ILLINOIS INSTITUTE OF TECHNOLOGY

CHEMISTRY ELEMENTS

A publication of the Chemistry Division at IIT

Photo by Bonnie Robinson

Chemistry Group photo, Welcome Lunch 2013-14

Fall 2013

Letter from the Chair

We are pleased to present the inaugural issue of Chemistry Elements, the newsletter of IIT Chemistry. This issue celebrates the second anniversary of the creation of the new Chemistry Division within the Department of Biological and Chemical Sciences, showcasing achievements of our faculty, students, and alumni, and providing insights into recent developments.

This is an exciting time for chemistry at IIT, as the College of Science and Letters has just become the College of Science. This change, and the earlier deconstruction of the Department of Biological, Chemical, and Physical Sciences (which led to the birth of the new Department of Physics in 2010), reflects the new emphasis, expansion, and focus on the sciences in the new college. At the start of academic year 2012–13, we moved into our new Chemistry Division office—Life Sciences Suite 106—which coincided with the appointments of Gwynne Fox, the new department coordinator, and Associate Chair Maria Tanner. As you may have heard, a renovation of Life Sciences (and Engineering 1) will begin in late spring 2014 as part of the "Fueling Innovation" campaign.

We are now in the process of building a strong Chemistry Division with a number of new faculty appointments to strengthen research and teaching infrastructure, and other academic initiatives. We have added new instruments to the Chemistry Instrumentation Lab. And with two new state-of-the-art high-throughput computer clusters, plus the existing Pauling computer cluster, IIT Chemistry is now home to one of the finest computational facilities to support outstanding computational chemistry research and teaching activities at the university (see feature research article for more details).

As part of the curriculum revision, we have introduced a new co-terminal degree, a B.S. in Chemistry/Master of Food Safety and Technology (jointly with the Biology Division and the Institute for Food Safety and Health), a graduate certificate in Regulatory Sciences (jointly with the Biology Division), and a B.S. in Chemistry with Chemistry Teaching Certification (jointly with the Division of Math and Science Education). Our M.S. and Ph.D. programs, as well as the professional master's programs, continue to grow. Our recent Commencement event had 30 chemistry students graduating with B.S., Master's, and Ph.D. degrees, with a hooding ceremony for our five Ph.D. recipients.

We have increased our efforts to attract the best students, and are committed to providing the best-possible learning environment for our students. This past year we started a tradition of a student awards ceremony to give prizes to our top students at the close of the academic year. We are grateful to the family of former IIT Chemistry Professor Paul Fanta for a generous gift to enrich the graduate students' academic experiences in the department.

The research focus of this issue is materials for energy. We have several groups engaged in materials chemistry research, and I encourage you to read the feature article describing some of their work in this area.

Lastly, we pay tribute in this issue to Professor Peter Lykos and Professor Ken Schug, who have recently departed us after serving many years in the department.

We want to thank all of you for your support to keep the tradition of chemistry at IIT strong. Please share with us memories of your IIT days, as we always enjoy receiving interesting anecdotes and plan to include "Alumni Reflections" in our newsletter in future editions. We look forward to hearing from you (our new email is chemistry@iit.edu) and invite you to visit the new Chemistry Division sometime at your convenience.

Ishaque Khan
Chair, Chemistry Division
Department of Biological and Chemical Sciences

2012–13 KILPATRICK STUDENT AWARDS

Assistant Professor Aditya Unni presents the 2013 Kilpatrick Undergraduate Scholar Award to **Ethan Chang** at the 2013 Kilpatrick Lecture

The 2012–13 Kilpatrick Fellow, **Kadir Aydemir**, accepts the Kilpatrick Fellowship award from Chair Ishaque Khan

Assistant Professor Brant Cage presents the 2013 Kilpatrick Undergraduate Scholar Award to **Khwaila Falaneh**

Materials for Energy Research at IIT Chemistry

Energy is the lifeblood of the modern economy. Global energy demand has been increasing rapidly; it is expected to double by 2050. Ensuring a sustainable supply of energy without compromising our environment and jeopardizing our food supply chain remains a challenge.

The solution is intimately connected with advancements in new and efficient materials suitable for energy applications, especially for the storage and transport of energy, and for affecting energy-efficient industrial processes (e.g., low-temperature catalytic industrial chemical transformations). Chemistry, being the science of atoms and molecules, occupies a central place in the design and development of these materials with desirable properties and functions suitable to cater to the needs of industry and society.

A number of IIT chemistry faculty members are engaged in materials research with emphasis on materials for energy applications, covering all four critical areas—materials synthesis, characterization, evaluation, and computation and modeling:

Professor Ishaque Khan's group is taking a multidisciplinary approach, seeking a molecular-level understanding of the fundamental structure/property relationships needed for the identification and rational synthesis of new and efficient materials for energy applications. The research work in his group revolves around the following interconnected critical components, which mutually feed into each other, generating synergistic effects:

Materials design and synthesis: to develop a capability of fine-tuning materials and to achieve the desired framework architecture, porosity, surface composition, functionalities, and active binding sites

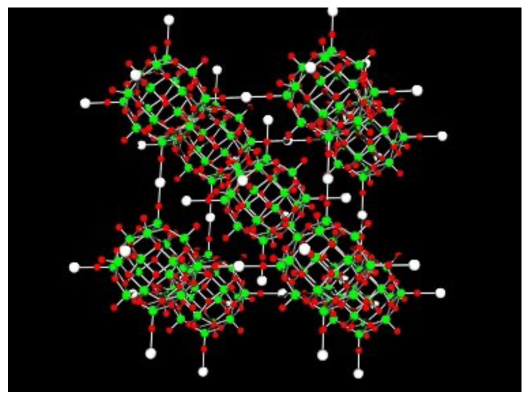
Materials characterization: to develop fundamental relationships between a material's structure and its energy applications (low-temperature catalysis, room temperature sensors, storage of energy)

Materials evaluation: to investigate properties such as hydrogen storage capacity, sensor sensitivity and specificity, catalyst reactivity and selectivity, and stability

Simulation and modeling: to understand the interaction between probe/substrate molecules and the surface/interfaces of materials.

Khan's research is focused on a new breed of nanostructured materials on which an integrated multidisciplinary approach to energy storage materials can be based. In particular his group is creating novel zeolitic systems (adsorbents for water purification, catalysis, hydrogen storage materials, sensor and other uses) for tailor-making materials with controllable properties and functions. They have recently prepared a series of nanostructured materials that include three-dimensional open-framework solids composed of arrays of the oxometalate molecular building blocks and novel inorganic-organic nanocomposites composed of oxometallic motifs and/or metal centers, cross-linked with robust rod-like organic ligands. These low-density porous framework materials contain well-defined channels and cavities similar to those found in conventional zeolites. Figure 1 shows the representative examples of this series of materials. They represent a new class of open-framework structure crystalline solids, whose structures are resolved at the atomic level. Besides their novel structural and topological features, these materials exhibit interesting and potentially useful sorptive, electronic, magnetic, catalytic, and chemical-sensing properties. The fundamental knowledge base gained may lay the groundwork for producing the next generation of energy storage materials, energy-efficient catalysts, and room temperature sensors.

Figure 1. Representative examples of the novel nanostructured materials: 1. a three-dimensional open-framework solid composed of nanoclusters, **2.** a nanocomposite with large channels, **3.** AFM image of a prototypical functional material



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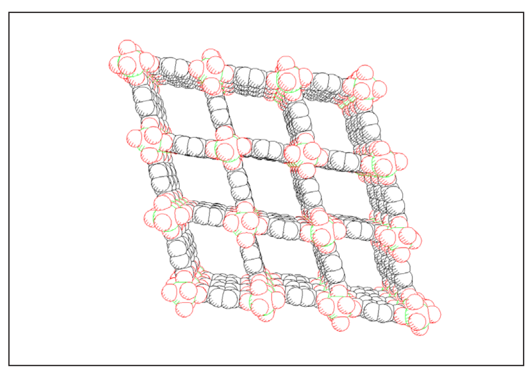

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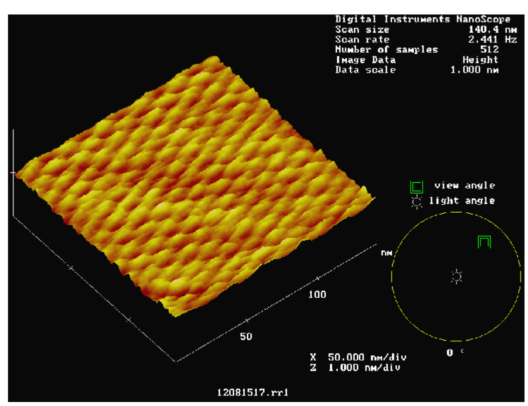

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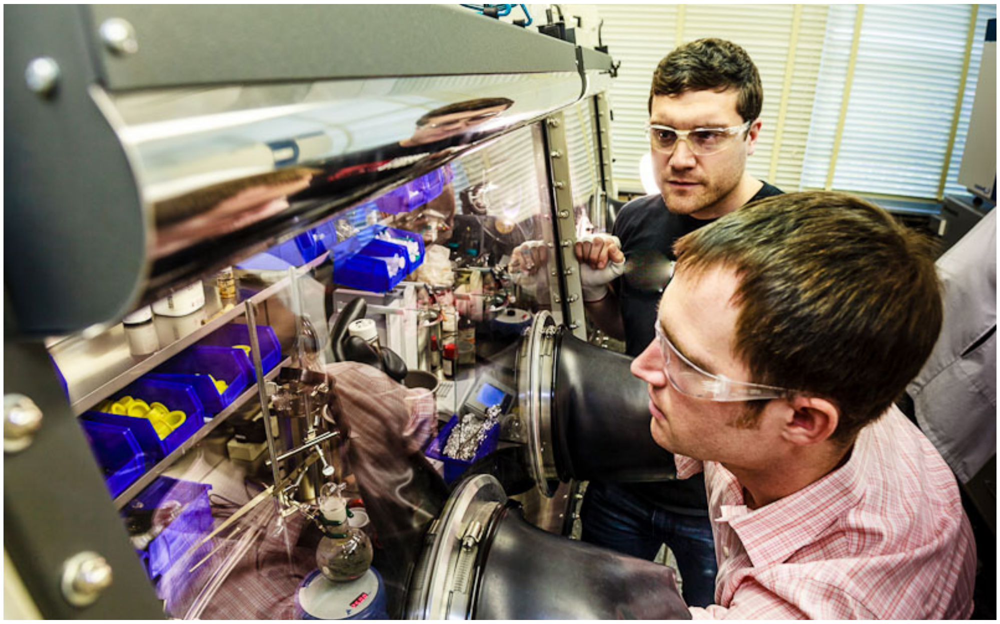


Assistant Professor Adam Hock and graduate student Matt Weimer working in an inert atmosphere glove box

The group led by Assistant Professor Adam Hock studies a variety of chemical systems such as catalysis (the acceleration of a chemical reaction by a catalyst), solar energy conversion, and electronic materials for next-generation computers and other devices. Many projects in Hock's research rely upon the ability to assemble these materials with near atom-level precision.

Synthetic chemistry often brings to mind bubbling beakers, pretty colors, and stirring liquids. While Hock certainly works with all of these aspects of chemistry, he also utilizes molecules and materials that react with oxygen and water in air. Due to this reactivity, a lot of these reactions are conducted in steel, glass, or other enclosures under nitrogen (the major component of air) that has been purified to remove the oxygen and water to part-per-million levels.

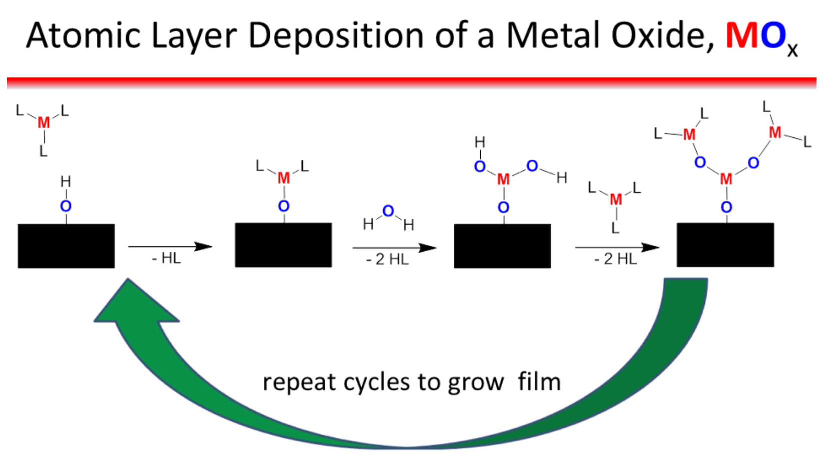
Hock describes his work in atomic layer deposition (ALD):

"A good deal of our work studies reactions of gases with solids. Some of these are gases that contain molecules we want to transform in order to study more efficient ways to make materials such as plastics. Other gases are specially designed molecules that are tailored so that they react in a very specific way with a solid surface, such as a (soon-to-be) microchip. In this process, the metal-containing molecule reacts with the surface and chemically sticks there in a way that other metal-containing molecules do not (e.g., those that are unreactive and bounce off). All of these molecules cover the surface to make a layer about one molecule thick. After this stoichiometric reaction we can remove any excess metal source molecules that are hanging around in the gas phase but are not chemically bonded with the surface by flowing inert gas. Think of blowing dust off a tabletop.

"Next we add a different reactant, for example, dihydrogen monoxide (H_2O). The water will react with the metal molecules on the surface via proton transfer, transforming them into metal species that have bound OH ligands. Any extra water molecules just bounce off like extra metal ones did before. After we remove the extra water you can again introduce a metal-containing molecule that will react with all of those OH's and react with the surface. However, once you use up all the OH's you are back at the same situation where the excess metal-containing molecules can be removed. This process relies upon well-behaved chemical reactivity with no uncontrolled thermal or other surface chemistry. The repetition of these well-defined chemical reaction cycles over and over can literally build a film of material one atomic layer at a time. Hence the name: atomic layer deposition."

ALD is used in several of the steps to make modern electronics, and the field is incredibly exciting as new applications are being discovered and developed every day in solar cells, flash memory, catalysis, and energy conversion. The ability to control the surface chemistry to grow in this layer-by-layer manner means that you can evenly coat rough surfaces, too. The ability to coat trenches, holes, or other nanoscale geometries is ALD's advantage over other deposition techniques. The nanoscale features in modern chips are so small that this technique is possibly the best way to control all the interfaces—the atom-on-atom location where one material stops and another starts. These interfaces dominate many of the electrical and other properties in devices, and combined with the ability to coat almost any geometry, one can see why ALD technique is so useful for building all kinds of nanoscale devices. And it all relies on controlling the surface chemistry as the material grows. Studying these reactions can be quite challenging!

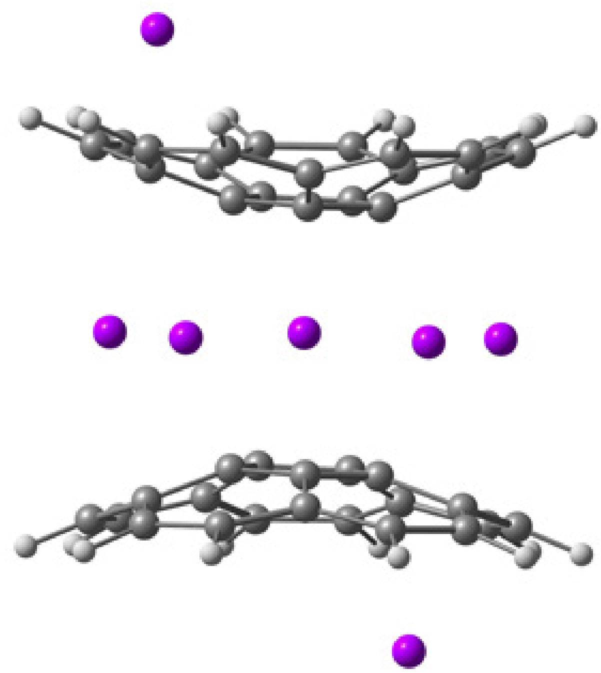
Hock has a joint appointment at Argonne National Laboratory, run by the United States Department of Energy, in the catalysis group. His work there is primarily in the area of catalysis, where he is studying new catalysts and reactions, and developing new materials for efficient energy production. IIT's close relationship with Argonne is invaluable to our division's studies in all of these areas.



Assistant Professor Andrey Rogachev's research involves performing theoretical searches for new types of batteries. Nowadays, the most efficient batteries (with large capacity) are those based on lithium ions intercalated between graphite layers. However, the given electronic structure of graphite monolayers (a.k.a. graphene sheets) limits the Li:C ratio (lithium per carbon ratio) to be as high as 1:6. Rogachev's study focuses on the new, curved polyaromatic systems (Figure 1), for which one can reach at least 1:5 ratio. These results are promising for a better capacity of new Li-batteries. The mechanism of formation of these interesting systems as well as the search for new ways to stabilize even higher Li-per-C ratio are the primary goals of his theoretical efforts.

Another direction of Rogachev's research is the detailed theoretical investigation of luminescent properties of lanthanide complexes used in LED (light-emitting diode) devices. LED devices can convert up to 60–70 percent of electricity to the light in comparison with traditional incandescent bulbs that do only 5–7 percent conversion (the rest of electricity goes to heat). Thus, LED consumes far less electric energy. Luminescence of each lanthanide ion covers a narrow range of light spectrum ("pure" color) due to their very specific transitions between f states (f representing an electronic state of the emitting center), albeit altogether they (lanthanides) cover the whole spectrum, from red to blue regions. However, the forbidden nature of f-f transitions as well as their small absorption coefficient makes the direct excitation of LnIII ions (lanthanide ions) very inefficient. Therefore, to achieve efficient luminescence, one must sensitize the metal center. The most effective sensitization of metal emission is through the use of "antenna effect" provided by highly absorptive appropriate organic ligands (organic molecules bound to the metal center). Such sensitization incorporates three major steps; see Figure 2: (1) absorption of light by organic ligands, (2) energy transfer from the ligand to the metal center, and (3) light emission by the lanthanide ion. Successful development of the model of light-harvesting ligands for lanthanide metal centers will guide experimentalists to create new materials with highly desirable luminescent qualities, such as pure color and efficiency, while eliminating metal-ligand combinations of poor luminescent characteristics. Better qualities of new materials provide higher efficiency for LED devices and, as a result, save more energy.

Figure 1



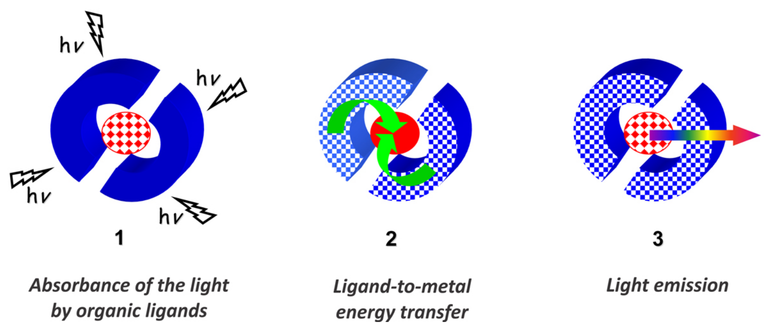


Figure 2. *The sensitization scheme in lanthanide complexes*

Congratulations to Our New Ph.D.s!

Kadir Aydemir
Advisor: Ishaque Khan
Thesis: Vanadium Oxide-Based Materials as Oxidative Dehydrogenation Catalysts: Synthesis, Characterization as Properties

TaeYoung Kim
Advisor: Rong Wang
Thesis: Biocomposite Nanomaterials: Characterization, Manipulation, and Application

James Halley McNeely
Advisor: Brant Cage
Thesis: Analysis of Low-Dimensional Magnetic Systems Containing Chromium (III) and Cobalt (II) Ligated by the Squarate Ligand: Magnetic Characterization, Biological Characterization, Instrumental Development, and Software Development

Naga Ravikanth Putrevu
Advisor: Ishaque Khan
Thesis: Synthesis and Structural Investigation of Polyoxovanadate Systems for Semiconductor NOx Gas Sensing

Xiang Sun
Advisor: Huyn-Soon Chong
Thesis: Formation of Aziridinium Ions and Their Synthetic Applications

New Faculty Appointments

David Minh

IIT welcomes **David Minh** and Andrey Rogachev as assistant professors in computational chemistry.

Minh's research involves developing new computational methods to quickly and accurately characterize protein-ligand interactions, especially binding affinities. Unlike most existing algorithms, which are based on geometry, these methods build upon a rigorous foundation in statistical mechanics. Minh plans to apply these methods in diverse ways, including the design of specific chemical probes for biological processes such as protein-protein interactions, developing a quantitative understanding of functional selectivity in G-protein coupled receptors, and predicting the selectivity of kinase inhibitors. After completing an undergraduate degree from the University of California, Berkeley, Minh earned his doctorate at the University of California, San Diego under J. Andrew McCammon, a well-known expert in computational biochemistry. Minh continued his scientific training with postdoctoral experiences at the National Institutes of Health, Argonne National Laboratory, and Duke University, where he built upon his previous training in theoretical and computational chemistry and branched out to experimental biophysical chemistry using isothermal calorimetry, X-ray solution scattering, and neutron spin echo.

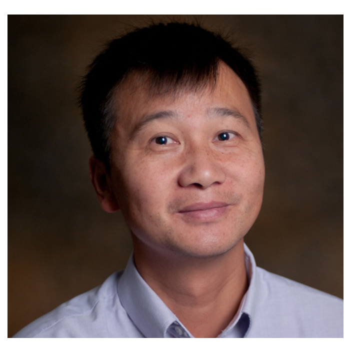
Andrey Rogachev studied chemistry at Moscow State University and received his diploma and Ph.D. degrees in 2002 and 2006, respectively, working with Professor Alexander Nemukhin and Professor Natalia Kuzmina on the synthesis, reactivity, structural analysis, and theoretical modeling of mixed-ligand heterobimetallic complexes of lanthanides and 3D-transition metals. He successfully defended his Ph.D. thesis in two fields of chemistry at once—inorganic and physical (computational) chemistry. In 2006, he joined the teaching

Andrey Rogachev

and scientific community of State University of New York at Albany as an invited lecturer for the graduate course Advanced Synthesis and started his longstanding collaboration with the group of Professor Marina Petrukhina on the chemistry of fullerene fragments, or buckybowls. In 2007, he joined the group of Professor Peter Burger at the University of Hamburg as a postdoctoral associate. His research interest at that time was focused on the chemistry and physics of systems with unusual bonding such as N-oxides and metal-oxo multiple-bonded species. In 2010, he joined the group of Professor Roald Hoffmann (Nobel Laureate 1981) as a postdoctoral associate at Cornell University, where he used a variety of modern theoretical methods and approaches to shed light on chemical bonding in different systems and molecules, from very simple to quite complex.

Professor Xiyun "Richard" Guan arrived in the fall of 2012 from the University of Texas at Arlington. Guan received his Ph.D. in chemistry from the University of Kentucky. His expertise is in bioanalytical and biophysical chemistry. One aspect of Guan's research is to develop nanopore techniques for various applications in biotechnology at the single molecule level. The engineered nanopores have a variety of new functional properties that could be used as a basis for making sensors. Since the data obtained are not obscured by the average values that are inherent in conventional chemical and biochemical experiments, single-molecule detection provides information about the distribution and time trajectories that would otherwise be hidden by the statistical mean. Guan's group is especially interested in the development of biosensors for bioterrorist/biodefense chemicals, environmental pollutants, toxins, DNA, and protein molecules.

Guan is interested in moving biosensors out of the laboratory and into commercial applications, for example, to develop sensing techniques that could be employed in the analysis of environmental and



Xiyun Guan

Benjamin Zion

biological samples, and for the application in field detection.

Benjamin Zion, lecturer in chemistry, came to IIT in the fall of 2012. He received his Ph.D. from the University of Chicago and was formerly involved in the area of reactions at surfaces. His current focus is chemical education and course development with special attention to instrumentation. Zion oversees the care of our instrumentation lab.

Martha Tanner

Martha "Maria" Tanner, who started in the fall of 2011, is now serving as associate chair and leads our efforts in undergraduate curriculum and admissions. Tanner has her Ph.D. from the University of North Carolina at Chapel Hill and her interests are in chemical education, science communication, and also organometallics, catalysis, and polymer synthesis.

In Memoriam

Peter Lykos

Kenneth Schug

Our longtime colleague and ACS Chicago Section director, Emeritus Professor of Chemistry **Peter Lykos** passed away on July 16, 2013. Lykos joined the IIT chemistry department in 1955 and had a distinguished academic career as a physical chemist with a strong interest from the earliest days in computers in chemistry—what has come to be known as computational chemistry. He was a pioneer in the use of computers in the classroom, bringing them to IIT in 1959.

Lykos was also passionate about IIT's signature program, Interprofessional Projects (IPRO) Program. His last IPRO course offering was Global Warming and Community Outreach. He was conscious of the well being of the department, and was instrumental in raising an endowment honoring colleagues Martin and Mary Kilpatrick.

Lykos took a leave of absence from 1971–73 to serve the National Science Foundation, to create a new Computer Science Division section called Computer Impact on Society. He was an active member of the American Chemical Society, where he helped to create the ACS Division of Computers in Chemistry in 1974, and in 2011 he was elected as director of the ACS Chicago Section. He spearheaded the organization of the National Chemistry Week celebration at IIT in 1989.

In Lykos, we have lost a talented colleague and a chemist who liked to say, "chemists are the human element."

Kenneth R. Schug, longtime distinguished faculty member (and two-term chair) in IIT's Division of Chemistry, passed away on May 29, 2013. He was known for his love of teaching and generous community spirit. Schug joined the university in 1956, spent a sabbatical in Japan in 1964, and retired as professor of chemistry in 2012. He enjoyed teaching general chemistry and working on innovative learning methodologies.

In 1979, Schug was instrumental in establishing the Chicago Area Health and Medical Careers Program in an effort to increase the number of physicians and other health professionals from historically underrepresented minority populations. Seven years later, Schug spearheaded a structured series of summer and academic year-in-service courses for elementary- and secondary-school teachers as part of the Science and Math Initiative for Learning Enhancement Program.

With Schug's departure we lost a wonderful colleague and a science educator.

Faculty News

Associate Professor Hyun-Soon "Joy" Chong was awarded a renewal of her research grant from the National Cancer Institute of the National Institutes of Health. This research is on new bifunctional ligands for radioimmunotherapy.

Associate Professor Richard Guan served as chair of the Nanopore and Nano-channel Section for the conference on Advances in Microfluidics and Nanofluidics, in Notre Dame, Ind. His talk was on "nanopore detection of biological warfare agents." Guan also gave a talk at the ACS 2013 Great Lakes Regional Meeting, held in La Crosse, Wis., on "rapid and sensitive detection of copper ions by nanopore stochastic sensing."

Assistant Professor Adam Hock gave talks at the following meetings: Spring 2013 Materials Research Society National Meeting (San Francisco), 2013 North American Catalysis Society (Louisville, Ky.), 2013 Gordon Research Conference on Organometallics (Newport, R.I.), 2013 Department of Energy Frontiers at the Interface of Homogeneous and Heterogeneous Catalysis Meeting (Annapolis, Md.), and the Atomic Layer Deposition Conference (San Diego).

Professor Ishaque Khan was invited to join a select group of researchers from around the world in writing the monograph "New and Future Developments in Catalysis-Hybrid Materials, Composites, and Organocatalysts," published by Elsevier in 2013.

Industry Professor of Chemistry Diep Nguyen was chosen as a teaching fellow of the College of Science and Letters.

Associate Professor Rong Wang just returned from a year's sabbatical at Utah State University, where she worked on a research project involving spider-silk-inspired native and synthetic nanomaterials.

To contact the Chemistry Division, phone us at 312.567.3278 or email chemistry@iit.edu

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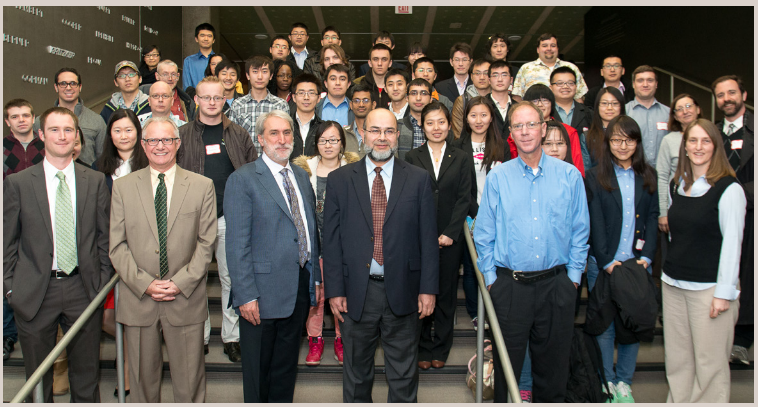
Creator of "Artificial Leaf" Delivers the 2013 Kilpatrick Lecture



Chemistry group photo at the 2013 Kilpatrick Lecture: [*front row*] Adam Hock, Dean Russell Betts, speaker Daniel Nocera, Ishaque Khan, Brant Cage, and Maria Tanner

A chemist whose "artificial leaf" was named one of the top inventions of 2011 by *Time Magazine* was this year's Kilpatrick Lecturer in Chemistry. **Daniel Nocera**, Patterson Rockwood Professor of Energy in the Department of Chemistry and Chemical Biology at Harvard University, spoke on "Alternative Energy for Society and Third-World Applications" on April 17, 2013. A reception and poster session followed the lecture.

A member of the American Academy of Arts and Sciences and the United States National Academy of Sciences, Nocera is developing innovative, inexpensive energy sources, including the artificial leaf—a silicon solar cell with different catalytic materials bonded onto its two sides that makes fuel from sunlight, capturing elements of photosynthesis.

Earlier artificial leaves successfully split water into hydrogen and oxygen but used expensive materials and were costly to produce. Nocera's leaf uses a nickel-molybdenum-zinc compound and a cobalt film, both much less costly, opening the door to use one day in developing countries.

"A research target of delivering solar energy to the poor with discoveries such as the artificial leaf provides global society its most direct path to a sustainable energy future," Nocera wrote in an article about his work in the American Chemical Society journal *Accounts of Chemical Research*.

Professor **Ishaque Khan** remarked that Nocera's work is "an excellent example of the power of chemistry to help solve society's most pressing problems."

George Whitesides, Woodford L. and Ann A. Flowers University Professor at Harvard University, was our 2011 Kilpatrick Lecturer in Chemistry. Whitesides has made his mark in the frontiers of basic and applied sciences, and has had one of the most prolific careers in science. Over his half-century of chemical acumen in academia and industry, and within a variety of governmental organizations, Whitesides has achieved an international reputation for his expertise in the technical and policy-based direction of chemistry and science in general.

Following the talk was a panel discussion—"Solving Problems or Satisfying Curiosity"—with Professor Ishaque Khan (moderator), Whitesides, College of Science and Letters Dean **Russell Betts**, and Armour College of Engineering Dean **Natacha DePaola**.

IIT's annual Kilpatrick Lecture honors Martin and Mary Kilpatrick, who were outstanding researchers and educators at IIT. Martin served as chair of the Department of Chemistry from 1947–1960, leading the department to national prominence in both undergraduate and graduate instruction and research.

[*From left*] Adam Hock, Ishaque Khan, speaker George Whitesides, Aditya Unni, and Provost Alan Cramb at the 2011 Kilpatrick Lecture