Department of Chemistry

In academic year 2013–2014, the Department of Chemistry had 26.5 full-time faculty (one dual faculty appointment with Biological Engineering): seven assistant professors, one associate professor, and 18.5 full professors. Three of our faculty (Catherine Drennan, Alexander Klibanov, and JoAnne Stubbe) have a secondary appointment in Biology or Biological Engineering. Four additional faculty (Arup Chakraborty, Barbara Imperiali, Susan Solomon, and Steven Tannenbaum) have a secondary appointment in chemistry. In addition to research in biological, inorganic, organic, materials and nanoscience, and organic and physical chemistry, the Chemistry Department continued its strong programs in undergraduate and graduate education, with 210 graduate students, 120 postdoctoral researchers, and 56 undergraduate chemistry majors.

Effective July 1, 2014, Alice Ting assumed the rank of full professor and Elizabeth Nolan the rank of associate professor without tenure. Assistant Professor Brad Pentelute holds the Pfizer-Laubach career development professorship effective July 1, 2014.

Faculty and staff of the department were deeply saddened by the death of two of its emeritus professors during the year. Robert A. Alberty, former dean of MIT's School of Science, whose seminal contributions to the thermodynamics and kinetics of biochemical reactions are still at the forefront of chemistry, passed away on January 18, 2014, at the age of 92. A member of the chemistry faculty since 1967, Alberty led the School of Science from 1967 to 1982, when he returned to teaching and research in physical chemistry. He became professor emeritus in 1991.

Irwin Oppenheim passed away on June 3, 2014, at the age of 84, following complications from heart surgery. Oppenheim joined the department in 1961 as an associate professor—notably, its first theoretical chemist—and was promoted to full professor in 1965. His research at MIT concentrated on a molecular description of relaxation phenomena in gases and liquids.

On July 1, 2014, Alex Shalek, a former postdoc in the Park Lab at Harvard University, Mei Hong, formerly the John D. Corbett Professor of Chemistry at Iowa State University, and Jeff Van Humbeck, formerly a postdoctoral fellow in Chemistry, joined the Department of Chemistry faculty. Gabriela Schlau-Cohen, currently a postdoctoral fellow at Stanford University, will join the department as an assistant professor on January 16, 2015.

Research in the Shalek group is directed towards the development and application of new technologies that will facilitate the understanding of how cells collectively perform systems-level functions in healthy and diseased states. The group leverages recent advances in nanotechnology and chemical biology to establish a host of core, cross-disciplinary platforms that will collectively enable them to extensively profile and precisely control cells and their interactions within the context of complex systems. The group will also focus on how cellular heterogeneity and cell-to-cell communication drive ensemble-level decision-making in the immune system, with an emphasis on "two-body" interaction (e.g., host cell-virus interactions, innate immune control of adaptive

immunity, tumor infiltration by immune cells). The goal is to not only provide broadly applicable experimental tools but also help transform the way in which we think about single cells, cell-cell interactions, diseased cellular states, and therapeutics so as to create a new paradigm for understanding and designing systems-level cellular behaviors in multicellular organisms.

The Van Humbeck laboratory aims to develop new methods for controlling catalytic reactions and the structure of organic materials. Encompassing many individual projects, three overarching research themes direct the lab's initial endeavors. One is selective oligomerization. By incorporating catalysts within restrictive supramolecular volumes, size-selective oligomerization will be pursued in the context of energy applications (i.e., biofuels upgrading) and medicinal chemistry (i.e., polyketide synthesis). In the area of catalysis, the effect of electrostatic elements will also be investigated. The judicious inclusion of charged units into catalyst structures will be investigated with a view to improving both efficiency and selectivity in new reactions. Ion pairing as a means of structural control has been explored to a much greater extent in polymers, with the typical units of charge resulting from proton transfer. As an alternative, the inclusion of inherently charged units that lack protons will be pursued, for both functional and structural organic materials. Additionally, the development of charge by electron transfer between redox active centers will be investigated for responsive materials.

Research in the Hong lab focuses on the development and application of solid-state NMR spectroscopy to elucidate the structure and dynamics of biological macromolecules, especially membrane proteins. Hong's research spans fundamental spectroscopy and applications to biology, pharmacology, and biomaterials. She has a long-term interest in ion channels and curvature-inducing membrane proteins. She is also interested in biological complexes such as polysaccharides and glycoproteins of plant cell walls. Magic-angle-spinning solid-state NMR spectroscopy is her principal tool for these biophysical studies because it provides atomic-resolution structural and dynamical information on noncrystalline and insoluble macromolecules in their native environments.

Faculty Awards and Honors

Professor Keith Nelson was elected to the American Academy of Arts and Sciences on October 12, 2013. 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, and education. The new class was inducted at a ceremony in October 2014 at the Academy's headquarters in Cambridge, Massachusetts.

Professor Stephen Buchwald, the Camille Dreyfus professor of chemistry, was awarded the 2014 Linus Pauling Medal Award for "outstanding contributions to chemistry meriting national and international recognition." The Linus Pauling Medal Award has

been given annually since 1966 by the American Chemical Society (ACS) Puget Sound, Oregon, and Portland Sections. The award is named after its first winner, Nobel laureate Linus Pauling, a native of the Pacific Northwest.

Professor Timothy Swager, the John D. MacArthur professor of chemistry, has been named faculty director of the Deshpande Center for Technological Innovation. His appointment, announced at the center's annual research showcase, IdeaStream, became effective May 1, 2014. "Professor Swager's background in world-class research and technology commercialization, and his leadership within MIT's Chemistry department will be great assets to the center," said Deshpande Center founder Desh Deshpande. "Tim's proven ability to impact the world with his ideas will allow him to play a key role in leading MIT's innovation agenda."

Professors Mircea Dincă and Jeremiah Johnson were selected to receive 2014 Alfred P. Sloan Foundation Research Fellowships. Since 1955, the fellowships have been awarded to early-career scientists and scholars whose achievements and potential identify them as rising stars, the next generation of scientific leaders. In addition, Professor Dincă was selected for a Cottrell Scholar Award. Dincă is one of a dozen outstanding early career teacher-scholars at PhD-granting institutions to be accepted into the Cottrell Scholar program following a rigorous peer-review process. The awards are presented to early career faculty who are committed to excel at both research and teaching.

Professor Nolan received a Camille Dreyfus Teacher-Scholar Award for her work in understanding the physiological role of peptides/proteins that bind metals and their function as antibacterial agents. The Camille Dreyfus Teacher-Scholar Awards Program supports the research and teaching careers of talented young faculty in the chemical sciences.

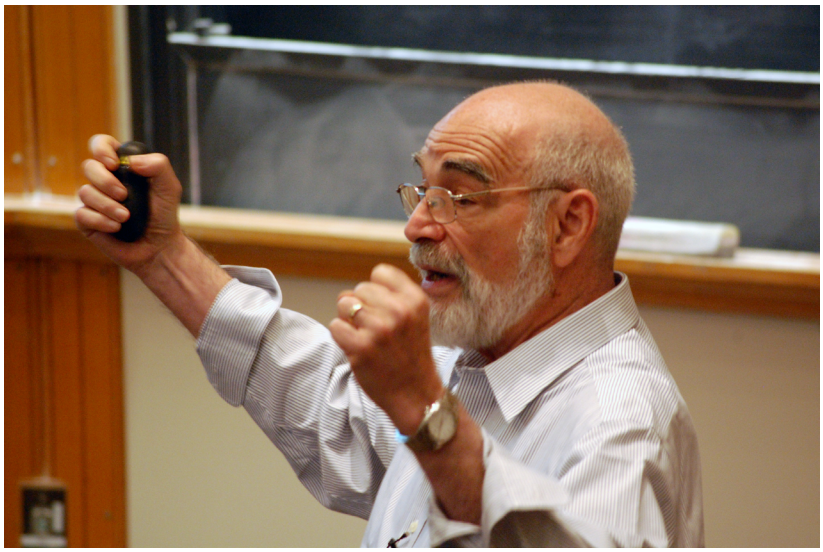
Professor Troy Van Voorhis was selected to receive a grant from the Camille and Henry Dreyfus Foundation under its Special Grant Program in the Chemical Sciences. The Special Grant Program in the Chemical Sciences provides funding for innovative projects in any area consistent with the Foundation's broad objective to advance the chemical sciences.

Professor Matthew Shoulders was selected to receive a three-year Smith Family Award for Excellence in Biomedical Research. For the past 21 years, the Smith Family Foundation has been supporting groundbreaking medical research through the Smith Family Awards Program for Excellence in Biomedical Research. Its mission is to launch the careers of newly independent biomedical researchers with the ultimate goal of achieving medical breakthroughs.

Named Lectures

The department welcomed the following named speakers during fall 2013 and spring 2014:

- Organic Chemistry Merck-Pfister Lectures: Makoto Fujita, University of Tokyo
- Sigma-Aldrich Lecture in Organic Chemistry Seminar: Sarah Reisman, Caltech
- Merck-Banyu Lecture in Organic Chemistry: Mamoru Tobisu, Osaka University
- A.D. Little Lectures in Physical Chemistry: Bruce Berne, Columbia University
- Buchi Lectures in Organic Chemistry: Phil Baran, Scripps
- Novartis Lectures in Organic Chemistry: Viresh Rawal, University of Chicago and Sejal Patel, Novartis
- Bristol-Myers Squibb Lectures in Organic Chemistry: Jeff Johnson, UNC & David Kronenthal, BMS
- Davison Lectures in Inorganic Chemistry: Chi-Ming Che, University of Hong Kong
- Pfizer-MIT Lecture in Organic Chemistry: Melanie Sanford, University of Michigan
- Biological Chemistry Seminar Series: TY Shen Lectures: Carlos Bustamante, University of California at Berkeley



Bruce Berne, Higgins professor of chemistry at Columbia University, delivers the A.D. Little Lectures in Physical Chemistry.

Serving the Institute

The Department of Chemistry provides key educational service to the Institute. During the 2013–2014 academic year, the department taught 1,910 undergraduate students in the areas of biochemistry and inorganic, organic, and physical chemistry. The

department also was the home for 57 Undergraduate Research Opportunities Program (UROP) students, providing important mentoring relationships for students from a number of departments, including chemistry, biology, mathematics, physics, chemical engineering, biological engineering, electrical engineering, and materials science.

Class of 2014. Back row (l to r): Megan Cherry, Alice Choi, Chyleigh Harmon, Julia Berk, Sumin Kim, Anubhav Sinha, Suan Tuang, Jacob Laux, Katherine Silvestre, Tatiana Berger, Vincent D'Andrea, Erika Ye. Front row (l to r): Grace Tuyiringire, Daniel Mokhtari, Alexandra Wrobel, Sasilada Sirirungruang, Arunima Balan, Aileen Johnson. Not pictured: Sean Karson.

Chemistry Majors

We continue to consistently attract a very talented group of undergraduates to Course 5, with a total of 56 majors across the three years. This year, 18 students received SB degrees in Chemistry. Exit surveys indicated that 50% of the Class of 2014 is bound for graduate school and 17% expect to attend medical school; 33% are planning to seek employment.

Undergraduate Recognition and Awards

Undergraduate awards were given at the 2014 Undergraduate Senior Recognition and Awards Banquet in May.

CRC Freshman Chemistry Achievement Award For outstanding academic achievement in chemistry: Minwoo Bae, Tomohiro Soejima

Outstanding Sophomore Achievement Award For outstanding achievement in academics, research, and service to the Department of Chemistry: Lily Chen: Diptarka Hait

ACS Analytical Chemistry Award For outstanding achievement by a junior in experimental chemistry: Martin McLaughlin

Strem Prize For outstanding undergraduate research and in recognition of the best presentation at the 2014 Chemistry UROP Symposium: Alexandra Wrobel

Alpha Chi Sigma Award For outstanding achievement in scholarship, research, and service to the Department of Chemistry: Daniel Mokhtari, Katherine Silvestre

Research Award For outstanding contributions in the area of research: Arunima Balan, Tatiana Berger

Frederick D. Greene Teaching Award For outstanding contributions in the area of teaching: Arunima Balan, Suan Tuang

ACS Inorganic Chemistry Award For excellence in inorganic chemistry: Alexandra Wrobel

Undergraduate Research Opportunities Program

The Undergraduate Research Opportunities Program continues to be the capstone experience for our undergraduates. More than 90% of our majors work in a research group at least once during their degree program, conducting research alongside faculty, postdocs, and graduate students.

Chemistry Teaching Assistants

Our graduate student teaching assistants (TAs) are among the best at MIT. This year, students rated 78% of our TAs a 6.0 or higher on a 7.0 scale. Of that group, half were rated 6.5 or higher. The following teaching assistants received TA Awards: Alyssa Antropow, Salima Bahri, Jessica Carr, Deborah Ehrlich, Ethan Evans, Daniel Franke, Allena Goren, Eric Metzger, Alexander Mijalis, Julia Stauber, Wesley Transue, Yu-Pu Wang, Anna Wuttig, Chi Zhang.

The department has introduced a new award, the Department of Chemistry Award for Continued Excellence in Teaching. Recognizing sustained service and excellence in teaching within the department, this prestigious award is presented to graduate students who have taught for at least three terms and have previously won the Department of Chemistry Award for Outstanding Teaching. The inaugural winners of the Department of Chemistry Award for Continued Excellence in Teaching are Phil Hamzik, Marco Jost, Ken Kawamoto, and Molly Sowers.

Excerpts from TA Evaluations:

"One of the best TAs I have ever had at MIT. Cares about her students, and makes sure that they understand the subject material. Easy to contact, and very thorough in her answers."

"Best recitation leader! Your review sessions and summaries of all the reactions for a single unit were invaluable and the reason our recitation always did so well was because of how clearly you explained all the concepts and worked us through practice problems. I hope you become a full time chemistry teacher someday because you'd be a great lecturer!"

"[NAME] was probably one of the best TAs I've had in course 5. She was able to answer any questions I had and made me really interested in what I was doing. She had a strong handle on the lab procedures and was always prepared."

"He was an excellent TA and helped me understand the material. He genuinely cares for his students and encourages us to put in more effort. I also enjoyed how he always answered students' questions and focused on each of our problems rather than just completing a set of questions. He has great teaching skills and I learned a lot from recitation!"

"Displayed an amazing amount of charisma and taught very clearly. Showed a deep understanding of the subject and went out of his way to make sure the students understood the material. Addressed the students and their problems individually, even outside of class, which takes a tremendous amount of time and effort, truly a unique quality. Definitely an amazing TA."

"[NAME] put a lot of time into making really great powerpoint presentations that did a great job of reinforcing the lecture material. He was very clear and thorough, promptly answered his emails, and was always eager to help. He also recommended that I seek additional help in the class through tutoring when my performance worsened, which proved to be a helpful recommendation."

"The best chemistry TA I've had here at MIT. His excitement for the material rubbed off on students and made lab time a true pleasure. [NAME] is not only enthusiastic about the material, but also very approachable and good at explaining the material. He was very responsive to email. If he decides to pursue academia, his students will be a very lucky bunch."

"[NAME] was incredibly on top of everything, always. She was by far the most organized TA. She would come in early to write up lecture notes on the board before lab, was very helpful during office hours, and made sure to thoroughly explain the experiments to her students. She was not only a wonderful TA in lab, but was also very responsive via email. Great at explaining things, and very committed to her students."

Graduate Student Awards

Armburst, Kurt: Boston Symposium on Organic and Bioorganic Chemistry Best Paper Award

Azzarelli, Joseph: Lemelson–MIT National Collegiate Student Prize Competition, "Use-It" Category, Top 5 Finalist

Berman, Chet: Daniel S. Kemp Summer Fellowship and the Robert T. Haslam Presidential Fellowship

Branon, Tess: Dow Fellowship

Chileveru, Haritha: Richard R. Schrock Summer Fellowship

Coropceanu, Igor: National Science Foundation Graduate Fellowship Program

Cox, Kurt: National Science Foundation Graduate Fellowship Program

DiChiara, Andrew: Masamune Memorial Graduate Fellowship

Evans, Ethan: Presidential Fellowship and National Science Foundation Graduate Fellowship Program

Fennell, John: US Army Advanced Civil Schooling Fellowship

Frank, Daniel: Presidential Fellowship

Funk, Michael: Amgen Scholars travel fellowship

Grell, Tsehai: National Science Foundation Graduate Fellowship Program

Halkina, Toma: BMS Graduate Fellowship

Hamzik, Philip: Kenneth Gordon Summer Fellowship

Heckman, Laurel: National Science Foundation Graduate Fellowship Program

Jackson, Megan: National Defense Science and Engineering Graduate Fellowship

Jiang, Jun: R. C. Lord Memorial Summer Fellowship

Kohn, Alexander: Presidential Fellowship

Korzynski, Maciej: Fulbright Fellowship

Liu, Sophie: National Science Foundation Graduate Fellowship Program

Luppino, Sarah: National Science Foundation Graduate Fellowship Program

Manke, Kara: AAAS Mass Media Fellowship at NPR

Metzger, Eric: Presidential Fellowship

Mijalis, Alex: National Science Foundation Graduate Fellowship Program

Moore, Christopher: Walter Hughes Memorial Summer Fellowship

Nakashige, Toshiki: National Science Foundation Graduate Fellowship Program

Nelson, Brandon: Dean of Science Fellowship

Niljianskul, Nootaree: PPT Public Co Ltd (Thailand) Fellowship

Ong, Wen Jie: A*STAR Fellowship

Park, Sarah: National Science Foundation Graduate Fellowship Program

Phillips, Angela: Strem Family Graduate Fellowship and Presidential Fellowship

Piephoff, Daniel: Presidential Fellowship and National Science Foundation Graduate Fellowship Program

Shin, Sucheol: Kwanjeong Educational Foundation of Korea Fellowship, Steinfeld Summer Fellowship, and American Conference for Theoretical Chemistry Best Poster Award

Transue, Wesley: Dean of Science Fellowship

Velian, Alexandra: Organometallic Gordon Research Conference Graduate Student Poster Award

Vinogradov, Alexander: Amgen Summer Graduate Fellowship

Vinogradova, Ekaterina: IPMI Bright Futures Student

Wang, Yu-Pu: Amgen Summer Fellowship

Wong, Madeline: Amar G. Bose Research Grant

Wellborn, Matt: American Conference for Theoretical Chemistry Best Poster Award

White, Kathleen: National Science Foundation Graduate Fellowship Program

Wuttig, Anna: National Science Foundation Graduate Fellowship Program and Presidential Fellowship

Zhang, Chi: George Büchi Summer Fellowship

Zhu, Rong: Wellington and Irene Loh Fund Fellowship

Zhukhovitski, Alex: 2014 Intel PhD Fellowship

Dedication of the Silbey Education Office

Tuesday, October 22, 2013, was a special day for the Department of Chemistry. It marked the day the Chemistry Education Office was named for the late dean of science and professor of chemistry Robert J. Silbey. Not by coincidence, on the same day the first of two A.D. Little Lectures in Physical Chemistry was delivered by theoretical chemist Bruce Berne, Higgins Professor of Chemistry at Columbia University, and a lifelong friend of the Silbey family. Bob and Bruce attended school together in Brooklyn, NY, and later carried out their graduate studies at the University of Chicago. They remained the closest of friends until Bob's death in 2011.

Before delivering his lecture, titled "The Role of Water in Molecular Recognition and in the Kinetics of Hydrophobic Assembly," Professor Berne spoke about Silbey's illustrious career. Room 6-120 was filled to capacity with current students and postdocs, along with Silbey's colleagues, former students and postdocs, friends, and family.

Bruce described Bob's scientific accomplishments in electronic energy transfer in condensed phases, in radiative properties of molecules near surfaces, and in the physical origin of polymer conductivity. He also shared with the audience his enjoyment of Bob's witty sense of humor.

The Silbey display case outside the new Chemistry Education Offices.

At the conclusion of the lecture, a crowd gathered outside the recently refurbished Chemistry Education Office, located in 6-205, for a ribbon-cutting ceremony. Presiding over the event were Professor Sylvia T. Ceyer, head of Chemistry; Professor Susan S. Silbey, the Leon and Anne Goldberg professor of sociology and anthropology at MIT; and Dr. Theresa C. Kavanaugh, former Silbey graduate student and partner at the law offices of Goodwin Procter.

Professor Ceyer described how appropriate it was to dedicate the education office in Bob's name because of his extraordinary teaching talent, his devotion to his students, and the wonderful relationship he had with his colleagues.

Dr. Kavanaugh, expressing enormous affection for her former advisor, referred to an amusing sign Bob kept in his office that read, "Stop whining," and his advice to her to act like an adult—" words of wisdom," she said, "I draw on anytime I feel a whine coming on."

Professor Silbey—Bob's wife—declared that Bob would not have approved of the honor of a dedicated office, but said it was a fitting tribute to a man who was so devoted to science and education. "The honor of the naming of this office is not for Bob," she said. "It is for all his children—his academic children, and his daughters and grandchildren—who now know his memory will be honored in perpetuity." The education office will now formally be referred to as "the Robert J. Silbey Chemistry Education Office."

Doctoral and Master's Degree Recipients

September 2013

Joshua Baraban	PhD	Field
Rachael Buckley	PhD	Stubbe
Raoul Correa	PhD	Bawendi
Laura Gerber	PhD	Schrock
Weslee Glenn	PhD	O'Connor
Samantha MacMillan	PhD	Peters
Jessica McCombs	SM	Johnson
Arturo Pizano	PhD	Nocera
Stephanie Tumidajski	PhD	Danheiser
Thomas Willumstad	PhD	Danheiser
Susan Zultanski	PhD	Fu

February 2014

Michael Blair	SM	Ceyer
Stephanie Cheung	SM	Imperiali
Jian Cui	PhD	Bawendi
Daniel Liu	PhD	Ting
Evgeny Markhasin	PhD	Griffin
Michael Morrison	PhD	Imperiali

June 2014

Nathaniel Brandt	PhD	Nelson
Angela Gao	SM	Johnson
Timothy Johnstone	PhD	Lippard
Mackenzie Martin	SM	Hammond
Ta-Chung Ong	PhD	Griffin
Chunte Peng	PhD	Tokmakoff
Jeremy Setser	PhD	Drennan
Mingjuan Su	PhD	Buchwald
Stephanie Teo	PhD	Nelson
Erik Townsend	PhD	Schrock
Darcy Wanger	PhD	Bawendi
Hyunsuk Yoo	SM	Lippard
Tengfei Zheng	PhD	Nolan

Faculty Research Highlights

Stephen L. Buchwald. The Buchwald group has made outstanding progress in the design and development of new ligands and precatalysts used in the formation of carbon-carbon and carbon-heteroatom bonds. In particular, mechanistic studies have resulted in new catalyst systems for C–F bond formation and for the selective formation of complex nitrogen-containing molecules. The techniques developed are general and practical, and have highly diverse applications. Recent collaborations include synthesis of potential therapeutic compounds for neurodegenerative diseases, synthesis of organic light-emitting diodes for electronic displays, and methods for the continuous flow manufacturing of pharmaceuticals.

Sylvia T. Ceyer. The Ceyer group has observed that hydrogen dissolves into the bulk of an 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 covalently bound surfaces that serve as a reactant.

Rick L. Danheiser. During the past year, the Danheiser lab reported several new methods for the chemical synthesis of nitrogen heterocyclic compounds, a class of organic compounds that includes a number of biologically and medicinally important compounds.

Mircea Dincă. The Dincă group has discovered a new two-dimensional material with an unprecedented combination of high surface area and high electrical conductivity, with potential applications in energy storage technologies. They have also demonstrated the utility of a large class of compounds known as metal-organic frameworks for reactivity with small oxidant molecules of relevance to industrial oxidation catalysis.

Catherine L. Drennan. In 2013–2014, the Drennan laboratory published the first crystal structures of benzylsuccinate synthase, a glycyl radical enzyme that catalyzes the remarkable transformation of toluene and fumarate into benzylsuccinate. This reaction allows microbes to live in crude oil–polluted sand and mud by using toluene as their carbon and energy source. In doing so, these microbes contribute substantially to bioremediation of human-made pollution. Importantly, the lab's data revealed elements of the enzyme structure that are crucial for reactivity with toluene, an otherwise inert compound.

Robert W. Field. In the electronic spectrum of acetylene, the Field group revealed the universal signature of an isomerization transition state. The combination of two revolutionary technologies (chirped pulse millimeter wave spectroscopy and a buffer gas cooled ablation source) generates spectroscopic information one million times faster than the previous best methods. Using it, they demonstrated a powerful way to observe individual interaction mechanisms between an electron and a cation. Superradiance, a radiation field–mediated quantum mechanical interaction in a macroscopic system of gas phase molecules, is under investigation in a system with >100x the optical thickness of previously studied superradiant systems.

Timothy F. Jamison. The Novartis–MIT Center for Continuous Manufacturing team 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 Klavs F. Jensen and Allan Myerson (both of MIT Chemical Engineering), the Jamison group developed an integrated, end-to-end system for the continuous manufacturing of several (i.e., multiple) pharmaceutical substances in a refrigerator-sized system containing several new innovations and technologies for continuous flow synthesis. Potential applications include disaster relief, developing nations, green manufacturing, and orphan/neglected diseases. The Jamison group also developed a new family of nickel complexes that they expect will find broad utility in catalysis.

Jeremiah A. Johnson. In the past year the Johnson group developed a nanoparticle platform for the controlled delivery of three chemotherapeutic agents for ovarian cancer therapy. This approach opens new avenues for single nanoparticle drug delivery strategies based on clinically verified drug combinations; it also opens the door to discovery of novel drug combinations.

Stephen J. Lippard. The Lippard lab devised novel anticancer drug candidates, based on osmium, that selectively kill cancer stem cells, which are proposed to be responsible for tumor aggressiveness and metastasis. The lab elucidated principles governing the ability of methane monooxygenase, an enzyme that allows bacteria to grow on natural gas as their sole source of carbon and energy, to couple the consumption of oxygen with methane conversion to methanol. Paramount is the ability of the enzyme system to control access of oxygen to the active site pair of iron atoms by opening and closing a gate in a carefully timed manner. Finally, the Lippard lab devised a sensor to detect mobile zinc signaling in biology that emits in the red with virtually no background over a wide pH range, enabling studies of the roles of mobile zinc in the auditory, visual, and olfactory systems.

Mohammad Movassaghi. The Movassaghi research group continues to focus on the development of new strategies and technologies for complex molecule synthesis. They recently reported the first application of their diazene-based directed complex fragment coupling technology in the context of an alkaloid total synthesis. They also reported their complete chemical synthesis study of all known trigonoliimine alkaloids that enabled their first anticancer evaluation. Importantly, they completed and reported on a five-year study involving the first comprehensive structure-activity-relationship study of all known agelastatin alkaloids and discovered their potent activity against human blood cancer cell lines. The hallmark of their syntheses is their unparalleled efficiency and high level of stereochemical control in complex settings, taking full advantage of the inherent chemistry of plausible biosynthetic intermediates.

Keith A. Nelson. Keith Nelson's research group completed a decade-long experimental study of viscoelastic behavior, showing for the first time that the very fast motions of molecules in the high-temperature, lightly viscous liquid can be systematically connected to the slower molecular dynamics in the cooler, viscous liquid and the extremely slow dynamics in the very cold glassy state. The results have implications

ranging from fundamental statistical mechanics of the liquid state to practical polymer processing. In other work, the Nelson group conducted the first experimental measurements in which terahertz-frequency light fields were used to induce a solid-state phase transition, and the appearance of the new phase was monitored directly through femtosecond time-resolved x-ray diffraction. Crystals of vanadium dioxide were driven from an insulating, monoclinic phase to a metallic, rutile phase, and the coupled electronic/structural phase transition was monitored directly. Finally, the Nelson group conducted experiments demonstrating that a novel quantum phase of matter, the exciton-polariton condensate, really is a Bose-Einstein condensate like those observed in liquid helium or ultralow-temperature atomic gases. It is formed from admixtures of electronic excited states (excitons) and photons, with effective masses so tiny that the condensates can form at room temperature rather than the usual extremely low temperatures. This opens up novel applications for quantum matter as coherent light sources and quantum information processing elements.

Elizabeth M. Nolan. The Nolan lab further elucidated the molecular basis for how the antimicrobial protein human calprotectin sequesters essential metal-ion nutrients from both gram-negative and gram-positive bacterial species in vitro, which results in growth inhibition. In studies of the cysteine-rich host-defense peptide HD6, which has been proposed to block bacterial invasion in the human gut by self-assembling into "nanonets" that entrap bacteria, the laboratory identified hydrophobic residues that are essential and thereby elucidated the molecular basis for HD6 self-assembly and innate immune function. In another thrust, siderophore-antibiotic conjugates that target pathogenic Escherichia coli species and provide antibiotic delivery across the gram-negative outer membrane via IroN, a siderophore receptor employed by pathogens, was achieved.

Bradley L. Pentelute. During this past academic year, the Pentelute research lab discovered a new mode to selectively modify proteins and peptides with agents that enhance their properties. They found that fluorinated arenes stabilize peptides and render them cell penetrating. Their technology is being applied toward the treatment of brain cancer. In addition, they invented a fast flow machine for the rapid synthesis of polypeptide drugs. This technology enables researchers and biotech companies to rapidly identify new compounds for the treatment of various diseases.

Matthew Shoulders. The Shoulders group leveraged model systems they developed to study collagen folding and misfolding to discover that activation of protein misfolding stress responses can resolve collagen secretion defects associated with osteogenesis imperfecta, potentially providing a new therapeutic entry point to the collagenopathies. They also established new methodology to explore the dependence of the adaptive capacity of HIV and influenza on human host cell protein folding mechanisms. Other highlights include elucidation of cellular mechanisms that shape the N-glycoproteome.

Timothy M. Swager. The Swager group continues to focus on the development of functional materials for electronics, energy conversion, and sensing. Their sensing efforts include the detection of chemical signatures of relevance to food and agriculture. Low-cost, low-power ethylene sensors from the Swager laboratory are undergoing

commercialization in an MIT startup company, C2 Sense. Swager's collaboration with Robert Griffin on the development of new radicals for dynamic nuclear polarization has created record enhancements in the detection of carbon signals from nuclear magnetic resonance (NMR). Enhancements of 620 were observed, which translates to a time saving in signal acquisition of more than 384,000. These new methods have great potential for new NMR and magnetic resonance imaging (MRI) technologies.

Alice Y. Ting. In the past year, the Ting lab has used the APEX (engineered ascorbate peroxidase)-based live cell proteomic mapping approach to determine the proteomic composition of the mitochondrial intermembrane space that lies between the inner and outer mitochondrial membranes. More than a dozen novel mitochondrial proteins were discovered in this study, and the labeling radius of APEX was determined to be ~10 nm. Several other cellular proteomes were also mapped, and analyses of these datasets is now under way.

Troy Van Voorhis. In the past year, the Van Voorhis lab continued their efforts to understand the electronic structure of photochemical and photovoltaic systems. Their biggest contribution in the past 12 months has been an understanding of the mechanism of singlet fission in organic photovoltaics. Their theory accurately predicts the rate of fission across many orders of magnitude and could facilitate the design of photovoltaic cells with efficiencies as high as 44%.

Adam Willard. The Willard group demonstrated that energy transfer in quantum dot thin films can be accurately modeled using simple coarse-grained models. Specifically, they showed that microscopic disorder within quantum dot films causes excited electrons to dissipate energy and slow down with time. The Willard group also showed that the orientations of water molecules at a liquid-vapor interface can be predicted from the average water density profile near the interface along with considerations of hydrogen bonding geometries. This theoretical treatment can be extended to quantify the ability of an aqueous substrate to disrupt water's preferred hydrogen bonding structure.

Sylvia T. Ceyer
Department Head