## Saturday morning – Abstracts WRM 267 - 348

### WRM 267

### High resolution MS proves that the developmental cancer drug, RRx-001, alkylates the hemoglobin beta chain

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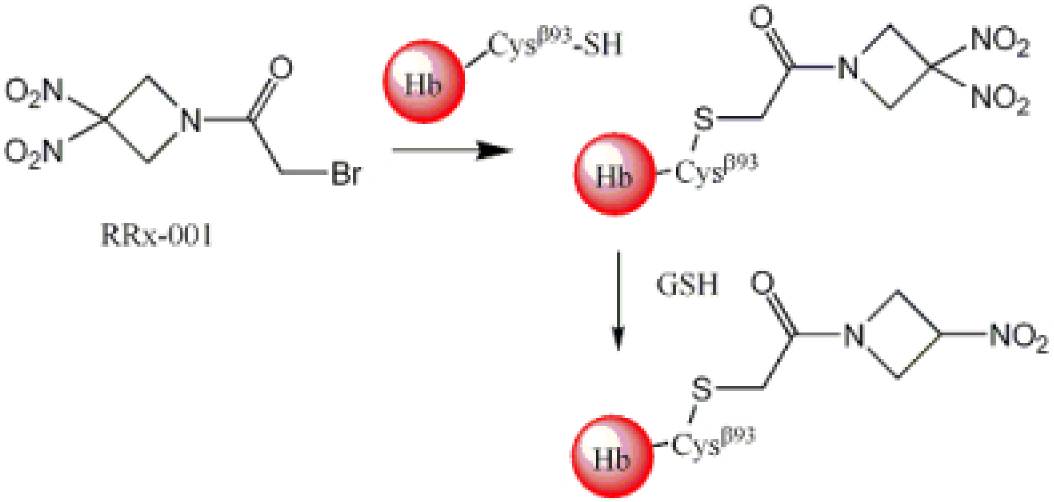
Human whole blood was incubated with RRx-001 at final concentrations of 0, 0.50 and 5.0 mM for 30 minutes. The hemoglobin was isolated by centrifugation, hemolysis and acetone precipitation. The alpha and beta chains were separated by LC for analysis by time of flight mass spectrometry. No evidence was obtained for alpha chain alkylation. 5 mM drug results in ∼50% conversion of beta chain to a +187 Da species (=$C_5H_5N_3O_5$ or 1 RRx-001 unit). A second species was observed at +142 Da which is attributed to a glutathione induced loss of nitro from the primary adduct.



At 0.5 mM minimal alkylation is observed above baseline. This method cannot be used at clinical uM concentrations.

### WRM 268

### Application of High Resolution Mass Spectrometry in Structural Determination of Natural Products Present in Withania Somnifera Fruits

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Withania somnifera is a rich source of biologically active secondary metabolites. Liquid chromatography (LC) coupled with high-resolution mass spectrometry (HRMS) with data-dependent and targeted MS/MS experiments were conducted to elucidate the structure of observed metabolites. A total of 62 metabolites identified included 32 withanamides, 22 withanolides, 3 steroidal saponins, 2 lignanamides, feruloyl tyramine, methoxy feruloyl tyramine and a diglucoside of hydroxyl palmitic acid. Applications of high resolution MS in drug discovery will also be presented.

### WRM 269

## Spectral Accuracy on High Resolution Mass Spectrometers and Application to Elemental Composition Determination

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Determining elemental compositions of unknown molecules is an important goal of analytical chemistry. The isotope pattern revealed by a mass spectrometer provides valuable information regarding the elemental composition of a molecule. The difference in the observed profile isotope pattern compared to the theoretical isotope pattern, denoted spectral accuracy, can be calculated mathematically using a computational algorithm. In order to employ spectral accuracy considerations for elemental composition determination, it is important to know how faithfully a mass spectrometer can record the isotope pattern and to understand the magnitude of the errors of the relative isotopic abundances. In this talk, results will be presented from the evaluation of spectral accuracy on an Orbitrap-XL and an AB Sciex 5600 Q-TOF mass spectrometer using 10 natural products and twenty-two drug molecules, respectively, in which spectral accuracy was calculated by the program MassWorks. In addition, discussion on the impact of the Orbitrap resolving power on spectral accuracy will be discussed along with how spectral accuracy can help obtain insight into the chemical nature of the analyte that may be otherwise overlooked.

### WRM 270

## MS proteomic characterization of the protein interface of nanoparticles

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Studies of nanoparticles in the environment and biological systems are complicated by the many chemical and physical changes they undergo upon release. This includes adsorption interactions with biological systems that leave the particle surface with little resemblance to the original engineered NPs. Of the most predominant surface modifiers in the environment, proteins selectively adsorb onto NPs to permanently alter environmental reactivity. Using mass spectroscopic proteomics approaches, we have characterized the biophysicochemical characteristics of proteins that dominate interactions with NPs of various sizes and surface coatings. To our knowledge, this is one of few comprehensive studies providing qualitative and quantitative analysis of the protein corona population, here enabled by analysis with comparative label-free LC-MS/MS. With this approach, we were reliably able to detect roughly 70 proteins tightly bound to the NP at low ionic strengths and more than twice that number in high ionic strength samples. Consistent with other studies, our analysis shows that the profile of NP bound proteins does not merely correspond to the relative protein concentrations of the greater protein population. Additionally, the data show that proteins close to or below detection limits in the larger protein sample (analyzed without NP exposure) were significantly enriched and reliably detected within the population of proteins tightly bound to NPs. This enrichment was condition dependent, with different proteins detected in greatest abundance within each sample analyzed. Functional and biophysical classification of the enriched proteins reveal trends indicating that protein interactions with NPs are driven by electrostatics, but the process is dynamic, with some proteins binding very tightly and found within many of the samples analyzed. These results provide insight into the surface chemistry of NPs within biological systems. The methodology applied here is also broadly applicable to drug targeting and other biomedical applications involving NPs.

### WRM 271

## Desorption electrospray ionization mass spectrometry imaging in biomedical research

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Desorption Electrospray Ionization Mass Spectrometry imaging (DESI-MSI) is one of a recently developed group of ambient ionization techniques in which samples are examined in the ambient environment with minimal pretreatment. Molecular imaging by DESI-MSI has been increasingly explored due to its outstanding capability of providing spatial information on the distribution of molecules with the specificity and the sensitivity that are characteristic of MS. In DESI-MSI, tissue sections are bombarded with microdroplets containing solvents that dissolve hundreds of lipids and metabolites. Then, the splash of secondary microdroplets containing the dissolved molecules are captured and analyzed by the mass spectrometer, allowing a detailed chemical map to be made of the sample. The experiment is performed in open air and takes less than a second per pixel, giving a large amount of information on one small spot on the tissue.

In this presentation, two novel biomedical applications of DESI-MSI will be discussed. With the goal of developing a MS method to evaluate the presence of cancer in surgical margins during gastric cancer surgery, DESI-MSI was used to investigate the molecular profiles of human gastric normal and cancerous tissues. The diagnostic ions that contribute to the discrimination between gastric cancer and normal tissues were identified using a statistical classifier and further characterized as complex lipids and small metabolites. To test the method, cross-validation and an independent set of samples were used, yielding high overall accuracy values of 99% and 97%, respectively. The method is currently being applied to evaluate tissue margins from gastric cancer surgery at Stanford Hospital. We have also successfully used DESI-MSI in drug development research to investigate the transdermal penetration efficacy of novel synthetic sodium channel blocker analogs. Our results demonstrate that synthesis allows us to modulate the depth of skin penetration of natural products by designing less polar synthetic analogs.

### WRM 272

### Using desorption electrospray ionization mass spectrometry to monitor ruthenium-catalyzed C-H functionalization

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Hydroxylation of C-H bonds can be achieved by using ($Me_3$tacn)$RuCl_3$ as a catalyst and $NaIO_4$ or CAN as the terminal oxidant. The reaction is important in that it provides specificity towards tertiary C-H bonds. However, it is known that the ruthenium catalyst comes to arrest after a certain number of turnovers. In this interdisciplinary project, we are using desorption electrospray ionization mass spectrometry (DESI-MS) to monitor the catalytic reaction in real time. The goal is to detect the active catalytic species and decomposition products of the reaction in order to improve the efficiency of the reaction.

The activated catalyst is dissolved in aqueous solution and spotted onto a substrate that is placed in front of the MS inlet. The reaction is induced by directing charged droplets of an oxidant-containing solution onto the catalyst. As the droplets hit the catalyst, secondary droplets are released from the surface, which contain the reacting compounds. The catalytic reaction takes place inside the secondary droplets and is quenched by evaporation of the droplets as they enter the MS. This method offers the exceptional possibility to get a picture of the reaction at a very early timescale, because detection by MS takes place only milliseconds after initiation of the reaction on the paper surface.

Two possible catalytically active species were detected, a mono-oxo and a di-oxo-ruthenium compound. An oxidant-dependent set of experiments has been carried out that suggests that the mono-oxo converts into the di-oxo with increasing oxidant-concentrations. Decomposition products of the catalyst were identified by looking at different incubation times from 30 min to 3 h. We found various catalyst dimers that increase in intensity with increasing incubation time. One example is an oxo-bridged ruthenium dimer. This finding leads us to speculate that catalytic arrest is caused by dimerization of the catalyst molecules.

### WRM 273

### Introduction to Funding Mechanisms

***David Mosby****, dave.mosby@k4academy.com. Keiretsu Forum Academy, San Francisco, CA, United States*

The investment landscape on every front has changed over the past 6 to 7 years. Entrepreneurs seeking seed and growth capital face circumstances that are at odds with the current mythology surrounding early stage capital acquisition. Angel investment capital is plentiful; entrepreneurs that are well prepared to meet investor expectations are not. This talk addresses the contemporary issues that constitute the major obstacles that contribute to investor's willingness to make investments. Learning how to prepare to address those obstacles helps entrepreneurs accelerate access to the capital and other resources they need to grow their businesses.

### WRM 274

### The Science of Crowdfunding

***Ethan Perlstein**, ethan@microryza.com.Perlstein Lab, San Francisco, California, United States*

Science crowdfunding allows the public to finance curiosity-driven research in exchange for front row seats to discoveries. I am part of a team that raised a record-setting $25,460 from an international coalition of micropatrons for an ongoing open pharmacology project called Crowd4Discovery. Since 2011, hundreds if not thousands of professionally trained and citizen scientists have experimented with crowdfunding, beginning with the SciFund Challenge pioneers, who modeled themselves after the artists and tinkerers who popularized Kickstarter. Today there are even crowdfunding sites dedicated to science projects, like the SF-based startup Microryza. The number of scientists who are crowdfunding is on the rise thanks to the bleak research funding outlook. At the same time, new equity crowdfunding opportunities are possible with implementation of the JOBS Act. In this brief talk, I survey the current science crowdfunding landscape in the style of blogger Nate Silver, distilling the statistical nuts and bolts of science crowdfunding campaigns. The emerging dataset of crowdfunded science projects reveals winning campaign strategies for goals spanning $1,000 to $1,000,000, though the balance is heavily tilted toward the low end. I conclude with a few predictions. The spectacle of crowdfund drives will cede to the stability of subscriptions. Equity crowdfunding will enable novel hybrid models that combine the best of academia and industry.

### WRM 275

### How to find angel investors

***David Mosby**, dave.mosby@k4academy.com. Keiretsu Forum Academy, San Francisco, CA, United States*

Angel investors are masters of hiding in plain view. Some do it on purpose, others by accident. However, this short talk illuminates specific strategies for early stage business leaders to both raise their business' visibility and identify tactics for locating specific investors to whom they might reach out. Along with this will be highlights of preparations to take in anticipation of a meeting with a potential investor.

### WRM 276

### SBIR Grants: What, Why, When and How

***Amy Boggs**, amy@grantsport.com. Grantsport, United States*

Non-dilutive funding is available through the Small Business Innovative Research (SBIR) grant program. Dr. Boggs will give an overview of the registration and application processes, and provide strategic advice for how to position your proposal. Learn about “grantsmanship,” and examine why and how to build a grants portfolio.

### WRM 277

### Securing venture capital funding for your company

***Tracy Saxton**, tracy.saxton@svlsa.com. SV Life Sciences, San Francisco, CA, United States*

Venture capital professionals source, evaluate and support investments in emerging companies. Drawing on experience gained from working at a start up biotech companies, and at SV Life Sciences, Dr. Saxton will provide insights on how to present your ideas to the VC community.

### WRM 278

### Key to Unlock: Getting your Newco Venture Funded

***Mike Powell**, powell@sofinnova.com. Sofinnova Ventures, United States*

There are several sources of capital for start-ups, and venture capital continues to be one of the major sources. But the criteria for getting funding has increased, and knowing what the new rules are is key to unlocking this source of capital.

### WRM 279

## Poeticizing Chemistry: Getting the general public interested in chemistry in a world of dirty power plants, pesticides, and chemical super-funds

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The media has frequently shown chemical hazards while rarely showing the benefits of the general field of chemistry. This has caused the public to be cautious about accepting chemistry as a positive science. It is a daunting task to reverse this perception. In the case of the Las Vegas poetry scene, the view of chemistry has improved upon finding out that I – a poet – have obtained my AS in chemistry; a modest accomplishment, but the perception of a poet with a degree in science, has been positive to the point of audience members having approached me to mention that I have prompted them to research topics brought up in my poems.

This presentation addresses the problem of the public perception of chemistry by using performance poetry. How do you poeticize chemistry in an aesthetic fashion? Can you keep full accuracy when doing so? How would the audience of a poetry reading react to certain information? Over the course of the past fourteen months, I have used the methods of writing poetry with topics of chemistry in mind and have presented these poems audiences of poetry readings around Las Vegas.

Poeticizing chemistry in this type of forum has yielded a positive trend of chemistry for those audiences who have witnessed it in Las Vegas, and a more widespread approach to this topic could be beneficial to the field of chemistry. This invites more widespread use of poetry to convey the beauty and benefits of chemistry to improve the public perception of chemistry.

### WRM 280

## Peer-led Team learning: A method for narrowing students' achievement gap in chemistry courses at San Jose City College

***Jennifer Parsons***, *jenjpar@yahoo.com, Madeline Adamczeski. Chemistry, San Jose City College, San Jose, CA 95128, United States*

The purpose of this project is to measure Peer Led Team Learning (PLTL) workshop's effects on academic achievement and retention, with special attention to underrepresented students enrolled in STEM Courses at our HSI community college. A PLTL workshop consists of a small group of students who voluntarily meet weekly and are assisted by a highly-trained student peer. As a team, with their Peer Leader (PL), students work on carefully structured problems to reinforce learning. Other goals of a PLTL workshop are to provide a supportive environment that fosters a sense of community, and help students gain confidence, competence, and tools that empower them to excel academically and personally. More than just a study group, where students discuss course content, a workshop is among six highly structured components of the PLTL program. In a workshop, guided by a PL, students assess, build, and orally communicate their understanding of the course material. The PL facilitates a workshop by implementing active learning strategies, and assisting students to stay engaged with the course material. A recent demographic study of the student PLTL participants (n=63/283) vs. non-PLTL participants (n=220/283) aggregated across four different chemistry courses at SJCC revealed that the achievement gap narrowed among several demographic populations. For those students who participated in PLTL workshops during the Fall 2011/Spring 2012 semesters, retention and success data shows that our Latino/a population has improvements, respectively, of 13%/15% and 17%/6%. Corresponding data for retention and success across all student demographics reveals respective increases of retention and success of 16%/14% and 18%/8% . This data demonstrates that success and retention of students who participate in a PLTL workshop significantly improves (eg. as compared to non-participants). Additional positive impacts obtain from surveys and focus groups can be attributed directly to the program and will also be included in this presentation.

### WRM 281

## Peer-led team learning: study on positive impacts that peer leaders provide toward student success, retention and faculty professional development in STEM courses at a Two-Year Hispanic-Serving-Institution

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The purpose of this project is to understand the impact on Peer Leaders (PLs) who serve STEM students, within San Jose City College's multifaceted Peer Led Team Learning (PLTL) program. Specifically, analysis of results from PL surveys and focus groups revealed several key indicators responsible for raising the success and retention of students enrolled in STEM courses. Conducted by an external evaluator and in cooperation with SJCC's Research Institutional Effectiveness division, focus groups and surveys are designed to solicit constructive criticisms and perceptions from all the participants, the results of which are used to: (a) guide the PLTL program components toward further improvement; (b) quantify student success and retention; and (c) demonstrate program effectiveness in order to procure appropriate institutional support and attain full financial sustainability. Simultaneous analysis of quantitative data, including student demographic, success, and retention is used in part to, drive decisions, for example in designating and/or increasing the number of STEM courses that are supported through PLTL workshops. The specific focus of this study is to evaluate the quality of the peer leader (PL) training components, including program-support learning structures adapted through both: (a) Peer-Assisted Learning models and (b) *On Course* active learning strategies. PL training blends a variety of interactive pedagogies to motivate and engage the participants' interest in STEM course content. PLs are afforded intensive weekly training collectively, and weekly in clusters according to STEM courses with lead faculty PLTL practitioners. There is an additional two-day pre-semester orientation that is mandatory as well. The trainings range from designing PLTL Workshop exercises, completing weekly planning sheets to conducting peer-to-peer observations. Weekly PL trainings and PL-faculty engagement sessions as well as the buddying-up of experienced with inexperienced PLs encompass leadership development, intensive mentoring, teacher-training as well as opportunities to engage in scholarly endeavors and personal growth.

### WRM 282

## Designing a comprehensive program management system to monitor the implementation of San Jose City College's peer-led team learning program

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The Peer-Led Team Learning (PLTL) program relies, for optimum students' success, on the careful implementation of its six critical components. Central among these core components is the highly trained Peer Leaders (PL) who facilitates PLTL Workshops (eg. a small group Peer-Assisted-Learning –PAL– pedagogy facilitated by a well-trained peer). Herein, we describe the technological tools and design that were developed to systematically archive all PLTL program materials and monitor program quality while supporting the peer leader position. We also demonstrate how PLs use the interactive management system to develop weekly planning sheets, measure, record and score student participation in PLTL Workshops.

Our attempts, over the last few years, at integrating commercial platforms to track participants, support the PL position, monitor program quality, and organize a multifarious set of program components yielded unsatisfactory results. To address the problem of managing a diverse array of programmatic elements, we envisioned an interactive tool that would be nimble, intuitive, and comprehensive. The result was the development of a robust PLTL electronic management system, designed in a cloud-based environment (eg. using a combination of five different scripting languages) that supports the PL position. This unique PLTL electronic management system, assists both PLs and program personnel to input data and track the program's effectiveness by

monitoring key performance indicators. As our intensive program undergoes continuous program review and expands beyond chemistry and into biology, physics and math courses this multidimensional tool will become increasingly more important for organizing and monitoring the growth and integrity of the program.

In this presentation we also include both quantitative and qualitative results with comparison impact data between PLTL-supported vs. PLTL-unsupported STEM courses. It is anticipated that the customized PLTL electronic management system described herein, can be adopted or adapted for use by other PAL programs with similar needs.

### WRM 283

### Teaching first and second semester general chemistry in the hybrid environment at a community college

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Harold Washington College is an urban community college located in downtown Chicago, IL. For the last several years, the chemistry department has offered first and second semester general chemistry in a hybrid format. In this mode of instruction, 50% of the lecture was conducted asynchronously and 100% of the lab was conducted face to face (f2f). During the asynchronous portion, students watched prerecorded lectures selected from the Internet, read assigned chapters from the text, completed electronic homework problem sets, and performed online simulations. The f2f sessions focused on interactive problem solving and small group work. To measure the efficiency of hybrid instruction, student outcomes in the hybrid courses were compared to the same measures in traditional, 100% f2f courses taught by the same instructors. As pretests, students from both hybrid and traditional sections took the California Chemistry Diagnostic (2006 version) and Lawson Test of Scientific Reasoning at the beginning of the course. As a posttest, all students took an appropriate ACS exam. For the first semester of general chemistry, the hybrid students were significantly less prepared than their peers in the traditional section by both pretest measurements ($p < 0.10$). Fewer of the hybrid students successfully completed the course (final grade of A, B, or C) and the ACS exam scores were significantly lower ($p < 0.10$). For second semester of general chemistry, the hybrid students and their peers in the traditional section were statistically identical by both pretest measurements ($p < 0.10$). The percentage of students who successfully completed the course was also approximately equal, but the ACS exam scores of the hybrid students were significantly lower ($p < 0.10$). These results will be discussed along with possible explanations for the lower student success in the hybrid sections. Suggestions for improving hybrid courses will be presented.

### WRM 284

### Organic chemistry in high school: A project in collaboration with a local community college

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Carlmont High School is a well-established public, four-year comprehensive high school located in Belmont, CA. Cañada College is a local community college located in Redwood City, CA, approximately ten miles from Carlmont High School. For the past few years, Carlmont High School has offered organic chemistry as a science elective course to its students either as a regular class or as an independent study option. Having this course offering option in high school is rare. The lecture portion of this class is taught at the high school campus using instructional materials comparable to those used at community colleges and four-year universities. Recognizing the value of laboratory skills but lacking the necessary facilities at the high school, a pilot project involving collaboration with Cañada College was explored. In this pilot project, 26 high school students came to the college's laboratory to conduct experiments one Saturday a month for eight months during the academic year 2010-2011. Instruction was delivered by their high school teacher. Students learned common microscale extraction, purification and analysis techniques, including IR and GC. Students responded satisfactorily to this experience in a post-activity survey conducted at the end of the pilot project. They expressed an increased interest towards chemistry. Furthermore, students who have transferred to four-year universities report positive feedback regarding the academic preparation they acquired through this project. The details of this collaboration along with the results of the project will be discussed in this presentation.

### WRM 285

### ChemEx$^2$ at Stanford

***Jean Lythcott****, jlythcott@gmail.com, Gary Benz, Kevin Doyle.Center for Study of Excellence in Teaching, Stanford University, Stanford, CA 94305, United States*

Stanford's new Summer Institute, ChemEx$^2$, is a highly respectful invitation to chemistry teachers to rethink their practice in behalf of their students. The grist of the two weeks Institute lies in separating the building of understanding about a chemical phenomenon from the prescribed set of actions and outcomes of a standard chemistry laboratory format. This is a radical, inviting, and productive departure from standard teaching practice. In the first year of ChemEx$^2$ 2012, one group of participants decided to re-sequence their entire chemistry curriculum as a result of some of the transformative thinking it sponsored for them, and to interesting success.
'ChemEx$^{2'}$ stands for 'Experiences' and 'Experiments' in 'Chemistry'. Several well-engineered phenomena, developed in the chemistry department at Stanford, are the Experiments of ChemEx$^2$. They are reliable, safe, and inexpensive, they can be used in multiple, chemistry curriculum contexts and for different outcomes, and they minimize the complexity or unreliability that often characterize laboratory activities to the distraction of students. The Experiences of ChemEx$^2$, developed by chemistry educators, involve queries about when a specific phenomenon could be used, in what different circumstances, for what different teaching purposes and outcomes, and to what advantage for students. It begins with the query: could students construct some deep chemical understanding from investigating a phenomenon on the very first day?
One specific focus of ChemEx$^2$concerns students creating their own arguments, from evidence they gathered, to a claim/conclusion of some new chemical understanding for themselves. Students then know not only what they know, but how they know it, and why they trust what they know. This focus on argumentation is highly supportive of key elements in the new science education reforms: National Science Education Framework, Next Generation Science Standards, and Common Core Standards for Literacy in the Content Areas.

### WRM 286

### Visualizing the Chemistry of Climate Change (VC3Chem): Interactive resources for teaching and learning chemistry through the rich context of climate science.

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Global climate change is one of the most pressing environmental challenges facing humanity. Taking this into account, we miss opportunities when connections to climate science and global climate change are not included in undergraduate chemistry courses for science majors. Many of the important underlying concepts of climate science rely on models built on a fundamental understanding of chemistry, and we have learned that they can be incorporated easily into undergraduate chemistry courses. In Visualizing the Chemistry of Climate Change (VC3Chem), newly developed and piloted modules address the gap and teach core chemistry concepts through the rich context of climate science. These interactive web-based digital learning objects enable students to learn about isotopes and their relevance in determining historical temperature records, IR absorption by greenhouse gases, and acid/base chemistry and the impacts on changing ocean pH. The efficacy of the tools and approach has been assessed through measuring changes in students' understanding about both climate change and core chemistry concepts.

### WRM 287

### Strategies to investigate microbial natural products from deep-sea hydrothermal vents

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The global crisis of escalating antibiotic resistance of micro-organisms strikes at multiple facets of human health and well-being, extending beyond infectious diseases to agriculture and commerce. It is recognized that in addition to finding new bactericidal antibiotics with unprecedented mechanisms of action, understanding microbial metabolism, community structures, and symbioses is critical to diverting the evolution of antibiotic resistance and inducing susceptibility to current antibiotics. Certain signaling molecules are produced solely during interspecies communication (quorum sensing cross-talk), and also under anaerobic/hypoxic growth conditions that mimic host environments. In addition to investigating unusual field collections of microbial assemblages from deep-sea hydrothermal vent sites, we have selected a multispecies co-culture strategy to elicit the production of functional (biologically active) natural products from phylogenetically characterized (16S rDNA) deep-sea vent isolates in the laboratory. Culture filtrates and cell mass extracts from both mono- and bi-species cultures are tested in microtiter 96-well plate format for differential bactericidal activity against a panel of clinically-relevant multidrug-resistant bacterial strains, and also in a newly-developed assay for inhibition of virulence mediated by the Type II Secretion (T2S) system in the model organism *Vibrio cholera*. The T2S system is widely distributed in bacteria causing disease in humans, animals, and plants. We have obtained more than 300 bacterial isolates from deep-sea vent collections at Axial Seamount (East Pacific Ocean) and NE Lau Basin (West Pacific Ocean), with over 70 actinomycete isolates. In the course of bi-species co-culture experiments with a number of these strains, we have found potent and selective bactericidal activity against the causative agent of gonorrhea, *Neisseria gonorrhoeae* and against methicillin-resistant *Staphylococcus aureus*.

### WRM 288

### New analogs of 6-deoxyerythronolide B and erythromycin A produced by precursor directed biosynthesis and in vitro reconstitution of the 6-deoxyerythronolide synthase.

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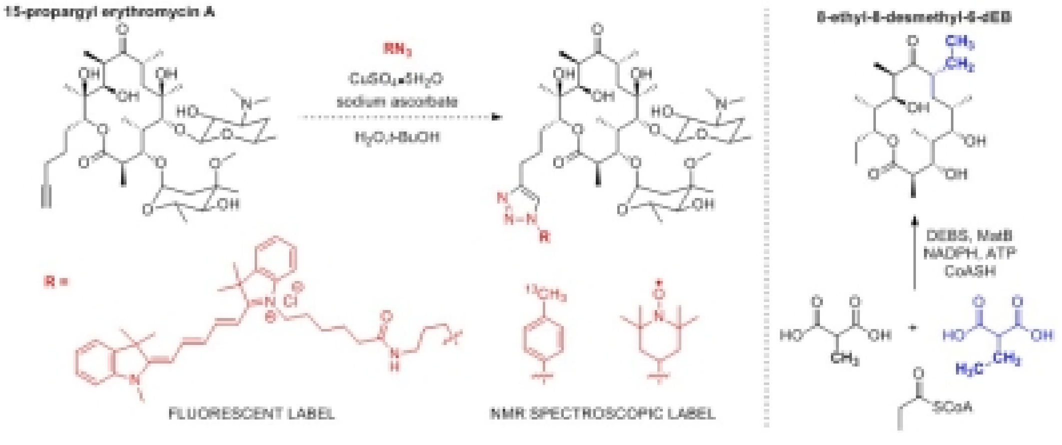

With the continual emergence of drug-resistance in bacteria, there is a constant need to develop new antibiotics. Macrolide antibiotics, such as erythromycin A, are widely clinically utilized and are known to function through inhibition of protein translation in bacterial ribosomes. In order to design the next generation of macrolide antibiotics, it is crucial to know the conformation of the macrolide when it is bound to the ribosome. Although X-ray crystallography has revealed the conformation of a variety of macrolides bound to ribosomes in the solid state, the conformational dynamics of macrolide-ribosome binding interactions have thus far not been elucidated. We report progress towards chemical modification of 15-propargyl erythromycin A, produced by precursor directed biosynthesis, in order to access fluorescent dye- and isotopically-labeled analogs of erythromycin. These new molecular probes will allow the characterization of macrolide-ribosome binding interactions through the use of fluorescence and nuclear magnetic resonance spectroscopy. New analogs of 6-deoxyerythronolide B (6-dEB), which is the macrocyclic precursor to erythromycin, can also be produced by changing the malonyl-CoA extender unit that is incorporated into the growing polyketide chain during biosynthesis. Towards this end, we have fully reconstituted the 6-deoxyerythronolide B synthase (DEBS) *in vitro* and biochemically characterized fundamental aspects of 6-dEB biosynthesis, including the turnover rate of the pathway. Furthermore, this new *in vitro* system was used to synthesize 8-ethyl-8-desmethyl-6-deoxyerythronolide B, in the presence of non-limiting concentrations of ethylmalonyl-CoA.

### WRM 289

### Use of high content molecular networks to profile and quantitate marine cyanobacterial metabolomes

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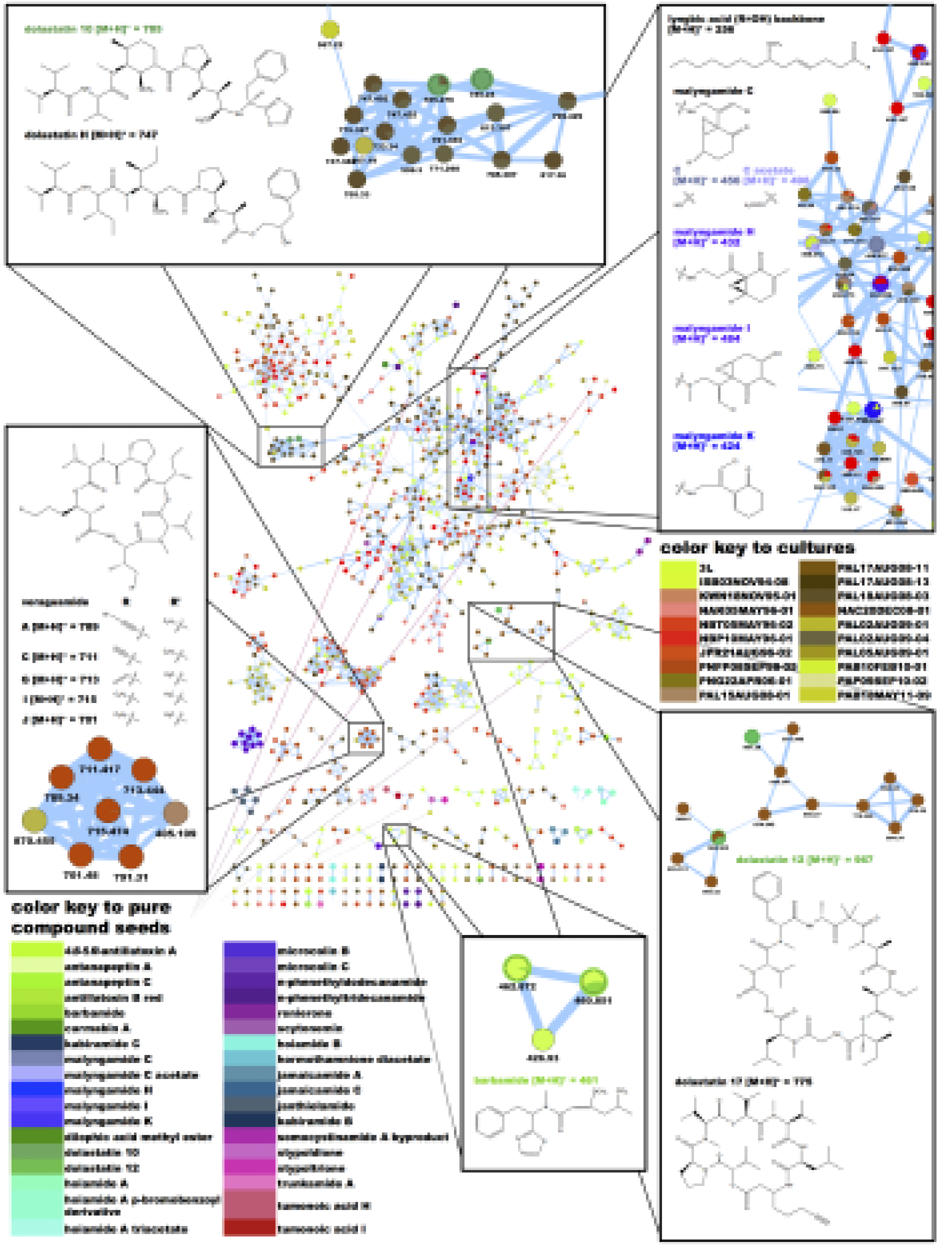
Liquid chromatography-mass spectrometry (LC-MS) is an ideal method for rapidly profiling crude natural product extracts, however, the quantity of data produced can become difficult to manage. Molecular networking based on MS/MS data provides an automated method for initial interpretation of these complex datasets. Here, we developed additional features for the Spectral Networks algorithm that provide relative and absolute quantitation of the amount of a specific compound in an extract. Motivated by a desire to find a malyngamide C producer among our cultured marine cyanobacteria for biosynthetic investigations, we combined the LC-MS/MS datasets for 20 lipid extracts and 60 pure compounds, including malyngamide C, to create a molecular network rich in content.



As an untargeted metabolomic survey, this network illustrates the chemical diversity present in the extracts of marine cyanobacteria. It is also a powerful tool for locating producers of specific secondary metabolites. Using new visualization techniques, we located a cultured strain of *Tropicamarinus tropica* from Panama that produced 0.054 mg of malyngamide C per mg crude extract (5.4% w/w) and this organism is now undergoing genome sequencing to access the corresponding biosynthetic machinery.

**WRM 290**

### Application of overlapping techniques to profile a well-studied cyanobacterial strain affords a richer understanding of its metabolome

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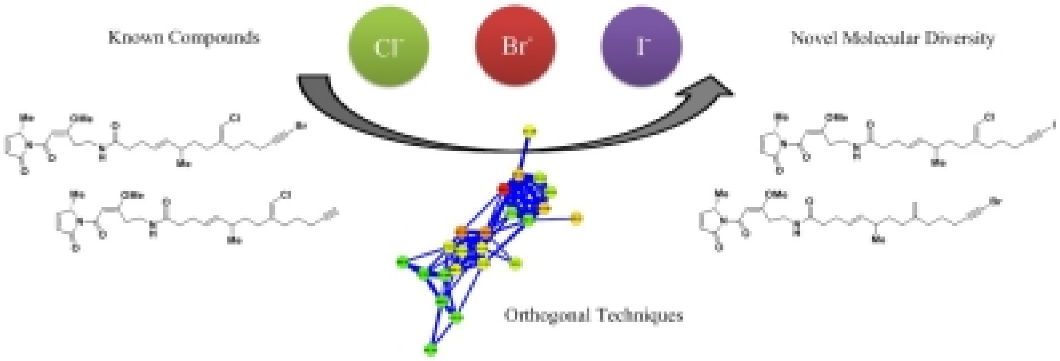
*Moorea producens* JHB is a strain of tropical marine cyanobacteria that has been extensively studied by traditional approaches in natural products chemistry. Previous bioassay and structure-guided isolations led to the discovery two exciting classes of natural products, hectochlorin and the jamaicamides A and B; however, these do not represent the full metabolic capacity of this organism. In an effort to expand our understanding of this strain's metabolome, we employed a variety of techniques that had never before been applied in the study of JHB. These included 'spectrometric networking' which allowed us to visualize the metabolome of JHB to both guide and enhance the isolation workflow. Additionally, we explored the metabolic capabilities of this strain by genome analysis and elicited the production of novel compounds by cultivation in modified media. These orthogonal analyses revealed diversity previously unreported in both the hectochlorin and jamaicamide family of compounds, as well as a novel compound outside of these structure classes, demonstrating that these tools are complimentary and enrich the profiling of secondary metabolomes of marine microorganisms from even well-studied strains.



### WRM 291

### Walking in the woods with quantum chemistry - Studying natural product biosynthesis with computational chemistry

***Dean J Tantillo***, *djtantillo@ucdavis.edu.Department of Chemistry, University of California, Davis, United States*

Applications of quantum chemical calculations to problems in natural products chemistry, including the determination of reasonable mechanisms for formation of complex terpenes, will be discussed.

### WRM 292

### Thiol-based probes for the discovery of electrophilic natural products from marine bacteria of the genus *Salinispora*

***Chambers C Hughes***, *chughes@ucsd.edu, Dongyup Hahn.Scripps Institution of Oceanography, La Jolla, CA 92093-0204, United States*

New methods for the rational discovery of biologically-active natural products are lacking. Traditionally, a bioactive compound is targeted with the aid of a biological assay (“bioassay-guided fractionation”), and mixtures are dereplicated with UV-detected liquid chromatography-mass spectrometry (HPLC-MS). Today, widespread overuse of this strategy often leads to the re-

isolation of known, highly UV-active, inherently “ionizable” metabolites and their derivatives. Since neither the extinction coefficient nor the potency of the targeted compound is known, moreover, little information can be gleaned concerning its actual abundance in the mixture.
“Reactivity-guided fractionation” aims to identify biologically-active compounds based on their reactivity and not their innate UV and MS characteristics. Chemical probes that consist of a UV or MS tag and a chemoselective reagent are designed and synthesized. A salient example of this method, we have prepared thiol-bearing probes that selectively react with a series of electrophile-containing natural products—for instance, penicillin G, clavulanic acid, parthenolide, andrographolide, epoxomycin, and salinisporamide. These same metabolites have been shown to react covalently with nucleophilic residues on their respective protein targets, so the reactivity of the thiol probe mimics the mechanism-of-action of the compounds. Current efforts are directed toward discovering new electrophilic natural products from marine bacteria of the genus *Salinispora*.

### WRM 293

### Inhibitory mechanisms of tannins on the enzyme Tyrosinase

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In our continued search for natural products the Patayuc plant from Guatemala was investigated as a potential insect control agent. Two Hydrolysable tannins isolated from the roots of *Fuchsia tetradactyla* Lindl were tested as tyrosinase inhibitors but failed to inhibit the enzyme in the predicted way. Both oxygen and spectrophotometer assays were used to follow the reactions. Neither tannin inhibited the oxidation of L-3,4-dihydroxyphenylalanine (L-DOPA) catalyzed by mushroom tyrosinase but were rather oxidized as soon as both were mixed with the enzyme. In addition, a large quantity of gallic acid (3,4,5-trihydroxybenzoic acid) was characterized from the plant roots. Gallic acid was oxidized by redox reactions to a quinone as a redox-cycler. Gallic acid has been previously identified as a tyrosinase inhibitor but these results suggest it is neither as a substrate nor an inhibitor.

### WRM 294

### Mass Spectrometry Based Investigations of Cheese-Derived Natural Products

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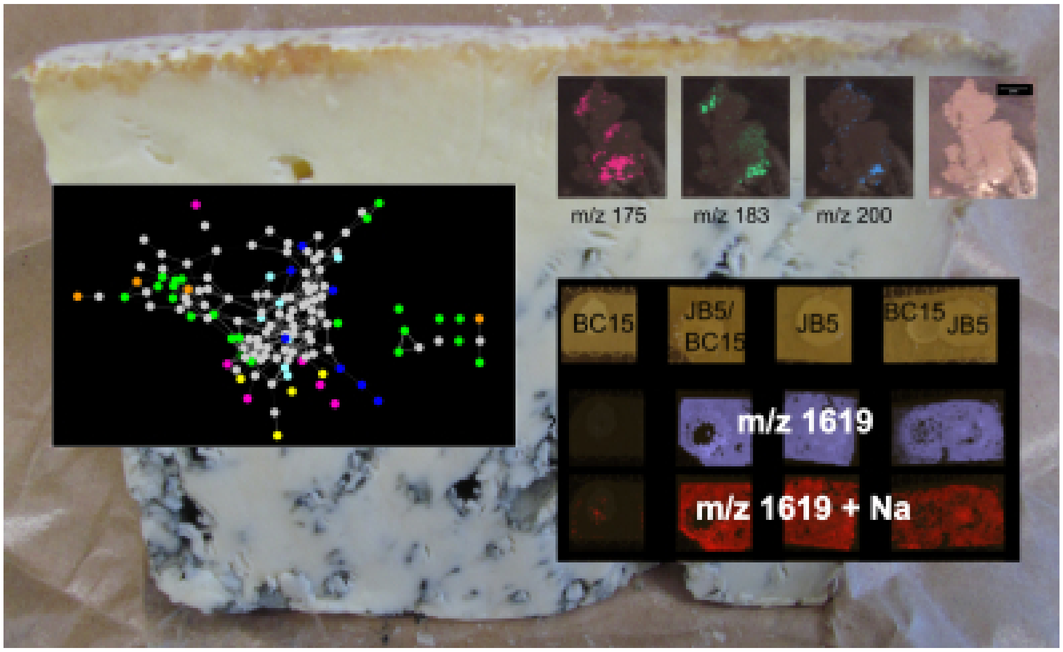
Natural products derived from complex microbial communities such as the lungs of cystic fibrosis patients are notoriously difficult to study due to the high level of heterogeneity in the microbial populations. We have chosen cheese rind communities as a less complex microbial community to study biofilm formation mediated by natural products. Metagenomic data of the Bayley Hazen Blue cheese rind shows that initially the rind is dominated with *Staphylococcus* spp.; then, as the cheese ages, *Brevibacterium* sp. becomes dominant. This microbial succession can be reproduced in a laboratory setting and can be interrogated using mass spectrometry tools developed in our laboratory.



One tool used to interrogate the biofilm is imaging mass spectrometry (IMS), which facilitates visualization of the spatial distributions of molecules in relation to the microbial communities. The second MS-based tool is molecular networking, which utilizes tandem mass spectrometry (MS/MS) fragmentation and creates a molecular fingerprint for natural products, allowing for their identification through seed known compounds, databases, or comparison of previously documented MS/MS spectra. Using IMS on the *in vitro* communities as well as the physical cheese rind itself, we have been able to identify natural products that are only produced by *S. succinus* and *Brevibacterium* sp. when they are in physical proximity to one another. These MS based tools have allowed us to gain insight into the complex world of cheese biofilm microbial communities and natural products.

### WRM 295

### Process development of PI3K inhibitor GDC-0980

***Theresa Humphries***, *humphries.theresa@gene.com. Small Molecule Process Chemistry, Genentech Inc., South San Francisco, CA 94080, United States*

We have developed a practical synthesis suitable for the preparation of multi-kilogram amounts of the PI3K inhibitor GDC-0980. The convergent sequence involves metalation / formylation and reductive amination followed by a metal catalyzed Suzuki-Miyaura cross-coupling to afford the API. A robust metalation protocol via triarylmagnesiate intermediates allowed formylation under non-cryogenic conditions. The cost of goods was significantly reduced through identification of a cheaper starting material and process development. Finally, a considerably more efficient and greener synthesis of a key raw material was developed.

### WRM 296

### A novel, versatile, and scalable general short synthesis for most of prostanoids has been achieved in our labs

***George Yiannikouros***, *george.yiannikouros@irixpharma.com. Department of Chemistry, IRIX Pharmaceuticals, Inc, Florence, SC 29501, United States*

A new, short, versatile, scalable, cost effective, and general synthesis for all prostanoids has been achieved in our laboratories. A cost effective process for the manufacturing of compound **I** in multi-kilograms quantity and its successful conversion, at scale, to compound **IV** , a suitable intermediate for the key, ring closure metathesis step, produced a ten-membered ring lactone **VI**

in ca. 70% overall yield. Upon the removal of the protective groups, following by a specific way lactone opening, the targeted prostaglandin API is produced
[figure 1]

### WRM 297

### Process optimization and scale up activities for preparation of an HCV NS5B polymerase inhibitor[1]

***Mohammad Masjedizadeh**, mohammad.masjedizadeh@principiabio.com. Chemistry and Manufacturing Control, Principia Biopharma, South San Francisco, CA 94080, United States*

An efficient, cost effective process for the multi-kilo preparation of an HCV NS5B Polymerase inhibitor will be presented. The process includes preparation of a bromo,chloroquinoline core using substituted chloroaniline and tribromopropanal followed by two Suzuki-Miyaura cross-coupling reactions and a selective dealkylation step. This process was scaled to generate 45 kg of the API.

[1] This work was conducted at Roche Nutley, NJ.

### WRM 298

### ELND006: Process Chemistry Improvements to the Key Enantioselective Step

***Michael S Dappen**, mdappen@comcast.net, Jacek J Jagodzinski, David A Quincy, Jing Wu, Lee H Latimer. Department of Chemical Sciences, Elan Pharmaceuticals, South San Francisco, California 94080, United States*

ELND006 is a gamma secretase inhibitor that entered clinical studies for the potential treatment of Alzheimer's Disease. The Medicinal Chemistry route involved 10 steps to initially produce racemic material. A route using the Ellman chiral auxiliary, *tert*-butyl sulfinamide, to control the stereochemistry of the single chiral center was demonstrated by Elan Medicinal Chemistry with modest diastereoselection (~76% de). This talk will report on the Elan Process Chemistry group improvements to the synthetic route, with a focus on reworking the Ellman chemistry (up to 95% de). After crystallization to upgrade the chiral purity, the new process produced ELND006 in 35% overall yield with greater that 99% ee.

### WRM 299

### Early process research strategies: evaluating multiple routes with multiple suppliers for addressing a key feature of a target molecule

***Michael Humora**, michael.humora@biogenidec.com. Department of Process Research and Development, Biogen Idec, Cambridge, MA 02142, United States*

The strategies that an organization uses to conduct early process research on a program can vary greatly depending on complexity of the molecule, specialization of partner technology, and a large number of similar variables. The program manager will adopt a specific strategy based on the needs of the project and play a significant role in how activities are coordinated and ultimately be a key driver for how the program is carried out. A case study describing how multiple contract manufacturing organizations, collaborating as integrated partners, with our team and with each other worked to address the formation of a key stereogenic center will be presented.

### WRM 300

### From few grams to multi Tons. Some tips

***Giorgio Bertolini**, GB.labochim@infagroup.com. Department of Technical Research and Development, Labochim SPA, a member of INFA Group ApA, Milan, Segrate ( Milano) 20090, Italy*

During the chemical process development, one of the key decision point is the synthetic route selection. However after this decision the way to transform a lab synthetic method to a chemical industrial process is a long exercise.

Beside the nature of starting materials and reagents, the number of steps and yields, many other parameters have to be considered during the optimization phase.

Based on our long experience on scale-up and industrialization of chemical processes both for generic APIs and for NCE, some of these new parameters will be suggested. The investigation

and selection of these parameters can be the key factor to discriminate from a good synthetic method and a real chemical process.

### WRM 301

### Autoignition chemistry of oxygenated molecules: Linking biofuel development with advanced engine combustion

***Craig A Taatjes***, *cataatj@sandia.gov. Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, United States*

The development of new biofuel production strategies that may reduce greenhouse gas emissions is occurring at the same time that new clean efficient combustion strategies are being designed for internal combustion engines. These combustion strategies are sensitive to fuel chemistry, and efficient conversion of lignocellulosic biomass will produce fuels whose combustion properties may difffer significantly from those of traditional petroleum-based fuels. Optimizing this system suggests a co-development approach in which new biofuel production methods are linked to the performance properties of the eventual fuel product. I will describe recent work aimed at developing a framework for this co-development. I will specifically focus on measurements of fundamental autoignition chemistry of oxygenated biofuels that represent classes of molecules that are produced from lignocellulosic biomass by endophytic fungi. These measurements are integrated with a larger effort that stretches from identification and exploitation of novel synthetic biology pathways based on fungal metabolism to combustion model development and testing in advanced engines. I will describe how the oxygen-containing functional groups alter the chemistry of autoignition.

### WRM 302

### Secondary organic aerosol phase and impacts on heterogeneous oxidation

***Christopher D Cappa***[1], *cdcappa@ucdavis.edu, Katheryn Kolesar*[1], *Chris Ruehl*[2,3], *Gina Buffaloe*[1], *Kevin R Wilson*[2]. *(1) Department of Civil and Environmental Engineering, University of California, Davis, Davis, CA 95616, United States (2) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States (3) Department of Environmental Science, Policy and Management, University of California, Berkeley, United States*

Secondary organic aerosol (SOA) forms in the atmosphere from the condensation of low-volatility products of gas-phase reactions of organic molecules. Recently, it has become evident that SOA does not always have the long assumed liquid phase, but instead exists as a solid or semi-solid (often referred to as “glassy”). There has been much speculation that the condensation of such glassy SOA onto pre-existing particles to form a coating will act as a barrier from heterogeneous oxidation due to the very high viscosity/low diffusivity of oxidants through the SOA coating. Here, this idea is directly tested through measurements of the OH heterogeneous oxidation kinetics of a model primary organic aerosol, specifically particles comprised of squalane, before and after coating with SOA. Squalane is a 30-carbon saturated hydrocarbon whereas the SOA, produced from the gas-phase reaction of a-pinene + $O_3$, is comprised of highly functionalized molecules. The effective reactive uptake coefficient of OH on pure squalane particles is known, with $\gamma_{eff,Sq}$ = 0.3. Upon coating, the effective uptake coefficient increases substantially with coating thickness, increasing by a factor of 4 for a 40 nm SOA coating. Thus, rather than the SOA coating serving to protect the POA from oxidation, in this case it actually enhances the chemical loss. Such an increase in $\gamma_{eff,Sq}$ demonstrates an important role for secondary reactions in the condensed phase, and suggests that there are strong differences in the reaction pathways available to organic radicals ($R^\cdot$, $RO^\cdot$ and $RO_2^\cdot$) for squalane self-reactions vs. squalane + SOA cross-reactions. Further, these results indicate that radicals are able to propagate through the SOA coating, despite its very high viscosity.

### WRM 303

### Molecular Understanding of Self-Cleaning and Depolluting Photocatalytic Processes on Urban Surfaces

***Hugo Destaillats***, *HDestaillats@lbl.gov, Mohamad Sleiman, Olivier Rosseler, Nahuel Montesinos, Damian Bikiel, Marta Litter, Hendrik Bluhm, Musahid Ahmed, Miquel*

*Salmeron.Indoor Environment Group, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Photocatalysis has been postulated as a promising approach for de-polluting urban atmospheres and preserving exposed surfaces clean. Building materials and coatings containing nanosized $TiO_2$ photocatalytic functionalities are gaining market share, including self-cleaning coatings, mortar, plaster, architectural fabrics and tiles. This presentation will describe results from two separate studies that used synchrotron-based surface spectroscopy and mass spectrometry to better understand the photocatalytic mechanisms that regulate the de-soiling and de-polluting activity. $NO_x$ removal was investigated by ambient pressure XPS, by identifying and quantifying surface and gas-phase species formed during adsorption of $NO_2$ on $TiO_2$ and subsequent UV irradiation at $\lambda = 365$ nm. The results illustrate how $NO_x$ chemistry on $TiO_2$ surfaces can be affected by the presence of water vapor, heteroatoms present as impurities, and carbonaceous soiling. The removal of black carbon (soot) deposited on irradiated $TiO_2$ surfaces was investigated by laser desorption coupled with time-of-flight (TOF) mass spectrometry synchrotron ionization and complementary analytical methods. Two different model soot samples were used as surrogates of urban grime to describe the mechanisms of photocatalytic soot oxidation and removal. Ancillary reflectance measurements were performed to determine the efficiency and kinetics of the overall process.

### WRM 304

## Dynamic perspective on optimizing charge transfer and transport in quantum dot sensitized metal oxide nanostructures for light energy conversion

***Jin Z Zhang***, *zhang@ucsc.edu. Chemistry and Biochemistry, University of California Santa Cruz, Santa Cruz, CA 95064, United States*

Nanostructured metal oxides (MO), such as $TiO_2$, $WO_3$, $Fe_2O_3$, and ZnO, are promising for light energy harvesting into electricity or chemical fuel such as hydrogen. Because of their large bandgap and thereby weak visible absorption, different strategies have been developed to enhance visible light absorption, including dye or quantum dot (QD) sensitization. On the other hand, charge transport in nanostructures is often limited due to a high density of trap states. We have recently developed new strategies to rationally introduce bandgap states, *e.g.* oxygen vacancies through hydrogen or other treatment of MO nanostructures, to substantially improve charge transport. Therefore, by using a two-pronged approach that combines QD sensitization for efficient charge transfer and chemical treatment of MO for enhancing charge transport, we can achieve synergistic enhancement in photocurrent generation. We carried out ystematic characterizations using a combination of techniques including photoelectrochemistry, electron microscopy, ultrafast laser, ESR, and XPS gain insight into the underlying fundamental mechanism. The approach is general and can be potentially useful for many different applications that require strong light absorption and efficient charge transport.

### WRM 305

## Sub-50 fs electron delocalization dynamics via resonant auger spectroscopy: The case of oriented organic semiconductor interfaces

***Alexander L Ayzner***[1,2]*, aayzner@slac.stanford.edu, Dennis Nordlund*[2]*, Do Hwan L Kim*[1]*, Zhenan Bao*[1]*, Michael F Toney*[2]*. (1) Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States (2) Department of Materials Science, Stanford Synchrotron Radiation Lightsource, Menlo Park, California 94025, United States*

It has now been established that the precise nature of the donor/acceptor interface in an all-organic heterojunction solar cell plays a critical role in determining such parameters as the open-circuit voltage and the short-circuit current. Nevertheless, experimentally relatively little is known about how the relative arrangement of donor and acceptor molecules determines the photoexcited electron dynamics and carrier localization at the heterointerface. Using the core-hole-clock implementation of resonant Auger electron spectroscopy, we attempt to answer the question of precisely how relatively orientation between model donor and acceptor molecules at the interface determines the rate of photoexcited electron transfer and hence the interfacial electronic coupling. We find that in the case where the donor and acceptor are oriented face-on with respect to each other, corresponding to substantial wavefunction overlap, we find that

photoexcited electron transfer times are below 50 fs. This is in contrast to the edge-on arrangement, where electron transfer is at least a factor of two slower. We explore the implications of these results for free charge carrier generation in blend organic photovoltaic devices.

### WRM 306

### Femtosecond x-ray spectroscopy studies of electronic excited states in coordination chemistry

***Wenkai Zhang***, *wenkaiz@slac.stanford.edu, Kelly Gaffney. SLAC National Accelerator Laboratory, Stanford PULSE Institute, Menlo Park, CA 94025, United States*

The ability of coordination complex to catalyze chemical reactions and absorb visible radiation makes them appealing targets for the development of photocatalysts. Identifying the chemical properties that dictate the electronic excited state dynamics of coordination complex will assist the design of molecular materials for solar energy applications. Suppression of charge transfer relaxation to high-spin ligand-field excited states would enhance the functionality of many earth abundant 3d transition metal complexes. I will present a femtosecond resolution x-ray fluorescence study of the impact of ligand field strength and solvent environment on the spin dynamics of a series of electronically excited $[\mathrm{Fe(CN)}_{6\text{-}2N}(\text{2,2'-bipyridine})_N]^{2N-4}$ complexes, with N = 1-3. These measurements verify the role of triplet ligand field excited states in the spin crossover dynamics from singlet to quintet spin configurations and demonstrate that modification of the ligand and solvent environment can lengthen the Febipyridal charge transfer lifetime by more than two orders of magnitude.

### WRM 307

### Peer-Led Team Learning at San Jose City College: A student-faculty partnership to transform the learning environment and promote student success, retention, leadership, teamwork, creativity, and critical thinking in STEM courses

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San Jose City College employs ***Peer-Led Team Learning (PLTL),*** a small group peer-assisted model that actively engages STEM students in solving carefully structured problems, facilitated under the guidance of a well-trained peer leader (PL). Students and faculty discovered that the tools acquired during these *free* PLTL Workshops are empowering, incredibly collaborative, and team building. Each person is encouraged to express creativity, demonstrate problem solving skills, and develop an openness to learn from their own mistakes. The PL's role is crucial in establishing a learning community, bonding with the instructor and their peers and sharing strategies for gaining competence and confidence in the subject matter. Additionally, PLs mentor students to effectively navigate and acculturate to academic life, all of which are well known characteristics that influence retention and success, especially among ethnic minority students. The PLTL model is nationally recognized and effective in improving student retention and success within institutions of varying size, location, and organizational structure. Although it can be adapted to reflect the individual needs and differences of any campus, there are fundamental principles that must be preserved to ensure program integrity and effectiveness.

| PLTL **Six Critical Components** |
|---|
| 1. The Workshop is integral to the course |
| 2. Course professors are involved in the selection of materials, training and supervision of PLs, and they review the progress of Workshops. |
| 3. PLs are selected, trained and supervised to be skilled in group work as facilitators. |
| 4. Workshop materials are appropriately challenging, directly related to tests, designed for small group work. |
| 5. The Workshops are held 90 minutes/week, contain 6-8 students, in a space suitable for small-group activities. |

6. PLTL is supported by the department and the institution with funds, course status and other support so that the method has the opportunity to be adopted across courses and disciplines

### WRM 308

### San Jose City College student ACS chapter: Community outreach and promoting interest and involvement in chemistry

***Sang Ngo**, ngo_ts@yahoo.com, **Loan Trac**, loantrac2711@yahoo.com, Madeline Adamczeski. Chemistry, San Jose City College, San Jose, CA 95128, United States*

The ACS Student Chapter in San Jose City College aims to promote an approachable introduction to science. Recent goals of our Club members have been to assist children, at a local transitional housing center, engage in the learning process and discover how much fun chemistry can be. This has been achieved by developing active learning workshop exercises and creating a welcoming learning environment. The workshop component of the Club's outreach program aims to inspire children to experiment with science in their everyday lives. Our ACS Chapter also actively hosts on-campus seminars, including recent guest speakers from the Heart 360 (ie. sponsored by the American Heart Association) and the Patient Navigation Program (ie. sponsored by the Asian Americans for Communication Involvement). In addition, members of the Chapter organize field trips including visits to UC Santa Cruz's Annual Joseph F. Bunnett Research Organic Chemistry Lecture series and monthly Santa Clara Valley Section-ACS meeting dinners. It is experiences like these, where we learn about cutting edge research and state-of-the-art scientific techniques and instruments. Our regularly scheduled fundraisers are multi-pronged whereby we promote chemistry, recruit new Club members, and raise funds to sustain these activities. It is also important to note that a significant number of club members also serve as Peer Leaders (PLs) and mentor STEM students in our Peer-Led Team Learning program. PLs help STEM students acculturate to college life and navigate the campus to foster both their academic and personal successes. Ultimately, the ACS Student Chapter at SJCC strives to stimulate interest in and gain appreciation for chemical sciences among members of the community and makes learning STEM subjects fun and intuitive.

### WRM 309

### Chemistry Club: A place to learn, share, and grow

*CSUS ACS Student Chapter, **Jessica J. Magpayo**, ghermanb@csus.edu, Angelica V. Carrazco, Alaina Kester, David Marcks, Allie Rummerfield, **Benjamin F. Gherman**, ghermanb@csus.edu, Cynthia Kellen-Yuen. Department of Chemistry, California State University, Sacramento, Sacramento, CA 95819-6057, United States*

The CSUS Chemistry Club aims to give students the chance to explore chemistry, through community outreach, on-campus activities, and professional development. Our club proudly sponsors youth outreach programs where we set up demonstrations as well as hands-on activities targeting elementary, middle, and high school students. During this past year, we twice hosted classes from local elementary schools for a day of chemistry-related activities on our campus in an actual Chemistry lab. We also put on an afternoon science experience for Native American high school students. In both cases, through activities such as microwave chemistry, cornstarch quicksand, and liquid nitrogen ice cream, we hoped to stimulate the students' interest and curiosity in science. We observed National Chemistry Week both by hosting a Mole Day celebration in our campus science building and also by having a booth for the CSUS homecoming festival. Our activities at these events allowed students and the greater campus community to learn basic chemical concepts like cross-linking which can be demonstrated by making everyone's favorite, “Slime.” Our club has shared potential career opportunities in chemistry by inviting alumni from professions such as optometry and pharmacy to come and offer career talks. We also went on field trips to two local wineries to learn about the role of chemists in wine making. Our student members, who come from many different backgrounds, enjoy their time in Chemistry Club and leave CSUS ready to be leaders in their field.

### WRM 310

## An Undergraduate Research Program for Deaf and Hard-of-Hearing Students

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We have a unique opportunity and resources to accommodate and promote deaf and hard-of hearing students in undergraduate research as part of their educational experience at the Rochester Institute of Technology/National Technical Institute for the Deaf (RIT/NTID). Our program provides students with opportunities to learn discipline-specific information while performing real-world research, contribute to the scholarship of their field, and work on projects utilizing the instrumentation they learn in the Laboratory Science Technology (LST) program. The program not only involves baccalaureate students in research, but also associate degree level students in undergraduate research projects. Success stories, lessons learned, and advice for implementing research activities for students with disabilities and early undergraduate students will be shared. Through this program, faculty at RIT/NTID are doing their part in involving diverse students in research experiences.

### WRM 311

## Get involved with the ACS Division of Chemical Education

***Cinzia Muzzi****, muzzicinzia@fhda.edu. ACS Division of Chemical Education, United States*

Want to know more about the Division of Chemical Education, want to learn how you can get more involved with DivCHED or learn about educational resources for chemistry? Want to find out how to apply for travel awards or meet and network with people from your region, nationally, and around the work who have similar interests? The Division of Chemical Education aims to serve as a means of focusing and enhancing the interest and efforts of all constituencies involved in the teaching and learning of chemistry at every level. If you have an interest in chemistry education, we want you involved in DivChed. Come visit our poster to learn more about the Division and all we have to offer, meet representatives from the Division, and let us know what you think the Division can do to better meet the needs of our members.

### WRM 312

## Anti-Science Legislation in California

***Immanuel J. Wilk****, sciencedocwilk@att.net. Menlo Park, CA, United States*

Two examples will be examined, Proposition 65, and Assembly Bill 1319. Both are anti-chemistry. Extensive use of public relations efforts was used to pass them. The wording of both will be examined. The anti-science organizations (ASOs) sponsoring such legislation are helped by the ignorance of the general public, the media, and politicians. When useful, the truth falls by the wayside. What might be the role of the American Chemical Society in combating anti-science and anti-chemistry attitudes

### WRM 313

## Is Conformational Flexibility Indicative of Compound Promiscuity?: A PDB Survey

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Selectivity is a primary consideration for small-molecule drug discovery. It is commonly believed that small molecules conformationally adapt to different binding pockets in order to optimize the free energy of binding. Consequently, medicinal chemists often try to either increase molecular flexibility to increase promiscuity or reduce molecular flexibility to improve selectivity. To further investigate the relationship between promiscuity and conformational flexibility, we mined the Protein Data Bank (PDB) to construct a manually curated dataset of 100 pharmaceutically relevant ligands crystallized in more than one protein target that bind each target with similar affinities (daffinity < 10-fold). After analyzing the individual molecular conformations of the 100 promiscuous compounds, we found that 59 compounds bound to different protein targets without significantly changing conformation (dRMSD < 0.45), suggesting that there is no distinct correlation between conformational flexibility and promiscuity within our dataset. The 41 promiscuous compounds that change conformation upon binding to different proteins generally bound to their protein targets with slightly lower affinities. Compounds that were crystallized in similar proteins (binding pocket sequence identity > 80%) were less likely to adjust conformation when binding. We were unable to identify a significant relationship between conformational change and either number of rotatable bonds, molecular weight, or calculated lipophilicity.

### WRM 314

### Characterization and Determination of Inhibitor Interaction with Streptomyces griseus Aminopeptidase

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Aminopeptidase is an enzyme that catalyzes the hydrolysis of amino acids of polypeptide chains from the N-terminus.*Streptomyces griseus*, a gram negative soil bacterium, releases aminopeptidase (SgAP) into the soil and its aminopeptidase demonstrates “enzyme catalytic promiscuity” in previous studies. SgAP has been found to hydrolyze peptide bonds and phosphoester bonds and its copper (II) derivative exhibits oxidative activities. This research project studies SgAP and its interaction against inhibitors with various functional groups. Purifications of the protein with a known procedure was performed. Then, using a Cary 50 Ultraviolet (UV)-Vision Spectrophotometer enzyme kinetics were determined as inhibitors were being introduces. Through Michealis-Menten kinetics, the SgAP's interactions with the inhibitors were analyzed. From the results of these interactions of different inhibitors with SgAP and further studies in the future, the enzyme catalytic promiscuity of SgAP could be better understood.

### WRM 315

### Using computational chemistry to design an optimal biomimetic ligand for the active site of the peptide deformylase enzyme

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Eubacterial proteins are synthesized with a formyl group at the N-terminus. Peptide deformylase (PDF), in a reaction catalyzed by an Fe(II) coordination complex in the active site, catalyzes the hydrolytic removal of the N-terminal formyl group from nascent proteins, making it of interest in antibacterial drug development. The goal of this research was to use computational chemistry methods (specifically, density functional theory) in order to find a biomimetic ligand for the enzyme active site which gives the most thermodynamically and/or kinetically favorable deformylation reaction. Beginning with a pyrazole-based ligand as a starting point for the model system of the enzyme active site, changes to the reaction energetics were examined when the ligand was changed to instead include imidazole, triazole, and pyrrole rings. The imidazole case was found to give the most thermodynamically favorable reaction. Electron-donating groups were then added to the ligands in order to make the various ring systems more electron rich and also to increase the nucleophilicity of a key thiolate group coordinated to the metal center. The activation energies and reaction energies with the various biomimetic ligands were correlated with changes during the deformylation reaction in the charge on the Fe(II) center and bond orders between Fe(II) and the protein substrate.

### WRM 316

### Investigating the folding dynamics of the RNA pseudoknot structural motif via massively parallel molecular dynamics

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RNA pseudoknots compose a three-dimensional structural motif that is present in the catalytic cores of some ribozymes, and are also capable of stimulating ribosomal frameshifts. Their complex topology and non-canonical hairpin-loop composition make pseudoknots an ideal structural motif with which to study the RNA folding process. Here we report our analysis of nearly 20,000 independent all-atom molecular dynamics simulations of the ribosomal frame-shifting pseudoknot of Luteovirus and the tmRNA pseudoknot from *Aquifex aeolicus*, which share global topology but have only ~50% sequence similarity. Using the Folding@Home distributed computing network and a novel Pathway Enumeration sampling method, a cumulative sampling time of over 115 μs was achieved for each of these pseudoknots. K-means clustering identified 27 conformational microstates for each pseudoknot, which reached conformational equilibrium after ~6 ns of ensemble sampling. Multiple folding metrics were used to identify 9 macrostates participating in the folding process, including previously undescribed misfolded and intermediate states. In agreement with our previous studies of tetraloop hairpins and tRNA, the similar folding behavior of these pseudoknots suggests that native state topology is a predominant factor in the RNA folding mechanism.

### WRM 317
### Synthesis of Lysyl Oxidase Inhibitors

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Lysyl oxidase (LOX) is a protein that aids in the proper formation of collagen and elastin in the human body. However, LOX also plays a role in the metastasis of cancerous tumors. Previous work has shown that by inhibiting the formation of the LOX protein with a molecule called beta-aminopropionitrile (BAPN), the spread of cancer throughout the body can be prevented. Unfortunately, BAPN is highly reactive and causes undesired side effects. The purpose of this project is to design small molecules capable of inhibiting the LOX protein by selectively delivering BAPN to the hypoxic environment of tumors. These molecules will be tested against lysyl oxidase and the gathered data will be used to design a more effective anti-metastasis drug.

### WRM 318
### Nontargeted profiling of the metabolome of a clockless mutant of Arabidopsis thaliana overexpressing a master regulator in the circadian clock, CCA1, reveals the holistic metabolic impact of locking plants in morning mode

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Our research question involves regulation of metabolic rates to maintain energetic equilibrium in A. thaliana. We hypothesized that the TCA cycle is under circadian control and that the transcription factor CCA1 affects the metabolome. Potential metabolic hubs were found by first exploring the literature. Seedlings at 7-days old were harvested at the morning and afternoon, representing maximum and minimum expression of malate dehydrogenase, chosen as a marker because it was both circadian regulated and identified as a metabolic hub. Significant differences between the Wild-type and CCA1 mutant fingerprints were revealed by principal component analysis (PCA) of 1H-NMR spectra. Key primary and secondary metabolites, sugars, and fatty acids were identified. GABA emerges as the most suitable choice for further analysis, as it differentially accumulates in the most treatments. This project illustrates the appropriate nature of NMR and GC-MS based metabolic profiling for hypothesis-driven studies.

### WRM 319
### Potential anti-tuberculosis components from an extract of a cellulose degrading marine bacterium

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The extract of a cellulose degrading marine bacterium, UA 774, was shown to inhibit the growth of *Mycobacterium marinum*, a close genetic relative of *M. tuberculosis.* The extract also had peaks of interest in the NMR spectra that could potentially be the source of the biological activity. The bacterium was grown on a 10L scale, centrifuged, filtered, then placed on a C-18 column. Elution was performed with 1:1 methanol:water (F1), followed by methanol (F2) and then ethyl acetate (F3). After bioassay, F2 was separated on a C-18 column with finer particles using a finer gradient. The most nonpolar components of F2 were interesting in $^1$H NMR and were shown to strongly inhibit the growth of *M. marinum*. HPLC separation resulted in further purification of the active components and spectroscopic analysis is underway.

## WRM 320

## Effects of Al-doping on the synthesis and performance of orthorhombic $LiMnO_2$

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To improve the stability of layered orthorhombic $LiMnO_2$, cathode material of lithium batteries, $Al^{3+}$ was doped using a solvothermal method; and the samples obtained were noted as W*x*E*y*-Al/Mn, where *x* and *y* refer to the volumes of water and ethanol, and Al/Mn is the molar ratio. As shown in Figure 1A, the $LiMn_{1-x}Al_xO_2$ solid solutionscan be synthesized at 150ºC for 36h (Figure1A(b) and (c)); and the Al/Mn ratios should be less than 1/5 in order to obtain a pure phase of $LiMn_{1-x}Al_xO_2$without $Mn_2O_3$(Figure 1A(d) and (e)). The cycle performance of the as-prepared W25E25-1/10 sample was investigated for up to 25 cycles at different C-rates with the voltage range of 4.3~2.0V(Figure1B). The cathode sample exhibited a high discharge capacity of 174mAhg$^{-1}$, higher than that(135mAhg$^{-1}$) of the sample without Al-doping reported previously.[1]The rate capability was noticeably improved and the discharge capacity reached about 100 mAhg$^{-1}$ at 0.5C. There was almost no capacity fading at the same C-rate cycles. Moreover, as the current density decreased from 0.5C to 0.1C, the discharge capacity can return to 168mAhg$^{-1}$, exhibiting a good electrochemical stability.

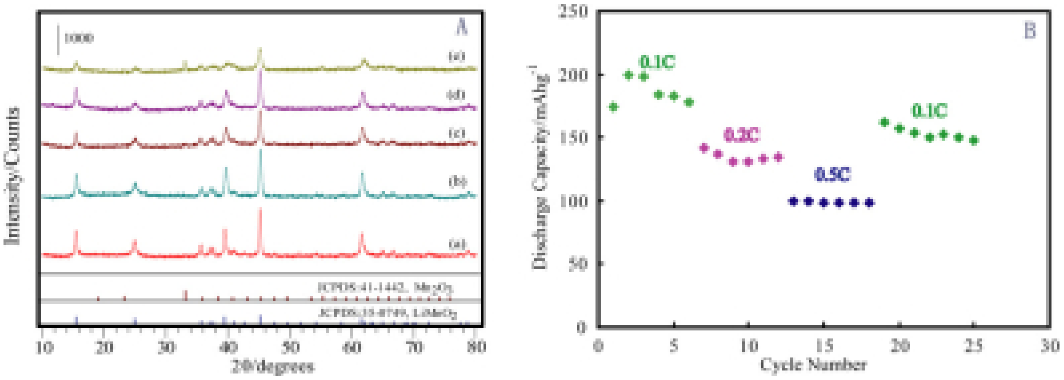

**Figure 1** .(A) XRD patterns of the as-prepared products:(a) W25E25,(b) W25E25-1/20, (c) W25E25-1/10, (d) W25E25-2/10 and (e) W25E25-3/10; (B) cycling performance of the W25E25-1/10.

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## WRM 321

## Photochemical degradation of fluoranthene in aqueous solution

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Polyaromatic hydrocarbons (PAHs) are widely distributed in natural water systems and marine sediments, and have been shown to be carcinogenic and mutagenic in animal models and human epidimiological studies. Photodegradation is the primary abiotic pathway for degradation of PAHs in aquatic environments. Photolysis rates for fluoranthene were measured in aqueous solution as a function of ionic strength (salinity), oxygen levels, and humic acid concentrations over the range of conditions found in fresh to marine waters. Solutions were irradiated using a solar simulator and concentrations of PAH were measured as a function of time using steady state fluorescence detection or HPLC with fluorescence detection. 3D excitation-emission matrix (EEM) fluorescence spectroscopy was used to identify potential photolysis products. Photolysis of fluoranthene followed first order kinetics, with degradation taking place on the timescale of hours. The variations of photolysis rates as a function of natural water variables will be presented and discussed.

### WRM 322

### Solvolyses in ionic liquid dual-solvent systems

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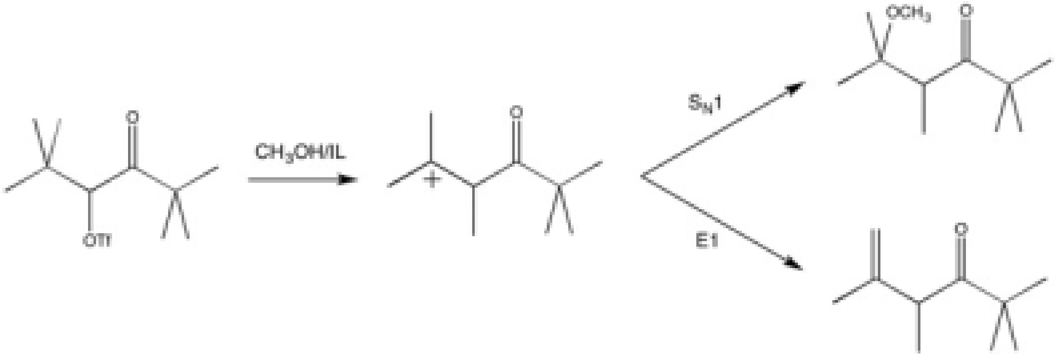
Ionic liquids have been studied as solvents in several types of reactions. In this work, the $k_{\Delta}$ solvolysis of pivaloyl triflate in an ionic liquid-methanol dual-solvent system was studied. The ratios of the substitution and elimination products were then measured by $^1$H NMR. For each of the ten ionic liquids studied, it was found that the addition of ionic liquid to the solvent system resulted in increased elimination product. The observed product distribution can be interpreted by applying the Kamlet-Taft solvatochromic parameters, α and β, of the ionic liquids. The mechanism of solvolysis was also investigated through computational studies.



### WRM 323

### Utilizing Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy to probe the solid state diffusion of cations through zeolite materials

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Zeolites are extremely porous aluminosilicate materials with pore sizes on the molecular scale. This feature facilitates applications involving diffusion of molecular and ionic species through these materials. We have been studying the kinetics of solid state migration of cations through zeolite materials using $^{29}$Si solid state NMR relaxation, X-ray diffraction, and diffuse reflectance infrared spectroscopy (DRIFT). Results from numerous experiments have increased our understanding of the migration process substantially. The work presented here illustrates that DRIFT can be utilized to follow the kinetics of solid-state long range intercrystallite diffusion in mixed zeolite systems. Preliminary results will be discussed in terms of the influences of temperature, zeolite pore system type, and cation character on the solid-state diffusion process

### WRM 324

### Synthesis and characterization of zeolite beta (BEA) and titanosilicate beta (Ti-BEA) using titanium(IV) tetrafluoride

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Ongoing global climate disruption stimulates research into methods that reduce, recycle, and/or store greenhouse gases. Titanium-substituted zeolites such as titanosilicate-1 (TS-1) and titanosilicate beta (Ti-BEA) are excellent oxidative photocatalysts and also exhibit photo-reduction chemistry. In this study, we focus on Ti-BEA because of its 12MR ring size, which facilitates the exchange of reactants and products, compared to the MFI framework (10MR). Our goal is to study the photocatalytic reduction of $CO_2$ and $H_2O$ to methanol using Ti-BEA powders.[1]
Pure silica BEA and Ti-BEA were synthesized according to modified literature methods[2,3]. Both doped and undoped forms of BEA were prepared and the growth conditions studied to compare and understand the growth rate and conditions of Ti-BEA. Progress of BEA crystallization from amorphous material to ordered beta zeolite framework was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Hydrothermal synthesis of Ti-BEA was modified to include the novel use of titanium(IV) tetraflouride as the titanium source, which reduces the needed amount of hydrofluoric acid[3]. Fluoride as a mineralizing agent produces nearly defect-free (few $Q^3$ sites) zeolite. XRD patterns and SEM images obtained before and after calcination show that pure monophasic Ti-BEA was obtained. UV-Vis and $^{29}$Si MAS-NMR spectroscopy were performed on calcined material and compared to published spectra[3]. Energy dispersive X-ray spectroscopy (EDS) was used to determine the amount of titanium incorporated into Ti-BEA. Future work will focus on the photocatalytic reduction of $CO_2$ using the Ti-BEA powders synthesized by this method.
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## WRM 325

## Analysis of peptoid tertiary-like structure through fluorescence spectroscopy utilizing the environmentally sensitive 4-DMN fluorophore

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Peptoids are N-substituted glycine oligomers with structures similar to those of peptides. The major difference between peptides and peptoids is the presence of variable side chains on nitrogen atoms in the backbone as opposed to side chains on the α-carbon. Peptoids are able to form helical structures similar to the α-helix in peptides despite the differing placement of the side chains. In addition to forming helical structures, peptoids have significant advantages over peptides, such as their ability to resist protease activity. It is important to explore different techniques for studying peptoid structure because it is difficult and expensive to use high resolution techniques such as x-ray crystallography. Fluorescence studies utilizing environmentally sensitive fluorophores as peptoid side chains reveal information about peptoid folding patterns[1], including peptoid tertiary-like structural features. Helical peptoids containing the environmentally sensitive fluorophore 4-DMN and an alkyne side chain were synthesized. Additonally, non-helical peptoids containing an azide side chain were synthesized. Helical and non-helical peptoids were dimerized via click chemistry through the azide and alkyne side chains. The peptoid dimers were studied via fluorescence and CD spectroscopy. Fluorescence and CD studies should reveal the associations between helical and non-helical peptoids and provide a picture of tertiary-like peptoid structure. It is important to use methods such as fluorescence and CD spectroscopy in order to understand the affinity of helical and non-helical peptoids.

[1] Fuller, A.A.; Seidl, F.J.; Bruno, P.A.; Plescia, M.A.; Palla, K.S. *Biopolymers* (*Peptide Science)* **2011** , *96*, 627-638

## WRM 326

## Understanding the cytotoxicity of transition-metal permalloy microdisks

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Nanomagnetic materials offer exciting opportunities when attempting remote control of biological processes. For example, ferromagnetic microdisks are able to induce apoptosis via magnetomechanical stimulus. Iron-nickel permalloy disks, which have these capabilities, are fabricated using optical lithography and metal deposition. They are removed from an array using organic solvents and are transferred to aqueous mediums for further applications. The permalloy disks can be made with a layer of gold on the top and bottom sides for the purpose of surface functionalization. The disks can bond with fluorescent dyes and biological compounds. Since the magnetic core of the disks consist of a transition metal alloy, there is a possibility of reactive oxidative species (ROS) forming in aqueous solution. This occurs through a Fenton reaction. The chemical stability of permalloy disks not coated with a gold layer were studied. ROS formation was detected using fluorescent probe hydroxyphenyl fluorescein, X-ray fluorescence microscopy, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). No significant levels of hydroxyl radical were detected at neutral pH. However, X-Ray fluorescence did detect leaching of nickel and iron from the disks through a model cancer tissue.

### WRM 327
### Synthesis of frustrated Lewis pairs based on ferrocenyl phosphines

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Electron deficient boranes behave as Lewis acids, reacting readily with Lewis bases to form Lewis pairs. Lewis acid-base pairs formed between $B(C_6F_5)_3$ and selected triarylphosphines reacts with hydrogen gas to form salts where the H-H bond has been heterolytically cleaved, i. e. into a proton, $H^+$, and a hydride, $H^-$. We have found that reaction between ferrocenyl(phenyl)phosphines ($Fc_xPPh_{3-x}$ x= 0-2) and tris(penta-fluorophenyl)borane, $B(C_6F_5)_3$, leads to Lewis pairs containing an electroactive iron (II) center. The products exhibit considerable intramolecular motion in solution as detected by $^1H$ and $^{31}P$ NMR spectroscopy.

### WRM 328
### New methodology toward the formation of highly substituted tetrahydropyranones

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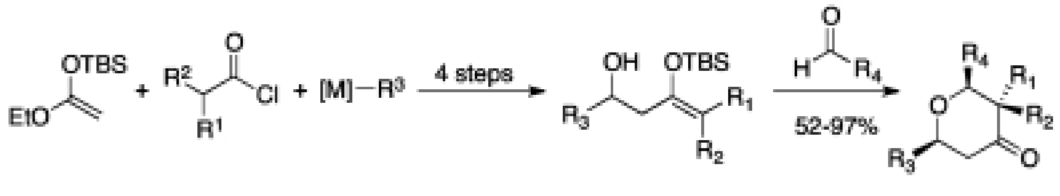
Cyclization between a hydroxy silyl enol ether and an aldehyde provides a new methodology for make highly substituted tetrahydropyranones (THPs) diastereoselectively. This modular synthesis can form up to three stereocenters and one quaternary center on the THPs. Formation of two of the stereocenters occurs during cyclization, which is promoted by TMSOTf or $BF_3$•OEt. The variation of the substituent comes from readily accessible precursors. This reaction tolerates many functional groups and it affords yields ranging from 52% to 97%



### WRM 329
### Enhanced photo-Bergman cyclization of an electron rich mono-substituted arenediyne

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The ability of acyclic arenediynes, such as 1,2-bis(phenylethynyl)benzene, to undergo photo-Bergman cyclization is well documented. These photocyclizations, however, typically require extensive irradiation times and often afford cyclized products in extremely low yield. In an effort to improve the photo-Bergman cyclization yields of simple acyclic arenediynes we have examined the effect of electron rich aryl substituents located on the enediyne alkyne. In particular, we have discovered that incorporation of *para*-methoxyphenyl substituents lead to improved photo-

Bergman yields ranging from 15-20%. In an effort to further improve these yields, we have prepared the corresponding mono-substituted derivative 1-ethynyl-2-(4-methoxyphenylethynyl)benzene. With reduced steric hindrance, this arenediyne undergoes rapid photo-Bergman cyclization with complete conversion of the enediyne within 90 minutes. The reduced irradiation time also leads to improved yields up to 26%. The synthesis of this mono-substituted arenediyne and our optimization studies for the subsequent photo-Bergman cyclization will be presented.

### WRM 330

### Design and synthetic approach towards novel quinoxalenediynes

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The Bergman cyclization of enediynes to produce 1,4-benzenoid diradical intermediates has been attributed to the potent ability of natural products like calicheamicin to cleave DNA. Our group is interested in the design and synthesis of highly conjugated enediynes to examine the effect of extended conjugation on enediyne reactivity. We recently prepared a series of aryl-fused 6,7-diethynylquinoxaline derivatives which were found to undergo thermal Bergman cyclization despite increased cyclization endothermicity predicted computationally. These computational studies also indicated that angular benzannelation as opposed to linear benzannelation may decrease cyclization endothermicity due to formation of a new aromatic sextet. To examine this influence experimentally we are currently exploring methods to prepare 5,6-diethynylquinoxaline and related aryl-fused 5,6-diethynylquinoxaline derivatives with extended conjugation. Based on our computational results, it is anticipated that the angular 5,6 diethynylquinoxaline derivatives will undergo more favorable cyclization energetics which may lead to improved yields for Bergman cyclization. Our synthetic approach towards terminal quinoxalenediynes as well as phenylethynyl quinoxalenediynes for enhanced photoreactivity will be presented.

### WRM 331

### Structural studies of water-soluble peptoids incorporating (*S*)-*N*-1-naphthylethyl side chains

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Peptoids, oligomeric *N*-substituted glycines, are a class of foldamers that possess the potential to adopt well defined secondary structures, making them attractive for use as biomimetics. Peptoids have been shown to be capable of adopting a helical conformation similar to a polyproline type I (PP-I) helix, and studies have shown that stable peptoid helices are promoted by inclusion of at least 50% *N*-α-chiral side chains, an α-chiral substituent at the *C*-terminus, and aromatic residues at *i* and *i*+3 positions. While the structures of peptoid helices with phenylethyl side chains have been well studied, the naphthylethyl side chain is suggested to be more strongly helix promoting. Peptoid helices comprising this residue have recently been studied in the solid state and in organic solvents. In order for peptoids to be incorporated into a biological system, however, it must be water soluble. Thus, our research lab has incorporated the naphthylethyl side chain into water soluble peptoids and is investigating its structure related effects.

We synthesized a length dependent series of peptoids, ranging from 6 to 15 monomeric units. These peptoids were then studied by fluorescence and CD spectroscopy. For both techniques, it was observed that spectral features changed as a function of peptoid length as well as the ionic character of the solvent. Longer peptoids showed an additional fluorescence emission peak near 400 nm, attributable to the formation of an excimer. The excimer emission peak could also be induced by increasing the salt concentration of the solvent. We have attributed the excimer to intermolecular assembly of the peptoid into aggregated states that exhibit a hydrophobic core, as supported by evidence from size exclusion chromatography and binding with 1,8-ANS. We will continue to explore the details of its intermolecular assembly.

### WRM 332

### Montmorillonite for the synthesis of substituted oxindoles

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The oxindole core is a key part of many biologically active compounds and substituted oxindoles are important targets for synthetic chemists. Montmorillonite is an acidic clay that can be used as a heterogeneous promoter, and is easily recycled, cheap, and environmentally friendly. In this project, the synthesis of substituted oxindoles is investigated using montmorillonite for the addition of nucleophiles to isatins. The reactivity of both K-10 montmorillonite and proton-exchanged montmorillonite (H+ mont.) is compared as a catalyst for these reactions. Montmorillonite was found to be an effective promoter for addition of indole to isatin. The ratio of single and double addition products was monitored for different reaction conditions. The addition of allylsilane nucleophiles to isatin was also investigated, where complete conversion to the allyl-oxindole product was observed. For the addition of allylsilanes, the use of H+ montmorillonite as a promoter drove the reaction more quickly than the normal montmorillonite and was also shown to be recyclable.

### WRM 333

### Isolating anti-tuberculosis metabolites produced by a unicellular marine bacterium

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While at first thought, many consider Tuberculosis (TB) a disease that, nowadays, is only a worry to those in third-world countries, new cases of multidrug-resistant tuberculosis (MDR-TB) are becoming prevalent in every country, industrialized or third-world. *Mycobacterium tuberculosis* is the bacterium that causes the common pulmonary tuberculosis but can infect other organs or tissues in the body. With the amount MDR-TB growing, the need for new drugs is constantly growing. This study examines the metabolites of a marine bacterium, strain UA-088, including their production, purification, some structure elucidation, and their inhibition of the growth of *M. marinum*, a close genetic relative of *M. tuberculosis*.

### WRM 334

### Novel oxime ether surfactants: Physicochemical characterization

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Several novel oxime ether surfactants were synthesized; each oxime ether was synthesized from a sugar and an alkoxyamine. The diversity of sugars and alkoxyamines provide a route to a variety of structures and physicochemical behaviors. Water solubility, thermal stability, melting thermodynamics, and surface adsorption of each surfactant were studied. Thermogravimetric analysis (TGA) was used to find the decomposition temperature. Differential scanning calorimetry (DSC) was used to determine the melting point, heat of fusion, and entropy of fusion. Surface tension-concentration adsorption isotherms for each surfactant were taken, and the resulting data were fit to the Szyszkowski equation; the surfactant head group area and free energy of adsorption were extracted from the fit parameters. Finally, the critical micelle concentration was determined for those surfactants that formed micelles. The goal of this project is to correlate these physicochemical properties to simple descriptors of molecular structure.

The synthesis of our oxime ether surfactants will be presented elsewhere.

### WRM 335

### The hydroxyl effect on the fate of fulvene endoperoxide decompositions

***John Basada**, ejbasada@mail.sfsu.edu, Ihsan Erden, Fupei Xu. Chemistry and Biochemistry, San Francisco State University, San Francisco, CA 94132, United States*

The thermal decompositions of unsaturated fulvene endoperoxides ordinarily proceed by way of allene oxide and cyclopropanone intermediates, affording mainly oxepin-2(*3H*)-one derivatives via an intramolecular 6p electrocyclization. We have now uncovered new pathways in fulvene endoperoxide decompositions where the presence of a hydroxyl group on the alkyl or aryl group attached to the exocyclic double bond has a profound effect on the fate of the dioxygen diradical derived from the unstable peroxide. The aromatic and aliphatic representatives of these hydroxyl-directed decompositions will be presented, along with discussions on the postulated mechanisms.

### WRM 336

### Analysis of Conformational Influences Within (2R,3R)-butanediol

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(2,3)-Butanediol is a simple polyol with two different isomers: the meso isomer and the racemic isomer. We examined (2R, 3R)-butanediol in different solvents and investigated its conformational preferences to determine the conformational influences present in (2R,3R)-butanediol. (2R,3R)-butanediol serves as a model molecule to understand the conformational influences in more complex compounds such as proteins. Some conformational influences we investigated are steric bulk, intramolecular hydrogen bonding, Coulombic attraction/repulsion, solvent effects, the polarity of the conformer versus polarity of the solvent, and hyperconjugation. This project primarily aimed to understand possible occurrence and effect of hyperconjugation between vicinal hydroxyl (OH) groups, which are present in (2R, 3R)-butanediol. Hyperconjugation is an interaction between sigma bond electrons and a vicinal, coplanar anti-bonding sigma orbital, which is thought to increases the stability of the system. The methodology employed was $^1$H NMR and $^{13}$C NMR on (2R, 3R)-butanediol in different solvents. Then, we simulated the experimental spectrum on gNMR to extract the coupling constants. We used the Altona equation in order to correlate the coupling constants with dihedral angles, thereby determining the conformation of the compound.

### WRM 337

### Synthesis of novel oxime ether surfactants

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Oxime ether ($R_2C=NOR$) functionality is formed through the condensation of alkoxyamine ($RONH_2$) and carbonyl (i.e., aldehyde/ketone) substrates. It is present in various natural products and pharmaceuticals (e.g., antibiotics). The stability and ease of formation of the oxime ether bond render it useful for various applications.

As part of our collaborative study on surfactant properties that affect the surface tension of water, we utilized the oxime ether bond to vary the surfactant properties in novel surfactants. The key step in our surfactant synthesis is the condensation of an alkoxyamine (carrying a hydrophobic alkyl chain) and a carbonyl substrate (carrying a hydrophilic sugar group). Our synthesis allows for the facile variation of both the hydrophobic and hydrophilic portions of the oxime ether surfactant.

The details of our synthetic approach will be presented. Thermal characterization and surface tension properties of our oxime ether surfactants will be presented elsewhere.

### WRM 338

### Identification and quantification of essential oils contained in hops (*Humulus lupulus*)

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An attempt was made to identify and quantify specific essential oils in Hops (*Humulus lupulus).* These specific essentials oils were alpha-humulene, caryophyllene and farnesene. The standard method for quantifying essential oils in hops is typically steam distillation, however, this study attempted to develop a new method of analysis by use of extraction in hexanes, followed by analysis with GC/MS. Analysis and quantification of specific essential oils was to be completed by comparison with standard curves. Samples of hops donated by ZP growers and analyzed included: Cascade, Magnum, Zeus and Brewer's Gold.

### WRM 339

### Optical properties of chromophoric dissolved organic matter (CDOM) in Southern California salt marsh pore waters

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Optical properties of chromophoric dissolved organic matter (CDOM) were measured in salt marsh as a function of vertical depth and distance from oil drilling activity in coastal Southern California. Absorption coefficients and fluorescence intensities increased with depth, while fluorescence:absorbance ratios (flu/abs) showed varying intensity between distances: higher values in pore waters collected at low depths for regions closest to the rig and surface interfaces for regions furthest from the rig. Flu/abs and spectral slopes showed a significant decrease as emission peak maxima were red-shifted. Terrestrial humic peaks A and C indicated increasing fluorescence intensity with depth for all distances from drilling activity. Lower anoxic regions form greater amounts of humic substance form as a result of the biodegradation of organic matter. The optical properties showed distinct bands for tryptophan-type and tyrosine-type, protein peaks T and B, respectively, at regions near the upper anoxic region. T and B peaks correspond to higher sulfate depletion and reduced Fe(II) species in samples closest to the rig as a result of anaerobic microbial activity. Fluorescence intensities for these samples were depicted using 3D excitation-emission matrix (EEM) fluorescence spectroscopy. CDOM optical properties and distribution suggest greater anaerobic microbial activity in salt marsh regions closest to oil drilling.

## WRM 340

### Mixed metal oxides for the desulfurization of jet fuel

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Removal of sulfur contaminants from fuel is important for creating feedstocks for hydrogen fuel cells. The standard desulfurization method, hydrodesulfurization, is energy consuming and not effective on the bulky sulfur compounds found in fuels such as JP-8. These hurdles have led to the field of adsorptive desulfurization to clean these challenge fuels. Mesoporous materials have shown to be efficient adsorbents for reducing sulfur content in fossil fuels. We have synthesized mesoporous mixed metal oxides under ambient settings using templating agents. The synthesis of these materials has been optimized by varying the precursor concentrations to yield materials with high sulfur adsorption capacities. The sulfur uptake of these materials loaded with silver was explored using model fuel before testing on JP-8 jet fuel. We will discuss how these material design factors affect the sulfur uptake and selectivity of the sorbents.

## WRM 341

### Electrochemical characterization of first-row transition metal corroles for use as oxygen reduction catalysts

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Fuel cell technology has become an important topic of research due to the increasing demand for alternative energy sources. Biomimetic molecules, such as porphyrins, corrins, and corroles, have been shown to be effective agents of oxygen reduction, a key reaction in fuel cells. Our group is studying substituted metallocorroles to characterize and quantify the effectiveness and mechanism of first row transition metallocorrole complexes in oxygen reduction. Rotating ring-disk voltammetry in aqueous media with metallocorroles physisorbed on high surface area carbon, spectroelectrochemistry, and stationary voltammetry in homogeneous, nonaqueous media were all used to determine electrochemical parameters. Of the systems studied, Fe corrole is most effective in 4-electron oxygen reduction. Both Co and Cu corroles were also characterized, with Co reducing $O_2$ through a 2-electron pathway and Cu showing an $E_{1/2}$ value at more cathodic potentials relative to Fe and Co, which show $E_{1/2}$ values at 0.41 V and 0.50 V, respectively (vs. Ag/AgCl).

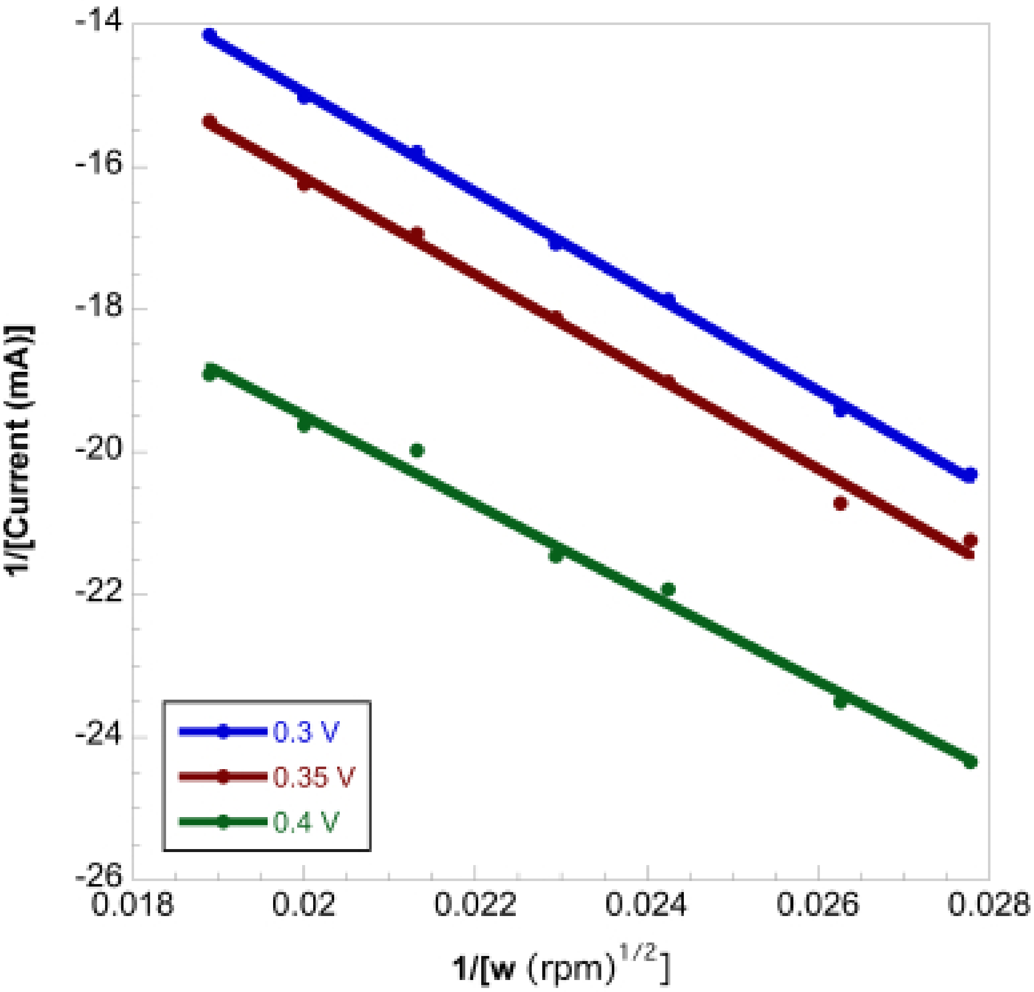

**Figure** : Koutecky-Levich plot of $O_2$ reduction catalyzed by cobalt 5,15-bis(perfluorophenyl)-10-*p*-methoxyphenylcorrole at different potentials (vs. Ag/AgCl)

### WRM 342

### NMR spectroscopic monitoring of transesterification catalyzed by triazabicycloguanidine

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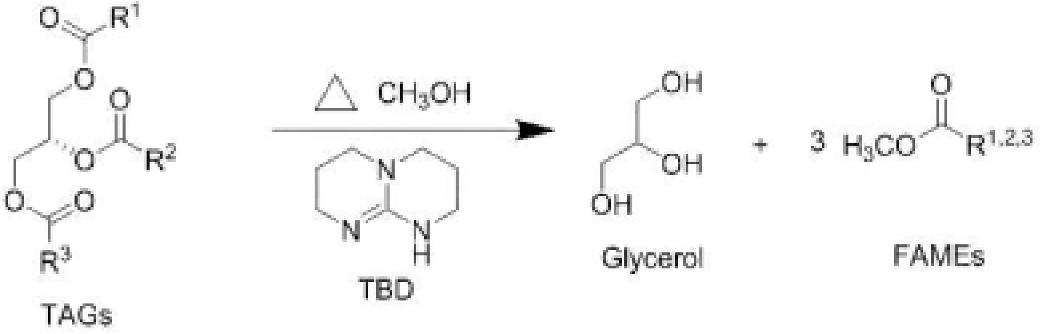

R$^{1,2,3}$ = fatty acid chain

The transesterification of triacylglycerols (TAGs) to fatty acid methyl esters (FAMEs) is a common reaction for the conversion of plant oils to biodiesel. Triazabicyclodecene (TBD) is a bicyclic, bifunctional guanidine base that has previously been demonstrated to be an efficient catalyst due to hydrogen bonding capabilities that facilitate transesterification. In this study, we use NMR spectroscopy to monitor transesterification reactions with TBD as a catalyst. The mechanistic process with TBD is being investigated with the goal of understanding and optimizing the conversion of TAGs to FAMEs, and understanding the potential of TBD as a catalyst for larger scale biodiesel conversion. NMR spectroscopy is utilized because it is efficient for analyzing the molecular interactions and kinetics of the reaction simultaneously. The effect of solvent, temperature, catalyst loading, and presence of intermediates and water were investigated to measure the efficiency and yield of the reaction. Experimental evidence suggests that the catalytic activity of TBD can be inhibited in the presence of water and intermediates, and elevated with higher solubility and catalyst loading.

### WRM 343

### Zinc-salophens as catalysts in electrohydrocyclization: Mechanism and stereoselectivity studies

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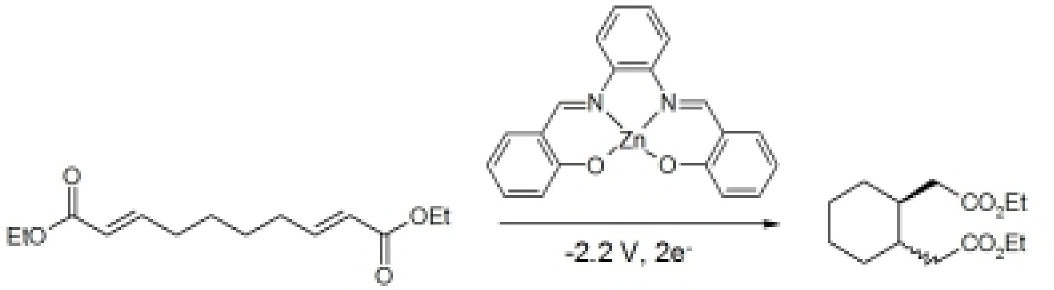
Electrohydrocyclization (EHC) reactions are intramolecular cyclizations between two β-carbons of α,β-unsaturated esters. EHC is very useful in the formation of biochemical molecules as it allows for efficient formation of many biologically active molecules. EHC reactions have also shown to allow for manipulation of the ratio of *cis:trans* product formed, which is very important in many biological molecules.

We are investigating the use of zinc salophen as a catalyst in EHC reactions. We would like to determine if zinc salophen produces a better reaction yield and allows for more steroselectivity than the Ni (II) salens previously studied by Dr. Miranda's research team. We have successfully synthesized and characterized zinc salophen. Its reduction potential has also been determined by cyclic voltammetry (CV). Bulk electrolysis of deca-2,8-dienedioic acid diethyl ester using zinc salophen as the mediator resulted in production of cyclized product at an 80.8% yield as well as an increase in the *trans* isomer produced. The increased stereoselectivity observed, the CV results, as well as computational chemistry suggest that zinc catalysts act as better ligand-centered radicals than nickel catalysts.



80.8 %; cis/trans 1:1.81

Mediated electrohydrocyclization using zinc salophen

### WRM 344

### Green Catalytic Activation of $H_2O_2$ by Organochalcogenide Compounds

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Organoselenide and organotelluride compounds are of great interest in “green” chemistry because of their ability to activate hydrogen peroxide. Hydrogen peroxide by itself is a slow oxidizing agent, but when activated, it is kinetically useful. While the organoselenide and telluride dendrimers prepared by Detty and colleagues have shown significant catalytic activation of $H_2O_2$, their catalysts were not water soluble and were prone to selenoxide syn-elimination. Various diphenyl selenide and diphenyl telluride species are being investigated because they lack β-hydrogens, and hold the potential to be water soluble when structurally modified. Using gas chromatography, the catalytic rate of $H_2O_2$ activation is evaluated with these different species. A blank rate is determined initially in order to standardize the efficiency of each catalyst. Diphenyl selenide does not show an increased rate of catalytic activity while diphenyl telluride shows a modest degree of catalysis. Pre-oxidation of diphenyl selenide results in no increase in the rate of $H_2O_2$ activation over the blank rate while 4,4'-dihydroxy substituted species show more catalytic activation than their non-hydroxylated counterparts.

### WRM 345

### Hypervalence in Monoxides and Dioxides of Superalkali Clusters

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$F_2Li_3$, a superalkali cluster, is characterized as having a lower adiabatic ionization energy than its elemental alkali counterparts and, coupled with the presence of complex molecular orbitals, suggests promise for novel bonding possibilities. CBS-QB3 composite method was used to study three distinct cluster isomers, as well as their cationic (+1) and anionic (-1) species, to identify energetic trends and observe geometric changes. Oxides were then generated from these clusters, of which three distinct monoxides and nine dioxides were obtained upon optimization. Identical calculations were performed for the oxide species and their charged counterparts. Some of the most stable oxides produced appear to possess hypervalent lithium and oxygen atoms forming unique structures with exceptional stability.

### WRM 346

### Imaging photoelectron photoion coincidence (i-PEPICO) investigation of furfural

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The dissociative ionization dynamics of furfural ($C_5H_4O_2$, furan-2-carbaldehyde) is investigated at the X04DB vacuum ultraviolet (VUV) beamline of the Swiss Light Source in Villigen. Threshold photoionization experiments are performed using the imaging photoelectron – photoion (i-

PEPICO) coincidence instrument at photon energies between 9 and 16 eV. Several ionic fragments are observed from the dissociative photoionization process of furfural. Data is reported in the form of time-of-flight distributions and breakdown diagrams. Ion time-of-flight distributions are fitted to obtain experimental appearance energies and dissociation rates.

### WRM 347

### Computational investigation of Stone-Wales isomerization in polycyclic aromatic hydrocarbons

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We report a computational investigation of Stone Wales-type thermal isomerizations in polycyclic aromatic hydrocarbons using coupled cluster and density functional methods. Such reactions are believed to occur in some systems under flash vacuum pyrolysis (FVP) conditions. Two mechanisms were investigated for each system: (i) a mechanism through a carbene-like transition state or intermediate and (ii) a mechanism through a cyclobutyl intermediate with multiple transition states. The mechanism through a perimeter carbene-like transition state or intermediate is preferred for the model reaction pentafulvalene-to-naphthalene (81 kcal/mol) and for the last two proposed steps leading from angular [4]phenylene to coronene, with barriers of 93-98 kcal/mol (M06-2X/6-31G*). However, in planar systems containing a pyracyclene subunit, such as dibenzopyracyclene, only the cyclobutyl mechanism could be located, with a barrier of 96 kcal/mol. For bowl-shaped molecules such as semibuckminsterfullerene, the barrier for both mechanisms is too high (110-150 kcal/mol) to be feasible under typical FVP conditions.

### WRM 348

### Characterization of Isobutanol + OH Reaction at Room Temperature via Multiplexed Photoionization Mass Spectrometry

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The OH-initiated oxidation of isobutanol is presented at room temperature using vacuum UV-radiation from the Advanced Light Source and a multiplexed mass-spectrometer at Lawrence Berkeley National Laboratory. Product species were identified primarily by their photoionization spectra and kinetic traces. All of the proposed mechanisms for these products involve H-abstraction initiated by the OH radical, followed by addition of O2. A reaction pathway is presented and discussed.