

A publication of the Chemistry Department at Washington State University

2012

A Message from the Chair



It has been a busy, demanding, and exciting year for the Chemistry Department. We saw our first 4000 plus class of entering freshman. They came, they saw, and they found classroom space! This was possible only through the imagination and dedication of our faculty and Scot Wherland, my Associate Chair for Undergraduate instruction. To give you some idea of the magnitude of the problem, in the fall of 2010 we were using all available lab rooms and we taught 76 sections (24 students per section) of freshman labs. Last year that number jumped to 88 sections, and we are expecting 92 sections of freshman labs this fall! In order to accommodate these new lab sections we are racing to convert two large rooms into freshman labs. They must be ready by September 3. I have a backup plan if the contractors don't make it, but I am not sharing at this point because it isn't pretty.

Next year the expansion bubble will hit our junior level classes. While the percentage increase may actually be slightly larger, the total number of seats needed won't be as bad. We have the rooms to offer more sections, what we don't have (yet) is the equipment we will need to run those extra sections. That is yet another growing pain that we are addressing. Fortunately, you don't need to worry about the quality of the lab instruction. Our recent rapid growth in our PhD program means that most of these labs will be instructed by PhD students. For other sections, we are hiring people with BS, MS, and even PhD degrees. Honestly, I think the quality of our lab supervision is as good, or better, than it has ever been.

Another exciting development for the department is the addition of Jonel Saludes to our faculty. Jonel is a terrific young organic chemist and you will find a brief introduction to him later in this newsletter. We are also looking to hire two more young faculty members for next year. One is a somewhat unusual combination of analytical and radiochemistry, the other is an inorganic chemist. The first position was made possible by a partnership between Sue Clark and our College of

Arts and Sciences (CAS) dean, Daryll Dewald. Sue wrote and won a grant for about half the radiochemist's start-up funding, and the dean provided the other half of the start-up. The faculty line for the position came from Herb Hill converting to half time. As our faculty ages, it is extremely important to replace them at a steady rate - the very high start-up costs for chemistry faculty (between \$400,000 to \$750,000 per assistant professor) makes it virtually impossible to hire more than one or two per year.

As always, I want to invite you to visit our department. If you are uncomfortable just stopping in, email Nikki Clark ahead of time and tell her who or what you would like to see (nikki@wsu.edu). She will do her best to arrange something appropriate.

Best wishes,

KW Hipps, Professor and Chair



The Expanding Role of Computational Science in Chemistry

by Dr. Aurora Clark

If it has been a while since your last foray into Chemistry you may be surprised by the notion that computer modeling and simulation is now broadly accepted as the third leg of the stool that defines chemistry as a central science. Applied computational methods allow us to investigate phenomena where economics, physical, or environmental constraints preclude experimentation, and they serve as a test-bed for the fundamental physical principles that govern the molecular world. Thus, Computational Chemistry bridges the experimental techniques and purely theoretical developments that form the basis for the chemical enterprise.

Progress in Computational Chemistry has been driven by dramatic advances in hardware capabilities and improved parallelization algorithms that enable routine calculations on thousands of processors with data processing speeds of one hundred trillion floating point operations per second. Research computing facilities are maintained by faculty on campus at WSU, and are also available at government sponsored supercomputing user facilities (for example the Environmental Molecular Science Laboratory at Pacific Northwest National Lab). In the broadest sense, there are two major branches of Computational Chemistry: a) one that utilizes time-independent information about the quantum mechanical nature of electronic interactions to accurately describe the physical properties of atoms and molecules, and b) one that uses statistical mechanics to describe and predict macroscopic phenomena that can be related to bulk observables. Both arenas serve an important role in technological and scientific advancement and they can be used synergistically to gain a holistic multi-scale understanding of a system and its behavior.

As an illustration, consider the interesting chemical story of water oxidation by the famous Ru “Blue Dimer” catalyst, [cis,cis-Ru(bpy)₂(H₂O)₂O]⁴⁺. Water oxidation, which follows the general reaction:



is of course considered a crucial component for generating hydrogen fuel using only water and sunlight, and the field was blown open by the discovery of the “Blue Dimer” in 1982. Yet this molecule has a long history in the literature because there are several different reaction pathways whose kinetic/thermodynamic favorability are modulated by experimental conditions. There are broadly two different mechanisms for the catalyst, one where the O₂ formation derives from one water and one of the ruthenyl oxo-atoms, and a second mechanism where both O-atoms derive from the solvent (Figure 1). The rate limiting step is believed to be H-atom abstraction from water, with the resulting nascent hydroxyl radical adding to the adjacent Ru=O to form a hydroperoxy/hydroxyl intermediate, or to the bipyridine to form a ligand radical intermediate. To explore this chemical system using computational methods based on quantum mechanics, accurate descriptions of atomic orbitals must be derived that account for the relativistic behavior of electrons near the Ru nucleus. Enter the realm of Edward R. Meyer Distinguished Professor Kirk Peterson, whose pioneering work on basis set development and kJ/mol accuracy calculations has provided the framework for accurately determining the differences in activation barriers between reactions (A) and (B) in Figure 1.

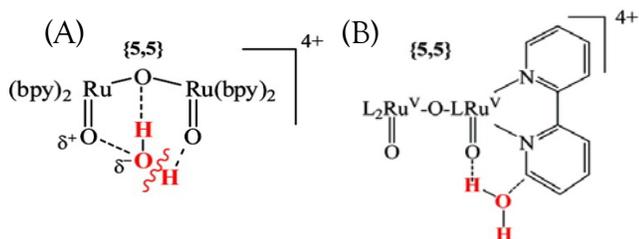


Figure 1.

But while the isolated molecular activation barriers and mechanistic studies are of great importance, the story doesn't end there. We must recognize that the species in Figure 1 do not exist in a vacuum and

that the dynamic arrangement of solvating water about Blue Dimer and the conditions of pH and counterions in solution also influence the catalytic turnover of this remarkable molecule. Recent work at University of Colorado and at MIT have indicated that proton relay chains can be formed about the ruthenyl core that alter the favorability of different water oxidation pathways. Thus, we must begin to include and explore solvation effects and how the dynamic behavior of water participates in the oxidation process. Toward this end, statistical mechanical simulations can be performed that examine how water constantly rearranges itself over time. Graph-theory based algorithms can analyze statistical mechanical data and can determine how often these proton-relay chains form and whether or not their formation can be statistically correlated to water oxidation. Thus, quantum mechanical and statistical mechanical methods can be combined to yield a multiscale, holistic understanding of the chemical reactivity of Blue dimer, that provides a vital complement to observations from experiment.

Faculty Highlights

Funding

Cliff Berkman, National Institutes of Health, “Probe Optimization for Prostate Cancer Detection,” \$459,037. Continuation.

Cliff Berkman & Margaret Black (Animal Sciences), National Institutes of Health, “Development of a Malarial Kinase-on-Phage Screening Platform,” \$218,850.

James Brozik, Department of Energy, “Model Membrane Assemblies and Membrane Proteins,” \$51,000. Continuation.

James Brozik, Department of Energy, “Genomics Enabled Sensor,” \$24,000. Continuation.

Sue Clark, Department of Homeland Security, “ARI: Improved Radiochemical separations for Actinide Forensic Signatures,” \$190,903. Continuation.

Sue Clark, Department of Energy, “Controlling Actinide Hydration in Mixed Solvent Systems: Towards Tunable Solvent Systems to Close the Nuclear Fuel Cycle,” \$150,000. Continuation.

Sue Clark & Ken Nash, Medical University of South Carolina-DOE, “Nuclear Forensics Education Program at Washington State University,” \$200,000. Continuation.

Sue Clark & Ivory Cornelius (Chemical Engineering & Bioengineering), Department of Defense, “Rapid, Ligand-assisted Capillary Electrophoresis Methods for Actinide Determinations by Mass Spectrometry,” \$359,503.

Sue Clark, Department of Energy, PNNL Subcontract, \$65,500. Continuation.

Aurora Clark, Paul Benny & Nathalie Wall, Battelle-DOE, “Rapid Computer Aided Ligand Design and Screening of Precious Metal Extractants from TRUOX Raffinate with Experimental Validation,” \$500,000.

Herb Hill, Science Applications International Corp.-DOD, “Reducing False Alarms in Ion Mobility Spectrometry Detectors –

Determination of Accurate and Precise Ion Mobility Spectrometry Constants,” \$252,281. Continuation.

Herb Hill, Department of Energy, “Evaluation of the Electrospray Ionization ion Mobility Time-of-flight Mass Spectrometer,” \$51,000.

Herb Hill, Excellims-DHS, “Fundamental Improvement of Ion Mobility Spectrometers for Explosive and Chemical Detection Using Structure Selective Ion-Molecular Interaction,” \$42,689.

KW Hipps, National Science Foundation, “Scanning Tunneling Microscopy of Temperature Dependent Molecular Processes at the Solution-Solid Interface,” \$125,000. Continuation.

James Hurst, Department of Energy, “Membrane-Organized Chemical Photoredox Systems,” \$130,000. Continuation.

Jeff Jones, National Institutes of Health, “Understanding the Metabolic Impact of Aldehyde Oxidase on New Drug Design,” \$258,683.

Ursula Mazur, National Science Foundation, “Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy Studies of the Structures and Energetics of Axial Ligand Coordination to Metal Porphyrins at the Liquid-Solid Interface,” \$294,000.

Ursula Mazur & KW Hipps, National Science Foundation, “Investigation of Structure and Electron Transport in Porphyrin and Phthalocyanine Aggregates,” \$470,000.

Jeanne McHale, National Science Foundation, “Controlling the Hierarchical Structure of Light-Harvesting Chromophore Aggregates,” \$463,142.

Ken Nash, Department of Energy, “Upgrading Lanthanide and Actinide Spectroscopy Capabilities at Washington State University,” \$84,299.

Ken Nash, Battelle-DOE, “NEUP Advanced Characterization of Molecular Interactions in TALSPEAK-like Separations Systems,” \$875,000. For more on the NEUP Program: <http://url.ie/fqpx>.

Ken Nash, Battelle-DOE, “Studies on Minor Actinide Separations,” \$75,000.

Kirk Peterson, Department of Energy, “Accurate ab Initio Thermochemistry and Spectroscopy of Molecules Containing f-block Elements,” \$145,000.

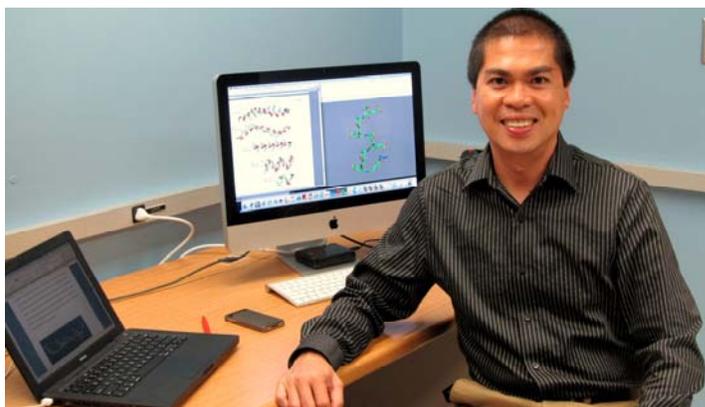
Nathalie Wall & Pete Reilly, Department of Defense, “Fast Ultra-Trace Detection of Fission Product Relative Isotopic Abundances,” \$376,069.

Ming Xian, National Institutes of Health, “Chemical Approaches for Detecting S-nitrosothiols,” \$274,724. Continuation.

Ming Xian, American Chemical Society-Teva USA Scholars Program, “Explore New Molecular Entities for Hydrogen Sulfide Research,” \$300,00.

Ming Xian, Burroughs Wellcome, “Collaborative Research to Develop New Chemical Tools for Signaling Molecules,” \$7,000.

New Faculty



Jonel Saludes joins our faculty in the Organic Division. Jonel earned his PhD in Organic Chemistry at the University of California, Davis. Under the supervision of Prof. Jacquelyn Gervay-Hague, ACS Fellow and Chair of the Department of Chemistry, Jonel designed, synthesized, and elucidated the solution phase NMR structure of novel chimeric peptides that mimicked the helical conformation of a cancer cell surface antigen called polysialic acid (PSA). Findings from his work provided the template for structure-based design of proteolysis resistant surrogates of PSA. He continued on with his training as a Postdoctoral Fellow in Bioorganic Chemistry and Chemical Biology at the University of Colorado Boulder in the laboratory of Prof. Hubert Yin. At CU, he demonstrated a creative proof-of-concept that designed peptides from the active site of lipid binding proteins could selectively tag nano-sized lipid vesicles, particles that are used by proliferating cancer cells to facilitate their movement to other body organs. Prior to engaging in peptide research, Jonel was trained on natural products chemistry and discovered antimycobacterial and antifungal secondary metabolites. Here at WSU, Jonel’s research program is focused on harnessing the potential of peptides to deliver bioactive molecules across the membrane bilayer, study cancer progression, and probe signal transduction. Specifically, efforts are focused on the design and synthesis of natural and unnatural peptides and the characterization of their interactions with membrane bilayers. Projects in the lab include the following: (a) designing chimeric, sialic acid-derived unnatural peptides as cell penetrating peptides, (b) capturing and detecting ultramicroscopic membrane-enclosed sacs called exosomes as an innovative way to diagnose cancer progression, and (c) probing ligand binding and oligomerization of prostate-specific GPCRs to understand the mechanism of protein activation that may aid in the development of peptide-based inhibitors of cancer signaling. In his spare time, Jonel likes to mountain hike and ride his road bike during summer and snowboard and cross-country ski in winter.

Awards and Achievements

Scot Wherland received the College of Sciences Boeing Distinguished Professorship in Science/Math Education.

Kirk Peterson was named Fellow of the American Physical Society and Fellow of the American Association of the Advancement of Science.

Nathalie Wall received the College of Sciences Young Investigator Award.

Don Matteson was recognized at the College of Sciences Award Banquet in honor of his retirement and for his 54 years of service to WSU.

Ursula Mazur has been selected to receive the College of Sciences Westinghouse Professorship in Materials Science.

Sue Clark was honored early this year by the ACS with the Garvan-Olin Medal. The Garvan-Olin Medal is awarded for outstanding service and leadership by women chemists. Dr. Clark was featured in an article in WSUNews: <http://url.ie/foeu>



2012 recipient Sue B. Clark (second from left) is presented her award by sponsor representative Judith Cohen (second from right), ACS Board Member Larry K. Krannich (right) and ACS President Basam Z. Shakhshiri (left).

Staff Member Receives Recognition

Nikki Clark received the College of Sciences Outstanding Staff Award. Nikki is the program coordinator for the General Chemistry Program.



Nikki Clark receives the College of Sciences Outstanding Staff Award from Chemistry Department Professor & Chair, KW Hipps.

Graduate Program News

Cougars Released Into the Wild

The University awarded doctoral degrees in Chemistry to more than a dozen students this year.

Mark Boggs, PhD

Committee Chair: **Nathalie Wall**

Dr. Boggs is postdoctoral researcher at Lawrence Livermore National Laboratory in Livermore, California.

Jessie Byers, PhD

Committee Chair: **Cliff Berkman**

Dr. Byers moved to Pittsburgh to begin a postdoctoral appointment in the School of Medicine, Department of Radiology at the University of Pittsburgh in Pittsburgh, Pennsylvania.

Veronica Chiu, PhD

Committee Chair: **Jim Schenk**

Dr. Chiu accepted a postdoctoral position in the Department of Neurosciences at the University of Toledo Medical Center in Toledo, Ohio.

Christina Crawford, PhD

Committee Chair: **Herb Hill**

Dr. Crawford is a Senior Member of the Technical Staff at Sandia National Laboratories in Albuquerque, New Mexico.

Upendra Dahal, PhD

Committee Chair: **Jeff Jones**

Dr. Dahal is a Postdoctoral Fellow at Pfizer Inc. He works in the Global Research & Development division located in Groton, Connecticut.

Eric Davis, PhD

Committee Chair: **Herb Hill**

Dr. Davis joined Fresno Pacific University as an Assistant Professor of Chemistry in Fresno, California.

Nelmi Devarie, PhD

Committee Chair: **Ming Xian**

Dr. Devarie is working as a postdoctoral researcher in the Xian Lab while he waits for his wife to finish her doctorate here in the Department.

Melissa Freiderich, PhD

Committee Chair: **Ken Nash**

Dr. Freiderich is a postdoctoral researcher at Oak Ridge National Lab in Oak Ridge, Tennessee.

John Freiderich, PhD

Committee Chair: **Ken Nash**

Dr. Freiderich is currently interviewing for a postdoctoral research position at Oak Ridge National Lab in Oak Ridge, Tennessee.

Travis Grimes, PhD

Committee Chair: **Ken Nash**

Dr. Grimes is a postdoctoral researcher at Idaho National Lab in Idaho Falls, Idaho.

Cortney Hoch, PhD

Committee Chair: **Ken Nash**

Dr. Hoch is working at Chemical Abstract Service, a division of the American Chemical Society, in Columbus, Ohio.

Jia Pan, PhD

Committee Chair: **Ming Xian**

Dr. Pan is a postdoctoral researcher at The Scripps Research Institute in Jupiter, Florida.

Lisa Wu, PhD

Committee Chair: **Cliff Berkman**

Dr. Wu is postdoctoral researcher in the Berkman Lab but will be moving on to a postdoctoral position in January at the University of Medicine & Dentistry of New Jersey in Newark, New Jersey.

Crosby & Dodgen Awards

In May, Prof. Glenn Crosby was on hand to present prizes named in his honor to four physical chemistry students. Jeremy Eskelsen (Mazur Lab) won the Crosby Award while Kevin Lewis (Kang Lab) was honorably mentioned. David Bross (Peterson Lab) won the Dodgen award and Dane Tomasino (Yoo Lab) was honorably mentioned.



Jeremy Eskelsen, Glenn Crosby Award winner for his seminar titled, *Investigation of Molecular Organization and Electron Transport in Ionic Binary Porphyrin Nanostructures*.



Kevin Lewis, Glenn Crosby Award Honorable Mention for his seminar titled, *High-capacity Ca²⁺-Binding by Calsequestrin*.



David Bross, Harold Dodgen Award winner for his seminar titled, *Quantum Chemistry with Chemical Accuracy: Thermochemistry of Transition Metal Containing Species*.



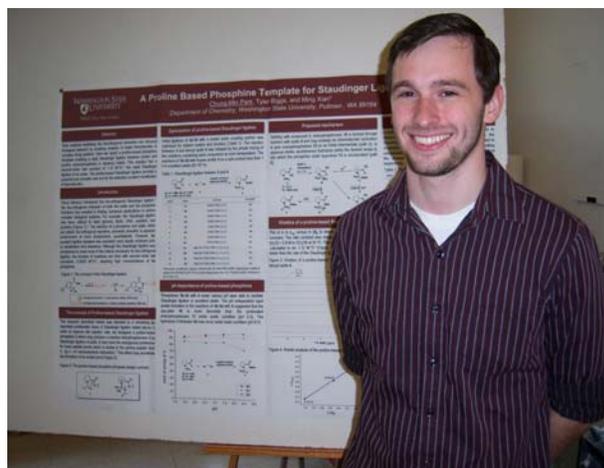
Dane Tomasino, Harold Dodgen Award Honorable Mention for his seminar titled, *Probing the Structures and Melting Curves of High-Density Fluids in-situ with Time-Resolved Spectroscopy*.

Undergraduate News

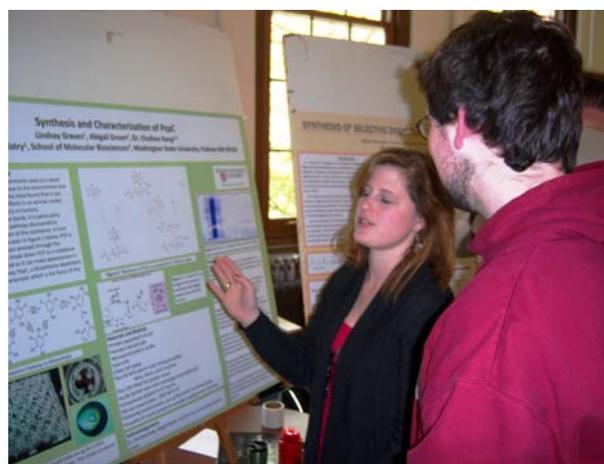


The May, 2012 graduating class. From left to right, Lindsay Graves, Nkohoua Yang, Jaclyn Sprenger, Mark Hopkins and Tyler Biggs.

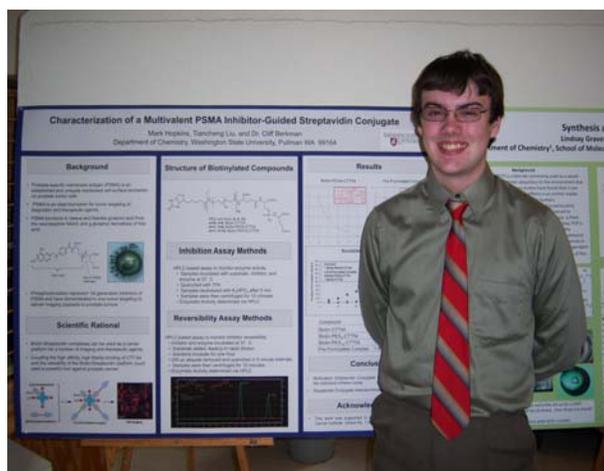
The capstone course for undergraduates earning a BS in Chemistry take Chemistry 495. In the class, students complete a research project conducted in one of the department's research labs and present a poster at the end of the semester. Students' grades are based on their poster and on how well they answer questions about their project as departmental faculty evaluate the students' posters.



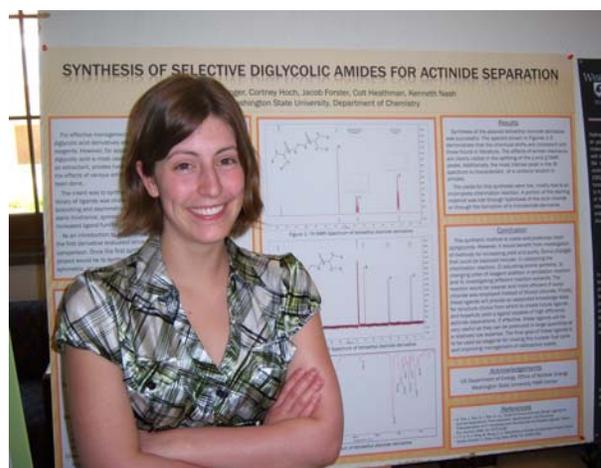
Tyler Biggs worked in the Mig Xian Lab and plans to attend graduate school.



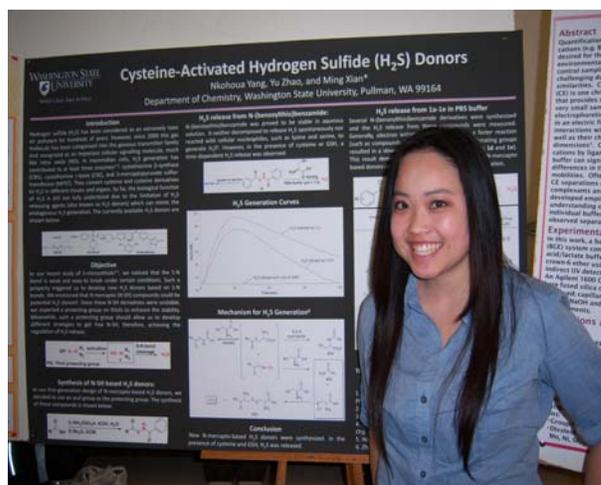
Lindsay Graves worked in the Ming Xian Lab and is employed by Merry Cellars Winery in Pullman.



Mark Hopkins worked in the Cliff Berkman Lab and is attending medical school at the University of Denver.



Jaclyn Sprenger worked in the Ken Nash Lab and is attending graduate school in chemistry at the University of Colorado, Boulder.



Nkohoua Yang worked in the Ming Xian Lab and is finishing coursework to apply for a degree in pharmacy.

Not pictured is **Nicholas Woods**, who graduated with a BS in Chemistry in August.

Breaking News

Pioneering Anti-Cancer Chemist to Receive WSU's Highest Alumni Honor

George R. Pettit, an organic chemist who pioneered the search for anti-cancer compounds in marine organisms, as well as insects and plants, has been awarded Washington State University's highest alumni honor, the Regents' Distinguished Alumnus Award.

The 1952 graduate (B.S., Chemistry) will be honored in a presentation and lecture on Sept. 20 from 1:30 to 3:30 p.m. in the CUB auditorium.