

## Department of Chemistry

In academic year 2011–2012, the [Department of Chemistry](#) had 27.5 full-time faculty (one dual faculty appointment with Biological Engineering): four assistant, three associate, and 20.5 full professors. Three of our faculty (Professors Drennan, Klibanov, and Stubbe) have a secondary appointment in Biology or Biological Engineering. Three additional faculty (Professors Chakraborty, Imperiali, and Tannenbaum) have a secondary appointment in chemistry. Of the department's 12 emeritus professors, two are Institute Professors. In addition to research in biological, inorganic, organic, and physical chemistry, the Chemistry Department continued its strong programs in undergraduate and graduate education, with 221 graduate students, 125 postdoctoral researchers, and 77 undergraduate chemistry majors.

Effective July 1, 2012, Troy Van Voorhis assumed the rank of full professor, and Alexander Klibanov became the Firmenich professor of chemistry and bioengineering. John Essigmann, the William R. and Betsy P. Leitch professor in residence and a professor in the Departments of Chemistry and Biological Engineering, was appointed the next director of the Center for Environmental Health Sciences. His appointment was effective April 2012.

Matthew Shoulders joined the faculty as an assistant professor on July 1, 2012. Shoulders was an American Cancer Society postdoctoral fellow in the laboratory of professor Jeffery Kelly at the Scripps Research Institute in La Jolla, CA. As a Department of Homeland Security and ACS medicinal chemistry graduate fellow, Shoulders worked under the guidance of professor Ronald Raines to obtain his PhD in organic chemistry from the University of Wisconsin–Madison in 2009. Shoulders graduated summa cum laude with a BS in chemistry from Virginia Tech in 2004, where he performed undergraduate research in the laboratory of professor Felicia Etzkorn. In his new lab, Shoulders is particularly interested in developing and applying chemical biology tools and bioorthogonal chemistry to elucidate how cells dynamically adjust the molecular identities of proteins in response to dysregulated protein homeostasis. His group's initial focus will be on cancer-related and stress-induced post-translational protein modifications such as N- and O-glycosylation. His lab will also work to understand the etiologies of and develop new therapeutic strategies for incurable orphan diseases that derive from missense mutations to extracellular matrix proteins, such as *osteogenesis imperfecta*. These disorders are powerful models for entire categories of protein folding-related diseases. As they discover and characterize pathways involved in cellular protein folding, researchers in the Shoulders group will also develop new chemical entities that modulate those pathways for treatment of protein folding-related diseases.

## **In Remembrance—Robert J. Silbey**

A celebration of the life of Robert J. Silbey, Class of 1942 Professor of Chemistry, former head of the Department of Chemistry, and dean of science from 2000 to 2007, took place on March 17, 2012, in the atrium of the Brain and Cognitive Sciences building. Professor Silbey died on October 27, 2011, after a battle with chronic lymphatic leukemia. He was 71. The atrium was a fitting venue to honor this remarkable chemist who, during his tenure as dean of science, oversaw the construction of the Brain and Cognitive Sciences building project, the Physics in-fill building, the renovation of Building 18, and the beginning plans for the new Koch Center for Integrative Cancer Research.

Family members, colleagues, and many friends filled the beautiful airy space to pay tribute to a remarkable man. Touching tributes, both poignant and entertaining, were delivered by all the speakers. Silbey's daughters, Jessica and Anna, regaled mourners with stories of their delightful childhood with a wonderfully attentive and loving father. They spoke of his devotion to their mother, Susan, and the joy and love he felt for his grandchildren. Susan Hockfield, president of MIT; former president Charles Vest; and former provost Robert Brown spoke of Silbey's extensive service to the Institute and his unpretentious excellence as an administrator. Susumu Tonegawa, Picower professor of biology and neuroscience, with whom Silbey worked closely during the establishment of the Picower Institute for Learning and Memory, delivered a heartfelt tribute to his colleague. Sylvia Ceyer, John C. Sheehan professor and head of the Department of Chemistry—to whom Silbey was a close friend, colleague, and mentor for over 30 years—talked of their wonderful friendship and spoke about how much his presence is missed in the Department of Chemistry. Bruce Berne, Higgins professor of chemistry and professor of chemical engineering at Columbia University, a life-long friend of Silbey (going back to their childhood and education in the Brooklyn public schools together), spoke fondly of the treasured relationship his wife and he enjoyed with Robert and Susan Silbey for over 50 years. Professor Jean Pierre Boon of the Center for Nonlinear Phenomena and Complex Systems, University of Brussels, who attended the University of Chicago with Silbey, spoke about their deep friendship and subsequent collaboration. James Kinsey, D. R. Bullard-Welch foundation professor of science emeritus at Rice University, chairman of the Welch Foundation scientific advisory board and former head of the Department of Chemistry at MIT (who was largely responsible for hiring Silbey as an assistant professor in 1966), spoke of their long friendship and collaboration. Alberto Suárez, professor of computer engineering at the Autonomous University of Madrid and a former graduate student of Silbey's, related the tremendous impact Silbey had had on his life and spoke of the precious last months they spent together when Suárez was able to assist him with his scientific writing. All spoke of Silbey's wonderfully successful scientific career, his deep love for his family, his terrific sense of humor, and his joie de vivre.

## **Memorial for H. Gobind Khorana**

A weekend of memorial events was held March 31 and April 1, 2012, in honor of the late H. Gobind Khorana, Alfred P. Sloan professor of biology and chemistry emeritus, who died on November 9, 2011. Uttam RajBhandary, Lester Wolfe professor in molecular

biology, organized the Saturday scientific symposium held at the Stata Center, where friends and colleagues traveled from as far away as India and Japan to honor Khorana. A short welcome by professor Chris Kaiser was followed by talks by friends and former colleagues. Many of the speakers were alumni from Khorana's years at MIT, including Judith Klein-Seetharaman, who was a PhD student in the Department of Chemistry. The talks included a mixture of descriptions of research in the speakers' laboratories along with reminiscences and remembrances of their experience working with Khorana. Many talked about his mentorship and guidance and how it influenced them in their scientific careers.

The session chairs and speakers included Sidney Altman, Yale University; Aseem Ansari, University of Wisconsin; Richard Calendar, University of California, Berkeley, who also read a tribute from Paul Berg, Stanford University; Nico Callewaert, Ghent University, Belgium; Marvin Caruthers, University of Colorado, Boulder; Parul Chakrabarti, Bengal Tuberculosis Association, India; Simon Chang, Louisiana State University; David Farrens, Oregon Health Sciences University; Hans-Joachim Fritz, University of Göttingen, Germany; Hara Ghosh, McMaster University, Canada; Hikoya Hayatsu, Okayama University, Japan; John Hwa, Yale University; Judith Klein-Seetharaman, University of Pittsburgh; Daniel Oprian, Brandeis University; Li Niu, State University of New York, Albany; Philip Reeves, Essex University, UK; Marsha Rosner, University of Chicago; Robert Sauer, MIT; Dieter Söll, Yale University; Sriram Subramaniam, National Cancer Institute; and Robert Wells, Texas A&M University. The talks can be accessed at <http://techtv.mit.edu/collections/biology:2698>.

Following the talks, a dinner was held in the biology building for about 70 friends and family. A wonderful collection of slides from Khorana's scientific career was collected and presented at dinner. Speakers at the dinner included Chris Kaiser and Khorana's son Dave.

On April 1, a memorial service to celebrate Khorana's life was held at the Tang Center. He was eulogized in an uplifting ceremony, with music by the Axis String Ensemble, who played pieces from Mendelssohn's *Songs Without Words* and a postlude by J. S. Bach. Speakers included Robert Randolph, chaplain to the Institute, and remembrances from Irving Goldberg, Uttam RajBhandary, and Marsha Rosner. Thomas Sakmar sent a wonderful tribute video. Alok Khorana, his great-nephew, and Julia Khorana, his daughter, shared their remembrances.

### **Faculty Awards and Honors**

Professor Jianshu Cao was appointed the Singapore research professor of biological physics for a one-year term beginning January 1, 2012.

Robert Griffin, professor of chemistry and director of the Francis Bitter Magnet Laboratory, was elected to the American Academy of Arts and Sciences. One of the nation's most prestigious honorary societies, the academy is also a leading center for independent policy research. Members contribute to academy publications and studies of science and technology policy, energy and global security, social policy and American institutions, the humanities and culture, and education.

The Awards Committee of the Royal Society of Chemistry's (RSC) Organic Division selected Professor Timothy Jamison for the 2012 RSC Merck Award. Professor Jamison was honored for his creative contributions to reaction development and natural-product synthesis, including pioneering work on cascade cyclizations, nickel-catalyzed carbon-carbon bond-forming processes, and flow chemistry.

Stephen Lippard, the Arthur Amos Noyes Professor of Chemistry, was awarded the 2012 Christopher J. Frederickson Prize for research in the neurobiology of zinc. The prize is awarded for the scientist who has broken the most important new ground in zinc neurobiology in the last three years. Professor Lippard received the prize jointly with James O. McNamara, MD, the Carl R. Deane professor at Duke University, with whom he co-authored the paper, "Vesicular Zinc Promotes Presynaptic and Inhibits Postsynaptic Long-term Potentiation of Mossy Fiber-CA3 Synapse," in *Neuron*, Volume 71, Issue 6, 1116–1126, 22 September 2011. Lippard was also awarded the Sacconi Medal from the Italian Chemical Society in conjunction with the Luigi Sacconi Foundation.

Professor Keith Nelson received the 2012 Ellis R. Lippincott Award in Vibrational Spectroscopy from the Optical Society of America for his innovations in the development of impulsive stimulated Raman scattering and its applications to the ultrafast vibrational spectroscopy of phonons and intermolecular liquid dynamics. The award is presented to an individual who has made significant contributions to vibrational spectroscopy as judged by his or her influence on other scientists.

In March 2012, JoAnne Stubbe, Novartis professor of chemistry and professor of biology, presented the 40th Annual James R. Killian Jr. Faculty Achievement Award Lecture, "Radicals: Your Life Is In Their Hands." She has devoted most of her career to elucidating the mechanisms behind small molecules known as free radicals. While most molecules need at least two electrons to remain stable, free radicals carry only one, an unstable configuration that makes them highly reactive and difficult to control. These molecules travel throughout the body and can react with anything they encounter. If they interact with a cell's DNA, free radicals can cause genetic damage that, over time, can contribute to aging and diseases such as cancer.

At an awards ceremony in New York during the spring of 2012, Professor Alice Ting, Ellen Swallow Richards associate professor, received the Vilcek Foundation Prize for Creative Promise in Biomedical Science. The award recognizes foreign-born artists and scientists who have demonstrated exceptional creativity and originality in the early stages of their careers. Two \$35,000 prizes, one in the field of biomedical science and one in a category of the arts or humanities designated by the foundation, are awarded each year.

Professor Andrei Tokmakoff received the 2012 Earle K. Plyler Prize from the American Physical Society for his pioneering work in the development and application of two-dimensional infrared spectroscopy.

## Named Lectures

The department welcomed the following named speakers during the fall of 2011 and spring of 2012.



*Professor Julius Rebek, director of The Skaggs Institute for Chemical Biology, and professor of chemistry at The Scripps Research Institute, visited the Department on May 3-4, 2012, to deliver the George Büchi Lectures in Organic Chemistry. Left to right: Professors JoAnne Stubbe, Julius Rebek and Rick Danheiser.*

- Abbott Lectures in Organic Chemistry: Gary A. Molander, University of Pennsylvania, and Michael J. Rozema; Andrew Phillips, Yale University, and Grier Wallace, Abbott Laboratories
- Arthur D. Little Lectures in Physical Chemistry: Beat H. Meier, Eidgenössische Technische Hochschule (ETH Zürich)
- Bristol-Myers-Squibb Lecture in Organic Chemistry: Amir Hoveyda, Boston College & Jaan Pesti, Bristol Myers Squibb
- Davison Lectures in Inorganic Chemistry: Fraser Armstrong, University of Oxford
- Eli Lilly Lecture in Organic Chemistry: Jean-Marie Lehn, Université de Strasbourg
- George Büchi Lectures in Organic Chemistry: Julius Rebek, The Scripps Institute
- MIT-Pfizer Lecture in Organic Chemistry: Andrew Myers, Harvard University
- Merck Banyu Lecture: Shigeki Matsunaga, University of Tokyo
- Merck Karl Pfister Lectures in Organic Chemistry: Craig J. Hawker, University of California, Santa Barbara
- Novartis Lecture in Organic Chemistry: Kenichiro Itami, Nagoya University
- T-Y. Shen Lectures in Biological Chemistry: Chris Dobson, University of Cambridge, UK

## Serving the Institute

The Department of Chemistry provides key educational service to the Institute. During academic year 2011–2012, the department taught 2,121 MIT undergraduates in biochemistry, inorganic, organic, and physical chemistry. The department also provided important mentoring relationships through the Undergraduate Research Opportunities Program (UROP), being home to 69 UROP students from a number of departments, including Biology, Chemical Engineering, Chemistry, Electrical Engineering, Materials Science, Mathematics, Mechanical Engineering, and Physics.

## Chemistry Majors

We continue to consistently attract an above-national-average number of students to Course 5, with a total of 84 majors across the three years. This year, 25 students received SB degrees in chemistry. In exit surveys we found that 48% of the Class of 2012 is bound for graduate school and 24% plan to attend medical school; 12% will seek employment and 16% are as yet undecided.



*Class of 2012. Back row, left to right: Nicholas Myers, Allison Hamilos, Brian McCarthy. Third row: Daniel Levine, Jennifer Hope, Ashli Davis, Paul Romer, Galina Mamaliga. Second row: Maryam Yoon, Elizabeth Min, Anna Levina, Kerry Ann Box, Karis Stevenson, Shion An, Anupong (Mee) Tangpeerachaikul. Front row: Sarah (Betsy) Flowers, Tara Mokhtari, Camille McAvoy. Missing from photo: Siraj Ali, William Doenlen, Abigail Koss, SangHyun Lee, Jamie Piedra, Thais Terceiro Jorge, Yuxin Xie.*

Undergraduate awards were distributed at the 2012 undergraduate senior recognition and awards banquet that was held on May 17 in the Stata Center. The following awards were presented:

ACS Analytical Chemistry Award for outstanding achievement by a junior in experimental chemistry—P. Bryan Changala

Alpha Chi Sigma Award for outstanding achievement in scholarship, research and service to the department—Anna Levina, Anupong Tangpeerachaikul

Chemistry Research Award for outstanding contributions in the area of research—Shion An, Brian D. McCarthy, Tara E. Mokhtari

CRC Freshmen Chemistry Achievement Award for outstanding academic achievement in chemistry—Khetpakorn Chakarawet, Alexander F. Siegenfeld, Martin I. McLaughlin

Department of Chemistry Service Award for significant contributions in service to the chemistry department—Daniel S. Levine, Brian D. McCarthy

Frederick D. Greene Teaching Award for outstanding contributions in teaching—Shion An

Merck Index Award for outstanding scholarship—Allison E. Hamilos, Shion An, Abigail R. Koss, Daniel S. Levine, Paul S. Romer

Outstanding Senior Thesis—Galina Mamaliga

Sophomore Achievement Award for outstanding performance in academics, research and service to the department—Eun Young Choi, Daniel A. Mokhtari, Suan L. Tuang

Strem Prize in recognition of the best undergraduate research presentation at the Chemistry UROP Symposium on April 28, 2012—Rocco L. Policarpo

### **Barry M. Goldwater Scholar**

P. Bryan Changala, a junior majoring in chemistry and physics, received a prestigious 2012 Barry M. Goldwater Scholarship. Changala plans to pursue a PhD in physical chemistry, in order to carry out research in molecular spectroscopy and teach physical chemistry at the university level. He has been carrying out research in the Field Group since his freshman year, studying small molecule gas-phase spectroscopy.

### **Undergraduate Research Opportunity Program**

UROP continues to be the capstone experience for our undergraduates. With over 90% of our majors working in a research group at least once during their degree program, they have the unique opportunity to conduct research alongside faculty, post docs and graduate students.

## Chemistry Teaching Assistants

This year students gave 67% of our graduate student teaching assistants (TAs) a 6.0 or higher on a 7.0 scale. Of those in this percentile, more than half received a 6.5 or higher



*Back row, left to right: Matthew Wellborn, Wankyu Lee, Colby Steiner, Jeffrey Martell, Lei Sun, Gregory Gutierrez. Third row: Alexandra Cok, David Grimes, Alex Zhukhovitskiy, David Song, Michael Huynh, Michael Mavros. Second row: Stephanie Tumidajski, Mingjuan Su, Jolene Mork, Whitney Hess, Kolby White, Phoom Chairatana, David Veysset. Front row: Markete Krikorian, Paula Ruiz-Castillo, Elizabeth Kelley. Missing from photo: Jenny Liu and Peter Thill.*

## Graduate Student Awards

Kurt Armbrust— National Science Foundation Graduate Research Fellowship Program

NSF GRFP

Pedro Arrechea—Dean of Science Fellowship

Thomas Avila—Dean of Science Fellowship, National Consortium for Graduate Degrees for Minorities in Engineering and Science (GEM) Fellowship

Joseph Azzarelli—Presidential Fellowship

Daniel Bediako—Martin Family Fellowship

Darin Bellisario—NDSEG Fellowship

Megan Brophy—Lippard Fellowship

Alan Burts—Hughes Memorial Fellowship, Dean of Science Fellowship

Phoom Chairatana—Outstanding TA Award, Royal Thai Government scholarship

Hang Chen—Norris Fellowship

Stephanie Cheung—Chapin Fellowship

Chern Chuang—Presidential Fellowship



James Colombe—Dow Fellowship, NSF GRFP  
Alexandra Cok—Outstanding TA Award, Davison Fellowship  
Igor Coropceaunu—Chapin Fellowship  
Kent Cox—Chapin Fellowship  
Galia Debelouchina—Raymond Andrew Prize for Outstanding Thesis  
Marcus Gibson—Martin Family Fellow  
David Grimes—NSF GRFP, Outstanding TA Award  
Gregory Gutierrez—Outstanding TA Award, Dean of Science Fellowship  
Robert Halbach—Davison Fellowship  
Chen Hang—Norris Fellowship  
Whitney Rochelle Hess—Eni-MIT Energy Fellowship, National Defense Science and Engineering Grant (NDSEG) Fellowship, Outstanding TA Award  
Elizabeth Hocking—Eni-MIT Energy Fellowship  
Victoria Hung—NSF GRFP, Wolfe Fellowship  
Michael Huynh—Outstanding TA Award  
Timothy Johnstone—International Precious Metal Institute Gemini Graduate Student Award, MIT-Harvard Center of Cancer Nanotechnology Excellence Graduate Award  
Elizabeth Kelley—Outstanding TA Award, Moore Fellowship  
Daniel Kozera—National Sciences and Engineering Research Council of Canada Fellowship  
Markrete Krikorian—NDSEG Fellowship, Outstanding TA Award  
Alyssa Larson—Martin Family Fellow  
Wankyu Lee—Outstanding TA Award, Presidential Fellowship  
Jenny Liu—Chapin Fellowship, Büchi Summer Fellowship, Outstanding TA Award  
Qing Liu—Wolfe Fellowship  
Jingjing Ling—Singapore Agency of Science, Technology and Research Fellowship  
Andrew Maher—Eni-MIT Energy Fellowship  
Jeff Martell—Outstanding TA Award  
Michael Mavros—NSF GRFP, Outstanding TA Award, Norris Fellowship  
Jessica McCombs—Dean of Science Fellowship  
Anna Mork—Outstanding TA Award  
Matthew Nava—Dean of Science Fellowship  
Nathaniel Park—NSF GRFP

Daniel Rolands—Corning Fellowship  
 Paula Ruiz-Castillo—Outstanding TA Award, La Caixa Fellowship  
 Kanchana Ravichandran—Eli Lilly Fellowship  
 Mark Simon—C.P. Chu and Y. Lai Fellowship, Davison Fellowship  
 Orly Slavin—Elie Shaio Memorial Award  
 David Yongmin Song—Chapin Fellowship, Outstanding TA Award  
 Julia Stauber—Presidential Fellowship  
 Colby Steiner—Outstanding TA Award  
 Paul Stevenson—Wolfe Fellowship  
 Mingjuan Su—Outstanding TA Award  
 Lei Sun—Davison Fellowship  
 Peter Thill—Outstanding TA Award  
 Stephanie Tumidajski—Outstanding TA Award  
 David Veysset—Outstanding TA Award  
 Matt Welborn—Chapin Fellowship, Outstanding TA Award, NSG GRFP  
 Kolby White—Outstanding TA Award, NDSEG, Dean of Science Fellowship  
 Wanqin Xie—Presidential Fellowship  
 Hsiang-Yu Yang—Presidential Fellowship  
 Yang Yang—Moore Fellowship  
 Aleksandr Zhukhovitskiy—Outstanding TA Award, NDSEG

## Doctoral and Master's Degree Recipients

### September 2011

|                    |     |                 |
|--------------------|-----|-----------------|
| Luis Arizpe        | SM5 | Fu group        |
| Ting-Kai Chang*    | SM5 | Degen group     |
| Galia Debelouchina | PhD | Griffin group   |
| Shaun Fontaine     | PhD | Danheiser group |
| Jeremy Johnson     | PhD | Nelson group    |
| Changhoon Lee      | PhD | Nocera group    |
| Jeewoo Lim         | PhD | Swager group    |
| Ye Tao*            | SM5 | Degen group     |

**February 2012**

|                  |     |                  |
|------------------|-----|------------------|
| Mimi Cho         | PhD | Stubbe group     |
| Margaret Flook   | PhD | Schrock group    |
| Peter Funke      | SM5 | Williamson group |
| Hee-Sun Han      | PhD | Bawendi group    |
| Amanda Kohnen    | SM5 | Danheiser group  |
| Nathaniel Silver | PhD | Tidor group      |

**June 2012**

|                        |     |                   |
|------------------------|-----|-------------------|
| Nicholas Bencivenga    | SM5 | Fu group          |
| Joseph Cotruvo         | PhD | Stubbe group      |
| Jason Cox              | PhD | Swager group      |
| Matthew Eddy           | PhD | Griffin group     |
| Sunkyu Han             | PhD | Movassaghi group  |
| Andrew Horning*        | SM5 | Tokmakoff group   |
| Harold Hwang           | PhD | Nelson group      |
| Kevin Jones            | PhD | Tokmakoff group   |
| Benjamin Kaduk         | PhD | Van Voorhis group |
| Timothy Kowalczyk      | PhD | Van Voorhis group |
| Julia Kozhukh          | PhD | Lippard group     |
| Joshua Lessing         | PhD | Tokmakoff group   |
| Alejandro Lichtscheidl | PhD | Schrock group     |
| Shuang Liu             | PhD | Swager group      |
| Jose Lobez-Comeras     | PhD | Swager group      |
| Michael Marshak        | PhD | Nocera group      |
| Ellen Minnihan         | PhD | Stubbe group      |
| Anna Mork *            | SM5 | Swager group      |
| Rebecca Parkhurst      | PhD | Swager group      |
| Jan Schnorr            | PhD | Swager group      |
| Albert Smith           | PhD | Griffin group     |
| Thomas Teets           | PhD | Nocera group      |
| Christopher Werley     | PhD | Nelson group      |
| Eric Zimanyi           | PhD | Cao group         |

\*Continuing as MIT graduate student

**Research Highlights****Moungi Bawendi**

Professor Bawendi and his students have been focusing on three broad areas of quantum dot research. First, they have been developing spectroscopic tools to investigate excitonic processes in single quantum dots and films of quantum dots that are used in both solar cell and light emitting applications, where they have made a number of important advances. Second, they have been developing technology to incorporate quantum dots into solar cell devices, in collaboration with the group of professor Vladimir Bulovic in Electrical Engineering and Computer Science. Third, they have made a number of advances in developing and applying quantum dots for biological applications, largely

in the context of in vivo applications geared towards understanding cancer in animal models. This last work has benefited strongly from many collaborations, especially with the Steele Laboratory at Massachusetts General Hospital, led by professor Rakesh Jain. Finally as a side project, professor Bawendi has collaborated with professor Ramesh Raskar from the Media Lab to demonstrate concepts of femto-photography, where all experimental data were taken in the Bawendi Lab.

### **Stephen Buchwald**

The Buchwald lab has continued its work on the development of new methods for organic synthesis that involve the formation of carbon-carbon, carbon-nitrogen, carbon-oxygen and carbon-halogen bonds. The techniques that the researchers have developed are widely used throughout academia and industry. Applications range from drug discovery and pharmaceutical manufacturing to the preparation of new electronic materials. In addition to the techniques themselves, they have been studying the fundamental processes that underpin them.

### **Sylvia Ceyer**

The Ceyer group is exploring the role of dissolved hydrogen in a Au-Ni surface alloy. This alloy is an excellent model for the Raney Ni alloy, used commercially in all heterogeneous catalytic hydrogenation reactions. The possibility of enhanced solubility of hydrogen in this Ni alloy, as compared to pure Ni, promises to make “bulk hydrogen” available for study by the larger community. The Ceyer group has also been probing the role of collisional lattice activation in the surface reactivity of Si. Preliminary results reveal that this mechanism for activation is a general one for surfaces that serve as a reactant.

### **Christopher Cummins**

The discovery was made that CO<sub>2</sub> binds reversibly to a titanium(IV) oxoanion complex in a manner that is counter-ion dependent; efforts were initiated to extend this carbon dioxide fixation modality to simple metal oxides. It was shown that macrobicyclic cryptand molecules could be hexadeprotonated with insertion of two metal(II) ions (M = Mn, Fe, Co, Ni, and Zn) and that the resulting bimetallic complexes bind small molecules such as cyanide ion. The same macrobicyclic hexacarboxamide cryptand molecules *sans* deprotonation were found to serve as receptors for the peroxide dianion, O<sub>2</sub><sup>2-</sup>, which could be generated electrochemically from molecular oxygen or chemically by induction of superoxide disproportionation. These new reactions have possible applications in metal-air battery technology. A mild new synthetic route to layered vanadyl pyrophosphate solid-state materials was devised, and a line of inquiry involving molecular complexes of cyclo tri- and tetra-phosphate ligands was initiated with the aim of discovering new oxidation reactions. A new class of bicyclic tetra-organo diphosphane (synthesized photochemically from elemental phosphorus) was found to engender self-assembly of bimetallic complexes of nickel, palladium, and platinum, and approaches were made to the generation of a mono-nuclear complex of P<sub>2</sub> as a ligand in coordination chemistry.

### **Mircea Dinc**

The Dincă group is concerned with the study and applications of hybrid materials known as metal-organic frameworks (MOFs) in energy related fields. During the past year, the group has shown that MOFs with permanent porosity can also display high charge mobility, providing the first solution to a long-standing challenge in the field, with potential implications in energy storage devices, electrocatalysis, and sensing. Relatedly, the group has established intrinsic mechanisms for fluorescence quenching in a wide class of organic chromophores and new synthetic techniques towards the construction of novel heterogeneous catalysts.

### **Catherine Drennan**

In collaboration with the laboratory of professor Stephen Ragsdale at the University of Michigan, the Drennan group published in *Nature* the long-awaited X-ray structure of all protein components required for the methyltransfer from folic acid (vitamin B9) to vitamin B12, a reaction necessary for maintaining pools of methyl donor S-adenosylmethionine as well for acetogenesis (*Nature*, Volume 484, 265–269, 12 April 2012).

### **John Essigmann**

The Essigmann lab is part of a collaborative multi-institutional group that has a drug candidate in Phase II clinical trials. The drug candidate is an antiviral agent that mimics the innate immune system by accelerating the rate of mutagenesis of viruses, causing the virus to go extinct within the host by a mechanism termed lethal mutagenesis. In other work, the group has discovered that 5-chlorocytosine, a product of nucleotide damage by inflammation, is mutagenic in living cells. Finally, the researchers have completed an analysis of the substrate range of AlkB, a DNA repair protein that counters the toxic effects of genome-damaging lipids.

### **Robert Field**

The Field lab's comprehensive spectroscopic study of the acetylene S1 electronic excited state contains a complete picture of the trans-cis isomerization barrier-proximal vibrational levels. The unique level-pattern signature of the location of the isomerization barrier is observed. Photofragment vibrational population distributions observed in chirped pulse millimeter wave (CPmmW) spectra are shown to sample the shape of the photofragmentation transition state. CPmmW spectra demonstrate the existence of previously unknown pyrolysis mechanisms. Superradiance and other inter-atom cooperative effects mediated by the radiation field are observed and exhaustively characterized in Rydberg-Rydberg transitions. A buffer-gas-cooled ablation source has been demonstrated to increase the yield of ablated species 100x and decrease the Doppler dephasing 10x. Each of these results is transformative in the field of molecular spectroscopy and dynamics.

### **Timothy Jamison**

The Novartis–MIT Center for Continuous Manufacturing team has demonstrated the first end-to-end continuous manufacturing of a pharmaceutical drug substance. The Jamison group developed the chemical synthesis sequence utilized in the process. In collaboration with professors Klavs Jensen and Allan Myerson (both of the Department of Chemical Engineering), the group developed a tabletop system for the continuous manufacturing of several pharmaceutical substances. Potential applications include disaster relief, use in developing nations, and green manufacturing.

### **Jeremiah Johnson**

Research in the Johnson group is focused on the design and synthesis of new materials for emerging applications. In the past year the group has developed new porous, degradable polymeric hydrogels that allowed the first measurement of loop imperfections in polymer materials. The researchers also developed a living sunlight-photoinitiated polymerization method for the synthesis of telechelic polymers and “flower-mimetic hydrogels.” They also developed functional N-heterocyclic carbene derivatives for modification of bulk and nanoscopic material surfaces.

### **Stephen Lippard**

The structure of soluble methane monooxygenase bound to its regulatory protein was solved by X-ray diffraction, revealing how methane, oxygen, and proton access to the active site of the hydroxylase enzyme is controlled. Phenanthriplatin, a monofunctional DNA-binding platinum anticancer drug candidate with unusual potency and cellular activity profile, was discovered. In a collaborative study with a group at Duke Medical School, the Lippard lab demonstrated that vesicular zinc promotes presynaptic and inhibits postsynaptic long-term potentiation of mossy fiber-CA3 synapse.

### **Mohammad Movassaghi**

Professor Movassaghi’s research program continues to focus on the development of new strategies and technologies for complex molecule synthesis. His group recently reported the first general approach to the total synthesis of gliocladin B and related gliocladins, including the first full structural assignment of any member of the methylsulfide-containing subfamily. The researchers also provided a generalizable solution to the aspidosperma alkaloids via the intermediacy of dicationic intermediates that allows unprecedented dimerization of complex alkaloids. In the area of fragment assembly, they developed a new synthetic strategy for directed union of two complex tryptophan-based molecules and have successfully applied this chemistry to the first enantioselective total synthesis and structural revision of the naseceazine alkaloids. The hallmark of their syntheses is the unparalleled efficiency and high level of stereochemical control in most complex settings, taking full advantage of the inherent chemistry of plausible biosynthetic intermediates.

### Elizabeth Nolan

The Nolan lab delineated the zinc- and manganese-binding properties of the antimicrobial protein human calprotectin, and discovered that this protein responds to physiological calcium gradients to morph into a potent transition metal chelator in the extracellular space where calcium levels are high. In another thrust, the group demonstrated that the ferric enterobactin transport machinery of *Escherichia coli* and the opportunistic human pathogen *Pseudomonas aeruginosa* may be utilized to bypass the outer membrane permeability barrier and deliver small molecule cargo conjugated to a monofunctionalized enterobactin platform to the cytoplasm of these organisms. In collaboration with the laboratory of professor Gerhard Wagner at Harvard Medical School, the group solved the NMR solution structure of a cysteine-rich human defensin peptide, HD5.

### Bradley Pentelute

This past year, Professor Pentelute established a new research group. Eleven members joined the group, including undergraduates, graduates, and postdoctoral fellows. The group discovered that a small transpeptidase was capable of attaching thioester functionalities onto proteins in a robust manner. This discovery will allow for the chemical modification of proteins.

### Richard Schrock

The Schrock lab has been involved in fundamental studies of the olefin metathesis reaction (new catalysts and mechanisms) along with applications of metathesis in polymer and organic chemistry. The group has also been attempting to prepare a catalyst for the reduction of molecular nitrogen to ammonia with protons and electrons.

### JoAnne Stubbe

The Stubbe lab continues its efforts to understand the mechanism and regulation of ribonucleotide reductases (RNRs), the enzymes central to DNA replication and repair and the targets of three clinically active anticancer drugs (gemzar, hydroxyurea and clofarabine) and a fourth (triapine) in phase II clinical trials. In collaboration with the lab of professor Catherine Drennan in Chemistry and the lab of associate professor Francisco Asturias at Scripps Research Institute, the lab has used complimentary biophysical methods (x-ray crystallography, cryo-electron microscopy, small-angle x-ray scattering, and analytical ultracentrifuge) to obtain the first structural insight into the inhibited states of the bacterial and hRNRs. The researchers have also developed methods to measure the rates of interconversion of the inactive and active states. They have shown unexpectedly that two drugs (Gemzar, a mechanism-based inhibitor of hRNR, and clofarabine, a slow tight-binding, reversible inhibitor of hRNR) both inhibit the enzyme by alteration of its quaternary structure in unexpected ways. Clofarabine di- and tri- phosphates, for example, trigger formation of kinetically persistent hexamers

of one of its subunits that remain in this state even subsequent to inhibitor dissociation. The lab has also demonstrated that hRNR is the most upstream target of the drug iron-triapipe and that it mediates rapid reduction of RNR's essential tyrosyl radical and then consequently its inactivation. This proposed mode of cytotoxicity is at odds with reports in the literature. The lab continues to investigate the mechanisms of cytotoxicities of these drugs and the function and regulation of RNRs, essential for life.

### **Timothy Swager**

In collaboration with the group of professor Robert G. Griffin of the Department of Chemistry and the Francis Bitter Magnet Laboratory, the researchers have developed nuclear magnetic resonance spectroscopy biracial polarization agents with record high signal enhancements by dynamic nuclear polarization. In collaboration with professor Vladimir Bulovic, they have demonstrated a novel method to create greater charge separation at interfaces and have produced higher efficiency organic photovoltaic cells. They have also developed new resistivity-based sensors for the plant hormone ethylene. This latter method can be readily implemented in a wide array of electrical platforms and ongoing efforts are directed at developing robust technologies that can reduce waste in the post-harvest fruit and vegetable management.

### **Alice Ting**

The Ting lab reports advances in site-specific protein labeling in cells, electron microscopy (EM) imaging of cellular proteins, and proteomic mapping of living cells in the past year. In its site-specific protein labeling work, the Ting lab published several papers describing the targeting of bright, photostable organic dyes to specific intracellular and cell surface proteins in the live cell context using engineered variants of lipoic acid ligase. In EM research on imaging of cellular proteins, a genetically encoded reporter for EM imaging of cellular proteins was developed and applied to resolve a literature dispute regarding the membrane topology of the mitochondrial calcium uniporter. For proteomic mapping of living cells, a method has been developed to map the molecular composition of different sub-regions of living cells with nanometer-scale spatial resolution.



**Andrei Tokmakoff**

The Tokmakoff group studies time-dependent changes of molecular structure in chemical reactions and biophysical processes through the use of two-dimensional infrared spectroscopy and molecular dynamics simulations. In the past year the researchers have developed a femtosecond infrared light source that allows them to directly monitor the transport of protons along hydrogen bonding networks in water. They also have studied biophysical dynamics problems, including protein-protein association processes and protein folding.

**Troy Van Voorhis**

The Van Voorhis lab predicted a novel mechanism for O-O bond formation in water splitting catalysts, developed a realistic model of electrochemistry and electron transfer in solution, and discovered fundamental connections between localization and structural disorder in organic semiconductors.

**Sylvia T. Ceyer**

**Department Head**

**John C. Sheehan Professor of Chemistry**