Luis Obispo, CA.

Our interest in the kinetics and regioselectivity of cyclopropane fragmentation has led us to explore the behavior of 1-arylbicyclo[4.1.0]hexanes in the presence of an electrophile. Heterolytic fragmentation along either of the cyclopropane bonds attached at the benzylic position yields an aryl-stabilized carbocation that is rapidly captured by an available nucleophile. Depending on the regioselectivity of addition, the five-membered ring may either remain intact or realize a one-carbon expansion event. We are currently studying the kinetic and regioselective response of the system to the presence of electron-donor and electron-withdrawing groups on the aromatic ring. The kinetics of each derivative can be conveniently determined by performing the reaction in an NMR tube.

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Synthesis of positively charged cytidyl ribonucleic guanidine (RNG-C)

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Synthetic oligonucleotides have been investigated for inhibition of gene expression by either antisense or RNAi mechanisms. Replacement of the negatively charged phosphodiester linkages of RNA with positively charged guanidinium linkages provides the polycationic ribonucleic guanidine (RNG). The primary goals in the design of such agents include increasing the binding affinity while maintaining the sequence specific, resistance to degradation by cellular nucleases, and improve cell membrane permeability. We report herein the synthesis of 3’-end, internal, and 5’-end monomers which are required for the synthesis of a cytidine-based ribonucleic guanidinum oligonucleotide. The production of the 5’-terminal monomer was accomplished through a 14-step process beginning with uridine. The end result is a transformation to a cytidine based nucleoside with protective groups for later linkage. The production of the 3’-terminal monomer was accomplished through a 10-step process using a benzoyl cytodine as a starting material. A 15-step process is required for the production of the internal monomer beginning with uridine. A final treatment of the internal and 5’-end monomers with fluoroenylmethyloxycarbonyl isothiocyanate is required for preparation of the cytidyl oligomer.
Palladium(II) Catalyzed Coupling of Bis-Vinyl Boronates

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Sponsored by Craig A. Merlic under the supervision of Robert Iafe

A new methodology has been developed for the ring-closing step when constructing polyene macrocycles by using palladium(II) to catalyze C-C bond formation between vinyl boronates. This methodology is an improvement on the standard palladium(0) coupling because it avoids the toxic vinyl halide intermediate, can be run at room temperature, and does not require differentiated coupling partners. It can be used to synthesize E,E-, E,Z-, and Z,Z- dienes with or without further conjugation. Macrocyclization can be followed by a transannular Diels-Alder reaction to provide access to polycyclic ring structures.
Novel approaches to the synthesis and purification of water-soluble curcumin analogues
California State University Channel Islands (Chemistry Department)
Jose Medina
Mentor: Phil Hampton

Recent studies have shown curcumin’s potential as a treatment for diseases ranging from various types of cancer to Alzheimer’s disease. However, this potential is limited by the molecule’s highly hydrophobic character and resulting poor bioavailability due to its inability to cross the blood-brain barrier. This research examines the synthesis of hydrophilic analogues possessing 2-aminoethyl substituents on the phenolic position. When attempts at direct alkylation of curcumin proved unsuccessful, a convergent synthesis of O-alkylated curcumin and curcumin analogs was examined. Enedione analogs of curcumin have been produced by O-alkylation of 4-hydroxybenzaldehyde, followed by condensation with benzoylacetone under reduced pressure. Based on this strategy a novel synthesis and purification has been developed. This process offers the advantages of significantly improved yields and higher purities over the methods reported in the literature.
The saponification of ethyl acetate with NaOH was studied in order to determine the reaction rate constant and reaction order. The reaction of ethyl acetate with two different feeds was investigated for producing sodium acetate: a NaOH aqueous solution and an alkaline wastewater. Biodiesel wastewater was selected as an example of alkaline wastewater. Sodium acetate production from biodiesel wastewater demonstrated higher NaOH conversion than from NaOH aqueous solution. It is believed that the presence of methanol in the biodiesel wastewater changes the saponification reaction mechanism and this change leads to the higher conversion. These results show that biodiesel wastewater might be a suitable feed for the production of sodium acetate.
Synthesis of derivatives of 1-(3,5-dialkoxyphenyl)-prop-2-yn-1-ol and their use in the generation of olefin metathesis catalysts

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Olefin metathesis is a fundamental chemical reaction involving the rearrangement of carbon-carbon double bonds catalyzed by transition metal complexes. This Nobel Prize-winning reaction finds a wide array of applications including the development of new drug candidates, novel polymers and materials, and processes to convert petrochemicals and bio-renewable resources (e.g., vegetable oils) into useful chemicals and materials. Currently, the most commonly employed olefin metathesis catalysts are based on ruthenium, because they show excellent activities and are tolerant of air, moisture, and many functional groups. However, their preparation is somewhat cumbersome involving several steps and requiring the isolation of the catalysts as crystalline materials. Our group has recently developed a very convenient one-step procedure for the in-situ preparation of active olefin metathesis catalysts.¹ The new method involves reacting Ru(p-cymene)Cl₂(PC₃) with prop-2-yn-1-ol compounds to make new ruthenium indenylidene complexes. Details on the synthesis of three different derivatives of 1-(3,5-dialkoxyphenyl)-prop-2-yn-1-ol, as well as their reaction with ruthenium starting materials and the activity of the generated complexes in ring-closing metathesis will be presented.

Synthesis of trinuclear titanium and zirconium complexes toward the activation of molecular nitrogen

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While nature manages to transform atmospheric nitrogen into ammonia under ambient temperature and pressure, the industrial production of ammonia known as the Haber-Bosch process requires very high temperatures (750-1,000 °F) and very high pressures (100-300 atmospheres). This industrial process is used to produce over 100 million tons of ammonia annually and is estimated to consume about 1% of the global energy. Most of the produced ammonia is converted into fertilizers to sustain about 40% of the global population. As such, this industrial reaction is both indispensable and highly energy-costly. Both the biological and industrial reactions are based on metal-containing catalysts, but their mechanisms of action are poorly understood. We are interested in testing the following hypothesis: "the cooperation of several metals in close proximity will lead to a more efficient nitrogen conversion catalyst". We have used a new approach to prepare new well-defined pre-assembled trinuclear titanium and zirconium complexes and have started to study their reactivity with reducing agents under a nitrogen atmosphere. Details regarding the synthesis and reactivity of these complexes will be discussed. These systems have the potential to increase our fundamental understanding of the biological and industrial nitrogen conversion catalysts and may ultimately lead to a more energy-efficient process.
Dehydration kinetics of 1,1-diaryl-1-propanol and 1,1-diaryl-1-ethanol

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Mentor: Eric J. Kantorowski, Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA.

Kinetics is a topic commonly covered in the undergraduate organic chemistry lecture, but is less common in the accompanying lab course. We are currently developing an NMR-based experiment that offers students an opportunity to explore reaction rates. In the experiment, a tertiary diaryl alcohol is introduced to an acid and the resulting dehydration reaction is followed using NMR spectroscopy. Varying the aryl substituents allows for study of the effect of electron-donating and electron-withdrawing groups on the reaction rate. The alcohols that we tested for viability were 1,1-diphenyl-1-propanol, 1,1-diphenyl-1-ethanol as well as substituted derivatives thereof, chosen based on their relative ease of synthesis and purification. Results will be presented for a variety of acids and NMR solvents.

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Computational Chemistry Methods Determine Diatomic Spectroscopic Properties

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Ab initio quantum mechanical computer codes have demonstrated an instrumental role in the refinement of many areas of chemical theory. Computational agreement with experimental results has proven to be the ultimate challenge of such efforts. Coupled-cluster approximation methods demonstrate the most promising approach for obtaining near-empirical accuracies of molecular properties. In this study, coupled-cluster methods are utilized to determine which spectroscopic properties may be computed to near-experimental accuracy at the lowest computational cost. The functions used to create the molecular orbits (the basis set) were varied (both in size and type) at each level of computation. Infared and Raman spectra property values of simple diatomics (BH, HF, CO, N₂, and F₂) were calculated, and the effects of the basis sets were determined. Results have revealed that at the highest coupled-cluster computational level, bond lengths are systematically overestimated with small (cc-pVTZ) basis sets, and medium-sized basis sets (cc-pVQZ) often provide satisfactory geometries. Dipole moments and dipole derivatives, which allow calculation of IR spectral intensities, show convergence within a few percent of large basis sets, using medium augmented basis' (which include diffuse functions for electric field property calculations). Overtone transitions, however, demonstrate erratic convergence behavior, suggesting contributions from 3rd or higher order terms to the molecular energy. Hyperpolarizability and related Raman spectra values, and the effect of core-electrons, were also studied. Results thus far demonstrate the unique influence of the type and size of basis sets on molecular property functions, and thus provide insight toward theoretical frameworks for property-function-specific computational algorithms.
Adsorption of Toluene on Graphite.

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Graphite is a very stable substance whose structure contains sheets of graphene (condensed aromatic rings of sp$^2$ hybridized carbon). This unique layered structure opens the door for many chemical compounds to interact with its surface through dispersion interactions. As a result, graphite like materials are often used as filters to purify water. The goal of our research was to carefully examine and understand the adsorption of toluene, a toxic aromatic hydrocarbon, on the graphite surface. In our experiment, highly oriented pyrolytic graphite (HOPG) (1 cm$^2$) was cooled to <85 K using liquid nitrogen in an ultrahigh vacuum chamber. A controlled amount of toluene was leaked into the chamber and adsorbed onto the HOPG surface. The temperature-programmed desorption (TPD) technique was used to quantify the adsorption energy of toluene. In the TPD experiment, the graphite sample was heated at constant rate and the partial pressure of molecules leaving the surface was measured by mass spectrometry. The data from TPD showed two separate desorption features of toluene, one at 160 K - 180 K and another one at 130 K - 150 K. Desorption in the higher temperature range was ascribed to toluene desorbing from the HOPG surface. The second, lower temperature feature, corresponded to desorption from multilayers of toluene; layers of toluene on top of each other.
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