

Department of Chemistry

Chemistry is the science of creation, discovery, and understanding at the molecular level. Its achievements continue to fuel advances in other branches of science, in medicine, and in engineering. Major new initiatives in the department include the synthesis of novel molecules to turn sunlight into chemical energy, nitrogen into ammonia, and carbon dioxide into useful reagents, the invention of new tools to investigate complex biological processes including neurochemical signaling, methods to characterize the dynamics of water and the unfolding of proteins in solution, and the design and synthesis of electronic polymers. In academic year 2004, the Chemistry Department continued its strong programs in undergraduate and graduate education. Associated with the department currently are 260 graduate students, 98 postdoctoral researchers, and 104 undergraduate chemistry majors. As of July 1, 2004, the Chemistry Department faculty comprised 31 full-time faculty members, including 6 assistant professors, 4 associate professors, and 21 full professors, including 1 Institute Professor. Effective July 1, 2003, Professors Jianshu Cao and Andrei Tokmakoff were promoted to associate professor without tenure. In the fall, professors Catherine L. Drennan and Timothy F. Jamison were promoted to associate professor without tenure, to take effect on July 1, 2004.

Major Faculty Awards and Honors

- Professor Mounji Bawendi was elected to the American Academy of Arts and Sciences.
- Professor Sylvia T. Ceyer was elected fellow, American Association for the Advancement of Science.
- Professor Catherine L. Drennan received the Presidential Early Career Award, the Dean's Educational and Student Advising Award, and the 2004 Edgerton Faculty Award.
- Professor Gregory C. Fu received the 2004 E. J. Corey Award for outstanding original contribution in organic synthesis by a young investigator from the American Chemical Society (ACS).
- Professor Barbara Imperiali became a MacVicar Faculty Fellow and was awarded the Class of 1922 chaired professorship.
- Professor Stephen J. Lippard received the 2004 Bader Award in Bioinorganic or Bioorganic Chemistry from ACS.
- Professor Mohammad Movassaghi was named Firmenich career development professor in chemistry and the Dale F. and Betty Ann Frey scholar of the Damon Runyon Cancer Research Foundation; he also received the Amgen New Faculty Award.
- Professor Sarah E. O'Connor was named Latham Family career development professor and Medical Foundation new investigator; she was also an MIT Innovation Fund and American Chemical Society PRF awardee.
- Professor Joseph P. Sadighi received the National Science Foundation Early Career Development Award.

- Professor Robert J. Silbey received an honorary doctorate from his undergraduate alma mater, Brooklyn College of the City University of New York in June 2004.
- Professor JoAnne Stubbe received the Repligen Award from the Biological Chemistry Division of the American Chemical Society and was elected to the American Philosophical Society.
- Professor Alice Y. Ting was an EJLB Foundation Scholar Research Program awardee.



Symposium speakers (left to right): Laura L. Kiessling, Eric N. Jacobsen, Thomas V. O'Halloran, Stephen J. Lippard, Peter G. Schultz, E. J. Corey, and William H. Rastetter.

Infrastructure Developments

The department celebrated completion of the three-year renovation of the Dreyfus Building (Building 18) with a symposium on Friday, September 5, 2003. Six distinguished alumni and former postdoctoral fellows and faculty returned to campus to speak at the all-day event to an audience of over 200 scientists and researchers. The symposium was held in Wong Auditorium. Featured speakers included Laura L. Kiessling (University of Wisconsin–Madison); Eric N. Jacobsen (Harvard University); Thomas V. O'Halloran (Northwestern University); Stephen J. Lippard (head of the Department of Chemistry at MIT); Peter G. Schultz (Scripps Research Institute and the Genomics Institute of the Novartis Research Foundation); E. J. Corey (Harvard University); and William H. Rastetter (IDEC Pharmaceuticals).

Work began in April on the refurbishment of a new lobby for the Dreyfus Building as a result of a generous grant from the Camille and Henry Dreyfus Foundation. The new design, by Goody, Clancy and Associates, will expand the lobby and significantly improve its character, finishes, and amenities to make it an inviting place to sit and discuss science or to hold a poster session or reception. The design concept involves expanding the lobby as a segmented half-circle



New lobby for Building 18.

in plan, picking up on the simple geometric forms that characterized Pei's design of the Dreyfus Building during the 1960s and 1970s. The revolving doors will be replaced with a pair of double-door vestibules, improving the environmental control of the space. This design will increase the lobby's area by about 50 percent, thus making it large enough to accommodate social gatherings, exhibits, or other department events. The project was scheduled for completion in August 2004.

Education

In the fall of 2004, 41 students will enter the graduate program of the Chemistry Department. From September 2003 through June 2004, the department awarded 38 PhD degrees and 3 MS degrees.

In the area of undergraduate education, 27 students graduated in June with BS degrees in chemistry. The 2004 Undergraduate Spring Awards Banquet was held on May 6 in the Hyatt Regency Cambridge. The following awards were presented:

- CRC Press Freshman Chemistry Achievement Award for outstanding academic achievement by a freshman in chemistry: Joel Yuen
- ACS Analytical Chemistry Award for outstanding achievement by a junior in analytical chemistry: Torsak Luanphaisarnmont
- Merck Index Award for outstanding scholarship: Elisa Calimano, Michelle Nyein, and Peng Wu
- American Institute of Chemists Foundation Award, presented in recognition of outstanding achievement ability, leadership, and character: Sonya Tang
- AMITA Nomination, Departmental Nomination for Association of MIT Alumnae Senior Academic Award: Sonya Tang
- MIT Chemistry Service Award for significant contributions in the area of service to the department: Neal Mankad
- Frederick D. Greene Teaching Award for outstanding contributions in the area of teaching: Jeremy Baskin, Neal Mankad, and Sonya Tang
- Strem Prize for excellence in undergraduate research: Neal Mankad
- MIT Chemistry Research Award: Kathryn Duffy, Jennifer Lee, and Neal Mankad
- Alpha Chi Sigma Award for achievement in research, scholarship, and service to the department: Jeremy Baskin



Left to right, front: Sonya Tang, Elisa Calimano, Michelle Nyein, Peng Wu, and Jennifer Lee; back: Neal Mankad, Kathryn Duffy, Joshua Baskin, Joel Yuen, and Torsak Luanphaisarnmont.

Graduate Student Awards and Honors

- William L. Stewart Jr. Award: Peter Rye, Essigmann Group
- NOBCChe E. I. Dupont Award: Bart Bartlett, Nocera Group
- 2004 BMS Fellowship in Synthetic Organic Chemistry: Elizabeth Colby, Jamison Group
- National Science Foundation Award: Emily Nytko, Nocera Group
- 2004 National Defense Science and Engineering Graduate Fellowship: Mathew Tantama, Licht Group
- Barry M. Goldwater Scholarship: Andrew Danford, Lippard Group
- CSBi-MIT/Merck Graduate Fellowship: ChiWang Lin, Ting Group
- NIH MARC predoctoral fellowship: Elsa Arocho-Quinones, Ting Group
- William Asbornsen Albert Memorial Fellowship: Jessica Vey, Drennan Group
- Teaching Assistant Award: Kevin Anderson, Buchwald Group
- Teaching Assistant Award: Wesley Austin, Danheiser Group
- Teaching Assistant Award: Jean Bouffard, Swager Group
- Teaching Assistant Award: Christopher Clough, Cummins Group
- Teaching Assistant Award: Andrea Gabert, Schrock Group
- Teaching Assistant Award: Kevin Maloney, Danheiser Group
- Teaching Assistant Award: Joseph Martinelli, Buchwald Group
- Teaching Assistant Award: Leslie Murray, Lippard Group
- Teaching Assistant Award: Venda Porter, Bawendi Group
- Teaching Assistant Award: Mala Radhakrishnan, Tidor Group
- Teaching Assistant Award: Ryan Reith, Sadighi Group
- Teaching Assistant Award: Zachary Tonzetich, Schrock Group
- 2003 Wyeth Scholars: Johann Chan, Jamison Group; Sarah Dolman, Schrock Group; Ivory Hills, Fu Group; Karen Villazor, Swager Group
- Martin Luther King Leadership Award: Hector H. Hernandez, Drennan Group
- ACS Division of Organic Chemistry Graduate Fellowship sponsored by Albany Molecular Research: Eric Strieter, Buchwald Group
- 2003 NSERC of Canada Graduate Fellowship: Andrea Gabert, Schrock Group; Valdas Jurkauskas, Buchwald Group
- DOE CSGF Fellowship from the Krell Institute: Mala Radhakrishnan, Tidor Group
- Pfizer Research Fellowship: Chudi Ndubaku, Jamison Group
- Lester Wolfe Predoctoral Fellowship: Charles Hamilton, Sadighi Group
- Enhance the Graduate Experience Award presented by the dean of graduate students, Issac Colbert: Peter Rye, Essigmann Group
- Anna Fuller Foundation Predoctoral Fellowship 2002–2003: Dong Wang, Lippard Group
- 2003 MIT Institute Fellowship: Ryan Altman, Buchwald Group
- 2004 Wyeth Scholars: Edward Hennessy, Buchwald Group; Diana Hunt, Movassaghi Group; Karen Miller, Jamison Group; Melissa Shults, Imperiali Group

Named Lectureships

- Sylvia T. Ceyer: Dreyfus Lecturer Series, Dartmouth University
- Robert W. Field: Frontiers in Spectroscopy lecturer at Ohio State University
- Gregory C. Fu: Closs lecturer, University of Chicago; Roche Lecture, University of Colorado; Novo Nordisk lecturer, Technical University of Denmark; Fuson visiting professor, University of Illinois; Neurocrine Lecture, Stanford University; Raphael Lecture, University of Glasgow (Scotland)
- Barbara Imperiali: Northwestern University, 2003 Myron Bender distinguished lectureship in organic chemistry; Cambridge University, 2003 Merck lectureship; University of Montreal, 2003–2004 Shire BioChem lectureship; National University of Ireland, Maynooth, 2003 Kathleen Lonsdale lectureship; University of Southern Illinois, 2003 Arnold lectureship; Hope College, 2003/2004 Neckers lectureship
- Alexander M. Klivanov: UNAM distinguished lectureship, National Autonomous University of Mexico (Mexico City)
- Stephen J. Lippard: Cherry Emerson lecturer, Georgia Tech University; Lemieux Lectures, University of Ottawa; John Stauffer Lecture, University of Southern California; Ross Lectures, Dartmouth College; Lewis Lecture, Cambridge University; Krebs Lecture, International Conference on Bioorganic Chemistry, Sheffield, UK
- Richard R. Schrock: Cady Lectures, University of Washington
- Robert J. Silbey: Stauffer lecturer at Stanford
- Joanne Stubbe: University of Minnesota Gassman Lectures; University of Pennsylvania Womens Trustees Lecture
- Andrei Tokmakoff: Crawford lecturer, University of Minnesota

The department was pleased to welcome the following lecturers to MIT during the academic year:

- K. Barry Sharpless, Scripps Research Institute, Wyeth Lecture, October 2003
- John Tully, Yale University, A. D. Little Lectures in Physical Chemistry, December 2003
- Samuel I. Stupp, Northwestern University, Karl Pfister Lectures, January 2004
- Barry Honig, Columbia University, T. Y. Shen Lectures, April 2004
- George McLendon, Princeton University, A. D. Little Lectures in Inorganic Chemistry, March 2004
- Peter Leadlay, University of Cambridge, Buchi Lectures, March 2004

Selected Research Highlights

The Catherine L. Drennan laboratory published the crystal structure of the enzyme biotin synthase in *Science*. This structure shows how “AdoMet radical” or “Radical SAM” enzymes use an Fe₄S₄ cluster and S-adenosyl-L-methionine to generate organic radicals. This work also provides insight into the mechanism of biotin synthase, an enzyme that has applications in the commercial production of the vitamin biotin.

The John M. Essigmann group, by tethering a beta-estradienone to a DNA-damaging agent, was able to circumvent the programmed cell death blockade that makes prostate cancer cells resistant to chemotherapy. The agent has been chosen by the NCI for development through its RAID program. They also defined the substrate range for the DNA repair enzyme, AlkB. This enzyme oxidizes off the side chains put onto DNA by many organic carcinogens. The oxidation reaction results in restoration of the normal base-pairing properties of DNA, thus avoiding cancer-causing mutations.

A definitive introduction to small molecule electronic spectroscopy and a bridge between the frequency and time domain communities, "The Spectra and Dynamics of Diatomic Molecules", was published by the Robert W. Field group. In acetylene, the vibration-rotation spectrum of triplet electronic states has illustrated the unexpected assignability and regularity of a molecule near the ergodic limit of vibrational excitation.

The Gregory C. Fu group developed palladium- and nickel-catalyzed cross-couplings of alkyl halides; described mechanistic studies of palladium-catalyzed coupling processes; developed catalytic asymmetric routes to important classes of biologically active compounds, including β -lactones, oxindoles, and benzofuranones.

A new program was initiated by Barbara Imperiali's group to investigate the integrated action of the biosynthetic enzymes that comprise the *dolichol pathway*. The enzymes in this pathway are all membrane bound and ultimately work in concert to afford a complex dolichol pyrophosphate-linked oligosaccharide (dolichol pyrophosphate-GlcNAc₂Man₉Glc₃), which is the major glycosyl donor for asparagine-linked glycosylation.

Using sensitive, intracellular ratiometric fluorescent sensors designed and synthesized in the laboratory, the Stephen J. Lippard group, in collaboration with the Sheng laboratory at MIT, detected mobilization of zinc in live neurons and slices from the hippocampus following treatment with a nitric oxide releasing chemical. They also reported the first reversible fluorescent sensor for NO, a dirhodium complex. The structure of the hydroxylase enzyme of a toluene monooxygenase was determined by X-ray crystallography.

The Daniel G. Nocera group described the first molecule to produce hydrogen photocatalytically from homogeneous solutions of hydrohalic acid. During the past year they worked out the details of the catalytic cycle. Nocera's research in energy conversion was featured this past year on the nationally broadcast television programs, *ABC Nightline* and *NOVA*.

Among recent advances made by the Joseph P. Sadighi group are the copper-catalyzed reaction of carbon dioxide with alkynes in the presence of a reducing agent and the functionalization of C–H bonds in benzene by sulfonyl azides.

A major advance in the Richard R. Schrock group was the discovery that triamido/amine complexes of molybdenum, substituted with terphenyl substituents, reduces dinitrogen catalytically at a single metal center. This is the first time that such chemistry has been

demonstrated for any metal in almost 40 years of transition metal dinitrogen chemistry, and it strongly supports molybdenum as the site of dinitrogen reduction in the FeMo nitrogenase.

The Jeffrey Steinfeld lab extended the IntraCavity Laser Absorption Spectroscopy instrument to carry out time-resolved measurements. This capability enabled the rate of the recombination reaction $\text{H} + \text{NO} + \text{M} \rightarrow \text{HNO} + \text{M}$ in a discharge flow system to be measured. They also carried out a survey of toxic chemical purchase and use patterns in the MIT Chemistry Department as a prelude to developing a system to encourage toxic use reduction and substitution of less hazardous alternatives wherever possible.

The JoAnne Stubbe group reported long-range proton-coupled electron transfer in ribonucleotide reductase for the first time by using intein technology to make one of the subunits semisynthetically. This methodology has allowed them to study the effect of pK_a and redox potential at a specific residue, Y356, providing compelling evidence that this amino acid is on the pathway and does form a transient radical. The group also obtained the structure of the 5th enzyme in the purine biosynthetic pathway, formylglycineamide ribonucleotide (FGAM) synthetase, in collaboration with the Ealick lab at Cornell.

The Timothy M. Swager group in the last year has, in collaboration with Professor Bulovic of the Department of Electrical Engineering and Computer Science, developed novel laser sensors for explosives based upon electronic polymers.

The Andrei Tokmakoff group's studies of liquid water revealed the time scales and mechanism by which hydrogen bonds break and reform through collective motions of many molecules. Transient infrared spectroscopy was also used to follow directly the unfolding of proteins in solution on nanosecond to millisecond time scales.

Stephen J. Lippard
Department Head
Arthur Amos Noyes Professor of Chemistry

More information about the Department of Chemistry can be found on the web at <http://web.mit.edu/chemistry/www/>.