Saturday afternoon – Abstracts 349 - 395

WRM 349

Nanodiamonds and taxon-specific biomarkers for mapping tight-shale sweet spots to optimize hydrocarbon production from fracking and for delineating mixed-source oil production

J. Mike Moldowan[1]*, moldowan@stanford.edu, Jeremy E. Dahl*[2]*. (1) Biomarker Technologies, Inc., Rohnert Park, CA 94928, United States (2) Laboratory for Materials & Energy Science, Stanford University, Stanford University, CA 94305, United States*

It is important in petroleum exploration to determine the source(s) of the known petroleum reserves. Advanced exploration geochemistry employs GC-MS-MS and GC-isotope-ratio-MS data to enhance the recognition of oil sources and potentiate the recognition and de-convolution of frequently occurring mixed oil. Understanding mixtures of thermally-cracked oil and non-altered oil requires particular attention.

The thermal conversion of oil to gas (oil-cracking) is critically important for determining tight-shale producibility by hydro-fracking, but is poorly estimated by using standard geochemical parameters. Diamondoid concentrations in tight shale core and cutting samples provide the only readily available direct indication of the extent of natural oil cracking. Diamondoids are hydrogen-terminated nanodiamonds present in all source rock extracts and oil. They have high thermal stability like macro-diamond making them ideal natural internal standards for studying oil cracking.

Liquids production by lateral drilling and fracking are most highly indicated where there is an intermediate amount of oil cracking. High levels of oil cracking mark regions of dry gas production with very little associated liquid. Furthermore, it has been shown by SEM that some types of shale may reach maximum porosity in the wet gas window (partial oil-to-gas cracking). This situation would allow for the optimal hydrocarbon production.

The estimated percentage conversion of oil to gas in the shale, which can be determined by diamondoids and corroborated by biomarker analysis, allows the natural internal pore pressure to be calculated. Our results show that if no hydrocarbons can escape from the rock, natural oil cracking can result in pressures exceeding those used to hydro-fracture the rock.

It is possible to map those regions where little or no production is possible, those where the shale will be productive but from only gas, and those regions where both gas and liquid can be produced and where adjacent oil fields might be found.

WRM 350

Mass spectrometric methods for studies of nicotine metabolism and tobacco carcinogen exposure: Applications in clinical research

Peyton Jacob*, peyton.jacob@ucsf.edu. Division of Clinical Pharmacology, University of California, San Francisco, San Francisco, California 94143, United States*

Despite education about the hazards of tobacco and the success of smoking cessation programs, smoking and exposure to secondhand smoke are still major public health problems worldwide. Measuring human exposure to nicotine, its metabolites, and various toxic substances in tobacco smoke is important for studies of tobacco dependence and its health consequences, for development of new tobacco dependence therapies, and for studies of secondhand smoke exposure needed to provide the scientific basis for public health policy.

Mass spectrometry is playing an increasingly important role in studies of nicotine pharmacology and tobacco toxicology. In this presentation, some recent applications of mass spectrometry in multidisciplinary clinical research will be discussed. These will include quantitative chromatographic – mass spectrometric methods in studies of individual differences in nicotine metabolism, studies of secondhand smoke exposure and its effects on symptoms and outcome of chronic and acute disease, and studies of carcinogen exposure in hookah smokers.

[Figure1]

WRM 351

New methods for solving fundamental challenges in Mass Spectrometry using DMS - Ion Mobility

***Elliott Bradley Jones**, elliott.jones@absciex.com.LCMS, ABSCIEX, 1201 Radio Rd, Redwood Shores, California 94065, United States*

Mass Spectrometry has evolved towards higher degrees of selectivity to solve limiations of mass analyzer resolution. One of the most promising hybrid technologies is coupling Mass Spectroscopy to Ion Mobility. A number of new configurations of Mass Analyzer and Ion Mobility have become commercialized in the last 5 years allowing for powerful new and advanced workflows. The benefit of this type of system is the ability to separate ions based on charge, chemical properties as well as mass differences. DMS (Differential Mobility System) affixed between the ionization source and the mass analyzer interface allows for species separation before entrance into an ion path. The power of this system allows for gas phase fractionation of the ions, thus providing a level of selectivity before MS and MS/MS of the species. Furthermore, the DMS technology is compatible with addition of volatile modifiers to further affect the analyte cluster states. The clustering and de-clustering of the modifiers with the analytes will amplify their mobility differences, thus enhancing their separation and increasing the overall peak capacity. This selectivity approach enhances MS workflows by eliminating interferences, improve signal-to-noise, provide faster potential HPLC separations, reduce sample preparation and provide better accuracy in analyte measurements. DMS is also showing great promise in application areas of key LCMS challenges such as lipids and endogenous metabolites. A brief overview of theory and technology as well as examples of interesting application data will be presented in this work.

WRM 352

Analysis of polar compounds using HPLC-MS

***Joseph J. Pesek**, joseph.pesek@sjsu.edu, Maria T. Matyska. Department of Chemistry, San Jose State University, San Jose, CA 95192, United States*

Biological, physiological, forensic, pharmaceutical, clinical and environmental samples are often complex so that it is necessary to have a means to separate them (chromatography) coupled to a method for identification (mass spectrometry). The presentation will focus on a new type of LCMS technology related to analysis of small polar molecules that are often challenging for traditional reversed-phase separation methods. The approach for analyzing these types of samples is referred to as aqueous normal phase (ANP) chromatography. This mode has the advantage of having both reversed-phase and normal-phase retention. The principles of ANP chromatography will be described in order to differentiate it from other separation modes. The types of columns that can retain both hydrophobic and hydrophilic analytes will be presented illustrating the versatility of the ANP methodology. In addition, examples of challenging applications, particularly those involving polar analytes, using recently developed methods with an emphasis on MS detection will be reviewed.

WRM 353

Automated Sample Prep, Ultra Fast Mass Spectrometry and Cloud Based Informatics Accelerate Modern Assay Development

***Kevin Krock**[1], kmkrock@shimadzu.com Jared Russel[1], Chris Gillies[2], Scott Kuzdzal[2]. (1) Shimadzu, Pleasanton, California 94566, United States (2) Shimadzu, Columbia, MD 21046, United States*

From environmental screening to clinical research, modern mass spectrometers provide highly selective and sensitive measurements. Increasing the throughput of LC-MS assays requires innovative technology to overcome loss of sensitivity, poor reproducibility, and cross talk at fast measurement speeds. The development of exceptional triple quadrupole scan speeds of 30,000 u/sec and the ability to perform polarity switching in 5 msec enables researchers to fully utilize the capabilities of UHPLC to develop faster and more informative assays. Applications of attogram sensitivity of ultra fast mass spectrometry will be presented.

This presentation will also show how manual, bench-top sample preparation steps used in protein analysis and peptide based SRM assays can be replace with a faster, more reproducible, fully-automated sample prep platform that incorporates cloud-based informatics. Incorporating the Perfinity Workstation dramatically increases assay reproducibility while enabling complete

digestion of plasma/sera samples in less than six minutes. A traditional peptide-based SRM sample prep workflow taking over 18 hours can now be performed in approximately 40 minutes, offering exciting new opportunities for future clinical chemistry and emergency department diagnostic assay development. Application to cardiac ischemia diagnostic assay development and future immuno-MS applications will be demonstrated.

WRM 354
The Story of ETS Laboratories
Gordon Burns, *gburns@etslabs.com. President and Technical Director, ETS Laboratories, Saint Helena, California 94574, United States*
ETS was established in 1978 by Gordon and Marjorie Burns, in the basement of their Main Street home, to provide the rapidly expanding California Wine Industry with technical assistance and laboratory support. At first, ETS concentrated on microbiological issues and routine chemical analyses.
As the industry developed in size and complexity, winery clients looked increasingly to ETS for more advanced analytical services. ETS responded by investing in modern equipment and facilities and hiring highly trained technicians and researchers. This effort allowed ETS clients to benefit from the latest in technological advances. Today ETS is one of the most advanced wine analysis laboratories in the world.

WRM 355
Stories from a Chemist/Chemical Engineer of several Life Science startups
Greg T Went, *gwent@adamaspharma.com. Adamas Pharmaceuticals, Inc., Emeryville, CA, United States*
Three things are needed to start and grow a successful company. To varying degrees, all have been present in the life science start-ups that I have founded across a variety of fields, including DNA analysis and genomics (CuraGen, Parallele), protein engineering/therapeutics (Catalyst Biosciences, Angelica), proteomics/diagnostics (Tethys), and drug delivery/combinations (Adamas). In this talk, I will outline what those three things are, and how to assess them, to help demystify the decision process.
Starting companies grew out of two of my intense desires: first, the love of simply figuring out something and second, working in teams. These themes led me to study chemical engineering, ultimately receiving a PhD in the field. The choice of school, research director, and focus on spectroscopy all derived from these desires. Starting companies to make a living turned out to be a logical, rewarding, and, albeit, highly risky path.

WRM 356
Apexigen - a spin-out story
Mark Nevins, *mnevins@apexigen.com. Business Development, Apexigen, Inc., Burlingame, California, United States*
Apexigen is a biopharmaceutical company in Burlingame developing monoclonal antibodies for the treatment of serious diseases. Created as a spin-out in July of 2010, Apexigen began its life with a license to a platform antibody technology, several preclinical stage drug programs, collaborations with companies in China and a small amount of cash. Today, two products are in Phase 1 clinical trials by its partners, two additional INDs have been filed, the lead immunomodulatory antibody for the treatment of cancer is moving toward IND filing, and a total of eight collaborations are in place. Recently Apexigen announced the conclusion of a series A1 funding of $20 million.

WRM 357
Start-up challenges: The Story of Mango Materials
Molly Morse, *molly@mangomaterials.com. CEO, Mango Materials, California, United States*
Mango Materials, a California-based start-up company, produces biodegradable plastics from waste biogas (methane) that are economically competitive with conventional petroleum-based plastics. Mango Materials uses excess methane gas from wastewater treatment plants or landfills

to produce a valuable polymer that is converted into a variety of high margin or high volume, eco-friendly plastic products such as children's toys, electronic casings, water bottles, and food packaging containers. Due to a rising preference for green products from both consumers and government agencies, demand for biodegradable and non petroleum-based plastics is growing rapidly. The competition uses either petroleum, which is low cost but produces non-biodegradable plastic, or sugars, which are expensive but produce biodegradable plastic. In contrast, Mango Materials uses affordable methane gas and a process that competes favorably with petroleum-based plastics to produce low-cost, biodegradable plastics. This technology gives methane producers another profitable use for their waste biogas while transforming a greenhouse gas into a valuable commodity.
Using funding from the National Science Foundation and DOEN Foundation and partnerships with USDA-ARS in Albany and SBSA in Redwood City, Mango Materials has scaled up the process from microliters to tens of liters and is working to produce commercial samples. This presentation will discuss the effort Mango Materials' team is putting into starting a company in the bioplastics space.

WRM 358
Is it worth starting your own company?
K Paulvannan, *kpaulvannan@tandemsciences.com. Tandem Sciences, Menlo Park, CA, United States*
Tandem Sciences is a chemistry contract research company located in Menlo Park. The challenges we faced and lessons we learned from starting this company with our own savings will be discussed.

WRM 359
From Full Time Employment to Consulting - Strategies for Successful Transition
Daniel E Levy, *del345@gmail.com.DEL BioPharma, San Mateo, California 94402, United States*
In today's difficult economy, many sectors have been impacted. Among the hardest hit are the biotechnology and pharmaceutical industries. With an unemployment rate disproportionate to the national average, these sectors present significant challenges to those wishing to contribute to the development of innovative solutions to healthcare problems. Utilizing and developing skills such as managing CRO activities, leveraging services for resources, networking and marketing, opportunities can be created leading to the development of successful consulting practices.

WRM 360
Anyone can do it…the democratization of the distribution of educational tools
Mark A Bishop, *mbishop@miis.edu. Department of Chemistry, Monterey Peninsula College, Monterey, CA 93940, United StatesNonproliferation and Terrorism Studies, Monterey Institute of International Studies, Monterey, CA 93940, United States*
Because of the development of easy-to-use computer tools (InDesign, Illustrator, Photoshop, Dreamweaver, Flash, Camtasia, etc.), easy access to the Internet for most students, and growing acceptance of electronic educational tools, including textbooks, it has become possible for individuals to develop and distribute educational materials without the aid of the large academic publishers. In my talk, I'll describe the evolution of my project, which includes two versions of my textbook (*An Introduction to Chemistry)* in several formats, including regular printed books and various forms on the Net: PDF, EPUB (for iPhones, iPads, and Android devices), MOBI for Kindle, and Flash-based PowerPoint-like presentations with me reading the text. I'll also briefly describe my book's many supporting tools, including animations, tutorials, online lectures, and more. All of these tools except the printed books are freely available with no user names or passwords at preparatorychemistry.com. The main goal of my talk will be to explain how you can do some or all of the things I've done. I'll describe the tools you'll need, where you can get them at the lowest cost, and some idea of the time it will take to create your own materials.

WRM 361

Drawing every electron and considering orbitals in chemical structures using Formularrows, a stepping stone language to Lewis structures

Julie Newdoll, *julie@brushwithscience.com. Brush with Science, San Carlos, CA 94070, United States*

A method for drawing chemical structures called Formularrows, which requires the student to fully understand what they are representing, will be introduced. Methods for using Formularrows to impart deeper understanding of the material, and making a transition to Lewis structures will be suggested.

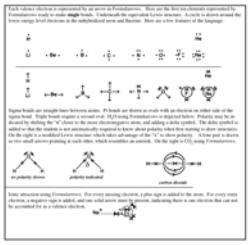
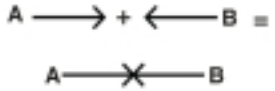
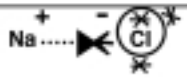
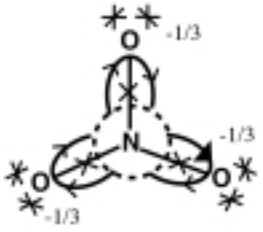
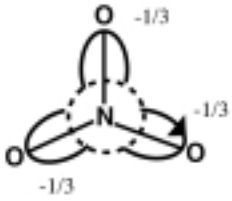


Table 1
Summary of Formularrows Symbols

Longhand symbol	Shortcut or alternate method	Description
		A bond where two atoms A and B are sharing one pair of electrons.
		Lone pair. Small version of two arrows meeting.
		Two lone pairs.
		A double bond between two atoms.
		A triple bond between two atoms.
		An extra charge in the system.
eg. 		Ionic bond attraction.
		Delta symbol used when location of electron arrowheads, the "x" on a bond, are to indicate polarity.
		Dative bonds.
 eg:		Delocalized orbitals are broken/ dashed circle around atom in question. There is one solid triangle per extra unit of charge in the system, and text is used to indicate atoms with additional charge where appropriate.
		Formularrows "pushing arrows" equivalent. Wavy line indicates newly forming bond.
		Two methods for drawing benzene. Symmetrical method uses "half electrons" on the right.

WRM 362
Implementing a free online homework system for first semester general chemistry
William J W Miller, *millerb@scc.losrios.edu. Department of Chemistry, Sacramento City College, Sacramento, CA 95822, United States*

Starting with QBank, a database of mainly multiple-choice questions available from the Journal of Chemical Education Digital Library, I have implemented an online homework system within my college's course management environment, Desire2Learn. This system allows multiple attempts at each question set of between 6 and 10 separate questions. In addition, approximately 50 new question sets (300 total questions) have been created. The majority of these newly created questions require numerical answers or contain chemical structures that must be interpreted, two things that are generally lacking in QBank. This system has been class-tested for two semesters. In this presentation, an overview of the process for implementation will be presented, including specific examples of the types of questions that have been created and the pros and cons of this system as compared to other commercially available online homework systems.

WRM 363

Online Homework with Targeted Instructional Feedback Leads to Improved Student Learning Outcomes

Scott Cowley, *scowley@mines.edu. Department of Chemistry & Geochemistry, Colorado School of Mines, Golden, CO 80401, United StatesSapling Learning, Austin, TX 78701, United States*

A disadvantage of out-of-classroom assignments is the lack of feedback available to students as they work through each problem. Consequently, instructors have become increasingly interested in online homework. While many homework systems offer similar advantages, such as online grading, and student statistics, few offer targeted instructional feedback that is proven to help students succeed in the classroom. Several efficacy studies were conducted to investigate the benefits of using Sapling Learning, an online homework system that offers “surrogate tutoring” feedback. When students were asked “would you like to use online homework again”, over 90% of those who had used Sapling Learning responded favorably. Furthermore, the ratio of successful to unsuccessful grades increased significantly when Sapling Learning was utilized. Another study observed that student engagement in Sapling Learning was positively correlated with their overall grade. This presentation will further discuss the benefits of using an online homework system with surrogate tutoring feedback.

WRM 364

New chemical methods for the selective, on-resin N-methylation of cyclic peptides to generate compounds with improved membrane permeability

Scott A Lokey, *slokey@ucsc.edu. Department of Chemistry, University of California Santa Cruz, Santa Cruz, California 95064, United States*

There has been a renewed interest in bioactive cyclic peptides and peptidomimetics, and new synthesis and screening technologies have enabled the discovery of potent macrocycles against a wide variety of biological targets. But while many cyclic peptides found in nature have suprisingly good cell permeability and even oral bioavailability, endowing synthetic cyclic peptides with “drug-like” permeability and pharmacokinetic properties has been relatively hit-or-miss. Cyclic peptide natural products often share a common chemical feature, backbone N-methylation, which serves to enhance lipophilicity and proteolytic stability, and our group has been interested in uncovering the relationship between N-methylation and membrane permeability. I will present new chemical methods for the selective, on-resin N-methylation of cyclic peptides to generate compounds with improved membrane permeability. I will also show unpublished results detailing the interplay of N-methylation and side chain functionality on cell permeability in cyclic octapeptides with molecular weights over 1000.

WRM 365

Natural products from the human microbiota

Mohamed Donia, *mohamed.donia@ucsf.edu. Department of Bioengineering and Therapeutic Sciences, University of California, San Francisco, San Francisco, CA 94158, United States*

The human microbiota is composed of hundreds of bacterial species covering all exposed surfaces of the human body. To date, very few studies have explored the microbial interactions within this complex environment and between the microbes and their human host. Natural products often mediate microbe-microbe and microbe-host interactions, as previously shown in

many symbiotic relationships. Here, we show that the human microbiome encodes a diverse array of complex natural products that mediate microbe-microbe interactions. These natural product pathways are widespread in almost all sites of the human body and are harbored by both commensals and pathogens. In addition, we show that some of these natural products play a role in human disease and in protection against pathogens.

WRM 366

Lead Diversification through a Prins-Driven Macrocyclization Strategy: Application to Functionalized B-Ring Bryostatin Analogues

Kelvin L Billingsley[1]*, klbillin@sfsu.edu, Paul A Wender*[2,3]*. (1) Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, CA 94110, United States (2) Department of Chemistry, Stanford University, Stanford, CA 94305, United States (3) Department of Chemical and Systems Biology, Stanford University, Stanford, CA 94305, United States*

Bryostatin 1 is a marine-derived macrocyclic polyketide that exhibits clinically relevant, highly potent, and diverse biological activities. Despite its promising therapeutic potential, bryostatin 1, like many natural products, is isolated in low and variable yields from its source. This work explores the design, synthesis and biological evaluation of a novel class of C13-diversified bryostatin analogues to establish whether modifications to the tetrahydropyran-based B-ring confer advantageous biological activity (e.g. increased potency, efficacy or therapeutic index). An innovative and general strategy based on a Prins macrocyclization-nucleophilic trapping cascade is employed to achieve late stage diversification. A lead candidate from this new class exhibited single-digit nanomolar affinity for the enzymatic target, protein kinase C. In addition, *in vitro* analysis of selected library members revealed that modifications of the C13 position of the bryostatin scaffold can be utilized as a diversification handle to regulate biological activity.

WRM 367

Enantioselective synthesis of (*R*)-homocitric acid lactone-1,2-$^{13}C_2$

Jared T Moore*, jarmoore@ucdavis.edu, Nadine V Hanhan, Maximillian E Mahoney, Stephen P Cramer, Jared T Shaw. Department of Chemistry, University of California, Davis, Davis, Ca 95616, United States*

Homocitric acid lactone in the hydrolyzed ring-open form is an essential component of nitrogenase, the enzyme responsible for fixation of atmospheric nitrogen by bacteria and archaea. Homocitrate is incorporated into the nitrogenase Fe-Mo cofactor, one of the most complex metal cofactors found in nature. To further study this mechanism, we have developed an enantioselective synthesis of (*R*)-homocitric acid lactone, complete with two ^{13}C isotopic labels at positions that are proximal to the molybdenum center in the fully formed cofactor. Specific labeling of these positions would open up a number of NMR, IR, and EPR/ENDOR experiments related to nitrogenase biosynthesis and mechanism. These isotopic labels arise from commercially available $^{13}C_2$-diethyloxalate. Asymmetry is addressed with a chiral allylic alcohol, available through enzymatic resolution, which sets the stereochemistry for the remaining synthetic steps. Other key transformations include a stereo-controlled Ireland ester enolate Claisen rearrangement followed by ring-closing metathesis, and finally a RuO_4 oxidative olefin cleavage to give (*R*)-homocitric acid lactone-1,2-$^{13}C_2$ in 95:5 er.

WRM 368

Exploring Class III HDAC Inhibitors from Marine Sediment-Derived Actinomycetes Using an HDAC-Based Yeast Screening Method

Taro Amagata*, amagata@sfsu.edu. Chemistry and Biochemistry, San Francisco State University, San Francisco, California 94132, United States*

We have recently developed an HDAC-based yeast screening method to identify class III HDAC (SIRT) inhibitors from actinomycetes separated from marine samples. In this presentation, the principle and application of the yeast screening and the SAR study for one of the SIRT1/2 inhibitors will be presented.

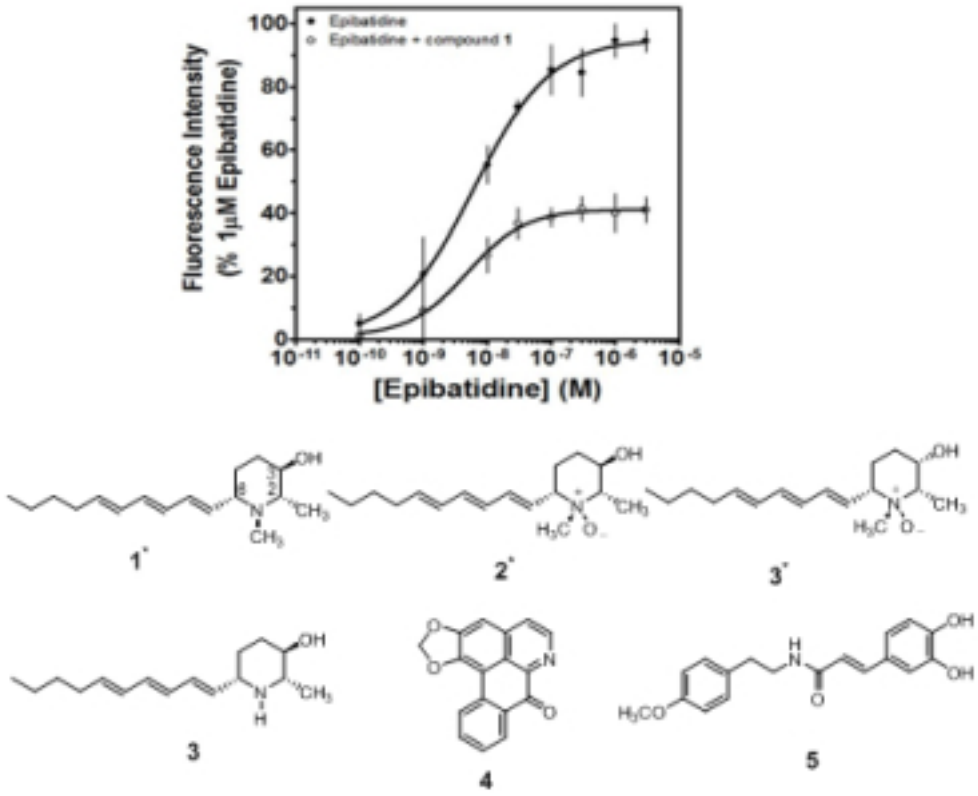
WRM 369

Alkaloids from *Microcos paniculata* L. with cytotoxic and non-competitive nicotinic receptor antagonistic activities: The transition from terrestrial plants to marine organisms

Patrick C Still[1,5], *pstill@ucsc.edu, Bitna Yi*[2], *Tatiana F González-Cestari*[2], *Li Pan*[1], *Hee-Byung Chai*[1], *James R Fuchs*[1], *Tran Ngoc Ninh*[3], *Djaja D. Soejarto*[4], *Brandon J Henderson*[2], *Dennis B. McKay*[2], *A. Douglas Kinghorn*[1], *Phillip Crews*[5]. *(1) Division of Medicinal Chemistry and Pharmacognosy, The Ohio State University, Columbus, OH 43210, United States (2) Division of Pharmacology, The Ohio State University, Columbus, OH 43210, United States (3) Vietnamese Academy of Science and Technology, Institute of Ecology and Biological Resources, Hanoi, Viet Nam (4) Department of Medicinal Chemistry and Pharmacognosy, University of Illinois at Chicago, Chicago, IL 60612, United States (5) Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, CA 95064, United States*

Microcos paniculata L. (Malvaceae) (voucher specimen: Soejarto et al. 14261) is a shrub or small tree that grows in Southeast Asia. Three new piperidine alkaloids, microgrewiapines A-C (1-3), and three known compounds (3-5), were isolated from separate chloroform-soluble extracts of the stem bark, roots and leaves of *M. paniculata*. Microgrewiapines A-C showed inhibition of the growth of the HT-29 human colon cancer cell line with IC50 values of 3-14 μM; and inhibited activation of human α4β2 or α3β4 nicotinic receptors, showing IC50 values in the low micromolar range. As a result of these studies, microgrewiapine A was found to be selectively cytotoxic, with noncompetitive inhibitory nicotinic receptor activity comparable to D-tubocurarine. This study represents the first report of cytotoxic and CNS modulatory piperdine alkaloids from genus *Microcos*. A transition from terrestrial plants to the underexplored marine myxobacteria is the current research focus with the aim of utilizing marine-sediment collections contained in the Crews group repository to obtain bioactive small molecules.

Microcos paniulata **field photo**
Courtesy: D. D. Soejarto



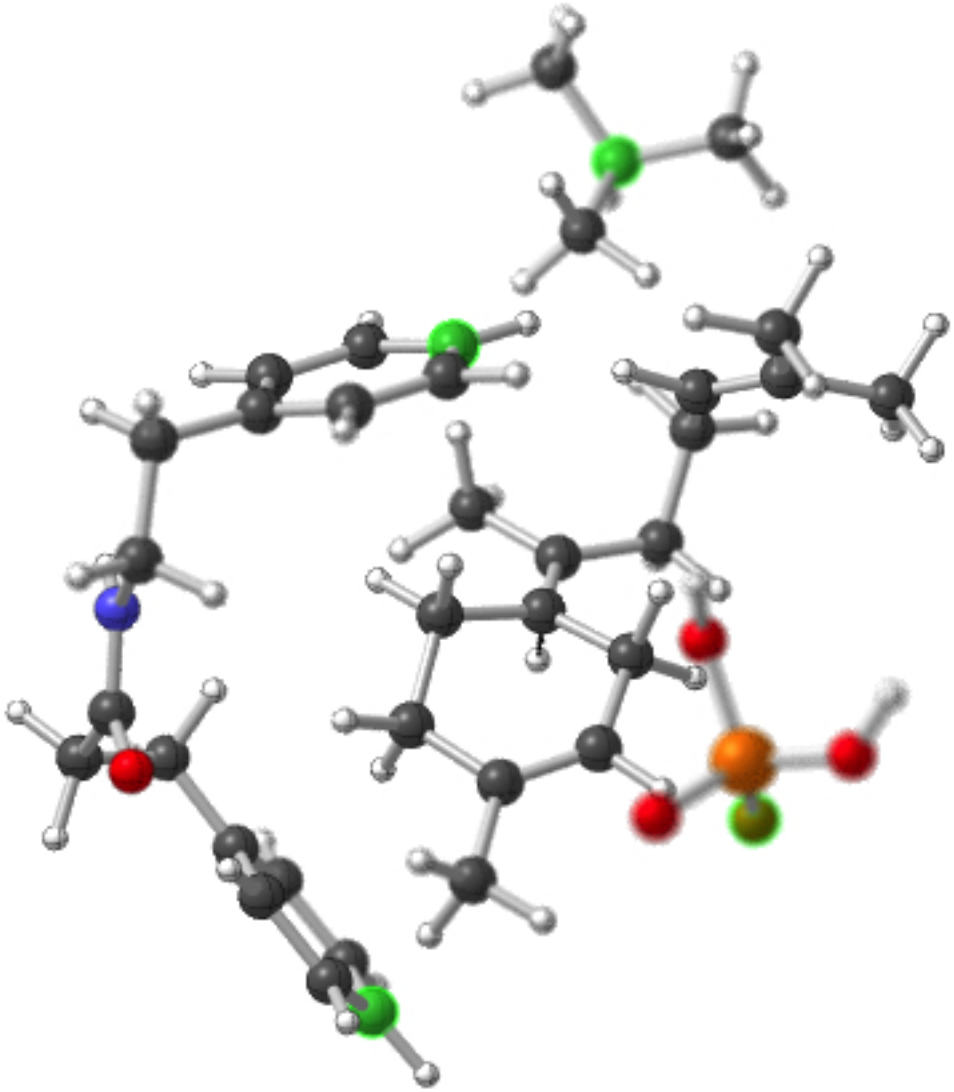
WRM 370

Probing terpene enzymatic functionality and the inherent dynamical preferences in carbocation rearrangements

Ryan P. Pemberton*, pemberton@ucdavis.edu, Dean J. Tantillo.Chemistry, University of California, Davis, Davis, CA 95616, United States*

Epi-isozizaene synthase is an enzyme that converts the sesquiterpene substrate, farnesyl diphosphate (FPP), to isozizaene. Biomechanistic studies of this conversion suggest that this process involved eleven elementary chemical events. Computational investigations are being applied to study this transformation using a variety of techniques, including (1) the traditional mechanistic study of the static structures and generation of the underlying PES, (2) the inherent dynamical effects associated with a particular geometry of a transition state along the reaction coordinate using QMMD simulations, (3) theozyme dynamics where a truncated active site is included in the trajectory calculations, (4) QMMM study that shows the effects that the enzyme has on the PES along the reaction coordinate, and (5) QMMMMD that goes beyond theozyme dynamics by considering the larger dynamical effects associated with protein dynamics.

A key transition state, lying along the multi-step reaction coordinate, has been identified and subjected to these various methods to access the function of the enzyme in each of the elementary processes. Theozyme dynamics will be the main area of focus, as we begin to unravel how the enzyme is able to accomplish this amazing feat. The concepts of conformational preorganization and the ability of an enzyme to alter the inherent dynamics and PES will be discussed, to explain how an enzyme can take a virtually linear substrate and turn it into a complex, polycyclic natural product.



WRM 371
Probing energy transfer and structural evolution during ultrafast charge transfer processes
Munira Khalil, *mkhalil@chem.washington.edu. Department of Chemistry, University of Washington, Seattle, WA 98195, United States*
The outcome of any ultrafast photoinduced charge transfer reaction depends on the complex interplay of atomic and electronic degrees of freedom on the timescale of a molecular vibration. In this talk, I will describe the role of coupled high frequency vibrations in probing charge transfer processes using nonlinear vibrational spectroscopy. The second part of my talk will focus on a combined transient X-ray absorption and TD DFT study to probe changes in the local electronic structure of molecular complexes in solution.

WRM 372
Revealing the electronic structure governing energy transfer through simulated spectroscopy

***David Prendergast**, dgprendergast@lbl.gov, Ioannis Zegkinoglou, Maria-Eleni Ragoussi, C. D. Pemmaraju, Phillip Johnson, David Pickup, Jose Enrique Ortega, Gema de la Torre, Franz Himspel.Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

X-ray absorption spectroscopy provides element-specific details of local electronic structure in materials. We have developed a first-principles framework based on density functional theory, to predict and interpret such spectra with the aim to reveal atomic-level details of energy transfer processes. Recently, this approach has been applied to photo-electrochemical processes in dye-sensitized solar cells. We report an analysis of Zn-porphyrin dyes, functionalized to enhance electron-hole separation upon photoexcitation, revealing the electronic origins of observed enhancement. We also report sensitivity of X-ray absorption spectroscopy to the demetalation of porphyrins potentially induced by coordination solvents.

WRM 373

The Role of Fast Charge Carrier Dynamics at the Catalyst/Reactant Interface: Water Oxidation on Transition Metal Oxide Surfaces

***Tanja Cuk**, tanjacuk@berkeley.edu. Department of Chemistry, University of California Berkeley, Berkeley, CA 94720, United States*

Charge carrier dynamics at the catalyst/reactant interface populate the catalytic surface with reaction intermediates that modify the surface as the reaction proceeds. Ultrafast charge carrier dynamics are thought to be associated with the very initial stages of charge capture by surface sites, modifying the surface bonding. We present *in-situ*, ultrafast transient absorption/transient grating spectroscopy that measures the optical signatures of this interfacial charge capture for two water oxidation catalysts: n-$SrTiO_3$ driven by a UV pulse and Co_3O_4 driven by an n/p GaAs photodiode with visible light. In n-$SrTiO_3$, we find that the carrier dynamics changes at the ultrafast, 10-100 ps time scale with applied voltages that do not alter the quantum efficiency for O_2 evolution under pulsed laser excitation. These changes with voltage therefore reflect interfacial charge capture, guided by Marcus theory, rather than the recombination and drift kinetics that dominate charge separation in the space charge layer. These results describe the kinetics of interfacial charge capture at potentials where a given surface population of intermediates is already saturated and does not influence the longer time scale kinetics; driving the reaction with visible light excitation would explore the kinetics at lower overpotentials. Transient grating spectroscopy on the engineered Co_3O_4/GaAs photodiode heterojunction shows that visible light can separate electron hole pairs and inject holes into the Co_3O_4 overlayer at the ultrafast time scale; *in-situ* measurements are ongoing.

WRM 374

Nonstoichiometric Oxides Surfaces Far from Equilibrium

***William C Chueh**, wchueh@stanford.edu. Materials Science & Engineering, Stanford University, Stanford, CA 94305, United States*

Surface electrochemical reactions are ubiquitous in many energy conversion systems. Of immense technological interests are solid-state electrochemical reactions that occur at the solid/gas interface in oxide electro-catalysts, such as those in oxygen-ion-conducting solid-oxide fuel cells and electrolyzers. Unlike their liquid counterparts, these electrochemical reactions involve the simultaneous transfer of ions and electrons between the solid and the gas. As such, the electro-catalysts need to catalyze both the oxygen-ion-transfer and electron-transfer reactions.

Under reaction conditions, perovskite oxides such as lanthanum ferrites and fluorite oxides such as cerium oxides gain and lose significant amounts of oxygen. It is well-known that oxygen nonstoichiometry control a vast number of properties in oxides, such as magnetism, the formation of 2-D electron gas at heterojunction, and superconductivity. Yet, the role of surface oxygen nonstoichiometry in electrochemical reactions remains largely a mystery due to difficulties in controlling and quantifying oxygen and valence electrons on the surface.

The fundamental question here is how does the surface oxygen nonstoichiometry control the electro-catalytic activity of oxides. In this talk, I will present several in-operando spectroscopic investigations of oxide surfaces using X-rays. We directly probed occupied and unoccupied

electronic states using surface sensitive techniques under reaction conditions, that is, under high temperature, pressure and bias.

WRM 375

Silicone elastomer modification using symmetric silicone macromers containing surface active pendants

***Jonathan Goff**, jgoff@gelest.com, Barry Arkles, Santy Sulaiman. Gelest, Inc., Morrisville, PA 19067, United States*

A facile technique was developed for a long-term increase in silicone elastomer surface hydrophilicity, eliminating the need for post-cure surface treatment (e.g. oxygen plasma or surface grafting). Well-defined silicones (1-4 kDa) with a central vinyl functionality and discrete PEG_2, PEG_3 and tetrahydrofurfuryl (THF) pendant endgroups were used as comonomers in Pt-catalyzed silicone RTV formulations. The modified silicone elastomers were optically clear and maintained the mechanical performance characteristic of this class of material. Intrinsic control of surface hydrophilicity was achieved, as the surface active pendant endgroups can orient on the bulk silicone elastomer surface. The elastomer surface changed from hydrophobic (contact angle $\sim 120^{o}$C) to hydrophilic (contact angle < 90^{o}C) at $\sim$5 wt.% comonomer loadings for prolonged time frames (> 5 months). The PEG_3 surface active pendants yielded a greater reduction in contact angle compared to the PEG_2 and THF pendants at similar comonomer loadings. Hydrolytic stability of the elastomer modifications at various pH followed the trend: PEG3< PEG2<THF. Coefficient of friction measurements of the modified silicone elastomers in water at physiological temperature revealed an increase in surface lubricity with comonomer loadings. The silicone elastomer comonomers were evaluated as additives in commercially available RTV formulations utilized in microfluidics and medical plastics.

WRM 376

Elastin-like Polypeptide Hydrogels with Grafted VEGF-Mimetic Peptides for Enhanced Endothelial Cell Function

***Lei Cai**, leicai@stanford.edu, Cong Dinh, Sarah Heilshorn. Department of Material Science and Engineering, Stanford University, Stanford, CA 94305, United States*

A pivotal requirement for successful tissue engineering is angiogenesis, the formation of new blood vessels from existing conduits. Angiogenesis requires a cascade of growth factor signaling to promote proliferation, organization, and differentiation of endothelial cells. However, the use of growth factors in polymeric scaffolds is often plagued by immunogenicity concerns, short *in vivo* half-lives, and quick diffusion away from the target site. To address these concerns, we aim to combine a small bioactive peptide into a tissue engineered matrix that provides sustained spatiotemporal cues to promote angiogenesis. An elastin-like polypeptide (ELP) that includes a cell-adhesive RGD sequence has been synthesized and further modified by covalent immobilization of QK, an angiogenic peptide mimicking the receptor-binding region of VEGF. Using a biocompatible, amine-reactive crosslinker, we precisely controlled the QK grafting density in the ELP hydrogels. Fluorescence recovery after photobleaching (FRAP) demonstrates that the QK diffusivity in pristine ELP hydrogels is 61 ± 5 $\mu m^2/s$, while covalent tethering QK to the ELP hydrogel effectively eliminates all QK diffusion. Compared with pristine ELP hydrogels, human umbilical vein endothelial cell (HUVEC) proliferation is significantly enhanced on ELP hydrogels immobilized with 1 nM or 1 μM QK, suggesting improved bioactivity of the hydrogels by encoding QK angiogenic signals. Current studies are investigating the three-dimensional sprouting behavior of HUVECs encapsulated within ELP-QK hydrogels. These results encourage the further development of biomimetic polymer scaffolds that can provide long-term biological signals to promote angiogenesis within tissue engineering scaffolds.

WRM 377

Engineering 3D microenvironments for pancreatic islets

***Crystal Nyitray**[1], crystal.nyitray@ucsf.edu, Gaetano Faleo[2], Ryan Chang[3], Qizhi Tang[2], Tejal Desai[1,3]. (1) Department of Pharmaceutical Chemistry, University of California, San Francisco,*

San Francisco, California 94158, United States (2) Department of Surgery, University of California, San Francisco, San Francisco, California 94143, United States (3) Department of Bioengineering, University of California, San Francisco, San Francisco, California 94158, United States

Islet transplantation in micro or macroencapsulation devices can be used to provide physiologic glucose-responsive insulin delivery. In the pancreas islets are surrounded by a complex microenvironment that is not recapitulated during islet transplantation, resulting in limited islet function. Creating a proper microenvironment to support islet secretory function within the macroencapsulation device is crucial for the success of this approach. To achieve this goal, we are developing: (1) a thin film polycaprolactone (PCL) macro-encapsulation device that protects the islets from immune destruction and (2) an islet microenvironment to better maintain islet function.

PCL is biodegradable polymer approved by the FDA for biomedical devices. We have fabricated a thin PCL device that demonstrates unhindered insulin kinetics, transplanted it in two animal models and shown protection against allo-rejection. Our data *in vivo* indicates that the thin-film devices demonstrate engraftment and alloimunity after a period of one month. No such engraftment was achieved with free islets. Since our devices demonstrate cell viability at one-month, we predict that alloimunity will be maintained indefinitely. Previous work from our laboratory has demonstrated superior insulin production per cell in larger 2-D and 3-D cell clusters. Additionally, we have shown a significant stiffness-dependent increase in the glucose stimulated insulin response per cell for 3D beta cell clusters grown on 0.1kPa scaffolds in comparison to 10kPa scaffolds. Our data suggests that the physical interactions with the microenvironment, including matrix stiffness, regulate insulin processing. We have seen an 8-10 fold increase in preinsulin mRNA after glucose stimulation on the softer scaffolds. By understanding the role of microenvironment on islet function we can better understand the therapeutics necessary to treat diabetes.

WRM 378

Nanoscale control of endothelial cell-matrix interactions on electrospun Elastin-like protein scaffolds

Shamik Mascharak[2]*, shamikm@stanford.edu, Patrick Benitez*[1]*, Sarah Heilshorn*[2]*. (1) Department of Material Science and Engineering, Stanford University, Stanford, CA 94305, United States (2) Department of Bioengineering, Stanford University, Stanford, CA 94305, United States*

Endothelial cells in the vasculature encounter various elastic, fibrous extracellular matrices, with fiber diameters as small as 10 nanometers. While it is clear that endothelial morphology and motility depend in part on interactions with such fibrous topographies, there exists a gap in knowledge concerning the precise effects of fiber size on endothelial monolayer physiology. Recombinant elastin spliced with cell-adhesive fibronectin sequences can be electrospun and crosslinked into a tunable, implantable fabric that is an ideal platform to observe the response of endothelial monolayers to different sized fibrous matrices. We report nanoscale control over electrospun elastin fiber width and its effect on the morphology and motility of human umbilical vein endothelial cell (HUVEC) monolayers. Cell-cell and cell-matrix junction morphology (immunostaining, quantification of confocal micrographs) depends on width of substrate fibers (0.8, 1.6, 3.0 μm) and location within the monolayer (peripheral, central). In the central monolayer, HUVEC expressed similar VE-cadherin levels across varying fiber diameters, but increased in spreading and nuclear cross sectional area on wider fibers. Contrastingly, HUVEC at the monolayer's leading edge expressed higher VE-cadherin levels within cell-cell junctions and nuclei on thinner fibers. Preliminary motility results indicate that HUVEC at the leading edge were more motile on larger fibers (time lapse microscopy of actin, nuclei). We hypothesize that such differences in morphology and motility require variations in VE-cadherin expression, which are driven by topography-mediated changes in apical-basolateral polarity. Ongoing work evaluates this hypothesis by assessing polarity directly (podocalyxin/collagen 4 distribution) and repeating described assays under VE-cadherin blockade.

WRM 379

Sorting bacterium cells using cell-imprinted polymer thin films: from concept to applications

Kangning Ren[1], kangning@stanford.edu *Niaz Banaei*[2], *Richard N. Zare*[1]. *(1) Chemistry, Stanford University, Stanford, CA 94305, United States (2) Departments of Pathology and Medicine, Stanford University Medical Center, Palo Alto, CA 94304, United States*

Cell imprinting is a recently developed technology that captures the structural and chemical information of the exterior of cells on a polymer surface through template-assisted assembly of functional groups. A polymer is cured around template cells that are removed subsequently, leaving complementary cavities that not only spatially fit but also chemically recognize the target cells {*ACS Nano*, 6: 4314, 2012}. The cell-imprinted materials thereby function as artificial receptors, which are considerably less expensive to produce and more durable than natural receptors and could potentially be broadly used for cell sorting. One promising potential application is the detection of pathogens causing infectious diseases. However, the involvement of pathogens in the production of the imprinted material as well as in the cell capturing process brings occupational risk of infection. Most recently, we discovered that inactivated bacteria can be selectively captured by a polymer film imprinted with the bacteria inactivated in the same way., avoiding the use of live virulent bacteria; moreover, the inactivation strategies, especially those utilizing chemical reagents, resulted in better selectivity of capture than when living cells were used {*ACS Nano*, 7: 6031, 2013}. This inactivation process may have played two roles: (1) to eliminate the secretion of extracellular matrix, which helps expose the surface of the cells during imprinting; (2) to fix the cells, which helps preserve the structural and chemical information on their surface. We are developing a rapid, culture-free, low-cost and high-sensitivity diagnosis for tuberculosis infection, which suffers the lack of effective diagnosis in low-income countries. Using wild type tuberculosis bacteria in an artificial sputum medium as sample, we established a diagnosis based on a cell-imprinted microfluidic device, which shows potential to offer a greatly increased sensitivity at similar cost compared with the most commonly used acid-fast microscopy test.

WRM 380

Tailored Polymers for Surface Coating of Silicone Devices

Jeffrey G. Linhardt[1], jglinhardt@google.com *Jay F Kunzler*[2], *Devon Shipp*[3]. *(1) Google X, Google, Inc., Mountain View, CA 94043, United States (2) Polymer Chemistry, Bausch & Lomb, Rochester, NY 14224, United States (3) Department of Chemistry, Clarkson University, Potsdam, NY 13699, United States*

Silicone hydrogels and elastomers have been used in a number of biomedical applications because of its favorable physical and chemical properties, and its biocompatibility. In a number of applications, one of the drawbacks of silicone materials is its inherent hydrophobicity. This lecture will discuss ways to make silicone materials more hydrophilic by a "grafting to" approach with tailored block copolymers.

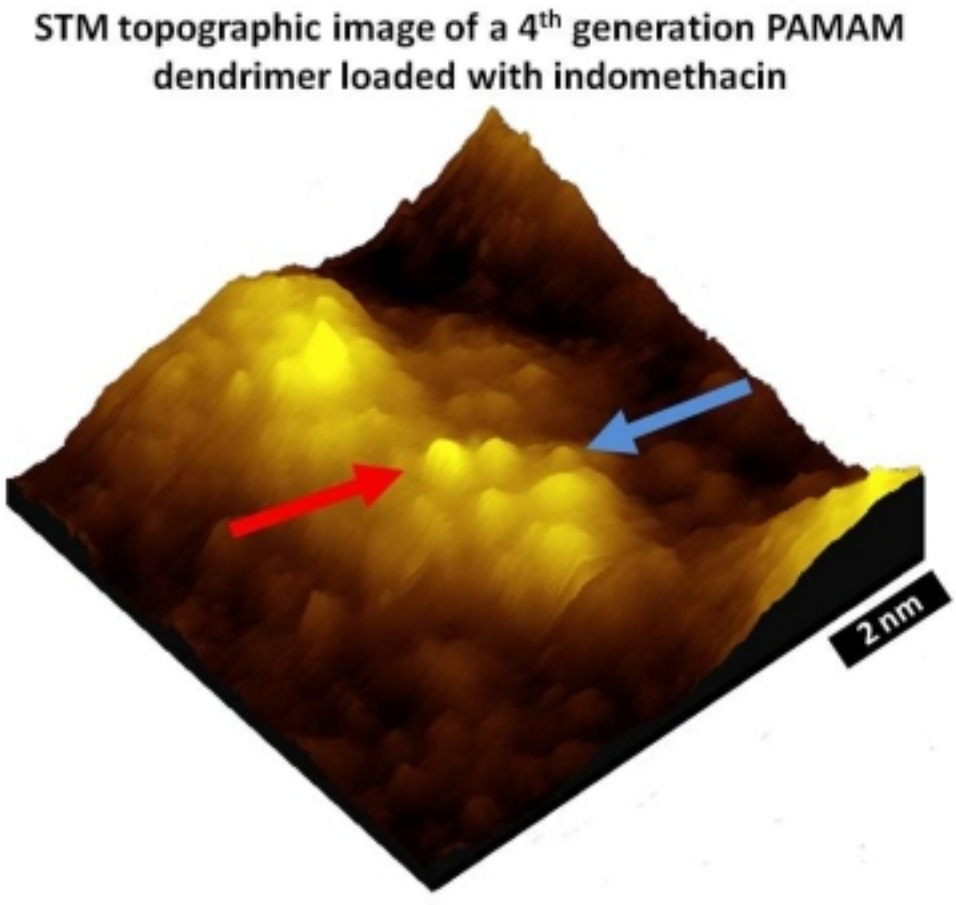
WRM 381

High-resolution imaging of dendrimers used in drug delivery via scanning probe microscopy

Shawn L Riechers[1], *slriechers@ucdavis.edu, Lifang Shi*[1], *Chirtopher J Fleming*[1], *Nai-Ning Yin*[1], *Juntao Luo*[2], *Kit S Lam*[2,3], *Gang-yu Liu*[1]. *(1) Department of Chemistry, University of California, Davis, Davis, California 95616, United States (2) Department of Biochemistry and Molecular Medicine, University of California, Davis, Sacramento, California 95817, United States (3) Department of Internal Medicine, University of California, Davis, Sacramento, California 95817, United States*

Polymer based vehicles for drug delivery have attracted much attention recently. Dendrimers and telodendrimer micelles represent two such classes, which have shown great promise. However, structural characterization at the molecular and sub-molecular level has been a challenge. This presentation introduces new approaches to address this challenge, i.e. high resolution imaging using scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Utilizing novel preparation protocols, high resolution STM imaging is attainable and important structural features

are revealed. These features include intramolecular dendrimer termini (blue arrow) and individual uploaded drug molecules (red arrow).



For extremely soft systems, such as telodendrimer micelles, immobilization and AFM imaging, without compromising structural integrity, has been achieved. High-resolution AFM imaging reveals the telodenrimer micelle morphology and volume, which has been utilized to determine the extent of drug loading. Work is in progress to visualize various functionalized dendrimer and teledendrimer systems. Revealing the nanocarrier structure and nanocarrier-drug interactions, via high-resolution imaging, facilitates the design and optimization of these emerging drug delivery systems for increased efficiency.

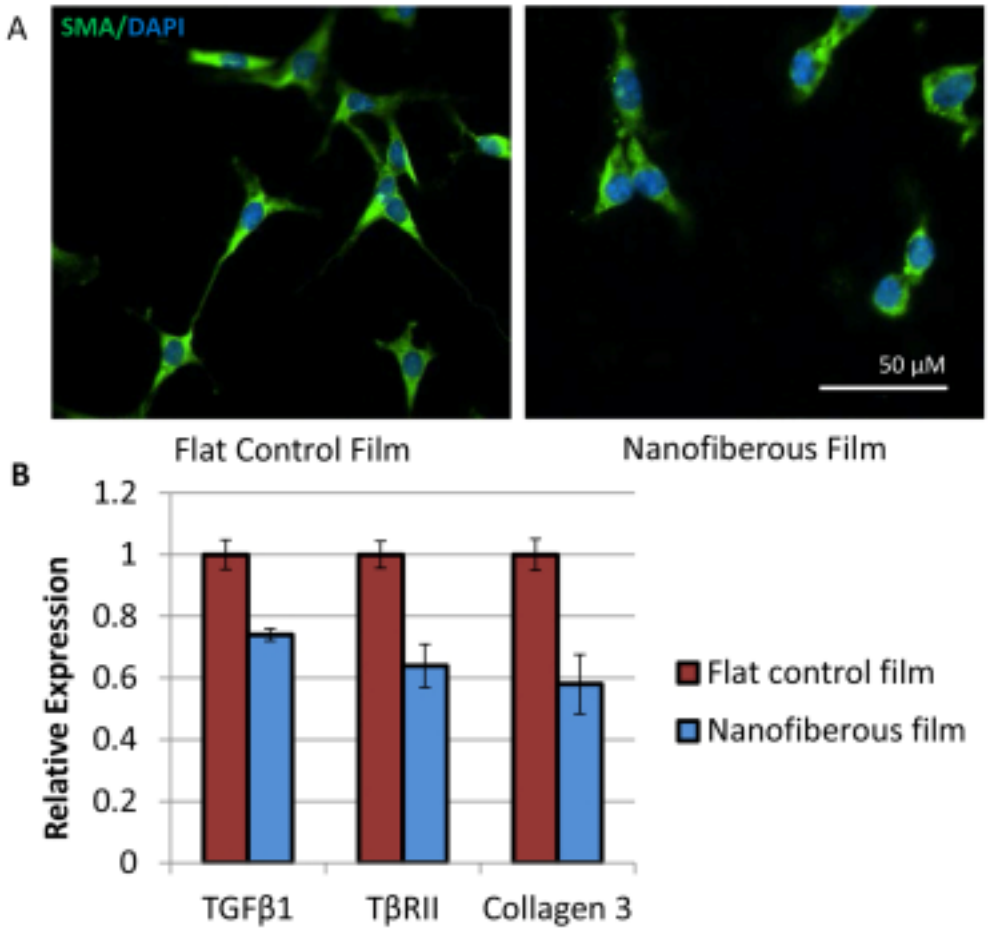
WRM 382

Nanofiberous polypropylene films reduce myofibroblast differentiation through the TGFβ pathway

Jessica L. Allen[1]*, jessica.allen@ucsf.edu, Jubin Ryu*[1,2]*, Tejal A. Desai*[1]*. (1) Department of Bioengineering and Therapeutic Sciences, University of California, San Francisco, San Francisco, California 94158, United States (2) Department of Dermatology, University of California, San Francisco, San Francisco, California 94118, United States*

Fibrosis is an altered wound healing response which causes significant clinical morbidity in nearly all affected organs. Within fibrotic tissue, fibroblasts undergo myofibroblastic differentiation, characterized by the expression of α-smooth muscle actin (αSMA) and increased production of extracellular matrix (ECM) components, such as collagen III. TGFβ signaling initiates myofibroblastic differentiation, but the mechanisms that regulate TGFβ signaling in fibroblasts are unclear. Biophysical cues, such as topography, have been shown to down regulate both

myofibroblastic differentiation and TGFβ signaling in fibroblasts. Currently, it is unclear the mechanism through which topography regulates myofibroblastic differentiation.
We have developed a series of nanofiberous films fabricated by laminating medical grade polypropylene through a nanoporous polycarbonate membrane. The fiber length and diameter can be reliably controlled allowing tunable topography. Upon cellular adhesion, longer nanofibers are easily deformed decreasing the generation of intercellular stress. Culture of a fibroblastic cell line on nanofiberous films leads to dramatic morphologic changes and decrease in αSMA protein staining (Figure 1a). Moreover, there is a significant reduction in Collagen 3, TGFβ1 and TGFβ receptor II (TβRII) in fibroblasts cultured on nanofiberous films compared to the flat film control (Figure 1b). These results indicate that nanofiberous films desensitize fibroblasts to TGFβ, thereby inhibiting myofibroblastic differentiation. A further investigation into the mechanisms behind the interaction between TGFβ and nanotopography may elucidate novel material design strategies that could be used to treat fibrotic diseases.



WRM 383
3-helix Micelles as a Drug Nanocarrier Platform: Cargo Loading and Biological Evaluation
Nikhil Dube, *ndube@berkeley.edu, Ting Xu. Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California 94720, United States*
Generating stable nanocarriers, 10-30 nm in size, with high drug content would have significant implications on their transport in blood circulation, tissue penetration and therapeutic efficacy. Our group has designed ultra small spherical micelles, 15 nm in size, based on self assembly of amphiphilic conjugates of poly(ethyleneglycol) conjugated coiled-coil helix bundle. These micelles

exhibit excellent *in vivo* kinetic stability, blood circulation half-life of 29 hours and reduced accumulation in liver and spleen. The favorable biological performance of 3-helix micelles combined with their unique structure indicates their promise as nanocarriers for drug delivery and imaging. We have investigated the drug delivery potential of 3-helix micelles through physical encapsulation of a range of amphiphilic and hydrophobic drugs. Doxorubicin loaded 3-helix micelles exhibit high encapsulation stability in biological environments and are cytotoxic towards a range of cancer cells. The peptide based shell of 3-helix micelles allows mediating proteolytic disassembly to enable drug release and clearance to minimize side effects. *In vivo* studies on local and intravenous administration of these stable 15 nm particles clearly demonstrated improved tumor half-life and reduced toxicity to healthy tissues from DOX-loaded micelles compared to free DOX. Furthermore, molecular parameters that control drug loading and encapsulation stability for nanocarriers in this size range were identified to tune the formulation of clinically relevant and structurally diverse drugs in these micelles. Drug loaded 3-helix micelles with size < 20 nm display extended stability, little drug leakage, substantial cytotoxicity towards cancer cells, favorable biodistribution and greatly reduced toxicity towards healthy tissues, and thus meet many of the critical requirements for safe and effective nanocarriers for cancer therapeutics.

WRM 384

Dynamics of conformational transitions of a water-soluble poly(3-hexylthiophene) derivative by surfactant complexation

Shanju Zhang, *szhang05@calpoly.edu. Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407, United States*

Transitions in the backbone conformation of conjugated polymers in organic solvents have been widely recognized to influence structures and properties of dried thin films. A well-studied system is poly(3-alkylthiophene)s, which have high charge carrier mobility and low energy bandgap. For instance, poly(3-hexylthiophene) has become a benchmark material used in the photoactive layer of polymer solar cells. However, such conformational transitions of water-soluble polythiophenes, with respect to their intramolecular versus intermolecular origin, remain largely unknown. In this research, we report on dynamic conformational transitions of a water soluble poly(3-hexylthiophene) derivative in aqueous cetyltrimethylammonium bromide. A coil-to-rod conformational transition of individual polymer chains is identified in diluted solutions. Study into the corresponding kinetics shows a unique rate law. Variation of conditions such as temperature, concentration and surfactant architecture has been investigated. A theoretical model is proposed to explain this new phenomenon and the mechanisms behind its influence on the optoelectronic properties.

WRM 385

Nanowire Solar Cells

Sarah Brittman[1,3], *brittman@berkeley.edu, Andrew Wong*[1], *Youngdong Yoo*[1], *Neil Dasgupta*[1], *Dandan Zhang*[1], *Peidong Yang*[1,2,3]. *(1) Department of Chemistry, University of California, Berkeley, CA 94720, United States (2) Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, United States (3) Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States*

Absorption of light and collection of photogenerated charges are the two essential tasks performed by a solar cell. Nanowires can improve the performance of these two tasks because their dimensions are on the same scale as the wavelength of visible light and the minority carrier diffusion lengths in many semiconductors. For example, core-shell nanowire arrays can improve charge collection by orthogonalizing the directions of light absorption and charge separation; they also exhibit low reflectivity and light-trapping effects for increased absorption. In the development of array devices, single-nanowire solar cells provide information about the material and junction quality of the system. The low cost and abundance of oxide and sulfide semiconductors make them attractive solar materials, and they are particularly well suited for nanowire solar cells because of their sub-micrometer minority carrier diffusion lengths.

WRM 386

Hybrid organic-inorganic core-shell nanowires toward high efficiency photovoltaics

Shanju Zhang, *szhang05@calpoly.edu. Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407, United States*

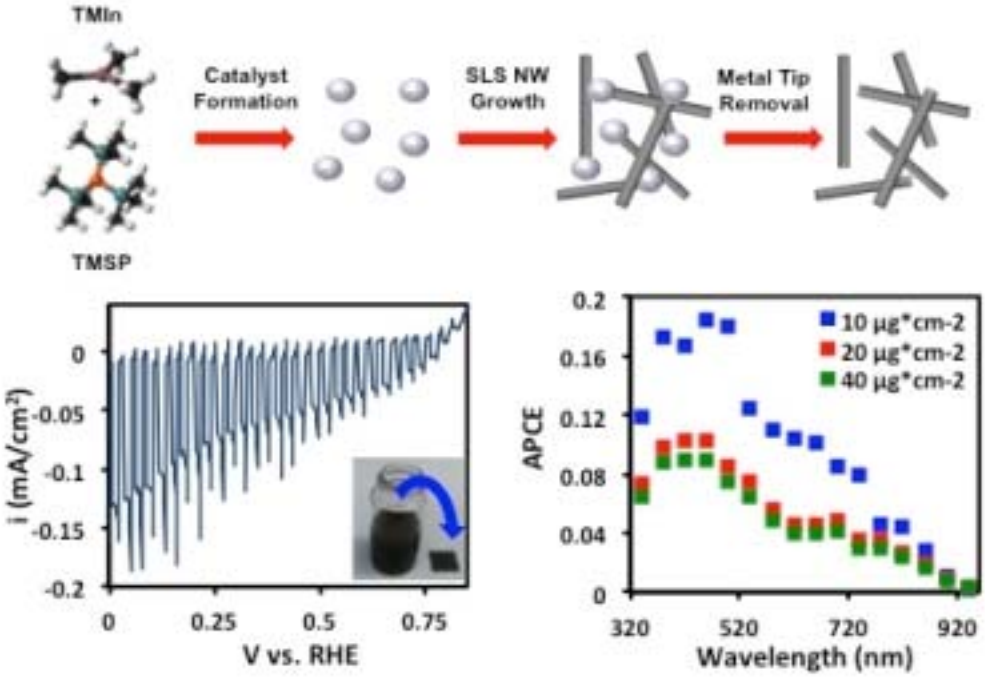
Hybrid organic-inorganic photovoltaics (PVs) are an emerging solar technology that could be processed using traditional printing/coating techniques from appropriate solutions. The ideal hybrid device possesses an ordered bulk heterojunction (OBHJ) in which donor and acceptor form vertically aligned periodic nanopatterns. Such an ordered motif has been the focus of recent interest, but its realization, particularly in a manner compatible with solution-based fabrication, remains challenging. In this research, we design and utilize novel hybrid organic-inorganic core-shell nanowires to produce ordered nanostructures of bulk heterojunctions. Hybrid nanowires consist of an inorganic semiconductor core and organic polymer shell with precise control of interface. Confined on the nanowire surface, polymer chains develop ordered crystalline structures. External fields are used to guide alignment of nanowires and unique optoelectric properties are achieved.

WRM 387

Solution phase growth of Indium Phosphide nanowires and their application for photoelectrochemical energy conversion

Nikolay Kornienko, *nick_kornienko@yahoo.com, Peidong Yang. Chemistry, UC Berkeley, Berkeley, California 94709, United States*

Efficient, large-scale, and cost effective solar-driven conversion of water into hydrogen and oxygen is one of the major challenges in current energy research. Materials that meet these requirements must simultaneously possess the correct band alignment and band gap, while using industrially compatible synthesis conditions. To address this challenge, Indium Phosphide (InP) nanowires were synthesized via a novel low temperature, surfactant-free, solution phase method. This synthesis was optimized to minimize kinking and achieve diameter control from 20 to 150 nanometers. The nanowires were doped p-type during the synthesis with through the incorporation of zinc. Photocathodes using a material loading of only 40 μg*cm^{-2} were subsequently fabricated from p-InP NWs, and optimized through Zn loading and NW thickness. The absorbed photon-to-current efficiency of these devices was tested and reached values of 20% at 500nm illumination for sub-monolayer InP photocathodes.



WRM 388

A direct thin-film path towards low-cost large-area III-V photovoltaics.

***Rehan Kapadia**, r.kapadia@berkeley.edu, Zhibin Yu, Ali Javey. UC Berkeley, Berkeley, California 94720, United States*

III-V photovoltaics (PVs) have demonstrated the highest power conversion efficiencies for both single- and multi-junction cells. However, expensive epitaxial growth substrates, low precursor utilization rates, long growth times, and large equipment investments restrict applications to concentrated and space photovoltaics (PVs). Here, we demonstrate the first vapor-liquid-solid (VLS) growth of high-quality III-V thin-films on metal foils as a promising platform for large-area terrestrial PVs overcoming the above obstacles. We demonstrate 1-3 µm thick InP thin-films on Mo foils with ultra-large grain size up to 100 µm, which is ~100 times larger than those obtained by conventional growth processes. The films exhibit electron mobilities as high as 500 cm(2)/V-s and minority carrier lifetimes as long as 2.5 ns. Furthermore, under 1-sun equivalent illumination, photoluminescence efficiency measurements indicate that an open circuit voltage of up to 930 mV can be achieved, only 40 mV lower than measured on a single crystal reference wafer.

WRM 389

Atomic layer deposited tunnel oxides stabilize silicon photoanodes for catalytic water splitting

***Andrew G. Scheuermann**[1], awsch829@stanford.edu, Christopher E.D. Chidsey[2], Paul C. McIntyre[1]. (1) Materials Science and Engineering, Stanford University, Stanford, CA 94305, United States (2) Chemistry, Stanford University, Stanford, CA 94305, United States*

A primary challenge limiting future grid-scale implementation of many renewable energy sources is their inherent intermittency. This problem is notably acute for solar energy, prompting interest in energy storage technologies that are viable at very large scale. As an alternative to batteries, synthesis of fuels from sunlight is one promising option, and requires optimized photoelectrochemical devices and materials. One fundamental challenge in this area, however, is the tradeoff between chemically stable semiconductor materials (typically wide band gap metal oxides) under oxidative conditions or efficient (typically less stable) solar absorbers with smaller

band gaps. In a prior report, [1] we protected silicon photoanodes with an atomic layer deposited (ALD) ultrathin TiO_2tunnel oxide and simultaneously achieved high efficiencies and lifetimes as well as avoiding the Fermi level pinning that is typical of many electrolyte/semiconductor interfaces. Here we discuss recent work [2] probing the effect of varying ALD-oxide thickness on water oxidation overpotential, and the applicability of both thinner and thicker oxides for this application due to bulk-limited hopping conduction with modest tradeoffs in efficiency for increased chemical protection.
[1] YW Chen, J.D. Prange, et al. Nat. Mater. 2011, **10** , 539-44.
[2] AG Scheuermann, et al. Energy Environ. Sci. 2013, **6** , 2487.

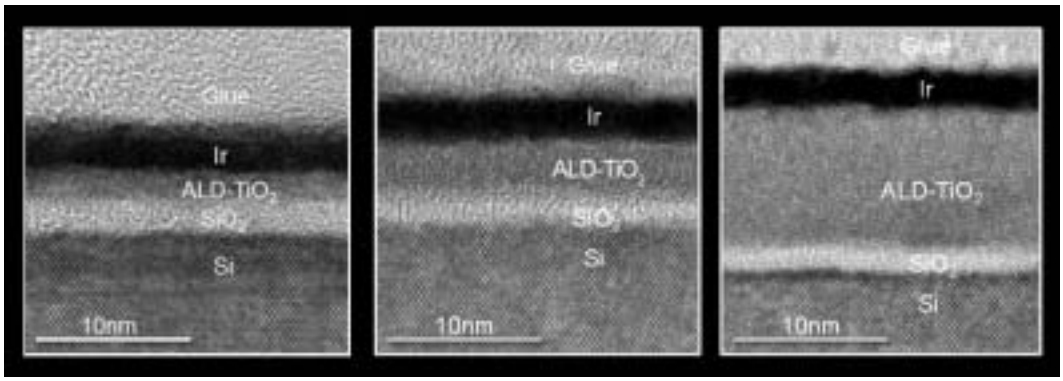


Figure 1: TEM analysis of three ALD-TiO_2 films of thickness 2nm, 5nm, and 12nm from left to right.

WRM 390
Relationships between structure and alkaline stability of imidazolium cations for fuel cell membrane applications
Samuel C Price*, samuel.c.price7.ctr@mail.mil, Frederick L Beyer. Weapons and Materials Division, Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, United States*
Alkaline exchange membranes have substantial potential to be useful in methanol fuel cells due to their potential to reduce electroosmotic drag of methanol and increase the oxidation rate of methanol. However, long term stability of the cationic moiety has been an issue, and imidazoliums have recently attracted attention as candidates for stable cations. The prevailing strategy for increasing the stability of the imidazolium has involved adding sterically hindering groups at the C2 position. Surprisingly, steric hindrance can often reduce the alkaline stability of the cation if it removes the acidic protons from the C2 carbon. We propose that the most important stabilizing factor for an imidazolium is the ability to form carbenes via deprotonation of this acidic proton. We compare the most stable imidazolium to date, 1,2,3-trimethylimidazolium, with a sterically hindered aliphatic ammonium cation, and find the aliphatic ammonium to be slightly more stable.

WRM 391
Women chemists at various stages of their careers-A graduate student perspective
Latisha Paw U*, latishapawu@gmail.com. Department of Chemistry, University of California-Berkeley, Berkeley, CA 94720, United States*
There are three main components that have shaped my life as a chemist so far: mentoring, getting involved with the community, and thinking about career paths early. Without wonderful mentors I would not have gotten to where I am. From my elementary school science teacher, whose passion augmented my parents' enthusiasm, to my undergraduate advisor, each taught me about science, but more importantly encouraged me to pursue it as a career. Getting involved in the community and being able to share science with non-scientists has been essential to my development. I have enjoyed helping community members of all ages understand science and

scientific thinking since childhood. Getting the chance to step back and show someone the bigger picture is also a reminder to me when I am caught in the details of a project. Communicating science in non-technical terms is nontrivial, and has often forced me to think in a different way. The last large influence on my path so far was thinking about careers early. Identifying areas I was interested in allowed me time develop skills and experience required for the field and to decide if it was actually what I wanted to do. As an undergraduate I knew I wanted to go to graduate school in chemistry so I made it a goal to work for different professors in different areas of research. These research experiences helped me develop my research abilities and determine what I wanted to study in graduate school. Thinking ahead has not only helped me gain useful skills and experience but has also helped keep me motivated when I am stuck on a project or frustrated with a class. While I will likely follow a career in industry, I am also considering non-traditional careers as I continue on my chemical journey.

WRM 392

Learn how to learn

Yaya A Zhu, *yayazhu@chevron.com. Department of Petroleum Material Characterization, Chevron Energy Technology Company, Richmond, CA 94801, United States*

The most important thing one can learn in any subject is to learn how to learn. No one is expected to remember every single thing they were taught, and some of us are just simply forgetful. It's not necessary to remember every single detail, but understanding the fundamental concepts is what leads to success.

After I graduated from college, I got a job at Chevron thus starting my career. However, my experience in college told me that laboratory experiments would be routine and uninteresting. Before I started working, I had no idea that chemistry could be so interesting. Practical experiments are very different from book learning due to the many unpredictable factors that one might encounter during the experiment. Complications occur even with the easiest experiment. When this happens, I need to understand the concept to be able figure out what happened. Therefore it's not important for me know or remember every reaction. Simply by understanding the concepts behind an experiment; I know which resources to consult in order to solve the problem.

WRM 393

Community colleges offer something beyond education to students

Iyun Lazik, *iyun.lazik@sjcc.edu. Department of Chemistry, San Jose City College, San Jose, CA 95128, United States*

The 112 community colleges in California offer opportunities for students to build a career, train in a new expertise, develop communication skills and complete UC and CSU transferable courses in smaller, student-centered environments. There are many advantages to taking classes in a community college: increased contact hours between students and instructors; greater opportunity for hands-on training in laboratory equipment; extended resources dedicated to teaching and learning; and lower tuition/room-and-board costs. The increased community college student success in sciences, especially in physics and chemistry, encourages many students to pursue a career in sciences. Whether you are a recent high school graduate or a life-long learner, pursuing a career in science is within your grasp at a community college near you.

WRM 394

Advice from a non-traditional chemist

Janet Schunk, *janet.schunk@siemens.com. Siemens Healthcare Diagnostics, Berkeley, CA 94710, United States*

Life has many paths . . . some are well worn and established; others not often taken; and then there are those paths still waiting to be explored. It does not matter which path you take (or maybe you will travel more than one), equip yourself for the journey. So, what should you take along on your journey as a chemist? Yes, you need fundamentals like organic, inorganic, calculus, and statistical courses. But you should also bring along the ability to go outside your comfort zone, to explore new areas (and not always science); to go beyond the “bench” by understanding your customer's needs or applicable regulations; to mix and mingle your interests

(do you like to write, or have an interest in public policy). And save some space (time) in your “back pack” to volunteer not only to meet others but to expand your leadership skills; to mentor and share knowledge both to those who are younger, as well as to those who are older than you (or those right there with you); to dream, to listen, to have fun. And remember most of all, nothing is engraved in stone. Your interests will grow, and mature, and change; life will change. Just reset your navigational beacon (GPS) for the new path and you will do fine.

WRM 395
Women Chemists Panelist
Trudy Lionel, *Trudy.Lionel@Bayer.com. QA GCPD, Bayer HealthCare LLC, Berkeley, CA 94710, United States*
Do you wonder how things work at a molecular level? From metabolism to the environment, from starlight to crystals: this is the excitement of chemistry for me. New areas of research and applications to society, coupled with the thrill of connections with young scientists have been a lifelong interest. I'll describe my winding path through academics, government and business, and encourage you to find work you enjoy. From the lone researcher to the team contributor, you can find your awesome career.