

Friday morning – Abstracts 130 - 225

WRM 130

Survey of Analytical Techniques Useful for Thin Film Material Evaluation in High Technology Applications

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The pervasive use of organic and inorganic materials to produce thin films in semiconductor, MEMS, Flat panel, and PV industries have challenged the sensitivity and specificity of modern analytical and physical chemical techniques. The necessity to continuously produce films of a consistent thickness, purity, and morphology requires analytical tools which are capable of measuring the required parameters quickly and accurately. As this symposium will concentrate on the application of a set of analytical methodologies, this talk will provide a guide to the techniques used.

It is important to characterize the composition of organo-metallic precursors via a gas chromatographic technique (GC-MS or TC-TCD/FID). Non-volatile thermally labile materials are typically analyzed using a liquid chromatographic approach (LC-MS). Trace metal (TM) content in precursor materials are accurately determined using a variety of Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) techniques. Once the thin film has been produced, TM measurements are performed utilizing LA-ICP-MS, dynamic SIMS or TOF-SIMS. Morphology is determined utilizing AFM, SEM or TEM techniques.

Other techniques will be discussed as appropriate.

WRM 131

Characterization of Precursors used in Semiconductor Manufacturing using a diverse set of Analytical Techniques

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The demands of cutting edge semiconductor manufacturing process technology require an ever-expanding range of materials to enable continued innovation for both processor performance and efficiency. While these novel materials may provide significant advantages for semiconductor processing, they also represent significant risk since they have not had the luxury of high volume usage or historical knowledge of legacy materials. As such, one of the key aspects of establishing a robust supply chain for these new materials is extensive characterization using a diverse set of analytical techniques. A wide variety of chemicals are used in semiconductor manufacturing, including liquids (wet chemicals, precursors), gases (process and specialty), solids (precursors, salts). Typical analytical techniques deployed for characterization (broad fingerprint) include Gas Chromatography- Mass spectrometry (GC-MS), Liquid Chromatography-Mass Spectrometry (LC-MS), Inductively Coupled Plasma- mass spectrometer (ICPMS), Nuclear Magnetic Resonance (NMR) Spectroscopy, Ultraviolet-Visible (UV-VIS) Spectroscopy, Fourier Transform-Infrared (FTIR)/Near Infrared (NIR), etc. Selection of the suite of analytical techniques for broad fingerprint depends on the nature of the chemistry and the limitations of the technique. GC-MS is used to fingerprint semi volatile/volatile organic components and contaminants. LC-MS is used to conduct qualitative analysis for detection and identification of non volatile contaminants. ICPMS is widely used to quantify (targeted metals) the trace contaminants in the chemicals. It can also be used in semi-quantitative mode to complete a screening for a broad range of metals. NMR is very useful in providing an assay for chemical and to fingerprint the contaminant profile. This presentation will focus on precursor characterization using various analytical techniques. Limitations and advantages of the application of analytical techniques to characterize precursors such as GC-MS, LC-MS, ICPMS, FT-NIR, and NMR will be discussed with relevant examples.

WRM 132

Analytical Characterization of Thin Films for ALD

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In the semiconductor industry, the demand of Moore's Law necessitates the use of high k precursors (e.g. Hf, Zr, Co) or low k (e.g. silanes) material thin films in place of the traditional Si or SiO₂. These films are deposited on wafers by atomic layer deposition (ALD) or chemical vapor deposition (CVD).

It is necessary to adequately characterize the analytical purity of the thin film precursors with the appropriate techniques in order to avoid device failure and meet the reporting limits listed on the certificates of analysis. Some of the analytical challenges associated with sample preparation and analysis of the precursors will be discussed. Most importantly, the analytical method must preserve the integrity and quantity of analytes present in the original samples. This presentation will describe sample preparation techniques (e.g. dilution and evaporation), trace element analytical methods (DRC-ICPMS vs. sector field ICPMS) and environmental regulations (RoHS and REACH).

WRM 133

Photovoltaic Materials Defect Characterization Techniques

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Novel PV materials require the development of advanced physical characterization techniques. A direct band gap material phenomenon optimizes using High Resolution Photoluminescence (HRPL) and Electron Beam Induced Current (EBIC) to precisely locate crystalline defects. Semiconductor Physical analysis techniques such as Focused Ion Beam (FIB) to specifically cross section the defect and Transmission Electron Microscopy (TEM) are then employed.

WRM 134

Trace Degradation Analysis in Li-ion Battery Electrolytes

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A decrease in lithium ion battery performance and cycle life results from the interaction between the electrolyte, anode, and cathode. Degradation products can include organic acids, polyphosphates, and other inorganic species. The presentation will discuss how IC, ICP, GC, and MS has aided in optimizing trace organic and inorganic analysis in lithium ion battery electrolytes.

WRM 135

Gas permeability and Klinkenberg effects in carbon micro and mesopores

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Molecular dynamics simulations were carried out to study gas permeability and the Klinkenberg effects of helium, methane, and carbon dioxide, in addition to their mixtures confined in carbon micro and mesopores. The structure was modeled using a slit pore as well as a three-dimensional pore network, generated atomistically using the Voronoi tessellation method, to represent the carbon-based porous structure of natural systems. Non-equilibrium molecular dynamics (NEMD) simulations were used with an external driving force imposed on the system. Simulations were conducted to determine the effect of pore size and exposure to an external potential on the velocity profile and slip-stick boundary conditions.

The results indicate that in micro and mesopores the particle-wall collisions may influence the velocity profile, which deviates significantly from the Navier-Stokes hydrodynamic prediction. In micro- and mesopores unlike in macropores (where continuum flow occurs), the gas velocity at the walls is non-zero. It is shown that the velocity profile is uniform for pore sizes less than 2 nm (micropores). As pore sizes increase to 10 nm parabolic velocity profiles are observed due to reduced interaction of gas molecules with carbon atoms of the pore walls. Also, the shape of the velocity profile is found to be independent of the applied pressure gradient in micropores. Simulation results are compared with experiments to understand both the merit and limitations of the simulation approach.

These fundamental studies have potentially important implications on gas transport in carbon-based porous materials and geologic formations which lead to an understanding of the

mechanism associated with gas transport in the confined spaces for carbon capture and sequestration applications.

WRM 136

International chemical identifier for reactions (RInChI)

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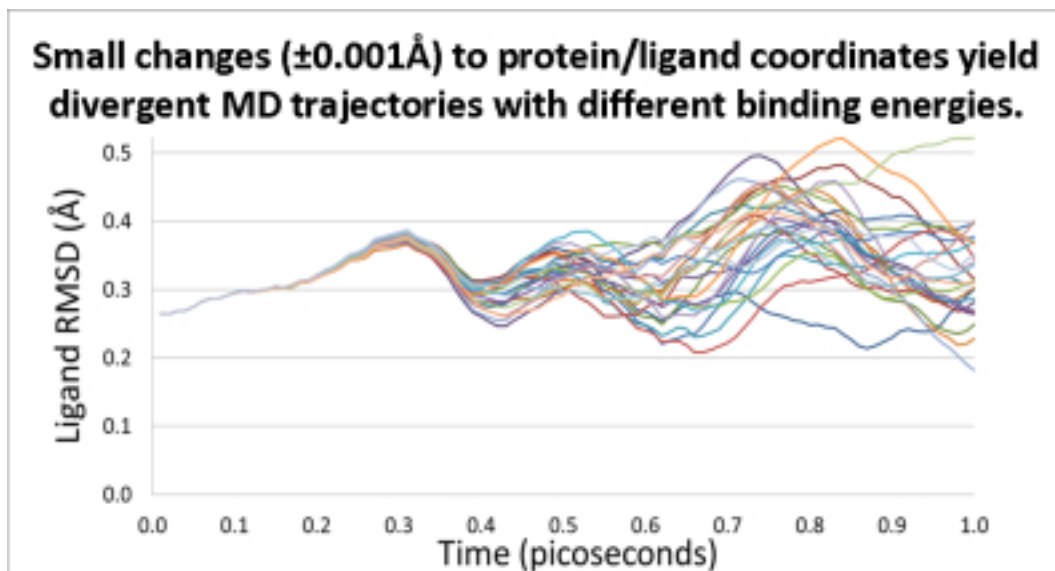
An open-access software for creating a unique, text-based identifier for reactions (RInChI) was developed at the University of Cambridge based on the IUPAC International Chemical Identifier (InChI) standard. RInChIs describe the substances (reactants, products, reagents and solvents) participating in a reaction with their respective InChIs. The structure of RInChIs is analogous to that of InChIs. In addition to generate RInChIs from widely used Rxnfiles and RDfiles, the software also includes the generation of long- and short-form, hashed representations: RInChIKeys. Furthermore, the software allows to reversibly convert between CT-files and RInChIs, to search for specific substances and their specific roles in reactions and to analyze databases. All these functions are available through web-based tools. An easy-to-use website has been developed at the University of Cambridge and is freely accessible at <http://www-rinchi.ch.cam.ac.uk/>. We will discuss details of the program and the status of the RInChI project.

WRM 137

Improved Ligand Binding Energies Derived from Molecular Dynamics: Replicate Sampling Enhances the Search of Conformational Space

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Does a single molecular trajectory provide an adequate sample conformational space? Our calculations indicate that for Molecular Mechanics - Poisson-Boltzmann Surface Area (MM-PBSA) measurement of protein ligand binding, a single molecular dynamics trajectory does not provide a representative sampling of phase space. For a single trajectory, the binding energy obtained by averaging over a number of molecular dynamics frames in an equilibrated system will converge after an adequate simulation time. A separate trajectory with nearly identical starting coordinates (1% randomly perturbed by 0.001 Å), however, can lead to a significantly different calculated binding energy. Thus, even though the calculated energy converges for a single molecular dynamics run, the variation across separate runs implies that a single run inadequately samples the system. The divergence in the trajectories is reflected in the individual energy components, such as the van der Waals and the electrostatics terms. These results indicate that the trajectories sample different conformations that are not in rapid exchange. Extending the length of the dynamics simulation does not resolve the energy differences observed between different trajectories. By averaging over multiple simulations, each with a nearly equivalent starting structure, we find the standard deviation in the calculated binding energy to be ~1.3 kcal/mol. The work presented here indicates that combining MM-PBSA with multiple samples of the initial starting coordinates will produce more precise and accurate estimates of protein/ligand affinity.



WRM 138

Interactive shape and pharmacophore similarity search enabled by GPUs

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Upon the completion of a high throughput or fragment screening campaign, project teams prioritize the hits for follow-up. One hit follow up strategy is to purchase close analogs to explore structure-activity relationships (SAR) of top-tier hits. Providing SAR information in a timely manner on hits allows project teams to narrow the list of compounds for medicinal chemistry expansion. This SAR by catalog method can be performed prior to obtaining crystallographic confirmation of binding poses.

Traditional methods like fingerprint similarity are frequently used to find analogs of HTS hits. However, searching a large database is slow and is not as successful with fragments due to their smaller size. Rapid Overlay of Chemical Structures (ROCS) is a ligand-based shape and pharmacophore feature similarity search tool. It takes advantage of the fact that molecular recognition is based on shape and feature complementarity to the receptor pocket. FastROCS is ROCS implemented to run on graphical processing units (GPU), which increases performance by two orders of magnitude. Searching a database of ~100 million small molecule 3D conformers becomes an interactive task on a GPU server. That interactive speed opens up possibilities for medicinal chemists to perform iterative fragment follow-up searches and evaluate results in real time.

We integrated FastROCS with desktop modeling software and made it a user-friendly tool for interactive 3D shape similarity search. Databases containing 4.2 million commercially available compounds and 1.1 million in-house compounds are searchable using FastROCS. We have successfully used FastROCS searches to find close analogs of fragment hits that provided SAR information for project teams. Medicinal chemists have used it as a scaffold-hopping tool to solve solubility problems. This work led to a tool compound for kinase project.

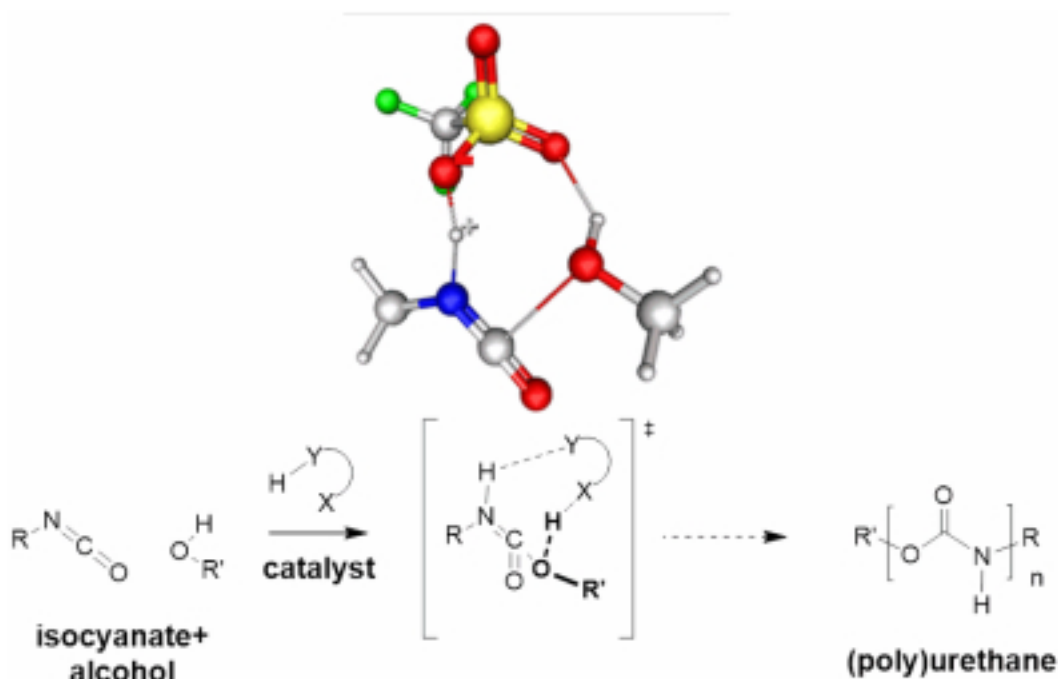
WRM 139

Organic Acid-Catalyzed Polyurethane Formation via a Dual-Activated Mechanism: Unexpected Preference of N-activation over O-activation of Isocyanate

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Using computational chemistry methods we propose mechanisms for the acid-catalyzed formation of poly-urethanes from isocyanates and alcohols. Trends in computed barrier heights for the N-activated carbamate formation agree with experimentally observed reactivities indicating that an acid catalyst's primary mode of action is the electrophilic activation of the isocyanate's carbonyl C through hydrogen-bonding to the isocyanate's N; this increases with the acid's acidity an acid catalyst's secondary mode of action is the nucleophilic activation of the alcohol through hydrogen-bonding; this increases with the nucleophilicity of the acid's conjugate base



WRM 140

Computer-aided design of permeable cyclic peptides

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Engineering passive membrane permeability is a critical challenge in developing macrocycle therapeutics. Many natural product macrocyclic drugs, such as cyclosporine, are passively membrane permeable and orally bioavailable, indicating that such drug-like properties are achievable beyond rule-of-five chemical space. We developed a computational approach to model permeability of macrocycles by utilizing a general physics-based membrane permeability model coupled with extensive conformational analysis in a membrane-like environment. Our permeability model is based on the biophysics of passive diffusion across membrane and is *not* trained on any particular types of permeability data or chemical class. The implementation is molecular mechanics-based, so the modeling only requires force field parameters and an implicit solvent model as inputs. By applying our method to screen virtual libraries of cyclic peptides designed with systematic variations of backbone stereochemical configuration pattern, backbone N-methylation pattern, and side chain substituents, we have designed permeable synthetic cyclic hexapeptides with MW ~ 750 that achieved permeability in *in vitro* cell-based assay and oral bioavailability in rat. Key parameters that contribute to passive permeation across membrane,

including conformational preference in membrane and intramolecular hydrogen bonding, were also examined.

WRM 141

Undergraduate research with community college students and how it supports student transfer

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For six years, the STEM-ENGINES Undergraduate Research Collaborative studied models that engage community college students in authentic undergraduate research that spans both a two-year and a four-year college. Our assessments have shown definitive gains in students' research skills, academic achievement, and attitudes towards further study in chemistry. In this paper, we will present case studies that illustrate how an undergraduate research supports student transfer beyond the community college and how it helps ease the shock of interinstitutional transfer. We will discuss how an authentic undergraduate research experience can not only promote the success of individual students, but also how it can contribute to broadening participation of underrepresented groups in the broader chemical enterprise. A new resource from the ChemEd Bridges group for understanding the complexities of student transfer, "Maximizing Our Impact in the World of Student Transfer: A Handbook for Chemistry Faculty" will also be presented and discussed.

WRM 142

ChemEd Bridges: Bridging community college chemistry faculty into the national educational community

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The ChemEd Bridges (CEB) project received four years of support from the National Science Foundation to improve the quality of community college (CC) chemistry education through a nationwide process of faculty development. A three-pronged approach was taken. We organized symposia and participatory workshops featuring topics of particular interest to CC faculty at National and Regional Meetings of the ACS, the Biennial Conferences on Chemical Education, and Two-Year College Chemistry Consortium Conferences. These served as focal points where tested innovations in chemical education were disseminated, and provided a space where two-year and four-year chemistry educators could develop new collaborative relationships. Through targeted mentoring of workshop participants, we helped CC faculty members institutionalize teaching reform at their colleges and assume leadership positions in national organizations. In the final year of the project, we organized a weekend workshop to discuss major problems that arise when chemistry students transfer from two-year to four-year colleges. Drawing on the workshop, CEB developed a practical handbook for assisting student transfer. This talk will focus on case studies of faculty development and discuss the Student Transfer Handbook, which is being disseminated by the American Chemical Society. At the end of the session, an interactive discussion of how to maintain this project will be held.

WRM 143

Strategies for successfully transitioning underrepresented minority students from two-year to four-year colleges

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Creating a smooth transition from a two-year to four-year college environment for any STEM undergraduate can be challenging, but for an underrepresented minority student who could be a first-generation college student, it can be an almost overwhelming experience. This paper will

focus on strategies that faculty and staff can use to help underrepresented students who are two-year college transfers prepare, successfully transfer and graduate from a four-year college. The discussion will include providing a supportive classroom environment, up-to-date academic advising and peer support services as well as student leadership opportunities. An electronic dashboard for monitoring underrepresented minority student progress to a four-year degree will be showcased as a tool to monitor milestones to a four-year degree.

WRM 144

Accessibility versus success: Challenges and benefits of teaching an evening hybrid general, organic, biochemistry course at a community college

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Cañada College is a diverse community college located in the San Francisco Peninsula. It enrolls over 10,000 students annually. Approximately 70% of students enroll in 6 units or less and 20% of students enroll in 6-11.5 units. In response to the need of our working students for evening classes that meet less frequently, the Chemistry Department began to offer an evening hybrid general, organic and biochemistry course in addition to its regular day time course offering. The evening class meets once a week reducing the number of face-to-face student-instructor interaction by half. Students are provided with an array of web-assisted resources and expected to work on lecture material independently with minimal instructor's guidance. The laboratory curriculum was adjusted to incorporate some experiments students can perform at home using household materials. Class meetings are planned to allow for relevant group discussions; to work on practice problems; and to introduce basic laboratory skills. Although we were able to address accessibility by offering a more convenient schedule, the nature of the schedule is such that only highly motivated and well organized students are able to keep pace with the expectations of the course. In this presentation we will discuss possible reasons leading to low retention and success rates in the evening hybrid course as well as offer suggestions for improvement.

WRM 145

Affirming the two-year college as a legitimate pathway to the baccalaureate and beyond and to careers in the chemical sciences, engineering and education

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The existence of research in two-year colleges is examined. How did we get to today and who helped us get there? Recent developments and headlines that thrust two-year colleges into the spotlight as legitimate pathways to STEM baccalaureate degrees and beyond leading to careers as professional technicians, scientists, engineers and educators are discussed with an historical perspective. Where do we go from here and what do two-year colleges need to get there, are suggested. Innovative enrichment of the chemical sciences curricula via undergraduate research, internships, poster presentations at professional meetings and standardized ACS examinations in General and Organic Chemistry are recommended in order to increase student retention and insure success in undergraduate transitions. Student recruitment both external and in-house must be monitored to keep it at a level that insures sustainability of the chemistry programs. A bibliography of relevant, recent journal, C&En and newsletter articles is included.

WRM 146

Aligning capital, scientific, and drug development interests: Lessons learned from Edison Pharmaceuticals

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The cost of developing drugs has been rising for over a decade, shaped by two dominant forces: cost and risk, both of which are very high. Bringing a new drug to market can cost >\$1 billion dollars, while a fraction of drugs in development achieve regulatory approval.

The challenge is even greater in rare pediatric neurological disease drug development. Despite the protective provisions of orphan drug laws, market sizes are extremely small and returns on investment can be difficult; many rare diseases are heterogeneous with little data on their natural histories; there is minimal regulatory experience with surrogate or clinical endpoints; and with lethal diseases in pediatric populations, the safety and ethics reviews are necessarily complex. Edison Pharmaceuticals has taken an innovative business, scientific and clinical development approach to solving these challenges. The company was founded in 2006 by a group of physicians, researchers, parents and foundations committed to finding treatments for rare pediatric CNS diseases. Initial capital came from the National Institutes of Health, three foundations, and angel investors that accepted the high development risk and longer time horizon for return on investment. Edison has engaged select partnerships, carefully managed its R&D portfolio and conservatively managed its capital. This has allowed the company to maintain its core mission of finding a first-in-class drug for lethal childhood diseases. Today, Edison has multiple therapeutics in advanced development stages and has steadily grown enterprise value.

WRM 147

How to Protect Your New Chemical Business

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Many entrepreneurs start a new business, get a loan or capital to fund that business and get to work. However, in the process, these businesses usually forget to protect the business by putting employment agreements, intellectual property agreements and independent contractor agreements into place. In addition, these new businesses think that they can wait to protect their intellectual property. This presentation will talk about corporate, employment and IP strategies for new chemical businesses. Resources will be provided at the presentation.

WRM 148

ACS Entrepreneur Founders: Choice of Entity, Funding and Founding Your Own Enterprise

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This presentation will focus on key issues to consider when founding a company. Areas of focus are choosing an entity (C corporation, LLC or partnership), thinking about founders' equity allocations and taking the right steps to building an attractive, "fundable" company.

WRM 149

Entrepreneurial programs and services from ACS

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The ACS Entrepreneurial Initiative is a members-only program with a broad reach into the entrepreneurial support community. ACS members and chemical entrepreneurs alike have benefitted from ACS's pilot experiment during the last 16 months. From the pilot, ACS members obtained materials and instruction about entrepreneurship from the Entrepreneurial Training Program and access to information, professional services, mentors, and sources of funding or partnering for their start-ups from the Entrepreneurial Resources Center. Program participants have stated that the pilot offerings made a big difference, and their collective voices have told us that ACS can and must do more. Program participants have in turn stimulated the broader entrepreneurial community, and the assets produced through the program are being more widely distributed to colleges and universities through partnerships with campus innovation and entrepreneurial centers.

Results from the ACS Entrepreneurial Initiative pilot will be presented along with an overview of programs currently available through ACS for its member entrepreneurs.

WRM 150

Finding and executing a business model for science based companies

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Startups are a crucial vehicle to enable translational research by facilitating the transition from groundbreaking science into marketable product. At QB3, we believe in empowering scientist entrepreneurs for this endeavor. In 23 months, our programs have created 150 well-structured companies and positioned them to attract funding. This talk will cover methodologies for building and executing a business model, including defining a value proposition, and decreasing market risk through customer development. We will also share some important lessons learned for early stage science-based companies.

WRM 151

Air dispersion modeling of volatile organic emissions from multiple natural gas wells in Decatur, Texas

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Air emissions of volatile organic compounds from operations at thirty-five natural gas processing facilities near Decatur, Texas were simulated using the air dispersion model AERMOD. A total of fifty-six wells were connected to the thirty-five condensate storage tank batteries that served as the primary emission sources in the model, and fugitive sources at each site were included as secondary.



The figure provided displays the proximity of the modeled natural gas sites with respect to the residential property receptor. Examination of industry investigations revealed that condensate storage tanks constituted the most significant contributors to localized air pollution in a region subjected to aggressive natural gas development. Respiratory and neurological human health hazards were evaluated based on the cumulative concentrations of volatile organic compounds reconstructed by the model from normal operating conditions at the sites. Results of air

dispersion modeling demonstrated that the human health hazards were of greatest concern in a topographically depressed location surrounded by the natural gas processing and byproduct storage facilities.

WRM 152

Isotopic forensic techniques for methane source discrimination

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Combustible gases, such as methane, in soil and shallow groundwater present a safety concern due to potential offgassing and accumulation in water well and plumbing systems that could lead to an explosion. Elevated concentrations of methane in enclosed spaces also pose an asphyxiation hazard. Methane observed in shallow subsurface environments can be derived from many potential sources including swamps, landfills, coal beds, and natural gas production and storage operations. Understanding methane provenance may be important for sites where methane hazards are present and multiple unrelated methane sources exist. Generation of methane and other light hydrocarbon gas occurs via three principal mechanisms; 1) biogenesis – microbial decomposition of organic matter (e.g., carbon dioxide reduction and acetate fermentation); 2) thermogenesis – thermal decomposition of deeply buried organic matter (associated with coal, oil, and gas formation); and 3) abiogenesis – formation of methane within Earth's mantle. These different methane generation mechanisms result in differing compositions of light hydrocarbon gases as well as in differing stable carbon and hydrogen isotope ratios which can be used to assess methane provenance. Carbon-14 (¹⁴C) age dating can further discriminate methane sources, as thermogenic gases are “fossil” carbon sources and do not contain measureable quantities of ¹⁴C, whereas biogenic gases are typically “modern” and contain measurable quantities of ¹⁴C. Methane forensic techniques were utilized to distinguish a single source of natural gas released from a Gulf Coast region salt dome cavern storage facility from other sources of methane known to occur naturally in the region. The natural gas release was caused by a breach of a storage well casing at an elevation above the storage cavern. Natural gas escaped through the well casing breach into overlying formations and migrated to the surface. Application of methane forensic techniques resulted in delineation of a significantly smaller affected footprint than originally interpreted.

WRM 153

Hydraulic fracturing and the impacts to groundwater and water quality: the importance of a monitoring program

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Hydraulic fracturing has been used to stimulate production of oil and gas since the late 1940's throughout the U.S., including California. In the late 1980's to early 1990's advances in horizontal drilling processes and fracturing techniques resulted in a significant increase in this enhanced production technique. Fracking techniques typically involve the injection of large quantities of water and proppant. The fracturing fluid chemistry is often complex, consisting of hundreds of chemicals designed to serve a variety of purposes, including corrosion and scale inhibitors, biocides, thickening agents, friction reducers, pH adjustment, and borehole and well cleaning. These chemicals can include diesel fuel, BTEX, 1,4 dioxane, ethylene glycol, and naphthalene. Groundwater can potentially be impacted from a number of different processes including faulty well construction, improperly abandoned wells, fault zones, releases from surface impoundments, leaks and spills, stormwater runoff, chemical storage, and underground injection of flowback water. Because of the large variety of chemicals potentially contained in the fracking fluid and flowback water, a comprehensive groundwater and surface watersampling and monitoring program should be designed and implemented. Included with this program should be a comprehensive baseline analysis of existing conditions to document any deleterious conditions that may exist prior to development.

WRM 154

**Protection of groundwater resources in the vicinity of hydraulic fracturing operations:
Lessons from New York State and the Marcellus Shale**

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While public concern over groundwater protection from hydraulic fracturing operations is beginning to grow in California, it has been at fever pitch for several years in New York State. The 2009 draft Generic Environmental Impact Statement hydraulic fracturing received 13,000 public comments and the Revised Draft received even more in 2013. On March 6, 2013, the New York State Assembly passed a bill to further suspend issuance of permits for high volume hydraulic fracturing until May 15, 2015. The focus of attention is the Marcellus and Utica Shales which, like the Monterey Formation, can produce tremendous volumes of natural gas with the aid of horizontal drilling and hydraulic fracturing. The major issues regarding groundwater protection will be reviewed in this presentation. A principle concern is whether pre-existing fractures and faults can transmit gas and fluids up to the groundwater. Some pre-existing fractures and faults are known to transmit gas in the near-surface under natural conditions. Inferences from microseismicity and other studies suggest that some deep faults at the horizontal drilling levels also have transmitted fluid at those levels. Avoiding such features is considered critical to prevent potential impacts to aquifers. Mapping and understanding the hydraulics of faults and fractures is not straightforward, however. For example, whether deep faults/fracture systems are 'open', and whether these systems are connected to shallow fault/fracture systems are not trivial determinations. Recent advances and potential research directions in fault studies will be discussed.

WRM 155

Analysis, treatment and tracing of frac and produced water

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While the environmental lobby is concerned with the chemicals that are injected into a well during hydrofracing, they have completely ignored the real potential environmental hazard; that of the production and flow back water. Frac fluid consists of a limited list of components, but the 'flow back' and 'produced water' contains hundreds of different chemicals. The majority of which are hydrocarbons along with a range of salts derived from minerals. Many of these organic compounds are classified as hazardous, but they are actually naturally occurring, being derived from high-pressure decomposition of plankton that lived in the Jurassic period. Analysis of various produced water has been accomplished by ICP-AES and GC-MS and the results will be discussed. With knowledge of the composition of produced waters, we have developed a simple approach to water recovery and recycling that has been scaled to field trials. Finally, how can industry and the public be sure that it is not a frac that is responsible for damage to the environment? The creation of highly mobile tracers that can be uniquely identified as compared to naturally occurring materials offers the possibility that a 'fingerprint' of a particular well can be created. Initial results in this area will be presented.

WRM 156

Analysis by ion chromatography of fracking flowback water from the Marcellus Shale using in-line conductivity and automated dilution

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The recent increase in U.S. natural gas production has been propelled by the extensive use of hydraulic fracturing (also known as fracking). This process extracts natural gas by drilling into bedrock (primarily shale) and then injecting fluid under high pressure causing cracks in bedrock, thereby releasing trapped gas, which can then be captured. While fracking provides financial benefits to both local and national economies, it has not been without controversy. Inadvertent spills or the dumping of fracking flowback (fracking solution that returns to the surface) into unlined collection ponds can contaminate ground water. One of the challenges with analyzing

flowback water is the high levels of dissolved solids as salts that are leached from bedrock. Injection of undiluted high ionic strength solutions can exceed the capacity of columns used in ion chromatography (IC), resulting in poor chromatography, peak suppression, and inaccurate reporting. Additionally, high concentrations may exceed the linear range for a particular analyte. To prevent column overloading by samples such as fracking flowback water, dilutions are performed. To minimize errors and reduce labor costs associated with manual dilutions, this process has been automated using in-line conductivity measurement, which then triggers dilution by an autosampler. This presentation describes the analysis of inorganic anions and organic acids in fracking flowback water using IC following in-line determination of sample conductivity and automated dilution.

WRM 157

Optimized Geochemical Modeling of Produced Fluids Provides Important Insight into NORM-Related Issues

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Although the formation of Naturally Occurring Radioactive Material (NORM) associated with oil and gas-related produced fluids is a widespread phenomenon the unanticipated discovery of NORM within tubulars (pipes, pumps, and tanks) and within former brine handling facilities, such as slush pits can, nonetheless, be a disconcerting and problematic event. To aid clients in predicting both NORM formation and likely locations of its formation within the plant and supporting facilities ARCADIS has developed an optimized geochemical modeling approach to assess the potential for NORM generation from produced fluids. Critically, a client may not have a comprehensive NORM-related geochemical data library immediately available consequently the modeling approach allows geological and geochemical insight into the fundamentals of produced fluid chemistry and NORM formation facilitating the modeling effort. Using the established knowledge associated with NORM constituent formation and combined with actual or estimated produced fluid geochemistry in terms of salinity, temperature, and individual constituent composition an initial geochemical solution can be developed for simulation of the subsequent geochemical changes induced by extraction and fluid handling processes. Specifically, the affects of cooling of the solution during extraction are modeled to assess the potential for barite (barium sulfate [BaSO₄]) precipitate formation and the co-precipitation of radium using a specially developed thermodynamic database. Combined with the use of Pitzer activity coefficient-based modeling estimates as to the potential mass and radioactivity of the NORM can be made as well as associated non-NORM-bearing scale potential. The above individual components of this geochemical modeling process and the value of the insight offered will be detailed within this paper.

WRM 158

Hydraulic Fracturing, Wastewater Injection and Unintended Earthquakes

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It has long been known that increasing the pore pressure within a pre-stressed fault can induce an earthquake by reducing the effective normal stress and thereby the frictional strength of the fault. Underground fluid pressures are routinely modified by a wide range of industrial activities including impoundment of reservoirs, mining, and petroleum production, all of which are known to have potential for inducing earthquakes. Recently, attention has been drawn to the earthquake hazard associated with the production of oil and gas from previously unproductive formations. Earthquakes can be induced as part of the process to stimulate the production from tight shale formations, or by disposal of wastewater associated with stimulation and production. By design, hydraulic fracturing induces numerous high-frequency microseismic events as part of the process of creating a connected fracture network to enhance formation permeability. Magnitudes are normally below zero for events in the target formation. Larger, unintended events sometimes occur and available evidence points to shear failure of pre-existing faults as their source. None have thus far have been large enough to cause structural damage. In contrast with hydraulic fracturing treatments, wastewater wells have induced earthquakes with magnitudes as large as

5.7 and have caused structural damage. However, it should be noted that only a small percentage of the more than 30,000 UIC Class II wells in the U.S. that are licensed for wastewater disposal are known to have induced earthquakes. Ultimately, better knowledge of the stress and pressure conditions at depth, the hydrogeologic framework, including the presence and geometry of faults will be needed to develop a predictive understanding of the hazard posed by induced earthquakes.

WRM 159

Many flavors of food chemistry

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Food chemistry covers a very broad range of topics within the chemical enterprise. Research can involve work on specific components in foods such as proteins, fat or carbohydrates or it can look into other properties of foods and how they change during processing. This presentation will review the broad area of food chemistry with examples of the widely diverse applications of chemistry to foods.

WRM 160

Culinary science: Deliciousness facilitated by scientific insight

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Chemistry, physics, and biology have governed everything that happens in the kitchen since before the kitchen was even invented. Only now are chefs and scientists coming together to gain greater understanding of food as a medium in order to better understand traditional cooking techniques and create novel combinations of aromas, textures, and tastes. This talk will explore the many ways that knowledge of chemistry in the kitchen is changing the culinary industry.

WRM 161

Wine flavor chemistry: From the vineyard to the bottle

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Wine flavor is comprised a mixture of hundreds of compounds interacting together to influence our perception of taste, aroma, color and mouthfeel. The flavor components arise in the grape as result of biochemical processes, during fermentation by yeast, and during storage as a result of chemical reactions. Many of the compounds that contribute to aroma are present at trace levels and so very sensitive analytical tools are needed to measure these compounds and relate their concentrations to sensory properties. This paper will review the chemistry of grape and wine flavor and discuss new analytical tools that allow for an improved understanding of the compounds that contribute to grape and wine aroma and flavor.

WRM 162

Eucalyptol and the "Eucalyptus" aroma in red wines

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Red wines from California sometimes display an aroma reminiscent of eucalyptus leaves. This aroma seems related to the presence of eucalyptus trees growing near vineyards. How volatile compounds from these trees could influence wine aroma, however, remained a mystery until ten years ago.

In 2003, ETS Laboratories conducted research with the main goal of finding an analytical marker for the "eucalyptus" sensory character in wine, and develop an automated analytical method to measure it routinely in wines. We analyzed the headspace of leaves taken from eucalyptus trees by SPME/GC/MS in Scan mode. As expected from literature, eucalyptol (1,8-cineole) was by far the main volatile compound found.

Next, we developed an automated Headspace SPME/GC/MS method in SIM mode. This method allowed detection at 0.3 ppb in a wine-like matrix, was linear up to 100 ppb, and showed excellent

precision in the low ppb range. Then, we analyzed wines displaying various levels of “eucalyptus” odor. Eucalyptol was found in all the wines where the odor was present. Amounts quantified, as high as 20 ppb, appeared strongly related to the intensity of the “eucalyptus” character perceived during tasting.

In order to investigate the actual sensory impact of eucalyptol in wine, we determined its odor thresholds in a California Merlot. The difference and recognition thresholds found were 1.1 ppb and 3.2 ppb, respectively. The comparison with eucalyptol concentrations in wines clearly demonstrated that eucalyptol is an “impact aroma compound” in wine.

Eucalyptol had never been reported in wine before, suggesting it is not a normally occurring grape compound. We demonstrated with a simple lab experiment that airborne transfer from eucalyptus leaves to grape berries could occur. Presence in wines may result from dissolution of eucalyptol molecules adsorbed on skins into red wine, during the winemaking process.

WRM 163

Determinations of inorganic anions and organic acids in beverages using suppressed conductivity and charge detection

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Organic acid profiles in fruit juices are important in the beverage industry to characterize flavor, maintain product quality, and to meet labeling requirements. To analyze organic acids and anions of strong acids, such as chloride and sulfate, which are also present in beverages, ion chromatography with suppressed conductivity is the ideal analytical method. Unlike the anions of strong acids which are fully ionized, organic acids are weakly ionized and can exhibit lower conductivity responses versus concentration than the strongly ionized anions. The new QD Charge Detector promotes complete disassociation of many weakly disassociated compounds by drawing a current at a fixed potential. As a result, the charge responses of singly-charged organic acids and doubly-charged and triply-charged organic acids are proportionally higher than conductivity.

Here we demonstrate separations of organic acids on a 4 μm particle size, capillary anion-exchange column. Four μm particle columns produce high efficiency separations but also have higher system backpressure, and therefore can only be used on a high-pressure capillary IC system. Capillary IC at $\mu\text{L}/\text{min}$ flow rates is always on and ready for analysis and requires only 5.2 L/yr of deionized water. The results show comparably higher QD response for organic acids compared to chloride and sulfate. Additionally, use of CD/QD ratios to assess peak purity is demonstrated, thereby improving reporting accuracy.

WRM 164

Meaningful Food Chemistry Innovation through Partnering

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This presentation will describe three processing technologies and associated products that were developed and applied to process fruits and vegetables in novel ways using food chemistry and engineering. The technologies are forming, casting, and ultraviolet light treatment and the associated products are fruit bars, fruit and vegetable wraps and films, and vitamin D enhanced mushrooms. Through partnering these technologies were transferred into commercialization where they now provide meaningful products which improve consumer health while providing new job opportunities for Americans and adding value to American grown specialty crops. This presentation will describe some of the challenges faced in moving these technologies and products from the laboratory into the marketplace. In addition it will highlight the opportunity food chemistry provides to add value and meaning to foods through effective partnering.

WRM 165 - withdrawn

WRM 166

Decacyclene-Based Materials: A New Frontier of Renewable Energy and Optoelectronic Research

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Renewable energy is becoming attractive because it is absolutely vital to establish a good candidate to replace fossil fuels considering the ongoing global energy challenge. In this context, the discovery of a new family of (organic) materials with interesting opto-electronic properties, namely organic semiconductors, is always a cause for celebration. We focused our attention on the chemistry of a new class of materials for organic electronics based on decacyclene.

We explored its inherent potential to support multiple functional groups by installing six amide groups via an unprecedented hexuple Friedel-Crafts carbamylation, thereby originating a new class of multivalent monomer and electroactive materials -- decacyclene trianhydride and triimides. These materials were shaped using the established chemistry of acenaphthene, naphthalene, and perylene cores. Owing to the extended π -surface of the triimides, these novel polycyclic hydrocarbons exhibit a propensity to self-assemble, and crystalline columns or ultra-long fibers are obtained by solely modulating the alkyl substituents.

As a further synthetic challenge, we also synthesized and investigated the properties of novel decacyclene triimide-based dendrimers for photonic applications. Thus, we are confident that this new class of dendrimers could easily find application in light harvesting antenna systems and catalysis.

WRM 167

Conclusion to the 22 year mystery of the fullerene (C₆₀) pentane solvate structure

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The pentane solvate of C₆₀ has been known since 1991 without a determined structure. Extensive infrared, differential scanning calorimetry (DSC), thermogravimetry-mass spectrometry (TG-MS) and X-ray diffraction studies had been carried out. The infrared data indicated that there was no electronic interaction between pentane and C₆₀. TG-MS and DSC experiments indicated a release of pentane and irreversible phase transition of the material. Crystallographic data indicated the compound's unit cell and a crystallographically forbidden "psuedotenfold symmetry*" as well as twinning of the solvate. Here we will present the fully ordered structure of C₆₀·pentane obtained with crystallographic data at 90 K, its analog C₆₀·diethyl ether, and the relationship between the two. The method that yielded the structures will also be described.

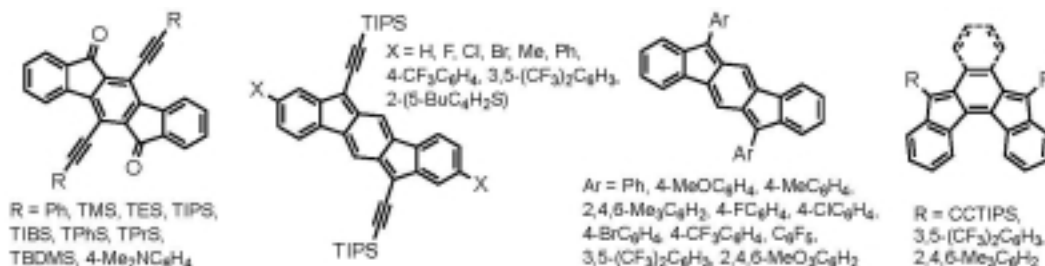
* Fleming, R. M.; Kortan, A. R.; Hessen, B.; Siegrist, T.; Thiel, F. A.; Marsh, P.; Haddon, R. C.; Tycko, R.; Dabbagh, G.; Kaplan, M. L.; Muijsce, A. M., PSEUDOTENFOLD SYMMETRY IN PENTANE-SOLVATED C₆₀ AND C₇₀. *Physical Review B* **1991**, 44, 888-891.

WRM 168

Indenofluorenes - a new class of electron-accepting materials

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This talk will present our synthetic, structural and materials studies of a new class of electron-accepting molecules based on the indenofluorene (IF) skeleton. The initial preparative route involved transannular cyclization of octadehydrodibenzo[12]annulenes to afford the pentacyclic ring system. Subsequent transformations generated the first stable examples of the fully conjugated, 20 pi-electron, formally anti-aromatic compounds. Optimization of intermediate IF-6,12-dione synthesis via a simple three-step process now permits access to IF derivatives in multigram quantities. Recent work has focused on 6,12-diaryllFs, where we demonstrated that single crystals of the pentafluorophenyl derivative could serve as an active layer in organic field effect transistors (OFETs) that exhibit ambipolar behavior. This presentation will focus on development of project as well as include the latest results from our lab.



WRM 169

Investigation on inhibition of polysulfides dissolved into electrolyte using porous carbon in rechargeable lithium-sulfur batteries

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Considering the fish-scale-based porous carbon with good adsorption capability, we designed a cathode using this carbon to inhibit the polysulfides dissolution. UV-visible spectroscopy was employed to study the soluble species in electrolyte and the data of PC (porous cathode, which was prepared by mixing 42 wt.% sulfur, 28wt.% porous carbon, 20wt. % AB and 10wt.% binder) were compared with that of CC (common cathode prepared by 42 wt.% sulfur, 48wt.% AB and 10wt.% binder). The UV-visual spectroscopy of soluble reduction products formed after the first discharge is detected as shown in Figure 1a—three peaks are detected which exhibit max absorbance at 237nm, 262 nm, 280 nm correspond to the long-chain reduction species. The soluble polysulfides in the electrolyte of PC decrease significantly with respect to CC. This result illustrates that using porous carbon is an effective way to restrain the polysulfides dissolve into electrolyte; meanwhile, the cycle performance is improved as it is shown in Figure 1b. The initial capacity of PC shows 1411mAhg⁻¹ and retains 878mAhg⁻¹ at 0.1C after 50cycle.

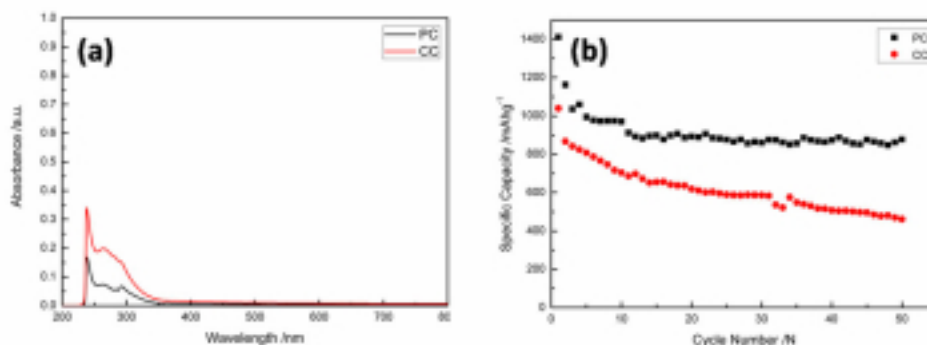


Figure1. (a)UV-visible adsorption spectra of PC and CC cathodes obtained after the first discharged; (b) Cycle performance of lithium/sulfur batteries using PC and CC at the rate of 0.1C. A solution consisting of 0.5 M LiTFSI and 0.4 M lithium nitrate in 1,3-dioxolane and 1,2-dimethoxyethane (1:1,v/v) as the electrolyte.

WRM 170

Heat-induced coarsening of gold nanoparticles on graphene

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Glutathione-capped gold nanoparticles of size 1, 3, and 10 nm were synthesized and bonded to graphene oxide to study their coarsening behavior upon heating. Graphene is a planar, single-layer sheet of sp^2 -hybridized carbon atoms exhibiting extremely high surface area ($2600 \text{ m}^2/\text{g}$). The nanoparticle-graphene hybrid materials were heated up to 600°C , and the surface nanoparticles would undergo coalescence to become larger particles. UV-Vis results show that gold nanoparticles have a plasmonic peak at 550 nm, which shifted to higher wavelength after heating. This is due to increased metal-metal interactions among the nanoparticles, after the vaporization of glutathione at approximately 200°C . Nanoparticle-graphene hybrid materials were also used to study the effect of covalent and non-covalent interactions between gold nanoparticles and graphene oxide during coarsening. Non-covalent interactions were studied by directly adding graphene oxide to nanoparticle solutions, and covalent interactions were achieved by the coupling of COOH-functionalized gold nanoparticles with L-cystine modified graphene oxide using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and N-hydroxysuccinimide (NHS). Solvent effects were also studied by heating the hybrid materials with and without solvent. These engineered nanoparticle-graphene hybrid materials were further studied by transmission electron microscopy (TEM), infrared spectroscopy, and apertureless near-field scanning optical microscopy.

WRM 171

New advances in the construction of C–N and C–O bonds for organic synthesis

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The development of straightforward methods to construct carbon–nitrogen and carbon–oxygen bonds using operationally simple reaction conditions is described. Specifically, this lecture will focus on a dysprosium (III) trifluoromethanesulfonate catalyzed cascade rearrangement of activated furans to 4-substituted cyclopentenones via a 4p electrocyclization. This method allows for the fast preparation of a variety of highly functionalized cyclopentenone products from furfural, a readily available starting material. Recent developments in nitrosocarbonyl chemistry using a copper-catalyzed aerobic oxidation of hydroxamic acid derivatives will also be described. In these reactions the highly reactive and transient nitroso species is generated catalytically under mild reaction conditions, which helps avoid previously reported problems associated with nitrosocarbonyl chemistry and has led to the development of new synthetic transformations.

WRM 172

Asymmetric Catalysis with Cations and Anions

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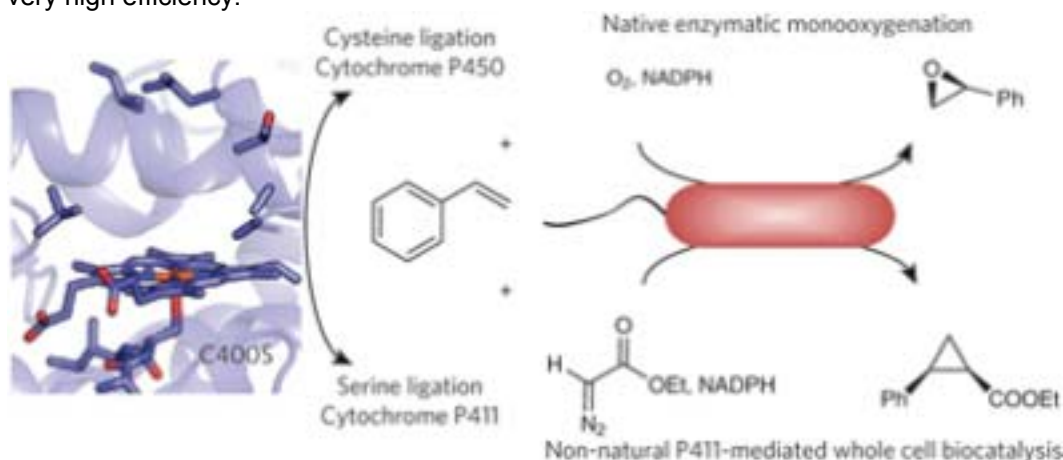
The past decade has witnessed remarkable development in the use of cationic gold(I) complexes as homogenous catalysts for the transformation of carbon-carbon π -bonds. Several years ago, we demonstrated that the reactivity of these complexes could be controlled by modification of the counter anion to these cationic transition metal complexes. This discovery provided a general platform for inducing enantioselectivity in reaction not only using cationic transition metal complexes, but also with reactive cationic reagents and intermediates. For example, we have applied this concept towards the development of enantioselective electrophilic fluorination under chiral anion phase transfer conditions. The use of these ionic interactions to control selectivity of cationic species has generally relied on small molecular anions. As an extension of this concept, we have been exploring the use of supramolecular assemblies as the anionic component in reactions catalyzed by cationic transition metal complexes.

WRM 173

Engineering Cytochrome P450 for Cyclopropanation

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The ability to genetically encode catalysts for non-natural chemical reactions will open new routes to sustainable production of chemicals. In nature, cytochrome P450 catalyzes the oxidation of organic substrates with oxygen to produce epoxides and alcohols. This transformation proceeds through an iron-oxene complex (Compound I), which is generated in the presence of NAD(P)H and molecular oxygen. Inspired by this catalytic cycle, we hypothesized that a similar process could be used to generate an iron-carbenoid specie from diazo compounds that could enable olefin cyclopropanation. Toward this end, we have been able to evolve a unique serine-heme ligated cytochrome “P411” that catalyzes formal carbene transfers from diazoesters to olefins with very high efficiency.



Proximal cysteine to serine substitution in a bacterial cytochrome P450 gives a signature ferrous-CO Soret peak at 411 nm, raises the resting state Fe^{III}/Fe^{II} reduction potential, abolishes monooxygenation activity and significantly allows NAD(P)H-driven cyclopropanation. The serine-heme enzyme performs up to 60,000 turnovers *in vivo*, is highly stereoselective, and is even more active than the purified protein at the same concentration.

WRM 174

Total Synthesis and Glucokinase Activating Properties of Tatanans A-C

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Tatanans A-C are new, structurally distinct sesquiterpenes that have recently been reported to potentially activate glucokinase. GK activation has been an important approach to the treatment of diabetes. We developed a short, scalable, and robust total synthesis of tatanans A-C in enantiopure form. The central part of the synthesis is metal-catalyzed stereoselective allylic dearomatization, controlling four stereogenic elements during the cyclization process. The synthetic material was extensively tested with regard to GK activating properties.

WRM 175

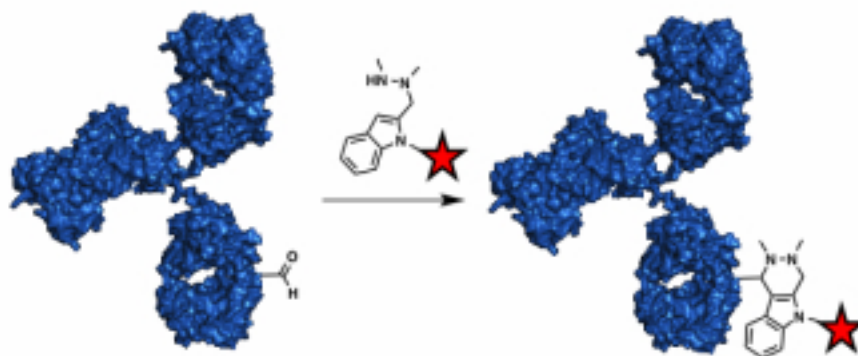
Hydrazino-iso-Pictet-Spengler Ligation: A new method for the generation of stable ADC's

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Antibody-drug conjugates (ADC's) are a promising new therapeutic option for cancer treatment. ADC's offer the promise of targeted drug delivery with increased efficacy and safety. Currently approved ADC's are heterogeneous mixtures resulting from nonselective ligation of drug to either cysteine or lysine residues. This heterogeneity complicates the pharmacokinetics and pharmacodynamics of these drugs.

Technology being developed at Redwood Bioscience affords the ability to create homogeneous ADC's with controlled payload stoichiometry and placement. Novel ligation chemistry has been

employed that exploits a genetically encoded amino acid “aldehyde tag” sequence. This new reaction, the hydrazino-iso-Pictet-Spengler (HIPS) ligation, possesses two distinct advantages over current carbonyl ligations. First, the HIPS ligation proceeds quickly at near neutral pH in the absence of catalysts, allowing for one-step labeling of aldehyde-functionalized proteins under mild conditions. Second, HIPS ligation products are very stable in human plasma relative to an oxime-linked conjugates. Thus, the HIPS ligation exhibits a combination of stability and speed at near neutral pH that is unmatched by current carbonyl bioconjugation chemistries. The “aldehyde-tag” in conjunction with the HIPS ligation is now being used to create homogeneous, site-specific, stable antibody drug conjugates.



WRM 176

Rational design of inhibitors targeting the drug resistant influenza A virus M2 (A/M2) proton channel

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The influenza A virus M2 proton channel (A/M2) is the target of the antiviral drugs, amantadine and rimantadine, whose use have been discontinued due to widespread drug resistance. Among the handful of drug-resistant mutants of M2, S31N, V27A and L26F were found in more than 99% of the currently circulating viruses. The small set of transmissible mutants argues that M2 is a highly conserved drug target compared to other viral proteins, rendering it an ideal target for anti-flu drug development. However, the discovery of inhibitors of these M2 mutants has been hampered by the lack of structural information and their limited sizes, polarity, and dynamic nature of their drug binding sites. Nevertheless, using an integrated approach including medicinal chemistry, molecular dynamics simulation, solid/solution-state NMR, X-ray crystallography, and pharmacological characterizations, we have discovered small molecule drugs that inhibit mutant M2 (S31N, V27A and L26F) with potencies greater than amantadine's potency against WT M2. The inhibitors were tested by two-electrode voltage clamp assays and the activities of potent

compounds were further confirmed in viral replication assays. A few compounds exhibiting EC₅₀ around 100 nM are advanced to mice model studies. Structural characterization of S31N drug binding by NMR shows the drug bound in the homotetrameric channel, threaded between the side chains of Asn31. The S31N inhibitors, like other potent WT M2 inhibitors, contain a charged ammonium group. The ammonium binds as a hydrate to one of three sites aligned along the central cavity that appear to be hotspots for inhibition. These drug binding hotspots along the channel axis provide a general model of M2 inhibition that can be used to guide the design of other channel blockers.

WRM 177

Liquid handling and dilutions profoundly affect biological assays

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Dispensing and dilution processes can profoundly influence estimates of biological activity. Published data show IC₅₀ values obtained via tip-based serial dilution and dispensing versus acoustic dispensing with direct dilution differ by orders of magnitude with no correlation or ranking of datasets. We generated pharmacophores based on data derived by both acoustic and tip-based transfer. The pharmacophores differ significantly depending upon dispensing and dilution methods. The acoustic dispensing-derived pharmacophore correctly identified active compounds in a subsequent test set where the tip-based method failed. Data from acoustic dispensing generates a pharmacophore containing two hydrophobic features, one hydrogen bond donor and one hydrogen bond acceptor. This is consistent with X-ray crystallography studies. In contrast, the tip-based data suggest a pharmacophore with two hydrogen bond acceptors, one hydrogen bond donor and no hydrophobic features. This pharmacophore is inconsistent with the X-ray crystallographic studies. In short, tip-based dispensing processes are an important source of error in high-throughput screening. These findings have far-reaching implications in biological research.

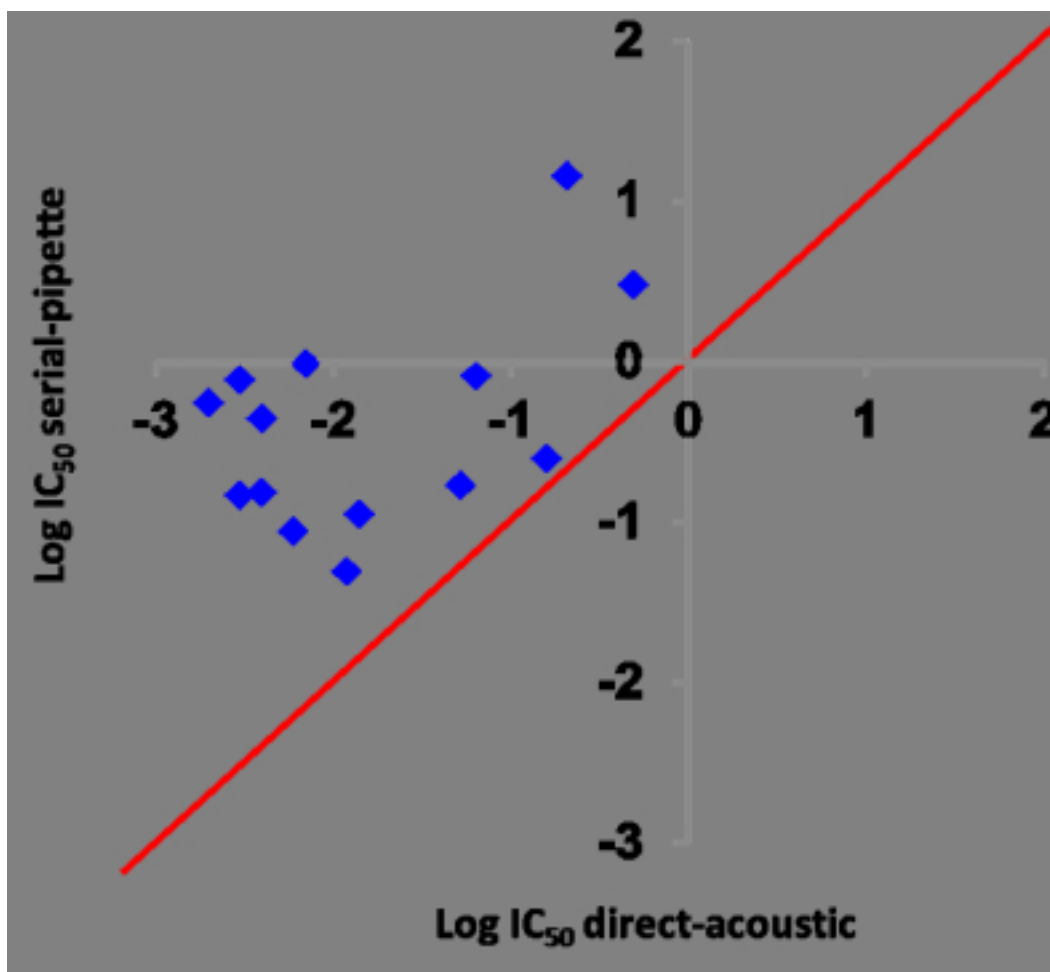


Figure 1. Without exception, all 14 compounds reported in patents WO 2009/010794 A1 and US 7,718,653, showed greater biological activity (i.e., lower IC₅₀ value) when concentration gradients were developed via direct dilution facilitated with acoustic transfer than when concentration range was developed with traditional serial dilutions with pipettes.

WRM 178

Optimizing synthetic access to the quorum sensing substrate S-ribosylhomocysteine (SRH)

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The phenomenon of quorum sensing (QS), through which select species of bacteria communicate intercellularly using small organic autoinducers (AI's), can be responsible for the coordination of group behaviors from biofilm formation to bioluminescence. Of particular interest is the involvement of QS systems in the expression of virulence in a range of human pathogens, including *E. coli*, *S. aureus*, and *V. cholerae*. QS circuits in species such as these provide particularly attractive medicinal targets due to the potential for these treatments to result in non-lethal cessation of virulence through behavioral manipulation rather than pathogen eradication, thus generating lower selective pressure towards resistance development. The small molecule (4S),5-dihydroxypentane-2,3-dione (DPD) serves as the precursor to AI-2, the 'communicative' autoinducer/s utilized in interspecies System Two quorum sensing. *In vivo*, DPD is biosynthesized from the metabolite S-ribosylhomocysteine (SRH) by the action of the LuxS

enzyme. Therefore, LuxS is a clear target for the exploration of anti-QS strategies, and SRH is requisite to these studies. With few chemical preparations of SRH reported in the literature, access to this compound may be expanded by an improved synthesis employing robust precursors and straightforward chemical manipulations. Moreover, a systematized knowledge of the underpinnings of an efficient chemical synthesis of SRH is also of value. This is particularly true considering the potential application to the preparation of rationally-designed analogs of SRH which may be hypothesized as modulators of interspecies QS. Here, a systematic investigation into the chemical synthesis of SRH is undertaken to identify optimal components and conditions for its efficient preparation, with an eye to eventual application to the preparation of interesting analogs. Implementations of the benchmark *in vitro* assay for LuxS activity for the identification of inhibitor candidates will also be presented.

WRM 179

Adventures with AKT: Small molecule inhibition and mechanism of activation

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The PI3K-AKT-mTOR signaling pathway is central to many cellular events and its mis-regulation is a common driver of enhanced growth and proliferation in cancer. We report the discovery and optimization of a series of 6,7-dihydro-5H-cyclopenta[d]pyrimidine compounds that are ATP-competitive, selective inhibitors of Protein Kinase B (PKB)/Akt. The use of co-crystal structures of inhibitors in complex with AKT and the closely related Protein Kinase A (PKA) was crucial to developing selective inhibitors of AKT. One such compound (GDC-0068) is a potent inhibitor of all three AKT isoforms, shows poor inhibition of other AGC kinases, blocks phosphorylation of multiple downstream targets of AKT in cancer cell lines and a dose-dependent anti-tumor response in xenograft models where the PI3K-AKT-mTOR pathway is activated. GDC-0068 is currently in human clinical trials for the treatment of cancer. A detailed model for the activation of AKT based on mechanistic studies with inhibitors, analysis of full-length AKT crystal structures and design of constitutively active AKT mutant proteins will also be presented. These studies have important implications for the ability of AKT mutations to give resistance to ATP-competitive and allosteric inhibitors.

WRM 180

Viscoelastic characterization of a thin film biopolymer of phenylalanine glycine repeat domains using the Quartz Crystal Microbalance with Dissipation Monitoring

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By monitoring the changes in resonance frequency and dissipation of a piezoelectric quartz sensor in real-time, the Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) can measure mass, thickness, and viscoelastic properties of solvated thin films of polymers and biomolecules. In this study, QCM-D was used to characterize the thickness and viscoelasticity of a thin film of natively unfolded phenylalanine glycine repeat domains (FGRDs) of the yeast nucleoporin Nsp1p. FGRDs are thought to be key facilitators of transport across the nuclear membrane and *in vitro* assays have shown that FGRDs can form hydrogels. Rheological analysis of FGRD films can provide insight into the morphology of nucleoporins and a viscoelastic treatment of these films via QCM-D can serve as a model for other thin polymeric films. His-tagged FGRDs were bound to a QCM-D sensor modified with a His-tag capture surface and the ensuing film was modeled as a homogeneous viscoelastic layer with thickness d , density ρ , and frequency-dependent storage ($G'(f)$) and loss ($G''(f)$) moduli. The modeled thickness at maximum grafting density determined via QCM-D (30 ± 4 nm) agreed well with the value determined via an AFM nanoindentation assay (30 ± 5 nm) and both the storage and loss moduli were found to be frequency-dependent (i.e., non-Newtonian) throughout the course of film formation. Results showed that the relative difference between G' and G'' decreased with

increasing surface coverage, meaning that the FGRD film became increasingly elastic with time. A comparison of the modeled results to theoretical predictions for a solution of entangled long-chain polymers revealed that the frequency range accessible by the QCM-D allows for viscoelastic characterization of polymeric films from the transition zone where G' is greater than G'' (i.e., the film is more viscous) towards the plateau zone where G' is greater than G'' (i.e., the film is more elastic).

WRM 181

Hybrid Elastin-like Polypeptide-Polyethylene Glycol (ELP-PEG) Hydrogels with Improved Transparency for Three-dimensional Cell Culture

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Elastin-like polypeptides (ELPs) engineered with bioactive and structural motifs have shown great promise in a variety of biomedical applications. In particular, ELP hydrogels, which can be tuned to mimic the biochemical and physical characteristics of native extracellular matrices, have been constructed to encapsulate various types of cells to create *in vitro* mimics of *in vivo* tissues. However, ELP hydrogels become opaque at body temperature because of ELP's inherent hydrophobic and thermo-sensitive properties, greatly obstructing observation and in-depth investigation of the morphology and behavior of encapsulated cells. In order to improve the transparency of ELP hydrogels for better imaging, we have designed a hybrid ELP-polyethylene glycol (PEG) hydrogel system that rapidly crosslinks with tris(hydroxymethyl) phosphine (THP) in aqueous solution via Mannich-type condensation. Compared with pure ELP hydrogels, the newly formed hybrid ELP-PEG hydrogels showed significantly improved light transmittance. The addition of the PEG component decreased the size of the ELP hydrophobic domains at 37 °C, as observed by Coherent Anti-Stokes Raman Scattering (CARS) microscopy. Adipose-derived stromal cells (ASCs) encapsulated in these hydrogels show high viability after 7 days of culture. High-resolution confocal microscopy of encapsulated ASCs is being used to explore the effects of matrix stiffness and integrin ligand density on ASC behavior in three-dimensional environments.

WRM 182

One-step conjugation of bioactive peptides to elastin-like hydrogels to form tunable tissue engineering scaffolds

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Bioactive peptides are simple and cost-effective to synthesize; however, their short half-lives and quick diffusion rates through tissue make them difficult to translate to *in vivo* settings. To overcome these limitations, we developed a one-step procedure to simultaneously crosslink an elastin-like polypeptide into a hydrogel while conjugating bioactive peptides into the same hydrogel network. To demonstrate this protocol, we tethered a small bioactive peptide (QK, 2.1 kDa) to a large elastin-like polypeptide (ELP, 37 kDa). Using genetic engineering technology, we designed the ELP to contain 14 lysine residues, each with one primary amine functional group. The ELP was recombinantly synthesized in *Escherichia coli* and purified by inverse temperature cycling. The original QK peptide contains two lysines that were protected with acetylation, while one N-terminal lysine was added as a conjugation reaction site. At room temperature, we mixed together tetrakis(hydroxymethyl)phosphonium chloride (THPC), an efficient amine reactive crosslinker, with ELP and QK in a phosphate-buffered saline (PBS) solution. Left undisturbed at room temperature for 20 minutes, the reaction creates a stable gel. Using spectroscopy, we found a consistent 80% conjugation efficiency, making it simple to tune the final concentration of QK in the hydrogel. Through a Fluorescence Recovery After Photobleaching (FRAP) analysis, we confirmed that QK is covalently bound to the network and has negligible diffusion. Human umbilical vein endothelial cells (HUVECs) cultured on ELP hydrogels with immobilized QK peptide had increased proliferation rates compared to pure ELP matrix. Due to the high efficiency and speed of the THPC crosslinker and the cell-friendly temperature of the reaction, this scaffold can simultaneously encapsulate cells during the crosslinking process. This one-step conjugation

technique provides a simple and quantitative way to optimize ELP hydrogels with a broad range of bioactive peptides for customized tissue engineering applications.

WRM 183

Synthesis and characterization of functionalized gold nanoparticle-cored dendrimers (NCDs) with average core sizes of 3, 10, and 17 nm as a theragnosis device for cancer treatment

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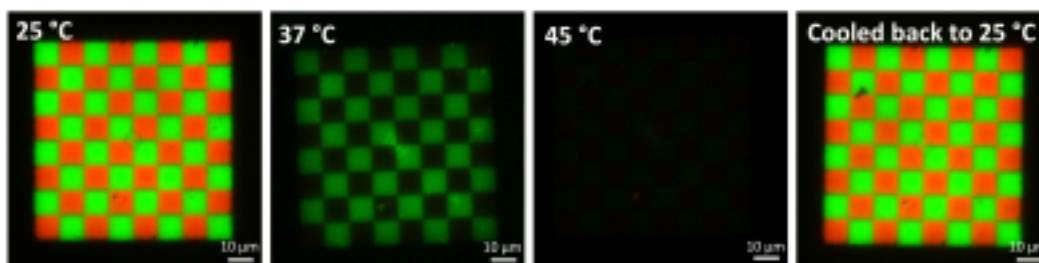
Gold nanoparticle based technologies have recently become very popular in biotechnology and medical research, and are looking to be more promising in detection and treatment of cancer. However, one of the problems with gold nanoparticles is their tendency to aggregate in aqueous solutions. This poster describes our attempt to synthesize water-soluble gold nanoparticle-cored dendrimers (NCDs) with various average core sizes, and evaluation of stability and cytotoxicity of these materials. Our synthetic method is based on a strategy in which the synthesis of monolayer ligand-capped gold nanoparticles is followed by adding dendrons on the particle surfaces by single coupling reaction. The produced gold NCDs were characterized using various instruments including transmission electron microscopy (TEM), FT-IR, UV-VIS spectroscopy, DLS, ICP-MS, and ICP-OES. The stability of gold nanoparticles and NCDs in solutions of different pH and salt concentration was determined by monitoring changes in surface plasmon bands of gold using UV-VIS spectroscopy. The NCDs were found to be more stable than other gold nanoparticles and most stable at higher pH and lower salt concentrations. The improved stability of NCDs suggests that the further improvements in biocompatibility and physiological stability of gold nanoparticle-based materials can be achieved by post-functionalization of gold nanoparticle surfaces. Preliminary cytotoxicity studies with gold nanoparticles and NCDs were also performed by examining cell viability for NIH 3T3 mouse embryonic fibroblasts using a MTT cell proliferation assay.

WRM 184

Thermoreversible fluorescence switching of hydrogel patterns generated by e-beam lithography

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Stimuli-responsive hydrogels are highly interesting for a wide range of applications, such as sensors, actuators, diagnostics, and tissue engineering. In this study, we prepared fluorophore conjugated thermoresponsive hydrogel patterns that show fluorescence switching in response to temperature changes. Oligo(ethylene glycol) methacrylate-based thermoresponsive polymers with amine end-groups were prepared by atom transfer radical polymerization (ATRP). The lower critical solution temperatures (LCSTs) were tuned by altering the length of oligo(ethylene glycol) side chains or by adjusting the ratio of monomers with different lengths. The polymers were patterned on silicon surfaces by electron beam lithography, followed by the conjugation of self-quenching fluorophores to the patterned hydrogels utilizing the amine end-groups. At room temperature, the hydrogels were brightly fluorescent in water. Upon increasing the temperature to values above the volume phase transition temperature (VPTT) of the respective gel, a dramatic decrease in the fluorescence intensity was observed due to self-quenching of fluorophores in the collapsed state of the gel. Importantly, the temperature-induced fluorescence switch is reversible. In a similar manner, we generated morphing structures that reversibly display different messages at different temperatures. We have investigated the fluorescence switching behavior of the hydrogels for up to ten cycles and the swelling-collapse behavior by AFM analyses. The presented platform could be highly useful in applications such as sensors and encryption.

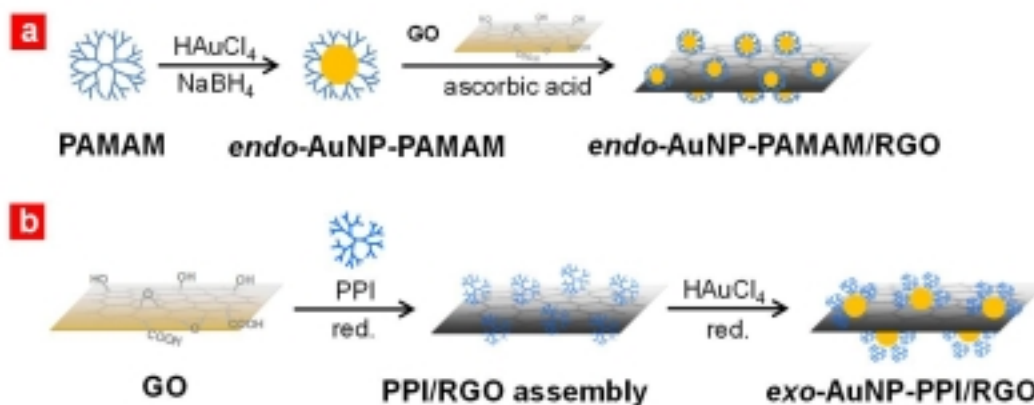


WRM 185

Formulation of soluble chemically reduced graphene oxide through noncovalent approach with various aliphatic polymers

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Soluble chemically reduced graphene oxide (RGO)/aliphatic polymer assemblies are formulated through noncovalent approach. σ - π interaction between aliphatic polymer chains and RGO plates might contribute to the formation of stable RGO/polymer assemblies with dispersion stability. While various functional RGO/polymer assemblies showing stimuli-responsibility have been formulated, detailed morphological features of assemblies were also evaluated by using gold nanoparticle encapsulated aliphatic dendrimers as molecular probes.



WRM 186

A Journey to Metal-Containing Polymers

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Metal-containing polymers have promising application as catalysts, biomaterial, conducting material and optically active material, due to the special activities exhibited by the metal centers. Ru and Ni-containing polymers from two different methods were investigated. For the first method, an organometallic monomer containing a ligand with a vinyl moiety was synthesized and purified, then polymerized with organic co-monomers. For the second method, an organic polymer - composed only of the polymerizable vinylic ligand and the organic co-monomers - was synthesized first, then coordinated to metal salts. Products from the two methods show distinct properties. SEM images were taken to assess the polymers' size, shape, and thin-film topography while confocal spinning disk microscopy confirmed fluorescent activity of discrete polymer nanoparticles. Polydispersity indices of synthesized polymers were obtained via dynamic light scattering. UV-Vis spectroscopy and spectrofluorimetry was used for assessment of electronic properties of the polymers.

WRM 187

Characterization of light-controlled graphene-elastin composite actuators

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Protein based polymers (PBPs) are valuable for biological research because of their intrinsic biocompatibility. Additionally, they can be designed and customized as needed to contain functional groups to interact with organic as well as inorganic materials. In this work, we utilize elastin-like polypeptides (ELPs) to create stimuli responsive hydrogels. ELPs, derived from natural elastin, are able to undergo coacervation based on conditions such as temperature, pH, and salt similar to tropoelastin in addition to being highly elastic. We also genetically engineered ELPs with an aromatic amino acid containing sequence, previously found in our lab to bind carbon nanotubes, to enable ELP to physically bind reduced graphene oxide (rGO) nanosheets. The rGO nanosheets act as photothermal heaters absorbing near infrared (NIR) light to produce heat. Using rGO nanosheets and ELP, we have designed fast and controllable light-responsive composite hydrogels.

These composite hydrogels heat up upon exposure to NIR light causing ELP chains to collapse. Anisotropic structure of the gels with porous and solid layers allows for different swelling/deswelling ratios across the gel thickness and causes them to 'flex'. The focus of our work has been to characterize the structure and function of these gels with varying compositions of rGO, ELP and the crosslinking agent. We use atomic force microscopy to observe the hydrogel micro-structure and surface mechanics as well as perform tensile tests to obtain bulk hydrogel properties. Such hydrogel actuators have applications in drug delivery, mechanotransduction, and soft robotics.

WRM 188

Comparative study of the loading capacity of preparative 5 μ m Gemini NX-C18 and Kinetex XB-C18 columns

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A core-shell particle has a solid non-porous core that is surrounded by a layer of porous material, which essentially have the same physicochemical properties of conventional porous particles used as packing media in chromatography[1]. The implementation of superficially porous particles in analytical HPLC has shown improvement in efficiency when compared to fully-porous particles of the same size on both HPLC and UHPLC instrumentation [2]. The success of superficially porous particles in analytical applications leads to question if the potential gains can be translated to preparative HPLC applications. A recently introduced preparative 5 μ m superficially porous Kinetex XB-C18 was compared to a preparative 5 μ m fully porous Gemini NX-C18 by means of evaluating the loading performance of the two columns using various small molecules. From this study it was observed that although superficially porous particles show improved efficiency on the analytical scale, fully-porous particles was superior for preparative separations. The possible causes for this observation are later discussed.

References

- [1] A. Cavazzini, F. Gritti, K. Kaczmarek, N. Marchetti, G. Guichon, *Anal. Chem.*, **2007**, 79, 5972.
- [2] A. Fanigliulo, D. Cabooter, G. Bellazzi, D. Tramari, B. Allieri, A. Rottigni, G. Desmet, *J. Sep. Sci.*, **2010**, 33, 3655.

WRM 189

Counter ion analysis with Ion Chromatography in small molecule drug candidates

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Counter ion analysis with Ion Chromatography in small molecule drug candidates were studied. The salt content in pharmaceutical products are critical. FDA has issued new guidelines to regulate the ID, content, etc. This study will reveal the impact of solvent used to dissolve pharma samples on the chromatogram and test results on a suppressor-equipped ion chromatography.

WRM 190

Temperature independent free energy relationships for three ionic liquids based on the trifluorotris(perfluoroethyl)phosphate anion

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Experimental data have been collected from the published literature for the gas-to-ionic liquid partition coefficients and molar enthalpies of solvation for over 100 solutes in the ionic liquids 4-(2-methoxyethyl)-4-methylmorpholinium trifluorotris(perfluoroethyl)phosphate, 1-(2-methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)phosphate, and 1-(2-methoxyethyl)-1-methylpyrrolidinium trifluorotris(perfluoroethyl)phosphate over the temperature range 318 K to 383 K. The logarithm of the gas-to-ionic liquid partition coefficient, log K, for each ionic liquid have been correlated to a temperature independent free energy relationship utilizing known Abraham solvation parameters. Molar entropies of solvation have been calculated from the molar enthalpies and log K values and correlated with the Abraham Model. Temperature independent free energy relationships derived from the Abraham Model correlations for the molar enthalpies and molar entropies of solvation show similar predictability as temperature independent free energy relationships based on log K.

WRM 191

Trace analysis of hydrazine in pharmaceuticals by reversed phase HPLC

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Hydrazine is a highly reactive molecule widely used in organic synthesis of starting material, intermediates and active pharmaceutical ingredients (APIs). However, hydrazine is a human carcinogen which causes genetic toxicity. According to EMA and FDA guidelines, the intake of genotoxic impurity must be controlled to no greater than 1.5 µg/day when a drug is taken for more than 12 months. Therefore, the level of hydrazine in drug substance often requires control to low ppm levels.

Many methods have been developed for the analysis of hydrazine in air, water, human plasma and urine by various spectrometric methods, however, these methods can not be directly applied to pharmaceutical samples due to matrix interference. Due to the lack of a UV chromophore, the detection of hydrazine in pharmaceuticals at low ppm is challenging. Special instrumentation and deuterated reagents have been used for hydrazine analysis in pharmaceuticals.

We developed and validated a simple, selective and sensitive method by using reversed-phase HPLC for determination of hydrazine in pharmaceutical materials at low ppm levels. 2-Hydroxy-1-Naphthalaldehyde (HNA) was chosen as a derivatization reagent, and the derivative has a maximum UV absorbance at wavelength of 406/424 nm which is in the visible range. Since most APIs have UV absorbance ranging from 200-400 nm, interference from the matrix was minimized and the appropriate selectivity was obtained.

The sample preparation is simple and fast. Chromatographic separation was carried out on a reversed-phase column with acetonitrile-water (0.05 % TFA) as mobile phase. Linearity of hydrazine ranged from 2-200 µg/L with $R^2 = 1.0000$. The spike recoveries of hydrazine at 1 ppm level were between 95-113% in various APIs tested, which demonstrated minimal matrix interference. The formed derivative is stable at ambient conditions up to 3 days.

This method has been applied as a generic method to determine hydrazine for pharmaceutical process control and drug material release.

WRM 192

Application of DFT methods for three way catalyst modelling

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Three Way Catalysts (TWC) are used in simultaneous conversion of automotive exhaust pollutants HC's, CO and NO_x to harmless CO, N₂ and water vapor. A conventional TWC consists of noble metals Pd, Pt and/or Rh placed on CeO₂ - Al₂O₃ support. Zirconia doping is also effective

in enhancing thermal resistance and catalytic activity. Density Functional Theory (DFT) is a powerful tool to accurately investigate structure and energetics for oxidation and reduction reactions on TWC systems. The objective of the study is to model novel efficient TWC catalysts for CO and NO conversion with lower Pd or Rh content and enhanced oxide support activity. Activity of various Pd and Rh substituted or cluster adsorbed CeO_2 and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ surfaces are compared.

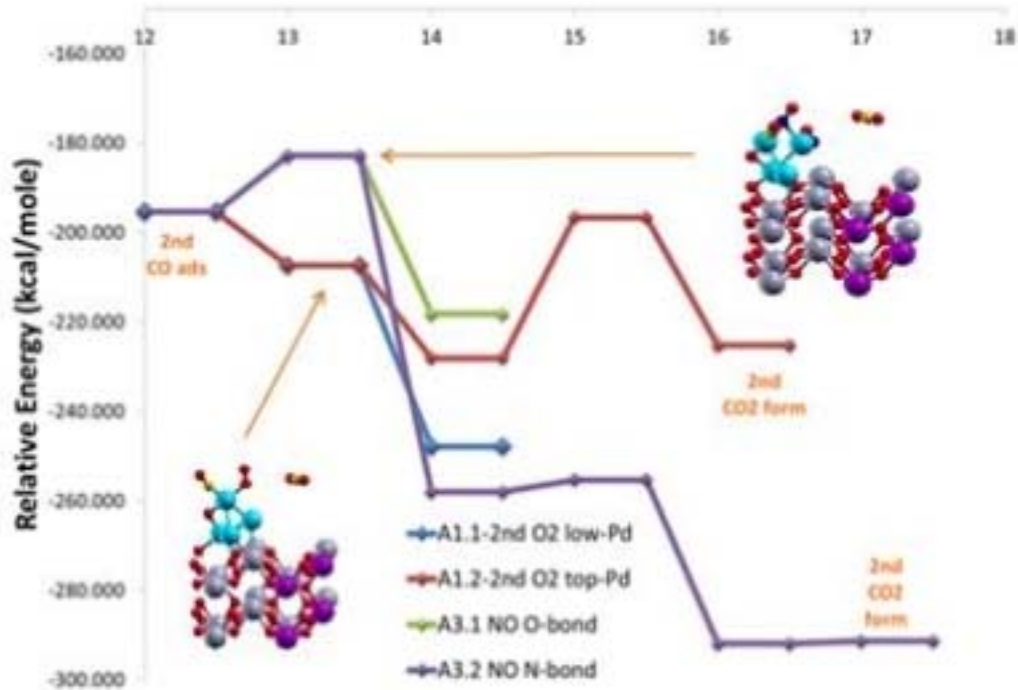


Figure 1. Energetics of CO conversion with O_2 or NO on $\text{Pd}_4\text{-Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$

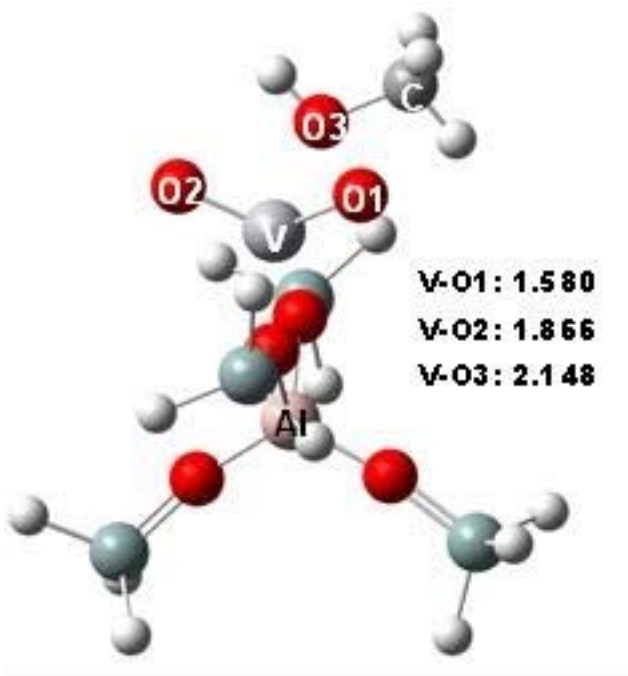
WRM 193

DFT study: Direct methanol oxidation to formaldehyde by N_2O on $[\text{VO}]^{1+}\text{-ZSM-5}$ cluster

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The aim of this study is to analyze the catalytic reactivity on $[\text{VO}]^{1+}$ sites in ZSM-5 zeolite for the catalytic oxidation of methanol to formaldehyde formation by N_2O via DFT. All calculations were based on DFT B3LYP/6-31G(d,p) as implemented in the Gaussian suite of programs. All atoms of the cluster (except H atoms used to terminate the terminal silicon atoms), and the reactant and product molecules were kept relaxed. Energy profile, equilibrium geometry, and transition state calculations were performed for the determination of the activation barriers and relative reaction energies. Based on the theoretical results it is concluded that $[\text{O-V-O}]^{1+}$ site formed after N_2O decomposition in ZSM-5 catalyst has a key role on the catalytic direct oxidation of methanol to formaldehyde which can clearly be considered a potential green chemistry process.

Figure 1 Optimized geometry of adsorbed methanol



WRM 194

Controlling activity of ligand-capped Pd nanoparticle catalysts: effects of thiolate ligand structure and functionality

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In the prior studies, stable and isolable palladium nanoparticles (PdNPs) were synthesized by employing sodium S-dodecylthiosulfate ligand precursors. Interestingly enough, this methodology yielded dodecanethiolate-capped PdNPs due to the cleavage of the SO_3 moiety during the passivation of growing PdNPs. Such PdNPs were capable of catalyzing a wide array of organic reactions due to the overall lower ligand surface coverage and henceforth the high accessibility to the reactive Pd surface. In this study, the effects of the structure of thiolate ligands on catalytic activity and selectivity of PdNPs were investigated. First, the distinct thiosulfate ligand precursors (sodium S-hexylthiosulfate, sodium S-cyclohexylethylthiosulfate, and sodium S-phenylethylthiosulfate) were synthesized from their alkyl halide counterparts by simple nucleophilic substitution reactions. Second, PdNPs capped with these ligands were synthesized using a modification of two-phase Brust reaction protocol. Systematic variations such as the reactant equivalents of tetra-n-octylammonium bromide (phase transfer agent), sodium boron hydride (reducing agent), and/or sodium S-alkylthiosulfate were attempted to control the core size and surface ligand density of these PdNPs. Each variant was characterized using transmission electron microscopy (TEM), thermogravimetric analysis (TGA), FT-IR, UV-Vis, and ^1H NMR spectroscopy. Moreover, the catalytic activity and selectivity of PdNPs with similar core size and ligand coverage but with distinct ligands were compared by analyzing the results obtained from the hydrogenation and/or isomerization of allyl alcohol and propargyl alcohol.

WRM 195

Expanding the scope of light-driven P450 biocatalysts: from non-natural substrates to other members of the P450 superfamily

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The Cytochrome P450 superfamily of heme-thiolate enzymes catalyzes a myriad of selective oxidation reactions using two reducing equivalents and molecular dioxygen as the source of oxygen atom. Our laboratory is developing hybrid P450 enzymes as light-activated biocatalysts for the selective aerobic oxidation of unactivated C-H bonds. The hybrid enzymes contain a Ru(II)-diimine photosensitizer covalently attached to non-native cysteine residues of the P450 heme domain. Upon visible light excitation and under flash-quench conditions, the photosensitizer is able to provide the necessary electrons to the heme domain and sustain photocatalytic activity. Using the model substrate lauric acid, we have demonstrated that an optimized hybrid P450 BM3 enzyme is able to achieve high catalytic activity (i.e. high total turnover numbers and initial reaction rates), among the highest values obtained for alternative electron delivery approaches using P450 BM3 enzymes. We are currently expanding the scope of reactivity of the hybrid enzymes and we will present our current efforts towards the light-driven oxidation of non-natural substrates as well as the application of the hybrid enzyme approach to other members of the P450 superfamily.

WRM 196

Understanding the Electron Reorganization along the Thermal Isomerization Reactions of Cyclobutenes. Origins of Inward Pseudodiradical Torquoselectivity.

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The thermal isomerization reaction of trans-3,4-dimethylcyclobutene (3,4-DMC) **1** to yield the isomer (2E, 4E)-hexadiene **2** have been studied using density functional theory (DFT) at the B3LYP/6-31+G level. For this reaction, two different channels of the conrotatory torquoselectivity allowing the formation of two isomers (E,E) and (Z,Z) have been characterized.

The isomer (Z,Z) occurs through the outward conrotatory mechanism, whereas the isomer (E,E) occurs through the inward conrotatory mechanism. The inward conrotatory is favored by 11.3 kcal/mol with respect to outward conrotatory one. This behavior is consistent with enthalpy, free energy and entropy values calculated for both reaction pathways. The topological analysis of the electron localization function (ELF) for the inward conrotatory transition state rationalizes the electronic reorganization as a process *pseudodiradical* {2n + 2p}, and not a pericyclic reorganization.

Acknowledgments

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References

1. Hulot, C.; Amiri, S.; Blond, G.; Schreiner, P. R. and Suffert, J. J. Am. Chem. Soc. 2009, 131, 16587–16587.
2. Fukui, K. Molecular Orbital in Chemistry, Physics and Biology, New York, 1964.
3. Criegee, R.; Seebach, D.; Winter, R. E.; Börtzen, B and Brune, H. A. Chem. Ber. 1965, 98, 2339.
4. Berski, S. ; Andres, J.; Silvi, B. and Domingo, L. R. J. Phys. Chem. A, 2003, 107, 6014–6024

WRM 197

In-Silico Combination of Docking, QM/MM analysis and MD Simulations for Tetrahydrobiopterin Analogous: Binding Towards Non-Heme Active Site of Phenylalanine Hydroxylase and A313T Mutant Type for Neurological Cascades

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Phenylalanine hydroxylase (PAH) belongs to BH₄ dependent aromatic amino acid hydroxylases enzyme family in which BH₄ is an important protein co-factor which promotes hydroxylation of neurotransmitters. Hence, BH₄ deficiency leads to imbalance in neurotransmitters synthesis and

thus causes neurological disorders. In present study we have utilized *in-silico* methodology for modifications in parent skeleton of nonreduced BH₂ on the basis combined analysis via Docking, QM/MM analysis and MD simulations, best pose of high affinity co-factor was obtained and QM/MM optimization leads to square-pyramidal coordination of non-heme active site. The specific recognition of protein target showing binding similarity of modified analogues with natural nonreduced co-factor. We have studied the binding of various structurally modified co-factor (dihydrobiopetrin) analogues with phenylalanine hydroxylase enzyme and its A313T mutant via docking studies. The altered co-factors were found to show interactions with important phenylalanine hydroxylases residues: Arg270, Glu280, Thr278, Pro279, Gly346, Ser349, Glu353, Val379 and Fe425. After the docking of these modified molecules with PAH molecules with high affinity were subjected for further analysis with the mutant phenylalanine hydroxylase enzyme. Hence, results suggested the therapeutic application of these modified co-factors. Also, for these metalloproteins, QM/MM and MD simulations analysis revealed the coordination environment of active site and thus depicted more descriptive abilities for it. The structural and energetic information obtained from the time-averaged MD simulation of co-factor-metalloprotein complex results that co-factor binding do not perturb the coordination environment of iron residing in 2-Histidine and 1-Glutamate triad. QM/MM optimization showed promising picture of active site QM environment which remained stable during simulations. Thus, we can conclude that these compounds could be potential selective co-factors of PAH amino acid hydroxylases that can be experimentally validated. Therefore, the acceptability of these analogues can be validated by synthesis and *in vitro* approaches to investigate their biological activity to validate our *in-silico* results.

WRM 198

Theoretical study of formation routes and dimerization of methanimine: implications for the aerosols formation in the upper atmosphere of Titan

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Methanimine is an important molecule in prebiotic chemistry since it is considered a possible precursor of the simplest amino acid, glycine, via its reactions with HCN (and then H₂O) or with formic acid (HCOOH). According to this suggestion, the simplest amino acid can be formed 'abiotically' starting from simple molecules relatively abundant in extraterrestrial environments, such as the interstellar medium, and, possibly, primitive Earth. Interestingly, methanimine has been observed in the upper atmosphere of Titan, the massive moon of Saturn. Methanimine can be produced in the atmosphere of Titan by the reactions of N (²D) with both methane and ethane, as well as by other simple processes, including the reaction between NH and CH₃ or reactions involving ionic species. Recent models derived a larger quantity of methanimine than that inferred by the analysis of the ion spectra recorded by Cassini Ion Neutral Mass Spectrometer. Growing evidence suggests that nitrogen chemistry contributes to the formation of the haze aerosols in the Titan upper atmosphere. In this respect, since imines are well-known for their capability of polymerizing, CH₂NH is an excellent candidate to account for the nitrogen-rich aerosols of Titan through polymerization and copolymerization with other unsaturated nitriles or unsaturated hydrocarbons. Since the first step of polymerization is dimerization, in this contribution we report on a theoretical characterization of methanimine dimerization. Electronic structure calculations of the potential energy surfaces representing the reactions of electronically excited atomic nitrogen, N(²D), with methane and ethane are also presented, as they are possible formation routes of methanimine under the conditions of the upper atmosphere of Titan.

WRM 199 - withdrawn

WRM 200

Charge transfer and ionic hydration

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Charge transfer (CT) is the shifting of small amounts of electron density ($< 0.1 e$) between non-bonded pairs. Intermolecular CT has remained largely unexplored, especially for systems which need to be studied using molecular dynamics (MD), i.e. those with large system size or long time scale events. For aqueous systems, CT becomes important when water's hydrogen bond symmetry is broken, for example in ionic solvation shell and at interfaces. A method for including charge transfer in MD simulations has been developed for water and ions. The method successfully predicts the (non-integer) ionic and (non-zero) water charges which are also found by ab initio molecular dynamics. The effects of CT on the ion solvation structure and ion adsorption to the liquid-vapor interface of water have been explored. The interface is investigated using an instantaneous surface definition, and how the curvature of the interface influences ion adsorption is also considered. Interesting results include charge distributions around ions and ionic effects on the long-range structure of water.

WRM 201

Theoretical investigation of OH reaction with Styrene

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Ab initio molecular orbital calculations have been conducted to investigate the reaction of styrene with hydroxyl radical. Both addition and abstraction reaction pathways were explored at the vinyl group of styrene molecule. The molecular structures of reactant, transition state, and products were located at the MP2/6-311G** level of theory, and the energetics of the reaction was estimated by single point calculation at MP4/6-311++G(2d,2p) level of theory using the geometry optimized at the MP2/6-311G** level of theory, with corrected zero-point energy (ZPE). The favorable pathway was found to be the addition of hydroxyl radical onto the double-bonded carbon atoms outside of benzene ring of the styrene molecule, which is consistent with the experimental observations. Reaction mechanism including the intramolecular migration of hydrogen of the OH-adduct products were also explored to give further insight on the experimental results observed from mass spectroscopy and infrared spectroscopy of the reaction products.

WRM 202

Efficient and precise techniques for parallelization of kinetic Monte Carlo techniques.

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The Kinetic Monte Carlo procedure, or BKL algorithm, is ideally suited for a wide variety of modeling challenges, such as activated process simulation. A careful theoretical treatment is required, however, to address parallelization challenges of the simulation, in both shared and distributed memory environments. We present an approach that builds on the synchronous KMC procedure, which advances the virtual time horizon in synchrony across multiple processors. We present a method that includes Markov Chain Monte Carlo techniques adapted to the KMC framework, and demonstrate that the procedure can be used to achieve highly precise synchrony while also preserving the underlying dynamics. The method is readily adapted to a wide variety of problems, and design considerations will be discussed.

WRM 203

Stability of oxidative products in Quinoa (*Chenopodium quinoa*) during accelerated aging

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The oxidative stability of lipids in processed quinoa was investigated in this study. Ground quinoa was subjected to accelerated aging for 30 days at 25, 35, 45, and 55°C. Three samples were removed from each temperature treatment every 3 days. Free fatty acids, conjugated diene hydroperoxides, and hexanal were used as indicators of lipid oxidation. Free fatty acids generally showed an increasing trend for the samples kept at 45 and 55°C over the period of the study, and a steady increase in conjugated diene hydroperoxides was observed at all four temperature treatments up to a maximum on day 9. However, all hexanal values dropped slightly at day 3, and

only minor fluctuations were observed over the 30-day sampling period for the 45 and 55°C samples. Storage time and temperature had significant effects ($p \leq 0.05$) on all three parameters, while the interaction between storage time and temperature was not significant for conjugated diene hydroperoxides produced. The results from these tests suggest that quinoa lipids are stable for the period of time studied. With vitamin E as a naturally antioxidant occurring abundantly in quinoa, the potential for quinoa to be a new oilseed could be enhanced.

WRM 204

Phytonutrient analysis of fresh and cooked *Yucca* (*Yucca whipplei*) fruit pods and blossoms

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Native Americans use the blossoms and pods of the *Yucca* plant (*Yucca whipplei*) as a food source. The study objective was to obtain information of cooking impacts on nutritional and compositional attributes of fruit pods and blossoms of *Yucca whipplei*, a traditional Native American plant. Samples of the *Yucca* plant parts were harvested from a reserve in Southern California. Samples were sorted for quality; field heat removed and half of the samples were then cooked simulating traditional Native American methods of parboiling blossoms and roasting pods. Samples were weighed into whirl pak bags, treated with liquid nitrogen, and placed in ultra-low storage at -80°C for 48 hours for further triplicate analyses of pH, moisture, total soluble solids (TSS), and pigments (total chlorophyll, total carotene). *Yucca* plant parts were tested for pH, which showed both fresh and cooked pods and blossoms were slightly acidic with an average pH of 6.2 for blossoms and 5.2 for pods. Moisture content results showed that the *Yucca* plant parts have relatively lower moisture levels (~85-90%) vs. other edible plants (~95-99%). TSS results showed sugar content (%Brix) higher in the cooked vs. fresh plant material; with roasted pods having an average of 8% Brix while fresh pods had an average 4% Brix. For pigments, samples were extracted in methanol and analyzed for total chlorophyll and total carotene levels using a UV/VIS-Spectrophotometer. This analysis showed that pods have more chlorophylls and carotenoids compared to blossoms. Cooked samples have more carotenoids than fresh samples with roasted pods having an average of 12.814 mg/g D.W. compared to fresh pods average of 10.335 mg/g D.W. The Folin-Ciocalteu method was used to measure phenolics content. The phenolic content is higher in fresh pods 245.76 mg GAE g/D.W. vs 198.06 mg GAE g/D.W. In summary, cooking influenced composition of the *Yucca* samples.

WRM 205

Compositional analysis of stinging nettle (*Urtica dioica*) leaves

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The objective of this study was to analyze the chemical characteristics of the Stinging Nettle (*Urtica dioica*) plant and compare the differences in content between the fresh and cooked samples of the nettle. Stinging nettle was harvested in Southern California in the Mockingbird Canyon Reserve, sorted for quality, cooled and placed in treatments (fresh, roasted). Half of the leaves were air roasted and the other half were left uncooked. The two treatment groups of Stinging Nettle leaves were then weighed, separated, and treated with liquid nitrogen before being stored in ultra-low freezer (-80C) for 48 hours. Post storage, samples of each set of leaves

underwent a series of tests in triplicates to analyze composition (moisture content, total pigment, pH, and other active compounds) and to see the difference, if any, in the composition of fresh versus cooked leaves. Instruments used in the analysis of the leaves included a UV/VIS-spectrophotometer, refractometer, vacuum drying oven, and pH meter. The Folin-Ciocalteu method was used for total phenolic content. The results showed that the cooked Stinging Nettle leaves resulted in higher levels of sugar (1.1% vs. 0.9% in fresh), carotenoid content (3.884 mg/g D.W. vs. to 3.015 mg/g D.W.), a slightly higher total phenolic content (169.57 mg GAE/g D.W. vs. 162.20 mg GAE/g D.W.) and pH (8.66 vs. 8.93). The fresh nettle showed higher moisture (69.29% vs. 59.32%). Overall, results showed that the cooking treatment of the Stinging nettle shows apparent increases in pigment, phenolic, and sugars (Brix percentage) likely due to moisture loss during cooking.

WRM 206

Esculeoside A content of commerical tomato varieties

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The availability of tomatoes as fresh and processed products year-round makes them one of mostly widely consumed agricultural crops. Besides appearance and taste, some consumer preferences for tomatoes are influenced by the potential health benefits associated with consuming tomatoes. Compounds found in tomatoes associated with health promoting properties and that are well known among consumers include lycopene, vitamin C, and the flavonoid rutin. Lesser known to consumers is Esculeoside A, a glycoalkaloid also reported to possess health promoting properties found in some tomato varieties at concentrations greater than lycopene. An C-18 HPLC method utilizing nitrogen chemiluminescence for the quantification of Esculeoside A was developed and the applied to the analysis of a selection of fresh and canned tomato products purchased from local grocery stores. The concentration of Esculeoside A ranged from 43.8 mg/g FW (Beef Steak) to 255.1 mg/g FW (Cherry), with a median concentration of 108.6 mg/g FW (vine ripe). The glycoalkaloid was not detected in canned tomato products. These results suggest that a single 90-gram serving of Cherry tomatoes could result in a dose of almost 23 mg of Esculeoside A.

WRM 207

Nutrient and organoleptic properties of 10 vintage tomato varieties

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With an increasing consumer focus on the purported health benefits of fruit and vegetable consumption, producers require a broader, more in-depth resource on which to base their crop selection and development. Vintage tomato varieties were grown in two field replicates, each of two consecutive years. Our survey includes °BRIX, the quantification of individual carbohydrates by HPLC, and the colorimetric determination of total sugar content. We also report vitamin C content, tritrateable acidity (TA), organic acid levels, and total soluble phenolics (TSP), as well as antioxidant activity by both DPPH and ABTS assays. Antioxidant results for all varieties averaged 85.3 µmol Trolox equivalents/ 100 g fresh weight (µmol TR eq/100 g FW) by DPPH assay, and 147.59 µmol TR eq/100 g FW by ABTS assay. In TSP results, Colusa was significantly lower than Beall's Gourmet and Red Pear varieties, with average values of 354.4, 424.4, and 468.2 µmol galic acid equivalents/100 g fresh weight, respectively. In the total sugars assay, varieties Colusa, Ramsay, Sun 1643, and NC 8288 were significantly lower than Beall's Gourmet and Red Pear (18,428; 20,926; 21,371; 22,249; 28,518; and 30,708 mg fructose equivalents/L, respectively). As individual carbohydrates, fructose was always higher than glucose, with Red Pear showing the greatest difference (+4,196 mg/L, average) and having the highest combined level (34,948 mg/L, combined). Florida 7060 showed the largest difference between citric and malic acid, with a 13:1 ratio. Red Pear was highest on average in both citric (5,035 mg/L) and malic acid (865 mg/L). Breeders and producers can use this information to make more informed decisions in their

selection, development, and testing of tomato crops to deliver a nutritious, consumer pleasing product.

WRM 208

Mesoporous materials for adsorptive desulfurization of JP-8 fuel

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The development of hydrogen fuel cells as portable auxiliary power sources is of particular interest to the U.S. Army. JP-8 fuel is an ideal hydrogen source as it is readily available to the Army, safe to store and transport while being energy dense. JP-8 also contains organosulfur compounds, however, that poison catalysts in the fuel reformers and fuel cells. Sorbents capable of bringing the sulfur content to < 1ppm_w that could be used under ambient conditions in the field would make these portable fuel cells a reality. In this work we explore the synthesis of different mesoporous metal oxide frameworks and their use as desulfurization sorbents. These mesoporous materials are loaded with a variety of transition metals to study their adsorption capacities and selectivity for organosulfur compounds. We will also report the reusability of our materials using solvent regeneration techniques.

WRM 209

Importance of tetrahydrobiopterin mediated interactions in aromatic amino acid hydroxylases enzymes family: Assessing effect on biosynthesis due to effect of single site mutation on thermodynamic stability of hydroxylases

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The mammalian aromatic amino acid hydroxylases (AAHs), including phenylalanine Hydroxylase (PheOH), tyrosine Hydroxylase (TyrOH) and tryptophan Hydroxylase (TrpOH), are involved in important metabolic pathways neurotransmitters. Subsequently, defects in biosynthetic pathway have been reported in various neurological disorders such as phenylketonuria, Parkinson's disease, neuropsychiatric syndromes. The lower activities of these enzymes results into lower levels of catecholamine in various neurological diseases states including depression, hypertension and schizophrenia. Therefore, biosynthesis of neurotransmitters is important to study for the identification of aspects of defects in the pathways. In the present study we have utilized single site mutation induced effects on three aromatic amino acid hydroxylases of the metabolism pathway to study effects on biosynthetic pathways. Thus we have utilized atomic coordinates of AAHs, 1MLW, 1DMW, 2TOH and ternary complex, 1MMK from RCSB PDB. The resulting thermodynamic stability of these hydroxylases due to folding energy changes ($\Delta\Delta G$) in wild type and mutated protein was obtained along with total energy of the system. In all four cases, we have analysed two sets for each desired residue: one with highest (+) and lowest (-) $\Delta\Delta G$ (kcal/mol) values. Further preliminary docking studies were done to obtain protein-ligand interactions for mutated residues. MM-GBSA and metadynamics evaluation on most stabilizing and high scored mutation was done for analysis of BH₄ binding, iron coordinated active site, substrates specificity determinates residues. Therefore, a reasonable choice of collective variables for investigating conformational changes due to the mutation is provided by the backbone torsion angles phi and psi of the aromatic residues involved in co-factor binding which were later mutated to non-aromatic residues. Metadynamics analysis investigated more adequately the effect of mutations on the local structure and stability of the co-factor as confirmed from free energy surface.

WRM 210

Inhibition of stearyl-CoA desaturase drives uptake of exogenous fatty acids and sensitizes glioblastoma cells to lipoapoptosis

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Fatty acid synthase (FAS) is a multi-enzyme complex attributed with de novo construction of fatty acids from acetyl-CoA. FAS has been shown to be minimally expressed in normative adult tissue and cell lines, but has been shown to be active in malignant and benign neoplastic tissues. Elevated levels of fatty acid synthase in clinical samples of cancer have been associated with high pathologic tumor grades and poor clinical outcomes for numerous tumor types. These observations have led to the development of FASN inhibitors as potential cancer drugs. Through inhibition of FAS and related enzymes, pre-clinical trials demonstrated drugs targeting lipogenesis slow neoplastic cell growth. The sole product of FASN, palmitic acid, like other long chain fatty acids, has been shown to be cytotoxic. The toxicity of palmitic acid is ameliorated intracellularly by stearyl-CoA desaturase (SCD), resident in the endoplasmic reticulum, that converts saturated long chain fatty acyl-CoA into monounsaturated fatty acyl-CoA. In particular U-251 and U-87 derived glioblastoma multiforme (GBM) human cell-lines have been previously shown to express high levels of FAS. Maintenance of fluidity of cell membranes is largely dependent upon relative concentrations of saturated and unsaturated fatty acids. Stearyl-CoA Desaturase (SCD) is a key enzyme in catalyzing the desaturation of de novo endogenous fatty acids most commonly at the 9th carbon terminus and SCD is ubiquitous in human cells. We present data that expresses cultured GBM cell lines are sensitized to lipoapoptosis induced both by exogenous heptadecanoic acid as well as by the accumulation of endogenous monounsaturated fatty acids through SCD inhibitor CVT-11127.

WRM 211

Development of Benzotriazine Oxides targeting replicating and non-replicating M. tuberculosis

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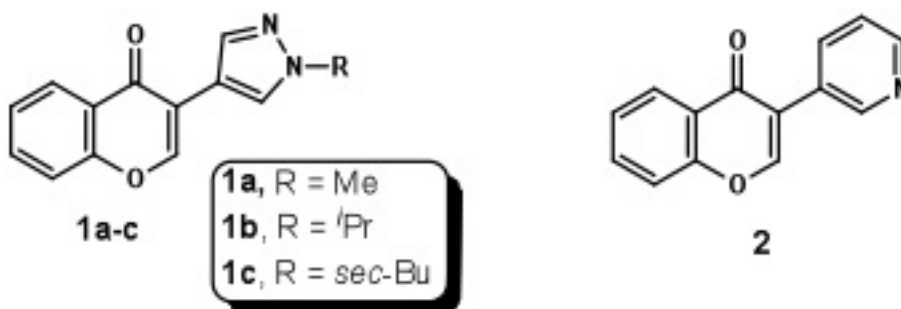
New classes of drugs are needed to treat tuberculosis (TB) in order to combat the emergence of drug resistance to existing agents and shorten the length of therapeutic regimens. Compounds that are bactericidal against both replicating and non-replicating *Mycobacterium tuberculosis* (Mtb) are particularly of interest because they may shorten the length of TB treatment regimens by eliminating infections more rapidly. Screening of a panel of antimicrobial and anticancer drug classes that are bio-reduced into cytotoxic species revealed that 1,2,4-benzotriazine di-N-oxides (BTOs) are potentially bactericidal against replicating and non-replicating Mtb. Medicinal chemistry optimization, guided by semi-empirical molecular orbital calculations, identified a new lead compounds from this series with an MICs < 0.5 µg/mL against H37Rv and a cytotoxicities (CC₅₀) against Vero cells of > 25 µg/mL. These leads also have equivalent potency against a panel of single-drug resistant strains of Mtb and remarkably selective activity for Mtb over a panel of other pathogenic bacterial strains. The BTOs have also been shown to have a very low frequency of resistance and are not antagonistic to the two frontline TB antibiotics, isoniazid (INH) and rifampin (RIF). An evaluation of the pharmacokinetic (PK) properties for the series indicates that most compounds are rapidly absorbed after PO dosing and have good bioavailabilities. The terminal elimination half lives of the compounds were shorter than our targeted values for once-a-day dosing and will require further optimization. These data along with measurements of the physiochemical properties demonstrate that BTOs have promise for the development of a new class of antitubercular drugs.

WRM 212

Synthesis of Azagenisteins for the cytotoxic evaluation towards Prostate Cancer Cell Lines

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Prostate Cancer is the second-leading cause of cancer-related deaths in the United States. Approximately 30,000 men die each year of hormone-refractory prostate cancer. There is no effective therapy when prostate cancer becomes metastatic and refractory to conventional treatments. Genistein, mainly isolated from soybeans, exhibited potential to prevent and treat prostate cancer. The barrier of genistein as a clinical treatment is due to its poor bioavailability. With the aim to develop improved genistein analogs for the treatment of advanced hormone-refractory prostate cancer, we have designed a series of heteroaromatic analogs of genistein. So far, we have successfully synthesized four target compounds including three new pyrazole analogs (structures **1a-c**) and one pyridine analog (structure **2**). Synthesis of the genistein analogs was achieved by Suzuki-Miyaura coupling reaction of the corresponding arylboronic acid (or boronic ester) with 3-iodochromone, catalyzed by a palladium (0) complex. The cytotoxicity of the synthesized genistein analogs will be evaluated against two human androgen-independent prostate cancer cell lines (PC-3 and DU-145). The design and synthesis of these heteroaromatic analogs of genistein will be presented.



WRM 213

Hit to lead discovery of novel N-methylated imidazolo-, pyrrolo-, and pyrazolo-pyrimidines as potent and selective mTOR inhibitors

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A series of N-7-methyl-imidazolopyrimidine inhibitors of the mTOR kinase have been designed and prepared, based on the hypothesis that the N-7-methyl substituent on imidazolopyrimidine would impart selectivity for mTOR over the related PI3K α and δ kinases. The corresponding N-Me substituted pyrrolo[3,2-*d*]pyrimidines and pyrazolo[4,3-*d*]pyrimidines also show potent mTOR inhibition with selectivity toward both PI3K α and δ kinases. The most potent compound synthesized is pyrazolo[4,3-*d*]pyrimidine **G-332**. Compound **G-332** shows a K_i of 1 nM against mTOR inhibition, remarkable selectivity (>2800/ >8000 \times) over PI3K α and δ kinases, and excellent potency in cell-based assays. When this work was done, a homology modeled was used built from three relevant PI3K gamma X-ray structures. There was a 21-24% sequence identity overall but significant correspondence in the ATP site. Recently the crystal structure of mTOR was published in the journal Nature(below) which validated our homology model.

Delivering large quantities of high purity compounds in the shortest possible time is the goal of a purification chemist. Two of the most popular purification techniques are Automated Flash Column Chromatography (AFCC) and Preparative HPLC. Traditionally, AFCC is characterized by the ability to load large amounts of material and short purification times, while Prep HPLC is valued for high resolution separations resulting in very pure products. As a result, AFCC is typically used as a complementary technique whereby the crude sample is enhanced to a higher level of purity before final purification using Prep HPLC.

With the recent advances in AFCC instruments and cartridges, the gap between 'high speed' flash purification and 'high efficiency' Preparative HPLC purification is rapidly shrinking. In many cases AFCC can deliver large quantities of product comparable in purity to Prep HPLC, with significantly less time and expense.

In this study, we evaluate the productivity advantages of AFCC over Prep HPLC, in terms of time, solvent and cost savings. We also demonstrate the benefits of AFCC both as a complementary technique to Prep HPLC, as well as a highly versatile stand-alone technique to deliver high purity separations in a cost-effective manner.

WRM 216

Discovery and optimization of small molecule AMPK activators

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Adenosine monophosphate-activated protein kinase (AMPK) is an essential regulator of cellular energy homeostasis. It exists as a heterotrimeric protein consisting of three subunits (α , β , and γ) that make the functional enzyme and is expressed in a number of tissues, including the brain, liver and skeletal muscle. AMPK activation stimulates hepatic fatty acid oxidation, inhibits cholesterol and triglyceride synthesis and modulates insulin secretion. We have identified and optimized a number of low nM small molecule activators of AMPK. In both cell culture and *in vivo* studies, our lead compound, structure 25, reduces liver fat content, enhances glucose uptake in cells and increases Glut4 expression in muscle tissue resulting in lowering blood glucose and insulin levels in both *db/db* and diet-induced-obesity (DIO) mice.

WRM 217

Novel quinolone inhibitors of NS5B Polymerase

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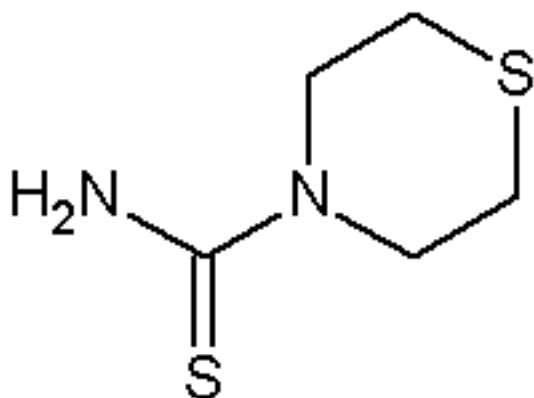
NS5b is a key enzyme in the Hepatitis C viral life cycle. The use of small molecule inhibitors of NS5b, alone or in combination with other HCV anti-viral compounds, has been clinically effective in treating HCV. A class of small molecule quinolones has been reported to be potent inhibitors of NS5b. We have designed, synthesized and tested a series of molecules based on this quinolone structural class that explores novel SAR at the C7 carbon.

WRM 218

Synthesis and characterization of an anti-tubercular Benzothiazinone derivative

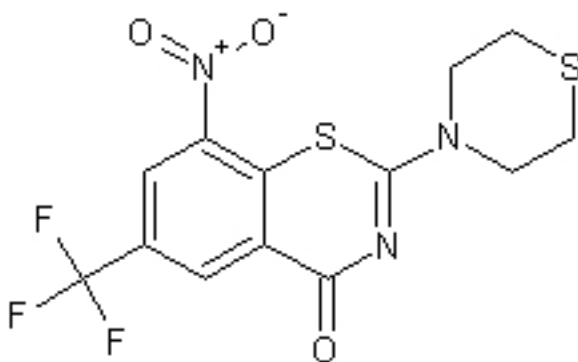
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Benzothiazinones are among the small group compounds that have activity against mycobacteria. BTZs are suicide substrate inhibitors of DprE1 and DprE2 enzymes. These enzymes lead to the production of mycolic acids that are essential to the mycobacterial cell wall. Analyzing the interaction of BTZ in the binding pocket, it is apparent that the R-group on the 2nd ring of BTZs is unspecific and can be changed to grant higher lipophilicity and possibly higher activity. A novel synthesis was devised to increase the lipophilicity and see what other effects may take place. The compound to introduce the R-group was synthesized using benzoyl chloride and yielded thiomorpholine-4-carbothioamide.



thiomorpholine-4-carbothioamide

In BTZ synthesis the starting compound was AR-96, which is 2-chloro-3-nitro-5-(trifluoromethyl)benzoic acid. It was reacted with the thiomorpholine-4-carbothioamide to yield the final BTZ SB-2.



BTZ SB-2

Both the SB-1 and SB-2 compounds were confirmed by ^1H NMR and ESI mass spectrums. Solubility and MICs will be taken and then will be compared to other BTZs.

WRM 219

Evaluation of Aloe and Cactus for burn treatment by comparison of anti-oxidant properties and free radical inhibition.

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There has been a great interest in natural compounds, which can help with problems faced in the medical field. There are many plants, which are used by indigenous populations for the treatment of skin disorders including Aloe Vera and other succulents, which are high in antioxidants.

Antioxidants play major role in various aspects of health from the reduction of wrinkles all the way to the treatment of burn victims. The goal of this research is to identify and examine the

antioxidant powers of fresh and lyophilized Aloe Vera and Nopal Cactus. These natural extracts were then compared with over the counter burn treatments. The compounds of interest were extracted with acidified methanol using both Solid-Liquid extraction as well as Soxhlet extraction. The functional groups of the extracts were identified by using Fourier Transform Infrared Spectroscopy as well as Ultraviolet-Visible Spectroscopy. Once the compounds were identified, Total Phenolic Content and 2,2-diphenyl-1-picrylhydrazyl radical assay were performed which was used to quantify the amount of phenolic compounds present as well as the antioxidant powers of the extracted compounds -- all results being compared to the results of the burn cream. The intention of this ongoing research is better understand the chemistry involved in topical antioxidants.

WRM 220

Improved isolation and purification of natural products by automated flash chromatography

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Natural products can play an important role in the development of new drugs for medicinal purposes. A crude extract typically contains lead compounds among many other components in the matrix, requiring multiple steps to isolate and purify. Conventional flash purification techniques can fail to detect those compounds that are non-chromophoric or lack the necessary sensitivity often required for detection of low level components. Advances in automated flash purification system technology, including the integration of evaporative light scattering detection, have given chemists the ability to purify samples containing both chromophoric and nonchromophoric compounds with much greater speed and efficiency than previously possible. In this work we demonstrate the benefits of integrated evaporative light scattering detection for flash purification of several naturally-derived samples.

WRM 221

Combustion Products of Ethyl Tert-Butyl Ether using Synchrotron Photoionization

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The photolytically initiated oxidation reaction of ethyl tert-butyl ether (ETBE) was carried out at the Advanced Light Source located in the Lawrence Berkeley National Laboratory. Using the multiplex photoionization mass spectrometer data were collected at the low pressure (4 Torr) and temperature (298 – 700 K) regimes. Data analysis was performed via characterization of the reaction species photoionization spectra and kinetic traces. A reaction schematic including branching ratios determination is presented as discussed.

WRM 222

Investigation of methyl & ethyl formate combustion reactions by photoionization mass spectrometry

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Simple esters methyl formate and ethyl formate are considered possible biofuels because of their combustion characteristics, as well as low environmental impact. The combustion reactions of methyl and ethyl formate have been investigated using pulsed-photolytic CI-initiated oxidation with analysis of reactions by time-resolved tunable synchrotron photoionization mass spectrometry under low-pressure (4 Torr) and temperature range of 293-700 K. Formation of formaldehyde was observed for reactions of methyl formate, while reactions with ethyl formate saw formation of propene and acetaldehyde. Branching fractions are calculated, showing formation of major products from internal hydrogen abstraction chemistry.

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Photocatalytic Properties of Oriented, {001} Faceted Anatase TiO₂ Films

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The photocatalytic properties of oriented, (001) faceted anatase films were investigated under UV-A light using terephthalic acid (TA) as a hydroxyl radical ($\dot{\text{Y}}\text{OH}$) trapping molecule and the generated 2-hydroxyterephthalic acid (TA-OH) adduct as a fluorescence probe. The anatase films were prepared by hydrothermal synthesis onto gold and titanium substrates that were evaporated onto silicon (Au/Si) and Pyrex (Ti/SiO₂) respectively. It was found that annealing the anatase films at 600 °C lowers the effectiveness of $\dot{\text{Y}}\text{OH}$ production suggesting that this high temperature treatment increases the probability of e^-/h^+ recombination both on the surface and in the bulk. High temperature annealing improves crystallinity and decreases trap states for photogenerated charge carriers. Under ambient air and O₂, it was found that the anatase films generate sufficient $\dot{\text{Y}}\text{OH}$ radicals compared to the reference material, P-25, which typically expresses (101) surfaces. After surface areas were normalized using AFM and defect count analysis, the photocatalytic efficiency of the anatase films was considered to be greater than the P-25 films on a surface area normalized basis. In the absence of O₂ via Ar purging, it was found that the anatase films generate considerably less $\dot{\text{Y}}\text{OH}$. This suggests that the (001) facet is reductive and that O₂ is needed to produce $\dot{\text{Y}}\text{OH}$. However, P-25 films generate near equivalent amounts of $\dot{\text{Y}}\text{OH}$ under both aerated and deaerated conditions showing that the mechanism of $\dot{\text{Y}}\text{OH}$ formation for this material is different from the (001) faceted anatase films. Finally, it was found that anatase films synthesized on Ti/SiO₂ generate more $\dot{\text{Y}}\text{OH}$ than those synthesized on Au/Si suggesting that on an insulating substrate, photogenerated e^-/h^+ pairs in the bulk migrate more readily to the (001) surfaces to take part in photochemical reactions.

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Studies of non-Kekule heterocycles

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Ovchinkov's rule provides a simple way of predicting the ground state of non-Kekule hydrocarbons. To complement our studies of verdazyl free radicals and verdazyl containing ligands, we have been investigating how the presence of heteroatoms affects the predictions of Ovchinkov's rule. We report here our results with non-Kekule molecules based on pyrimidine and other nitrogen heterocycles

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Controlling photochemical electron transfer in rhodium-doped strontium titanate nanoparticles through surface modification

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The electrochemical properties and energetics of the photocatalyst material Rhodium-doped Strontium Titanate (Rh:SrTiO₃) have been tuned by modifying the nanoparticle surface with metal/metal-oxide particles (Cr,Rh). Effects of these modifications were investigated using cyclic voltammetry, surface photovoltage spectroscopy (SPV), and diffuse reflectance spectroscopy (UV-vis). Our data shows that the photovoltage and photo onset potential of Rh:SrTiO₃ nanoparticles can be adjusted by introducing metal/metal-oxide particles at the surface through simple aqueous deposition methods. The results of this study have possible impacts on the field of solar energy conversion with nanomaterials.