The Spectrum

Volume 18
Issue 3
Fall/Winter 2005

Michael Kasha "Renaissance Man"

a quarterly publication

The Spectrum

special feature

perspective on

viewpoint

in this issue

focus on

On the cover
Chemiluminescence observed by bubbling Cl_2 gas via a milliport sintered-glass filter into an alkaline H_2O_2 solution. Bubbles of glowing, excited molecules of singlet molecular oxygen are seen rising through the solution in the cylinder. This 1963 discovery by Ahsan Khan and Michael Kasha is now culminating in two current major papers on the red aurora seen at 11-year cycles at low latitudes to 30° N, S. Courtesy of Michael Kasha.

Center for Photochemical Sciences
Bowling Green State University
Bowling Green, Ohio 43403
419.372.2033

The Spectrum

Editor	Pat Green
Contributing Editor	Michael Woods
Production Editor	Alita Frater

The Spectrum (ISSN 1044-5536) is published four times yearly at no charge. For subscriptions e-mail photochemical@listproc.bgsu.edu

The Spectrum is available on the web at www.bgsu.edu/departments/photochem

The Spectrum is published by the Center for Photochemical Sciences at Bowling Green State University, Bowling Green, Ohio. The mission of *The Spectrum* is to disseminate the latest research and news in the photochemical sciences to a general audience worldwide.

viewpoint

This winter has started out cold and snowy in Ohio. Average temperatures for November and December have been well below normal and snowfall amounts above average.

With cold temperatures comes the realization that natural gas and heating oil prices have increased substantially since last winter. As I was writing this editorial, the chief HVAC maintenance engineer for the University dropped by to chat about an odor I'd noticed in one of our offices. He solved the problem over the weekend, but told me that Bowling Green State University spends $32,000 per day to heat its facilities. Supply and demand and two major hurricanes are apparently the reason for increased fuel costs. Most American homes and businesses in the north are heated with either fuel oil or natural gas. Persons with larger, older homes, individuals on fixed incomes, schools, and even inner city churches are really feeling the crunch.

It seems obvious to those of us who have watched Americans heat their homes first with wood, then coal, next with heating oil only to switch in the 1960s and 1970s to clean, safe natural gas that a paradigm shift must be coming. The only question is what will be the energy source of the future and when will it start to impact the average American?

The Germans are well ahead of the Americans in the use of alternative fuels. Windmill farms exist all over, and many new buildings are equipped with solar photovoltaic panels. The German government supports both with tax abatement plans.

I have been thinking about this more than usual because we are in the initial stages of planning a new building for the Center for Photochemical Sciences at Bowling Green.

The Boston architectural firm Payette and Associates has been engaged to create a development document; one of the first renderings is shown above.

In addressing the architectural planning committee and providing the architects with instruction I said, "We are a Center for Photochemical Sciences; we want to live with light, by light and in the light. Through your design of our building, help America see that paradigm shift from an economic engine driven by fossil fuels to an economic engine driven by alternative fuels. Design a facility that is transparent, open, flexible, environmentally green and safe. No person should ever change a light bulb or turn one on/off. LEDs sensed to be on when needed will bath the building in necessary artificial light. I dream of a building that is mostly energized by the power of the sun."

Our photosciences readers can really help us think about how the building of the future will be designed and powered. Even if you think your ideas are obvious, share them with us. And if you know of suppliers, engineers and experimenters willing to work with us on this opportunity, please just let us know.

D. C. Neckers

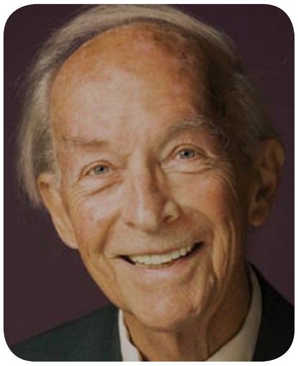
special feature

perspective on a renaissance man

an interview with **Michael Kasha**

As a scientist Mike is extremely creative in many different areas. He never stops being excited about science. It makes him young and he will always be young. I wish him many years of active life. He is a gift to science and education.

Mostafa El-Sayed, Julius Brown Chair and Regents Professor, Georgia Tech, at the 75th birthday celebration for Michael Kasha



Courtesy of Michael Kasha

Even the musically challenged realize at a glance that someone has been fiddling with this particular guitar. The traditional, rectangular bridge, for example, is now shaped like a wedge ("for optimized mechanical impedance"). And what the heck is it with that sound hole? Someone moved it from the usual centerline position to the upper right. Look inside the hole, and the internal bracing would make a luthier gawk.

You've heard of Kasha's Rules and The Kasha Effect? Meet the Kasha Guitar and Kasha Guitar Bracing.

When the American Society for Photobiology honored Michael Kasha with a 75th birthday symposium in 1996, speakers described the renowned Florida State University (FSU) scientist as a "Renaissance Man." Former FSU President Talbot D'Alemberte did the same upon renaming the Molecular Biophysics Building the Kasha Laboratory in June 2000.

Michael Kasha's broad intellectual interests and accomplishments in both the arts and the sciences certainly fit the definition. Kasha was the first person in Florida elected to the National Academy of Sciences and the first to serve on the National Science Board. He also was the first Floridian elected a fellow of the American Academy of Arts and Sciences. Hailed by the *Journal of Physical Chemistry* (May 2003) as founder (with George S. Hammond) of modern molecular photochemistry, Kasha has left a mark in an impressive array of other fields.

Among them are research on color in daylilies (leading to the discovery of proton-transfer spectroscopy of flavonoids), for instance, and the first new internal structure in 250 years in improving the acoustic properties of bowed string instruments of the violin family, from violin to bass viol.

In this interview with *The Spectrum*, Kasha reflects on a 67-year career (1938-2005) that began fresh out of high school as a "lab boy" at the Merck Research Laboratories, Rahway, NJ. Forty of the world's best organic chemists were racing to synthesize pantothenic acid (vitamin B_5) at Merck. Guess who did the key tests on each compound to decide which chemist had succeeded?

Kasha also discusses that monumental work on the phosphorescence of organic molecules that he did with Gilbert N. Lewis at Berkeley. It led to the then-controversial conclusion that delayed emissions in excited molecules are intrinsic molecular properties, originating from triplet states that seem to be forbidden by the laws of quantum mechanics. Kasha also recalls the day in 1946 when he discovered Lewis dead on the laboratory floor, liquid hydrogen cyanide pouring out of Lewis' experimental apparatus.

After Lewis' death, Kasha, the newly minted Ph.D., was left to defend the triplet state theory against skeptics that included the top spectroscopists and theorists of the era. Among them were Edward Teller (theoretical physicist, University of Chicago), Eugene Rabinowitch (photobiologist, University of Illinois), Robert Livingston (photochemist, University of Minnesota), and James Franck (molecular physicist, University of Chicago), all top scientists in their fields.

People often remark—rhetorically—about their luck in still being alive as the years pass. Kasha is lucky to be alive quite literally, after near misses with a major laboratory explosion and later working on the first fabricated plutonium mini-ingots during the Manhattan Project with nary a protective glove. Imagine pipetting (cotton plug "for safety") by mouth plutonium dissolved in hot concentrated perchloric acid (whose explosibility was controlled by added nitrate—also an explosive, serving to control chain reactions of the first) on a steam bath, running spectra in open optical cells, and dipping hands in a bath of chromic acid cleaning solution (to remove plutonium) before leaving the lab.

Michael Kasha was born December 6, 1920, in Elizabeth, New Jersey, to Ukrainian parents who were immigrants with only three to four years of schooling, and who did not value or trust higher education. His father, at one point, forbade Mike from attending high school. However, luck favored him again. His stubborn independence and drive finally led to his earning his B.S. in Chemistry at the University of

Michigan in February 1943, and subsequently on to U.C. Berkeley, where he was Lewis' only graduate student, completing his Ph.D. in February 1945 after an intensive two-year period (under WW II pressures).

Following Lewis' death, Kasha did postdoctoral research in U.C. Berkeley, U. Chicago, and U. Manchester, England. During this period, his insights into radiationless electronic excited state transitions led to his defining internal conversion and intersystem crossing transitions, and resulted in what became known as Kasha's Rules. He also showed that a solvent containing heavy atoms (e.g., ethyl iodide) could permit observation of singlet triplet absorption in organic molecules—the Kasha Effect.

In 1951, Kasha joined the FSU chemistry faculty; he is one of three University Professors at FSU and is a Lawton Distinguished Professor of Physical Chemistry. In 1960, he founded the Institute of Molecular Biophysics—with chemists, biologists, and physicists in integrated research projects—and served as director for 20 years. Today the Institute is in its 45th year and flourishing in all aspects of molecular biology and related areas.

Kasha has continued research in a number of areas, has supervised over 80 students for their Ph.D. or postdoctoral research, many of whom have gone on to distinguished careers.

Kasha began "fiddling" with guitars in 1964. This led to a parallel career in bowed string instruments, using vibration theory from physics, engineering physics, and acoustics. That work continues, using an anechoic (echo-free) chamber that Kasha designed and built in the Florida State University Center for Music Research of the School of Music.

Among his honors are the George Porter Medal for photochemistry, the Alexander Jablonski Medal for photophysics, and the Robert S. Mulliken Medal for molecular spectroscopy.

***The Spectrum*: What got you interested in science during childhood?**

Michael Kasha: I grew up in a Ukrainian immigrant community in New Jersey, where my first schooling was in a Ukrainian Catholic church school. One Ukrainian family lived in some isolated part of town and they would bring their son over on weekends to have some Ukrainian kids to play with. One day he came visiting and brought a paperback book of magic tricks. These were simple little scientific tricks involving some ideas from physics, chemistry, and biology. They were wonderful, and got me interested in knowing more about what the science was and how to understand it (I was about 10-12 years old then). My first mentor could be my cousin, John Ficula, whose family lived next door to us. Several immigrant families built new houses at the outskirts of Elizabeth, NJ, near the factory district (actually "across the tracks" of the main-line Pennsylvania Railroad, and across the tracks from the affluent people's neighborhood).

My cousin John was about three or so years older than I was, and very exploratory of the world beyond our tight Ukrainian community. There were no books in our house. John took me downtown to see the magnificent Carnegie Library, and to learn how to use it. It was my first real introduction to the world of books. What a pity that he did not go to a university! He had the curiosity and intellect. But there was almost no one from the quite large Ukrainian community who had the stimulation, family support, or even the concept of going further.

***The Spectrum:* Are kids today missing that kind of compelling, hands-on introduction to science?**

Michael Kasha at Merck Research Laboratories, 1939, carrying out microbioassay tests for pantothenic acid growth factor, measured by turbidity of *Streptococcus lactis* after overnight incubation.

Courtesy of Michael Kasha

Kasha: We have a famous guy on our FSU chemistry faculty now, Harry Kroto, a recent Nobel laureate in chemistry. Harry Kroto believes that the decrease in the population of science students in England is a direct consequence of the disappearance of the "Meccano" set for young people in England. In those early days, when he was a boy, you could put things together, and make them work. You learned how to screw things together properly, not too tight, not too loose, and you invented things. Hands-on experience with assembly of components puts reality to phenomena, which leads later to an intuitive understanding of their abstract treatment by mathematics and physical theories.

***The Spectrum:* Today's kids have computers....**

Kasha: They have computers, but that doesn't give them a hands-on feel for the subject. It is very crucial to feel, see, and make things with one's own hands, and to create new combinations.

***The Spectrum:* Most American kids don't get a real taste of that science-math mix until high school.**

Kasha: High school physics can be "an assault from which they never recover" if the mathematical intuition is not developed through tangible physical experience.

***The Spectrum:* Did you encounter teachers like that as a kid?**

Kasha: In junior high school we had Walter Shordiche as a science teacher, a most dedicated and generous man. He discovered that I knew how to do things, and he had me in his laboratory trying to invent little things to demonstrate to students. For example, for linear thermal expansion (instead of the "ball and ring" demonstration), I used a metal rod, about a yard long and threaded one end to simulate a gear, which then rested on a little geared wheel from a clock. A stiff piece of wire was soldered radially onto the wheel and it pointed up to act as an indicator. When a source of heat was brought near the rod at any position, the indicator would turn. Very sensitive. It acted as a thermometer. And Walter Shordiche was as proud of it as I was.

He gave me access to amazing things. At home, I got permission to partition off a small room in our basement which I used as a neat little laboratory. Shordiche let me bring home a fine Bausch and Lomb laboratory microscope. I used the microscope lamp to project images from microscope slides onto a piece of paper, and then I discovered that I could make pictures without a camera. I put sensitized photo papers there, exposed for 10 seconds, and developed it, and I got all kind of photomicrographs.

***The Spectrum:* Chemistry teachers?**

Kasha: Walter Shordiche was a big stimulus, and a fine teacher of physics and chemistry in junior high school. My high school chemistry teacher was totally uninspiring. He was a drill master, I was reading college books in chemistry on my own initiative. I've got to say, however, that one group of junior high school teachers really made a difference in my career start.

***The Spectrum:* In what way?**

Kasha: When I saw the film *My Big Fat Greek Wedding*, my father was just like that father. You had to live within the immigrant tribe and it was hard to break away. My father refused to let me go to high school. He said, "You stop at junior high and learn to survive." My father was struggling to save the house and worked hard—$10 a week was his depression-era salary for two or three years. He had to earn money on the side and he said the important thing was to learn how to survive, to learn a trade. Finally he said, "No high school."

So, four exceptionally diligent teachers from my junior high school came to the house after dinner one night to talk to my father. They were there for over two hours, arguing around the dining room table. They tried to convince him that this kid could learn anything. They said I was doing well in studying science, algebra, Latin, English, etc., and that I ought to be able to go on to high school. But my father said, "Never. Never!" So they figured out something. They said, "Suppose he took a course in the electrician trade?" There was a G.E. engineer, Maynard E. Hall, at the high school who was a magnificent teacher. So, I became an industrial electrician. I can wire factory circuitry—20 HP motor-generator pairs, 300 amp, large carbon-arc circuit breakers. I learned how to do it. And then my father allowed my continuing to high school. I could take an academic, scientific course if I wanted to, as long as I got an electrician's diploma. I did both, so that was the beginning of my freedom to go to academic things. And then I, of course, tried to go to college, and, of course, there was no way to go. There were 460 boys graduating from the high school. I was number 23 out of 460, and the first 22 got scholarships to Harvard, Yale, Princeton, wherever they wanted to go. They never asked number 23 where he wanted to go or what he wanted to do. They just completely disregarded me.

A word about my father, Stephen. He came from a farming family in the Carpathian Mountains. The mountain people had to be crafty to survive. My father showed great intelligence in what he was exposed to. He could converse in Polish, Slovak, and Hungarian (languages of countries that shared borders and people in Western Ukraine). He was enormously skillful and creative in manual skills. He taught himself English, and followed world news daily (in an American Ukrainian newspaper, Svoboda [Freedom]). He was a fine example, demonstrating that the amount of formal education is not a barometer of intellect.

***The Spectrum:* How did you find your way to Merck?**

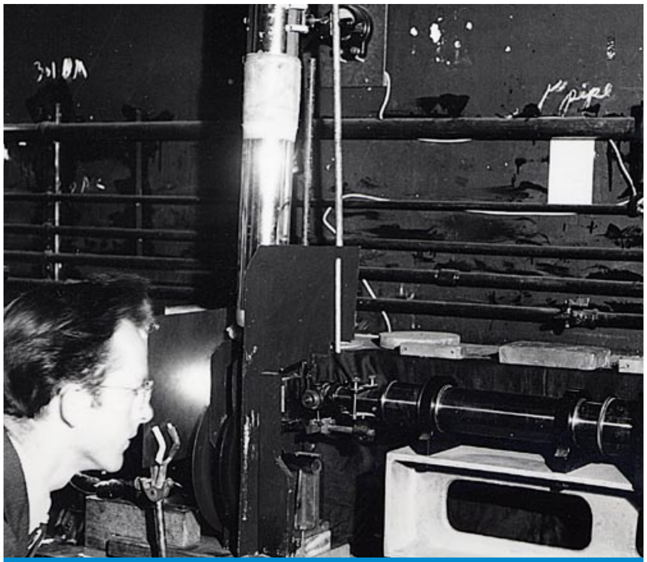
Kasha: I went to the high school employment office for advice. They said Merck had an opening for a lab boy, but it had been taken earlier that week, about two days ago. I jumped on a bus (Elizabeth to Rahway, about 10 miles). I got there at 4:30 on a Friday in August. People were anxious to get home on summer weekends. Karl Folkers, director of the Pure Research Division, was sitting at a desk, and agreed to see me. He made a quick decision; after 30 minutes, he said, "Well, you have the job!" But the job was taken, I said. He said, "Well, we'll give that boy some other job." And so I became the lab boy. I could handle equipment; and knew some chemistry. I would clean all the labs quickly in two days instead of five. The chemists learned about me and they all wanted me as an assistant. Folkers caught on, and made me his personal assistant. I did all kinds of stuff in that lab. I was taught microorganic techniques (by Folkers himself) which were needed in his erythrina-alkaloid chemistry. Once Folkers gave me a 100-gram sample of a crude erythrina-alkaloid mixture and told me to fractionate it. He left on a two-week vacation. When he came back, I had fractionated it into seven pure components, by optical-rotation standards, with a "chemical engineering" flowchart, showing each fraction. That was "pretty good for a high school graduate," he said.

Folkers justly claimed that he had "discovered" me as a potential scientist. Folkers became my lifetime mentor, and followed my career and gave enormous help and advice.

***The Spectrum*: How did you connect with G. N. Lewis at Berkeley?**

Kasha: Like many of the best changes of course in my life, it was quite accidental that I even considered going to Berkeley, 3000 miles from home. At the University of Michigan, Arthur Bueche and I were the top graduating seniors in chemistry, a large group of some 50 or so students. The chairperson of the Chemistry Department (whose name I omit to save the honor of University of Michigan) called both Art and me to his office. We had expected some great boost by being recommended to some great university for graduate work. We were surprised when he stated that he had arranged to send each of us to some out-of-the-way minor college. He was making a political payoff to some friends, and we were stunned, shocked! We quietly left his office. Outside his door, our disappointment and anger boiled over! Arthur stamped his foot and said, "I'll go to Cornell to work with Peter Debye!" And I did the same and said, "And I'll go to Berkeley to work with G. N. Lewis!" Until that point, Art and I, who were close friends, had only considered going to a well known major university in a nearby state. Did we succeed in our quick decision! A. M. Bueche *did* work with Peter Debye, later joined the G.E. laboratories, and rose to the very top, becoming C.E.O. of G.E., one of the world's largest technical industrial concerns. I was quickly accepted by Berkeley.

When I got to Berkeley, they gave me the list of the 18 chemistry professors. Students were supposed to go around and interview with each one. Lewis I saved until last. I didn't know it, but he had just lost his last three pre-war students. I told him I wanted to work with him. Lewis said, "I don't know you, and you don't know me, so why don't we have a trial period and after a month or so, see if we can work with each other?" He noticed I was nervous, he said, "Don't be nervous, I'm just going to tell you what I am interested in." He talked about all the work his laboratory had been doing. It was a nice way to approach a graduate student—totally different from the others. We agreed to work with each other. I was his only student for about the next 2½ years. Every day was exciting; we did new things; we did dramatic experiments; and it just went extremely well. We had a ball. Everyone knows the scientific outcome of that collaboration. I was fortunate to spend about six hours a day with Lewis directly. In my second year at Berkeley, World War II pressures for military service forced Wendell Latimer, Dean of the College of Chemistry, to assign me to



Michael Kasha operates the phosphorescence equipment used in the Lewis-Kasha triplet-state spectroscopy.

Courtesy of Michael Kasha

the plutonium chemistry project (known as the "Manhattan Project" under the Signal Corps), some 10 hours per day, so that I could continue to work with Lewis. So, from February 1944, to early 1946, my work with Lewis was during evenings, Saturdays, and Sundays. Lewis came in at 7:00 p.m. and worked until 11:00 p.m. every week day. Our first main paper (*J. Am. Chemistry. Soc.*, Dec. 1944) on triplet states was written in evenings on that schedule.

***The Spectrum:* Fewer people in the photochemical sciences community may be aware of your final day with Lewis.**

Kasha: It was a traumatic experience. Lewis died of a heart attack in 1946. He was working that Saturday afternoon after a faculty club luncheon. Lewis almost never came in for a faculty luncheon on Saturday, but he had a distinguished guest that day. I think the guest contributed to his condition, his heart attack.

***The Spectrum:* Who was the guest?**

Kasha: The man who came to lunch that day was a long-time "enemy" of Lewis...Irving Langmuir, the Nobel Laureate in chemistry. Langmuir had taken Lewis' ideas of complete octets and closed shells and made up his own chart and it became known as the Langmuir/Lewis chart. Langmuir had nothing to do with the original ideas; but he was a very dramatic speaker, going around the country lecturing with great enthusiasm. Lewis was a very modest personality, although he could give a vivid lecture, he didn't travel around much. He didn't go to conferences very often. So I think that meeting this man who had won the Nobel Prize (atomic hydrogen recombination) and who had made a very conspicuous public career lecturing and writing on the Langmuir ideas on electronic structure of atoms, served as a source of irritation to G. N. Lewis. I know that Lewis' and Langmuir's personalities clashed. I think that luncheon aroused the tension that could have precipitated a heart attack. That was my feeling about it. Lewis was very subdued and silent after the lunch. He was a heavy cigar smoker and they say that heavy smokers are more susceptible. In several cases I know, people who have died of heart attacks were provoked emotionally somehow.

Kasha classical guitars with asymmetric soundboard and bridge for frequency tuning (cf. J. S. Bach, *Goldberg Variations*, Sony Classical Recording, played by Kurt Rodarmer, using Kasha guitars).

Courtesy of Michael Kasha

***The Spectrum:* Did any involve other scientists?**

Kasha: That happened with James Franck when he went back to Germany. I had the good fortune to know Franck for about 20 years. I was in frequent touch with him the year I was in Chicago. My wife and I spent several summers in Woods Hole in Cape Cod, where I was working with Albert Szent-Györgyi. Franck was in residence there for long periods, and we talked for hours. What a wonderful person to get to know. I've written a biography of four people who, in my estimation, most influenced my career. I call it "Four Great Personalities of Science" (Franck, Lewis, Mulliken, Szent-Györgyi). Franck was, in my estimation, one of the greatest human beings, also one of the greatest scientists who ever lived. He was driven out of Germany by the Nazis. Years later, the city of Heidelberg invited him back. They wanted to give him the keys to the city. He accepted, going to Germany, and died there of a heart attack. All the old memories had come back.

***The Spectrum:* What happened the day Lewis died?**

Kasha: Lewis was doing a really neat experiment. He had found a *Trans. Faraday Soc.* article showing that liquid hydrogen cyanide changes refractive index by a huge amount over a certain temperature range. I don't remember the temperature range, but Lewis thought, "What a nifty way to look at the color effect!" And so he was making liquid hydrogen cyanide in quantity. He was going to study the dye by transferring the liquid hydrogen cyanide into a dye sample (vacuum bench distillation), alter the temperature to look at the color variation and presumably later measure it if we could keep the temperature constant at any point. The windows in the lab were closed when he was doing this experiment. There was one other person at the end of the hall that Saturday afternoon: Daniel Cubiciotti, who was working with Leo Brewer. Lewis, Dan, and I were the only people on the top floor that day. I walked back and forth from my lab to Lewis' vacuum bench lab at the end of the hall, seeing Lewis once in awhile. Once I came by and Lewis didn't seem to be there. So I stuck my head in and got a whiff of HCN; I knew the smell. I had heard about it. I saw his feet behind the vacuum bench. He had fallen flat on his back. I jumped back out and called Dan Cubiciotti for help and then I looked over the situation. There were some clay bricks near the door, so I clamped my nose and rushed in, threw the bricks through the window, and then I went back into the hall. I looked at the bench where he had been working and there was a pool of liquid there which looked a little viscous, so I got the safety bottle of sodium bicarbonate, dumped it on the liquid, and it bubbled fiercely. It was the liquid hydrogen cyanide from the apparatus, so I neutralized it. Windows had been broken and Cubiciotti called the police, who confirmed that Lewis was dead. They diagnosed that he had died of a heart attack.

***The Spectrum*: But weren't there stories circulating about suicide?**

Kasha: A heart attack. That was the autopsy, not hydrogen cyanide poisoning. One reason was that he did not appear cyanotic. People turn blue when hydrogen cyanide gets into their blood stream, and it kills quickly. Well, all over the country they said that Professor Lewis' death was a suicide with hydrogen cyanide. (The press reported that Lewis, the noted scientist, had died by hydrogen cyanide gas, a deadly poison.) That a suicide was involved was alarming to read because it was simply not true. And, by the way, he had been enthusiastic about the new research that we were planning to do: our talks about the coming year's research that morning, full of ideas and plans, had put Lewis in a very upbeat mood. The liquid HCN had begun to warm up in the ten or fifteen minutes after he died, and finally the pressure popped the reservoir of HCN off the glass vacuum system onto the table.

***The Spectrum*: After Lewis died you were left, a new Ph.D., defending the triplet state against some big-name doubters.**

Kasha: Yes. The negativism started right away and lasted and lasted. Lewis died just before a symposium that had been planned in his honor at Northwestern University for his 70th birthday by the American Chemical Society, so the committee asked me to come and present our work. They were kind enough not to say "your controversial work." Since people were forewarned that Lewis' assistant would come, they were armed to the hilt. People were saying, "Mike, there's an ambush set for you." Someone had seen Franck with our paper on his desk, and he had sections underlined in red, and for any visitors who would listen, he would pound the table, saying, "Ridiculous, absurd, impossible!" Edward Teller, the famous mathematical physicist,

Sand vibrational patterns on Kasha classical guitars at two frequencies (a, b), showing extended use of soundboard by long bass-coupling bars permitted by off-center soundhole.

Courtesy of Richard Schneider

was coming; Robert Livingston, the famous photochemist from Minnesota; and Rabinowitch, the photobiologist from Illinois, was fuming about the paper and he would also be there—all armed against this idea about the triplet state.

***The Spectrum*: How did you prepare to defend yourself and the triplet state? Any lessons for today's scientists who may face hostile fire like that?**

Kasha: Well, I was shaken, so I went to see Melvin Calvin, who said, "Don't worry, you know more about what you did than they could possibly know. Go there and present what you know and you'll be OK." Calvin had another idea that could be quite useful to others. He said, "If you're really worried, why don't you just look up what they have been writing and you will find out how to pre-answer their questions." That would do it. So I looked up Teller, who had written a very abstract, geometrical analysis in an article on what radiationless transitions really are like (*J. Phys. Chem.*, 1937). Well, Teller forgot his own work. It turns out that if he had really understood his own work in its spectroscopic consequence, he wouldn't have argued against us. He did not seem to realize that a radiative transition probability would not apply to radiationless transitions.

Michael and Lilli Kasha celebrating their 58th wedding anniversary and his 85th birthday.

Courtesy of Michael Kasha

***The Spectrum*: So what happened at the symposium?**

Kasha: I was invited to be the first speaker, and gave the prescribed short review talk of 20 minutes. I gave an outline survey of what we did, what we used, what effects we found, what proof of intrinsic molecular excitation we had, and so forth. Calvin said, "That sounded nice and clean." I sat down next to Calvin and he continued, "Let's see what happens." Then Franck got up. I had met him once before at Berkeley. He spoke without punctuation for 25 minutes. His sentences just went on and on and on. "I don't understand what he was saying," I lamented. He replied, "Don't worry; no one else does either." So, then Franck called upon Livingston, who got up and said that there was no evidence in all of photochemistry for a metastable state between the lowest excited state and a ground state. And Rabinowitch, the photobiologist, said, "There is no evidence in anything in photosynthesis or all of photobiology that requires a metastable state." Finally, Franck (in the role of chairperson of the Series) called upon Teller. I had never seen Teller in person before. He had a booming voice, his big black eyebrows constantly moving as he emphasized his words, and he kept stabbing the blackboard with the chalk as if he were dueling with it. Then he wrote all kinds of Q.M. equations and ended up writing that Latin triad often put at the bottom of a mathematical proof, "Q.E.D." (*quod erat demonstrandum*). The challenges had gone on for some 45 minutes.

***The Spectrum*: What were you thinking?**

Kasha: I thought, "How the hell do I answer?" Then an ascetic-looking, delicate man got up from the front row. It turned out to be Robert Mulliken. Teller was still standing there when Mulliken slowly walked to the blackboard and said, "Edward, why are you talking about atomic mercury?" Teller blushed. Oh, he got red. Mulliken said, "That has nothing to do with organic molecules; Lewis and Kasha have been talking about such organic molecules as benzene and derivatives of benzene, etc., and Hg doesn't relate at all." Mulliken said, "I think what Lewis and Kasha have been saying looks perfectly all right to me." Then he showed why. He showed, for example, that for the torsional potential of ethylene, the triplet singlet transition would be forbidden by the Franck-Condon (!) restriction, and could lead to retarded dynamics of emission! The simplistic argument was, "If the triplet-singlet emission is so forbidden, wouldn't the excited singlet-to-triplet excitation be equally forbidden? So, how could we ever observe it?" Wherever I went, people were still saying of the triplet state, "It shouldn't be observable."

The conference organizers were spooked by the four great experts' denunciation of the Lewis-Kasha work and by my new paper. So the *Chemical Reviews* journal issue for the celebration of Lewis' career tacitly suppressed my paper. It was demoted to be published last in the special volume, instead of first, in the order of presentation. But as it turned out, my novel appraisal of this subject included the first use of electronic state *internal conversion* and *intersystem crossing*, terms universally used today. And those were the keys to unlock the dilemma faced by the four experts!

***The Spectrum*: When did people finally accept it?**

Kasha: After 10 years, we had finally convinced most everybody. Franck was the first to change. He became my enthusiastic supporter, and even made a special trip to Tallahassee in 1953 to give a lecture on the triplet states in photosynthesis. Robert Livingston, then at the University of California at San Diego, wrote me a letter in about the 10th year, and said, "I'm writing to tell you that I'm going to now call the metastable state a triplet state, although I still don't believe it." That's being conservative! But, that was an interesting chapter. I have a streak of rebellion and when I think that something is right, I don't back down. I don't know where this rebellious streak came from, but I just did what I thought I should. We finally succeeded; my students at Berkeley (especially Donald McClure) and I did research which corroborated everything we had said and we were pleased about that.

***The Spectrum*: When we interviewed Nick Turro, he emphasized the importance of checking the literature—as have several other individuals. To what extent did previously published research help you and Lewis?**

Kasha: Lewis said, "Don't go culling the literature for all the past work; just think on your own and go ahead." Then, we had found these very narrow-band spectra unlike the broad structural luminescence bands of dye molecules. We thought no one had ever seen them before. So, when Lewis wasn't looking, I sneaked off to the library for a three-day weekend search. I went from *Chemical Abstracts* No. 1, Volume 1, up to the present at that time, and I filled a notebook full of references. I found papers from Poland, Germany, and France with myriads of bands that had been published. But they had everything backwards because there was no background of spectroscopy at their command. So, the origin of the band they thought was the lowest frequency emission band, instead of the highest frequency emission band (now recognized as the 0,0-band).

***The Spectrum*: We have learned that just in September 2005, The Tallahassee Scientific Society awarded you their Annual Gold Medal, with the inscription, "Michael Kasha, Ph.D. for his Unparalleled Scholarship in Multidisciplinary Scientific Research and His Outstanding Contribution to Education in the Sciences. 2005."**

So, what makes Michael Kasha tick?

Kasha: Beats me!

Editor's Note:

The interview appearing in the printed version of *The Spectrum* recently mailed was an earlier, unedited version of this interview with Dr. Kasha. There are mistakes and misspellings in that version.

The interview appearing here is the correct interview. For a PDF reprint of this interview, please email Pat Green, *The Spectrum* editor.

pat.green1@sbcglobal.net

two photon absorption in 1,4-bis([oxycarbonylphenyl]ethynyl)benzene chromophores

Evgeny Danilov, Dmitry Polyansky, & Douglas C. Neckers
Center for Photochemical Sciences, Bowling Green State University

Introduction

Though two-photon absorption (TPA) has been known since 1937,[1] experimental evidence only accumulated with the advent of lasers. Since the outset,[2] a variety of applications such as TPA-based microscopy and imaging,[3] data storage,[4] three-dimensional microfabrication,[5] photodynamic therapy, and optical power limiting[6] have been envisioned. Most chromophores are capable of TPA,[7] but inefficient two-photon absorbers require high light intensity and sample concentration to be observed experimentally. The necessity of high peak intensity and expensive laser sources remain the major complication in the commercialization of TPA applications, and more efficient chromophores continue to be a primary focus of TPA research.

Background

Although TPA is often referred to as a nonlinear process due to the second-order term in the differential equation describing the optical loss of a medium:

$$\frac{dI}{dz} = -a_1 I - a_2 I^2 \qquad (1)$$

(here a_1 is the linear absorption coefficient, a_2 is the two-photon absorption coefficient, I is the intensity of light, and z is a coordinate along the optical axis), its ties with nonlinear optics (NLO) are deeper. The mathematically rigorous and yet elegant theory of the connections between a_2 and a third-order nonlinear susceptibility $\chi^{(3)}$ says that a_2 is directly proportional to the imaginary part of $\chi^{(3)}$ [8,9,10,19] (a brief essay on this subject can also be found in the online version of this article). The main result of the theory is that for a third-order nonlinear process involving four waves of the same optical frequency ω, with $\omega_{ag} \approx 2\omega$, quantum mechanics provides the following expression for $\chi^{(3)}$:[10]

$$\chi^{(3)}(-\omega;\omega,-\omega,\omega) = \frac{N}{\hbar^3} B' \sum_{m,n,\nu} \frac{\mu_{gm}\mu_{ma}\mu_{an}\mu_{ng}}{(\omega_{mg}-\omega)(\omega_{ag}-2\omega)(\omega_{ng}-\omega)} \qquad (2)$$

Here N is the molecular number density, μ_{ij} are electric dipole transition moments, ω_{ij} are the energy gaps between molecular electronic levels, and B′ is a numeric constant. Due to the terms in the denominator of (2) containing frequency differences, $\chi^{(3)}$ can be resonantly enhanced. As with the linear susceptibility, the imaginary part of $\chi^{(3)}$ is responsible for the attenuation of an optical wave in the medium. The condition $\omega_{ag} \approx 2\omega$ ensures that the attenuation results from the resonance between two photons of radiation and a molecular energy level that is TPA. The final expression for the propagation of an optical wave under such conditions:[10]

$$\frac{dI(z)}{dz} = \frac{3\omega}{4cn(\omega)} \mathrm{Im}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)] I(z)^2 \qquad (3)$$

results in the already familiar nonlinear analog of Beer's law.

Because the two-photon absorption coefficient is associated with nonlinear susceptibility, strategies can be sought for the molecular engineering of chromophores with high TPA cross-sections. Susceptibility is directly related to molecular polarizability, so easily polarizable chromophores are better two-photon absorbers. The induced polarization of the medium can be represented as the sum of the individual dipole moments of the molecules in the medium: $\mathbf{P} = Ne\mathbf{x}$, where $\mathbf{x}$ is the vibrational amplitude of the electron oscillator. By definition, $\mathbf{P} = N\alpha\mathbf{E}$, therefore $\alpha = e\mathbf{x}/\mathbf{E}$. In other words, for a given charge and electric field strength, the larger the amplitude of oscillations, the larger is the polarizability. In atomic physics, the effect of high-order (up to about 100th) harmonic generation with unusually high intensity is explained assuming that an electron produces such harmonics when revolving in a wide orbit that is close to the ionization limit, sometimes even going to the continuum for part of the light wave period.[11,12] By analogy, one would expect that conjugated organic molecules like coumarin, Rhodamine and fluorene exhibit substantial nonlinear absorption because conjugation and delocalization of the electron density over the chromophore upon excitation provides the necessary freedom for the electron.

Efficient nonlinear chromophores also result from an increase in the electric moments μ in the numerator of (2). In addition to dipole moments, one could use the induced quadrupole moments of the molecule. Combinations of charge-donating and charge-withdrawing moieties result in substantial quadrupole moments upon excitation, and the π-system of the bridge provides the medium for delocalization. The most efficient molecular designs used for efficient NL absorbers follow donor(D)-bridge-acceptor(A) D-π-A, A-π-A, or D-π-D schemes. Efficient bridge chromophores include phenylene-vinylene, fluorene, and phenylene-ethynylene motifs. Calculations indicate that TPA cross-sections of phenylene-ethynylene compounds are not significantly different from their phenylene-vinylene analogs.[13] Work by Iwase et al. demonstrated that an introduction of linear diacetylene bridge led to an approximate twofold enhancement of the TPA extinction coefficient compared to the vinylene link of the same conjugation length.[14] Theoretical calculations of TPA of octuple molecules with phenylene-ethynylene linkages have predicted σ_2 values > 2×10^3 GM ($1\text{GM}=10^{-50}$ cm^4 sec phot^{-1} molec^{-1}).[15] Experimental measurements of TPA of D-π-A type fluorophores (where π is $-[\text{Ph-C}\equiv\text{C}]_n-$) demonstrated σ_2 values over 10^3 GM.[16] The TPA cross-sections measured for [60]fullerene-terminated phenylene-ethynylene compounds were about 140 GM. Significant improvement in the NLO properties of D-A systems can be obtained by exploiting dendrimer structures rather than their linear analogs.

Increases in conjugation usually lead to enhanced NLO properties. Theoretical studies[17] predict that for larger molecules the resonantly enhanced TPA cross-section σ_2 relates to the TPA coefficient a_2 as: $\sigma_2 = a_2 h\nu/N$ in GM units. This should scale as $\mathcal{N}^2$, where $\mathcal{N}$ is the effective number of electrons in the molecule. This effective number was calculated in the following manner: Two electrons were associated with each double bond along the conjugation path; each moiety outside the conjugation path was treated as a submolecule; the total effective number of electrons was found as $\mathcal{N} = ((\mathcal{N}_{\text{conj}})^2 + \Sigma(\mathcal{N}_{\text{sub}})^2)^{1/2}$. In the same work, fundamental limits for TPA cross-sections were estimated based on a quantum-mechanical sum rules treatment. Comparison with experimental data for a series of conjugated molecules using the most popular motifs, however, showed that measured TPA cross-sections scaled linearly with $\mathcal{N}$ and the TPA cross-section values fell about a hundred times below the fundamental limits as the number of electrons increased, implying that the additional electrons were not participating efficiently. If the cross-section followed the predicted trend, the σ_2 values from 3×10^5 to 10^6 GM for the molecules with $\mathcal{N}\sim25\text{-}50$ and about 10^7 for dendrimer structures can be expected.

Experimental Techniques

Because direct quantum mechanical calculations of NLO properties involve costly TD DFT algorithms,[18] combinatorial synthesis and the experimental measurement of TPA cross-sections remain popular options to test new design paradigms. Among the most practical techniques are TP-induced fluorescence and the measurement of nonlinear transmittance using either monochromatic *z*-scan or pump-white light continuum (WLC) probe. The setups for the last two, *z*-scan and WLC, were built in our Ohio Laboratory for Kinetic Spectrometry (OLKS). The idea behind each method is the same. One can calculate the TPA cross-section by measuring the dependence of the nonlinear transmittance of the sample on laser intensity. In the *z*-scan method, the same laser beam induces the nonlinear transmittance of the medium and probes it. In the WLC method, intense pump and broad-band probe pulses induce the nonlinear changes in transmittance while the broad-band pulse probes it. Although *z*-scan and WLC methods depend on different Cartesian components of the $\chi^{(3)}$ ($\chi^{(3)}_{\text{iiii}}$ and $\chi^{(3)}_{\text{iijj}}$, respectively[19]), researchers agree that the methods yield similar values for the TPA cross-section. Our results confirm this observation. While both setups use standard principles,[20,21,22] a brief description seems to be appropriate.

Z-scan setup

A schematic representation of the *z*-scan setup is shown in Figure 1. The output from a Spectra-Physics Hurricane laser (800 nm, 100 fs, 1 mJ, 1 kHz) or an optical parametric amplifier (variable wavelength) passed through a set of ND filters, focused (f = 250 mm) into a 2 cm quartz sample cell and then refocused again (f = 100 mm) into an EG&G UV-250080 photodiode. The sample cell was mounted on a computer-controlled Newport ILS250PP motorized linear stage and translated along the laser beam axis. The diode output was fed to a Stanford Research SR250 gated boxcar integrator and the integrated signal was digitized with a NI PCI-6023E DAQ board.

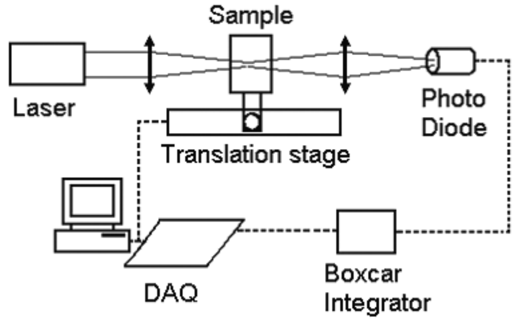


Figure 1. Schematic representation of Z-scan setup.

An in-house LabView program controlled data acquisition. Laser energy was kept as low as possible to avoid any response associated with non-linear effects in the solvent or sample cell. Control *z*-scan traces with pure solvents were recorded prior to all measurements. Data was acquired with a 0.5 mm step size and 250-pulse averaging. Transmittance (T) versus *z*-coordinate (x) curves were fitted according to the procedures described in the literature.[20,22,23]

WLC pump-probe setup

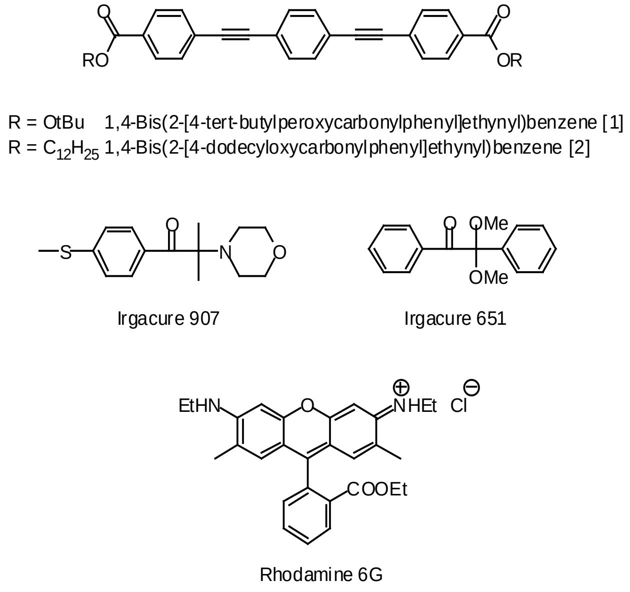
An ultrafast pump-probe transient absorption setup[24] was used with minor modifications for the TPA measurements.

The attenuated output from a Hurricane laser was used as the pump, while a white light continuum probe was generated in a CaF_2 crystal. The relative polarizations of the pump and probe beams were kept parallel. The pump and probe were spatially overlapped inside a 2 mm thick quartz cell containing a solution of the compound under study. The measured absorbance versus delay time curves were converted into transmittance (T) versus scaled delay time (τ) data and fitted according to the procedures described.[25]

Results and Discussion

TPA measurements for compounds with reported cross-sections and for model compound **2** were taken using the *z*-scan technique (Chart 1). TPA spectra for Irgacure 651 and Irgacure 907 were then measured using the WLC pump-probe technique and TPA cross-sections measured by the WLC method were compared with those measured by the *z*-scan at several wavelengths. Compound **1** was then used to demonstrate the 3-D microstructures created as a result of TP-initiated photopolymerization in trimethylolpropane triacrylate (TMPTA).

Chart 1. Chemical structures of compounds investigated in this work.



Z-scan measurements. TPA cross-sections σ_2 of Rhodamine 6G, Irgacure 651, Irgacure 907, and **2** were measured. The reactivity of **1** ($\Phi_{decomposition}$ = 0.6) under the experimental conditions precluded TPA cross-section measurement by the z-scan method. Typical z-scan traces for Rhodamine 6G and Irgacure 907 in methanol and the theoretical fits (T_{nl}) are shown in Figure 2.

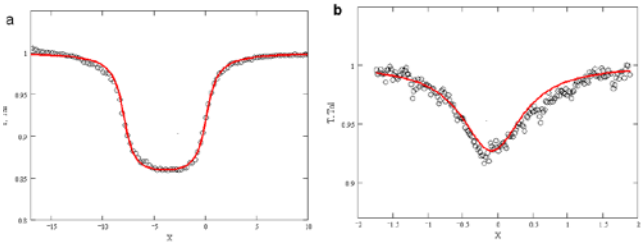


Figure 2. Z-scan traces (circles) and theoretical fits (red line) for 10 mM methanol solution of Rhodamine 6G dye at 800 nm (a); 43 mM methanol solution of Irgacure 907 at 594 nm (b).

The σ_2 values, experimental parameters, and literature data are summarized in Table 1. The σ_2 values obtained for Rhodamine 6G and Irgacure 907 are in good agreement with the literature. The TP cross-section of **2** was measured in chloroform at different wavelengths. The poor solubility of **2** in common organic solvents allowed for reliable TPA measurements only in the vicinity of the TPA maximum. The *z*-scan traces for **2** and the theoretical fits (T_{nl}) are shown in Figure 3.

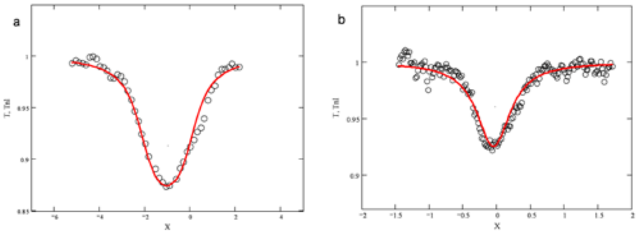


Figure 3. Z-scan traces (circles) and theoretical curves (red line) for **2** at 590 (a) and 594 nm (b).

WLC pump-probe measurements. Z-scan is a convenient and simple methodology for TPA measurements at a single wavelength. When spectral information is required, the WLC method[25] is used. The TPA spectra of Irgacure 651 and Irgacure 907 were measured using the WLC pump-probe method. Typical kinetic traces at several wavelengths and corresponding theoretical curves are presented in Figure 4. The graph shows the transmittance versus relative delay time (open circles) and the theoretical fits (red line) for several wavelengths of choice. Traces are shifted in the y-direction for better presentation. The TPA spectrum was reconstructed based on the σ_2 values obtained from the fits.

Table 1. Z-scan data for the set of compounds used in this study.

Compound	λ, nm	a_2, cm/GW	C, mM	σ_2, GM
Rhodamine 6G	800	6.7x10^{-3}	10	26.8 (36.0[26]; 16.2[27])
Irgacure 651	500	6.8x10^{-3}	160	2.7
	518	2.3x10^{-3}	160	0.9
	530	-	-	<20[28]
Irgacure 907	594	4.1x10^{-3}	43	5.1
	600	-	-	4.0[28]
2	590	4.1x10^{-3}	2.5	102.4
	594	4.2x10^{-3}	2.3	98.4

Two-photon spectra of the Irgacures measured by the WLC pump-probe and the *z*-scan techniques are overlaid with their single photon absorption (SPA) spectra in Figures 5-6. TPA spectra were plotted against the total energy of both pump and probe photons, expressed in nanometers. Excellent agreement was obtained between independent, absolute TPA cross-section values measured by the WLC pump-probe and the *z*-scan methods.

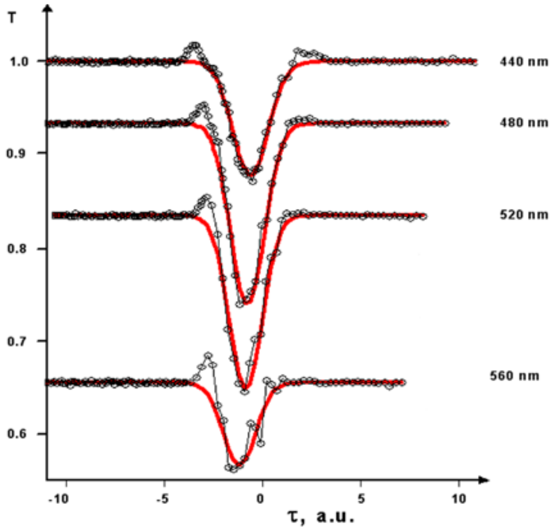


Figure 4. Kinetic traces obtained in the WLC pump-probe experiment with Irgacure 907.

The TPA spectrum of Irgacure 907 (Figure 5) overlaps with the SPA spectrum indicating that close lying excited states are involved in the transitions. However, no similar correlation was observed for Irgacure 651 (Figure 6). The red region of the TPA spectrum deviates slightly from the SPA spectrum probably due to larger energy separation between the states of different symmetry involved in both transitions.[29] Only the red wing of the TPA spectrum for Irgacure 651 was measured since at < 260 nm the SPA of the probe WLC grows in and suppresses the measurements. However, the TPA spectra below this wavelength can still be recorded using the *z*-scan since it requires two photons of the same energy. For example, instead of using a red + blue pair of wavelengths of which the blue is absorbed, the *z*-scan uses a green + green pair that does not invoke SPA. This example demonstrates that although the WLC method is well suited for measuring the complete TPA spectra and obtaining accurate values for σ_2, on some occasions *z*-scan methodology might be applicable even in a broader spectral range. On the downside, the *z*-scan method is substantially slower than the WLC since it uses point-by-point data collection. It was also found that the *z*-scan method is generally more destructive than WLC due to higher intensities and

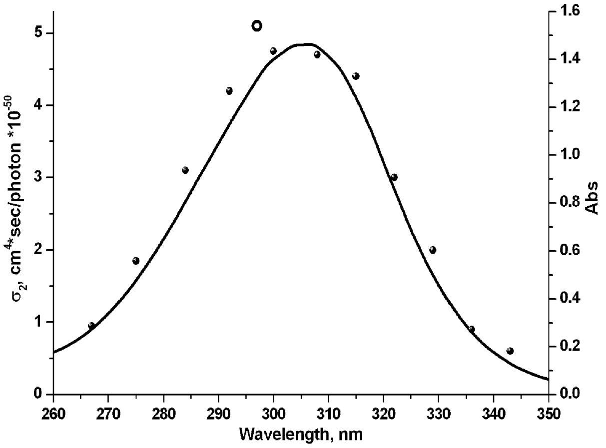


Figure 5. TPA spectrum of Irgacure 907 in MeOH measured by WLC (dots), Z-scan (open circle), and the single photon spectrum (solid line).

longer measurement times. This limitation is especially important for TPA studies of photolabile compounds.

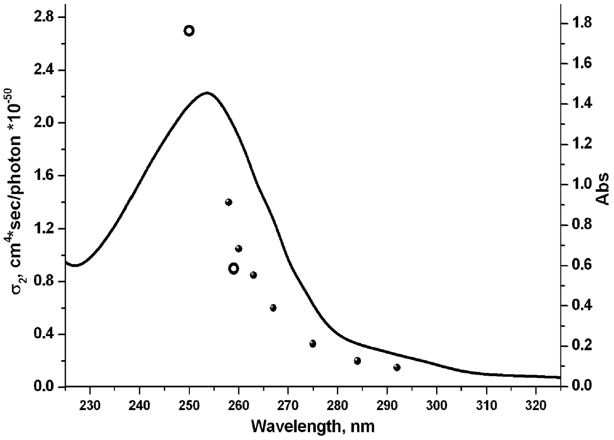


Figure 6. TPA spectrum of Irgacure 651 in MeOH measured by WLC (dots), Z-scan (open circle), and the single photon spectrum (solid line).

Photopolymerization experiments with **1** *as a photoinitiator.* 3-D microfabrication remains a possibly useful application of TPA. It has been successfully demonstrated with various photopolymer systems and good results were achieved in terms of spatial resolution and reproducibility.[30] According to (1), in a medium with high σ_2 that is transparent to light at the fundamental wavelength, absorption will take place only in the focal spot of the laser beam where the intensity is the highest. If the medium is a monomer containing an embedded TPA photoinitiator, polymerization will occur only in the focal spot. Figure 7 shows a microstructure fabricated by irradiating the mixture of TMPTA with 1%wt. of **1** with focused output from the 100 fs pulsed Ti:Sapphire laser at 800 nm. The irradiation of the monomer without the photoinitiator produced no changes indicating that polymerization was caused by the decomposition of **1**.

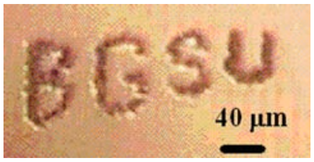


Figure 7. Optical microscope image of a microstructure obtained through the TPA-photoinitiated polymerization of TMPTA with 1%wt. of **1**.

Conclusions

TPA properties of a phenylene-ethynylene chromophore with carboxyl termini (compound **2**) exploiting the A-π-A design model (where π is –[Ph-C≡C]$_n$–) were studied and compared with the TPA data for known compounds. Compound **2** possesses a fairly large σ_2 value (110 GM) exceeding 20-40 times the σ_2 for the common commercial photoinitiators Irgacure 651 and Irgacure 907. Two methods, *z*-scan and WLC pump-probe, agreed very well on the σ_2 values for both Irgacures.

The TPA spectrum of Irgacure 907 overlaps with its SPA spectrum. The TPA spectrum for Irgacure 651 looked similar to its SPA spectrum but was shifted toward shorter wavelengths, implying that different excited states are involved in each case.

Photoinitiator **1** was used to produce 3-D microstructures by TPA-initiated photopolymerization of TMPTA.

Finally, the advantages and limitations of the *z*-scan and the WLC pump-probe techniques applied to organic nonlinear chromophores were demonstrated. Our results suggest that the techniques complement each other and should be used in parallel.

Acknowledgements

The authors thank Prof. Michael A. J. Rodgers, Director of the Ohio Laboratory for Kinetic Spectrometry, for providing necessary instrumentation. Dr. Sergey Voskresensky is gratefully acknowledged for the synthesis of **1**. DEP is thankful to the McMaster endowment for fellowship support.

References

1. Göppert-Mayer, M. *Ann. Phys.* **1937**, *9*, 273–294.
2. a) Kaiser, W.; Garret, C. G. B. *Phys. Rev. Lett.* **1961**, *7*, 229–231. b) Peticolas, W. L.; Rieckhoff, K. E. *J. Chem. Phys.* **1963**, *39*, 1347.
3. Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1990**, *248*, 73.
4. Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843.
5. a) Zhou, W.; Kuebler, S. M.; Braun, K. L.; Yu, T.; Cammack, J. K.; Ober, C. K.; Perry, J. W.; Marder, S. R. *Science* **2002**, *296*, 1106. b) Kuebler, S. M.; Braun, K. L.; Zhou, W.; Cammack, J. K.; Yu, T.; Ober, C. K.; Marder, S. R.; Perry J. W. *J. Photochem. Photobiol. A* **2003**, *158*, 163.
6. a) Ehrlich, J. E.; Wu, X. L.; Lee, I.-Y. S.; Hu, Z.-Y.; Röckel, H.; Marder, S. R.; Perry J. W. *Opt. Lett.* **1997**, *22*, 1843. b) He, G. S.; Xu, G. C.; Prasad, P. N.; Reinhardt, B. A.; Bhatt, J. C.; Dillard, A. G.

Opt. Lett. **1995**, *20*, 435. c) Walker, A. C.; Kar, A. K.; Wei, J.; Keller, U.; Smith, S. D. *Appl. Phys. Lett.* **1986**, *48*, 683.

7. McGowen, J. L.; Ajo, H. M.; Zhang, J. Z.; Schwartz, B. J. *Chem. Phys. Lett.* **1994**, *231*, 504.
8. Boyd, R. W. *Nonlinear Optics*, 2nd ed.; Academic Press: New York, 2003.
9. Bloembergen, N.; Lotem, H.; Lynch, R. T. In *Encounters in Nonlinear Optics: selected papers of Nicolaas Bloembergen, with commentary*. Bloembergen, N., Ed.; World Scientific: Singapore; River Edge, NJ, 1996, 263.
10. Milonni, P. W., Eberly, J. H. *Lasers*. Wiley: New York, 1988.
11. Lewenstein, M.; Balcou, Ph.; Ivanov, M. Yu.; L'Huiller, Anne; Corkum, P. B. *Phys. Rev. A* **1994**, *49*, 2117.
12. Tempea, G.; Brabec, T. *Appl. Phys. B* **2000**, *70*, S197.
13. McIlroy, S. P.; Clo, E.; Nikolajsen, L; Frederiksen, P. K.; Nielsen, C. B.; Mikkelsen, K. V.; Gothelf, K. V.; Ogilby, P. R. *J. Org. Chem.* **2005**, *70*, 1134.
14. Iwase, Y.; Kamada, K.; Ohta, K.; Kondo, K. *J. Mater. Chem.* **2003**, *13*, 1575.
15. Beljonne, D.; Wenseleers, W.; Zojer, E.; Shuai, Z.; Vogel, H.; Pond, S. J. K.; Perry, J. W.; Marder, S. R.; Bredas, J.-L. *Adv. Funct. Mater.* **2002**, *12*, 631.
16. Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. *Org. Lett.* **2004**, 6, 47.
17. Kuzyk, M. G. *J. Chem. Phys.* **2003**, *119*, 8327.
18. Tretiak, S.; Chernyak, V. *J. Chem. Phys.* **2003**, *119*, 8809.
19. Sutherland, R. L. *Handbook of Nonlinear Optics*. Marcel Dekker: New York, 2003.
20. Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.
21. Negres, R. A.; Hales, J. M.; Kobyakov, A.; Hagan, D. J.; Van Stryland, E. *Opt. Lett.* **2002**, *27*, 270.
22. Zang, W.-P.; Tian, J.-G.; Liu, Z.-B.; Zhou, W.-Y.; Song, F.; Zhang, C.-P. *J. Opt. Soc. Am. B* **2004**, *21*, 63.
23. Hermann, J. A. *J. Opt. Soc. Am. B* **1997**, *14*, 814.
24. Danilov, E. O.; Pomestchenko, I. E.; Kinayyigit, S.; Gentili, P. L.; Hissler, M.; Ziessel, R.; Castellano, F. N. *J. Phys. Chem. A* **2005**, *109*, 2465.
25. Negres, R. A.; Hales, J. M.; Kobyakov, A.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **2002**, *38*, 1205.
26. Kapoor, R.; Friend, C. S.; Patra A. *J. Opt. Soc. Am. B* **2003**, *20*, 1550.
27. Drexhage, K. H. Dye Lasers. In *Springer Series in Topics in Applied Physics*; Schafer, F. P., Ed.; Springer: Berlin, 1990; Vol. 1.
28. Schafer, K. J.; Hales, J. M.; Balu, M.; Belfield, K. D.; Van Stryland, E. W.; Haganb D. J. *J. Photochem. Photobiol. A* **2004**, *162*, 497.
29. Fisher, A.; Cremer, C.; Stelzer, E. H. K. *Appl. Opt.* **1995**, *34*, 1989.
30. Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, K. *Nature* **2001**, *412*, 697.

About the Authors

Evgeny Danilov studied physics at M. V. Lomonosov Moscow State University in Russia where he worked on ultrashort IR laser pulse generation techniques. After graduation he joined the Department of Quantum Electronics at P. N. Lebedev Physics Institute of the Russian Academy of Sciences as a researcher. Under the direction of Nobel laureate Nicolay Basov, Evgeny engineered high-power lasers. He received his Ph.D. in laser physics from Moscow State University. His research focused on the multiphoton IR excitation of small organic molecules by ultrashort laser pulses. Since 1999, Evgeny has worked in Bowling Green, first as a postdoc with Professor M. A. J. Rodgers, then as Research Assistant Professor and Research Coordinator of the Ohio Laboratory for Kinetic Spectrometry.

Dmitry Polyansky received his Ph.D. in Photochemical Sciences from Bowling Green State University in December 2005 after graduating from the D. I. Mendeleev University of Chemical Technology of Russia. In Bowling Green, Dmitry worked in D. C. Neckers' group doing time-resolved IR and visible nano- and subpicosecond studies of chromophores containing peroxide. He currently is a postdoctoral researcher at the Brookhaven National Lab.

Douglas C. Neckers is McMaster Distinguised Research Professor and the founder of the Center for Photochemical Sciences at Bowling Green State University. He is also current Executive Director of the Center and the founder of *The Spectrum*. Professor Neckers graduated from Hope College with his B.A. in Chemistry. He received his Ph.D. in Chemistry from the University of Kansas, and then did his postdoctoral research at Harvard University. Professor Neckers' research focus is in the area of photopolymerization and its applications.

a new generation of optical sensor materials

Manuel A. Palacios & Pavel Anzenbacher, Jr.
Center for Photochemical Sciences, Bowling Green State University

We live in a chemical world. At all times we are surrounded by chemical entities, molecules, and ions. Most of the time we are not particularly aware of that, however, there are circumstances when being able to detect or visualize chemicals is of utmost importance. Sensing materials harmful to humans or animals or toxic to the environment necessitates development of sensors for chemicals, that is, chemosensors.[1] Sensor materials and devices allow us to translate the presence of a chemical entity to a clearly distinguishable signal output, such as change in color, electrical properties[2] or luminescence,[3] to name a few.[4] In our research at BGSU, we focus mainly on the aspect of optical sensing, using change in color[5] and luminescence to relay the information about presence of chemicals.

In this brief article we describe an example of developing optical sensors for inorganic anions. In fact, numerous molecules and materials capable of sensing anions while providing optical output have been reported, but materials that are inexpensive yet capable of working with anions administered in the form of purely aqueous solutions are still rare.[6] This is because compared to isoelectric cations, anions often display tautomerism, adopt a wide range of geometries, and possess low surface-charge density, features that make the binding and sensing of anions less effective.[7]

In this paper we show how we have converted 2,3-di(pyrrole-2-yl)quinoxaline (DPQ) (Figure 1), a compound known in the literature since 1911[8] and only recently rediscovered as a potential colorimetric and fluorescent sensor[9] for anions, was converted into a viable sensor device. DPQ binds anions via concerted hydrogen bonding between the two pyrrole NH moieties and the anions. During the anion-binding process, changes in electronic density and conformation in DPQ result in a change in color as well as fluorescence (Figure 1).

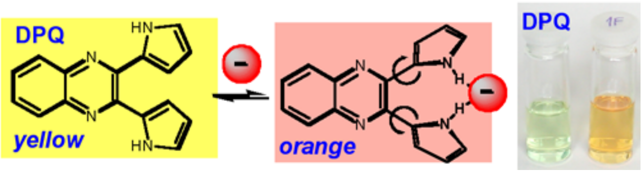


Figure 1. The structures of 2,3-di(pyrrole-2-yl)quinoxaline and DPQ-anion complex.

We have shown that the anion affinity and optical response of DPQ derivatives may be successfully tuned via attaching various substituents to the quinoxaline chromophore. In Figure 2, we show the anion-induced color and fluorescence in DPQ.

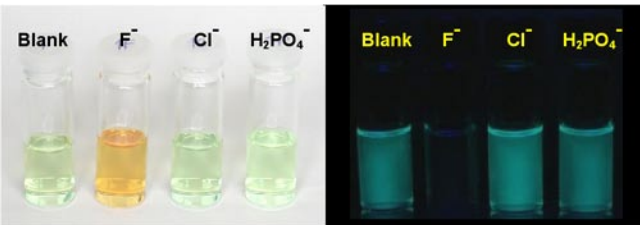


Figure 2. The changes in color and fluorescence of DPQ dichloromethane solutions upon addition of anions.

One can clearly see that the dichloromethane solutions of DPQ do change color, however, these changes are relatively weak. Also, the DPQ fluorescence is not very bright (quantum yield ~ 17%).

Because the fluorescence-based sensing is generally more sensitive, we decided first to improve the emissive properties of DPQ. This was achieved by attaching extended conjugated moieties to the quinoxaline chromophore either directly or via the acetylenic spacer, for example, in compounds in Figure 3.

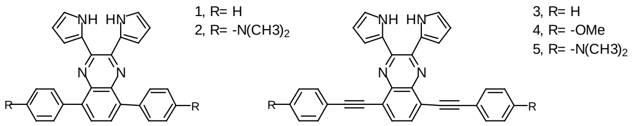


Figure 3. The structures of DPQ-related sensors with extended conjugated chromophore.

While extending of the conjugated DPQ chromophore improved fluorescence properties by increasing the quantum yields from circa 15% to 25-35% depending on a specific substituent, the resulting materials required additional improvements to render them water-compatible so the anions could be administered as solutions in water or a buffer. This was achieved by embedding the DPQ-based sensors in hydrophilic polyurethane matrices. Medical-grade hydrophilic polyurethanes (Tecophilic™ by Thermedics™ Polymer Products, division of Noveon, Lubrizol) were custom synthesized using the company's proprietary technology. These polymer matrices were designed and synthesized in such a way that they take up a certain amount of water, bringing the soluble salts including an anion into close contact with DPQ sensors embedded within the polyurethane matrix.[10] In a way, the matrix extracts the anions from the bulk environment, together with a limited amount of water. The exact amount of water depends critically on the hydrophilicity of the polyurethane resin. The resulting sensor-doped polyurethane was pressed into the shape of half-capsules of 20 μL capacity (diameter = 4 mm, height = 2 mm) (Figure 4A). The capsules may be introduced in multi-well dishes used in automatic plate-readers or used in a variety of holders with machined wells. The aqueous analytes are then introduced into the sensor capsules and incubated for 30 minutes, after which the clearly observable color pattern appears. This process may also be visualized by black light (Figure 4). Also, the incubation process may be shortened to less than one minute by developing the assay in a common microwave oven. Figure 4B shows a 16-well Teflon plate in ambient light while Figure 4C shows the same 16-well plate illuminated by black light (~365 nm).

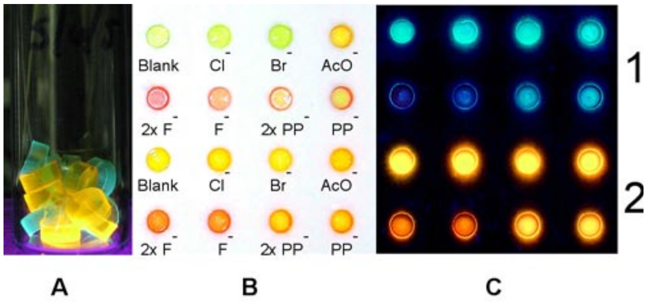


Figure 4. Panel A: Polyurethane capsules doped with sensors 1 and 2. Panel B: 16-well Teflon substrate with embedded capsules exposed to aqueous anion solutions. Panel C: The same 16-well assay illuminated by black light.

The multi-well capsule-based assay demonstrated numerous advantages of the polymer matrix-sensor approach, namely its flexibility in selecting the number and color/emission of the capsules to match the parameters of the detection instrumentation or, possibly, to circumvent colorant/fluorophore additives in food or beverages. However, the longer time required for swelling of the large capsule or required microwave heating to accelerate the process seemed somewhat impractical.

In the next stage, we have redeveloped this approach using micro-well plates. This new generation assays was fabricated by ultrasonic drilling of quartz slides to generate 500-750 μm round holes 750 μm deep (Figure 5). Polyurethane-doped sensors were solution cast to create about 100 μm coating in the respective hole. The light emission may be observed by the naked eye or recorded using a fiber-optic detector. The addition of 0.25-0.5 μL of an aqueous analyte solution to the micro-wells results in clearly observable color changes as well as changes in luminescence within seconds. The rapid response of the material is attributed to its small size and a thin sensor film, which is not limited by analyte diffusion. The micro-assay is shown in Figure 5. The capacity of each well is circa 1 μL, however, only 0.5 μL is required to develop clearly observable color and emission patterns. The changes in fluorescence may easily be recorded using simple fiber-optic detectors coupled to hand-held computers for sample evaluation.

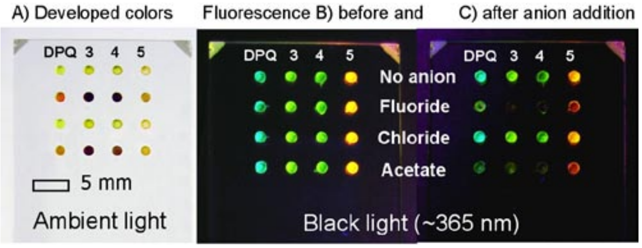


Figure 5. Microliter-scale assay. Sensors 3, 4 and 5 embedded in PU. Panel A: Clearly observable color patterns develop in the assay after anion addition. B: the micro-assay shows strong fluorescence from each micro-well. C: the addition of an analyte results in anion-induced change in fluorescence.

In summary, we show how the synergy in action between relatively ineffective colorimetric and fluorimetric sensors and polymer matrix results in a functional anion-sensor material and device. The beauty of this approach is that it does not require expensive synthesis, but rather relies upon simple mixing/matching protocols and is highly amenable to combinatorial optimization to meet various requirements of users and markets.

Acknowledgment

This work was supported by NSF (DMR-0306117, NER-0304320, SENSORS grants), BGSU (TIE and FRC grants), and a Kraft Foods, Inc. grant. Financial support was also obtained from the McMaster Endowment.

References

1. (a) Schmidt, R. F.; Thews, G. *Human Physiology*, 2nd ed.; Springer-Verlag: Berlin, 1989. (b) Marshall, W. J.; Bangert, S. K. *Clinical Chemistry*, 5th ed.; Elsevier: Edinburg, 2004. (c) Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, Wiley VCH, New York, 1999.
2. (a) Aldakov, D.; Anzenbacher, P., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 4752. (b) Anzenbacher, P., Jr.; Palacios, M. A.; Jursíková, K.; Marquez, M. *Org. Lett.* **2005**, in press.

3. (a) Anzenbacher P., Jr.; Tyson, D. S.; Jursíková, K.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 6232. (b) Pohl, R.; Aldakov, D.; Kubát, P.; Jursíková, K.; Marquez, M.; Anzenbacher, P., Jr. *Chem. Commun.* **2004**, 1282.
4. (a) Eggins, B. R. *Chemical Sensors and Biosensors*; John Wiley & Sons: Chichester, UK, 2002. (b) *Chemical and Biological Sensors for Environmental Monitoring*; Mulchandani, A., Sadik, O. A., Eds.; ACS Symposium Series 762; American Chemical Society, Oxford University Press, 2000.
5. Nishiyabu, R.; Anzenbacher, P., Jr. *J. Am. Chem. Soc.* **2005**, *127*, 8270.
6. (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Beer, P. D.; Gale, P. A. *Angew. Chem.,Int. Ed.* **2001,** *40,* 486.
7. Atwood, J. L.; Steed, J. W. In *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E.; Eds.; Wiley-VCH: New York, 1997; pp 147-215.
8. Oddo, B. *Gazz. Chim. Ital.* **1911**, *41*, 248.
9. (a) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438. (b) Anzenbacher, P., Jr.; Try, A. C.; Miyaji, H.; Jursíková, K.; Lynch, V. M.; Marquez, M.; Sessler, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 10268.
10. Aldakov, D.; Palacios, M. A.; Anzenbacher, P., Jr., *Chem. Mater.* **2005**, in press.

About the Authors

Manuel A. Palacios earned his B.S. in chemistry from the Simon Bolivar University in Caracas, Venezuela. He is a second year Ph.D. student in photochemical sciences at Bowling Green State University.

Pavel Anzenbacher, Jr. is an Assistant Professor of Chemistry at Bowling Green State University. A native of the Czech Republic, Anzenbacher was educated at the Charles University in Prague, where he received his M.S. degree from the Department of Organic Chemistry and earned a doctoral degree in organic chemistry from the Institute of Organic Chemistry and Biochemsitry of the Czech Academy of Sciences in 1997. He served as a podstodoctoral fellow at the University of Texas at Austin with Professor Jonathan L. Sessler. Anzenbacher's primary research interests include the development of advanced photonic materials in two main areas: supramolecular materials for molecular sensing and materials that can be used in the fabrication of flat displays. His e-mail address is pavel@bgsu.edu.

Bowling Green Photochemists Receive Awards

Dr. Pavel Anzenbacher, (see article pp 18-20), received an Alfred P. Sloan Research Fellowship, a highly competitive national award designed to identify those who show the most promise of making fundamental contributions to the development of new knowledge in the sciences.

"Sloan Research Fellowships is the oldest program of the Sloan Foundation, though those who receive the grants are among the youngest researchers the foundation assists," according to the Sloan Foundation.

Fellows receive $45,000 for a two-year period, to be used in setting up laboratories and establishing research projects. The Sloan funds give recipients the freedom to pursue whatever projects they feel are most compelling, and can be put to a wide variety of uses.

The foundation views the assistance of promising young scholars as an investment. "Financial assistance at this crucial point, even in modest amounts, often pays handsome dividends later to society," it states.

Anzenbacher has indeed shown promise. His research has already been recognized both by the University, with the presentation of the Outstanding Young Scholar Award in 2003, and externally, by his garnering of numerous support grants.

Dr. Felix Castellano was awarded the Olscamp Reseach Award which is given annually to a BGSU faculty member for outstanding scholarly or creative accomplishments during the previous three-year period. The quality of research is evaluated in terms of significance within the discipline, national and international import, artistic or scholarly creativity, and contribution to knowledge, culture or professional practice.

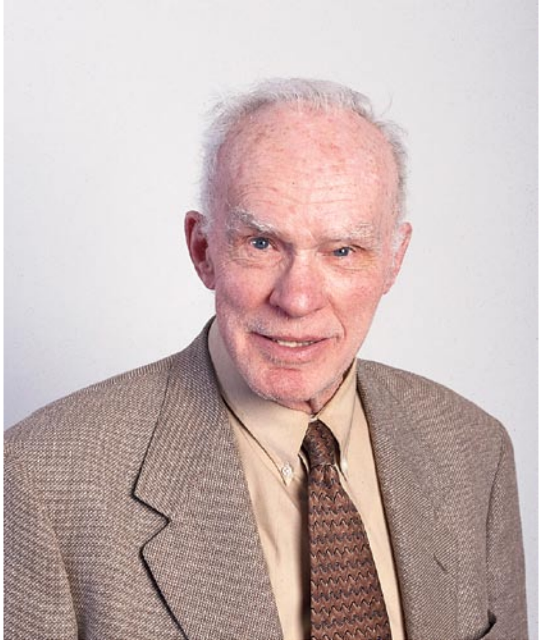
In the words of his nominator, Castellano has maintained an exemplary record over the past three years in a variety of research areas in his discipline of inorganic and organometallic photochemistry.

Since 2002, he has secured nearly $1 million in extramural research grants and contracts. He is the recipient of a prestigious five-year National Science Foundation CAREER award and has received funding from both the Air Force Office of Scientific Research and the Department of Energy. He currently maintains 10 active collaborations and his work is known both nationally and internationally, with collaborators as far away as Italy, Ireland, the United Kingdom, the Czech Republic and France.

In Memoriam

George Simms Hammond

Father of Organic Photochemistry



May 22, 1921 - October 5, 2005

organic dyes aggregation on TiO_2 surfaces

Elena Galoppini & Sujatha Thyagarajan
Department of Chemistry, Rutgers University

Introduction

Ru(II)-polypyridyl complexes have been studied for decades as sensitizing dyes of TiO_2 nanoparticles for solar energy conversion (Dye-Sensitized Solar Cells, DSSCs)[1] and remain among the most efficient sensitizers known to date (10.4%).[2] Figure 1 illustrates the configuration of a typical DSSC cell.

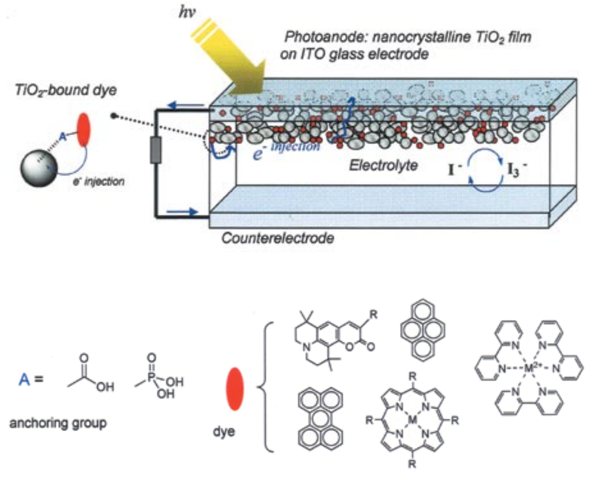


Figure 1. Schematic representation of the main components and electronic processes of a dye sensitized solar cell (DSSC). A few examples of dyes are shown.

Organic dyes such as porphyrins,[3] coumarins,[4-6] perylenes,[7-9] merocyanines,[10] phthalocyanines,[11-14] xanthenes,[15-17] cyanine dyes,[18-21] and squaraines[22] have been used and are considered highly promising. When compared to Ru complexes, however, organic dyes are often unstable under extended illumination, have sharp absorption bands and short excited state lifetimes. Some other properties, however, such as high extinction coefficients, low cost, availability and the possibility of unlimited structural modifications, are excellent for DSSCs applications. This explains the increasing effort towards designing and modifying organic dyes. Recent examples reported by Arakawa (coumarins, 7.7% efficiencies)[23] and Grätzel (porphyrins, 2.6% efficiencies)[24] and so forth clearly demonstrate that organic dyes are promising and can be improved to the extent that become competitive with inorganic sensitizers. Furthermore, organic dyes are excellent test systems for elucidating fundamental photophysics of charge injection and recombination processes at the molecule-nanoparticle interfaces. Willig's ultrafast electron transfer studies on perylene dyes are among the most elegant examples of this application.[25]

A common problem associated with the vast majority of organic dyes is their tendency to form aggregates on the surface of the semiconductor. Aggregation is not always a disadvantage, as in the case of chlorophyll derivatives bound to TiO_2.[26] However, the absorption spectrum and other photophysical properties of a dye change upon aggregation. For instance, face-to-face stacking of chlorine or porphyrin molecules (H-aggregates) leads to a blue shift in the absorption spectrum while side-by-side aggregates (J-aggregates) are red-shifted. In a classic example, excitation of the pyrene dimer leads to an excimer with a broad, featureless emission band in the fluorescence spectrum. Furthermore, there are numerous examples where stacking or dimerization is a disadvantage. In the case of photovoltaics, aggregation frequently results in decreased photocurrents and photovoltages though a variety of processes that compete with the photosensitization process. Energy transfer within π-stacks results in quenching processes that lead to a decrease in electron injection efficiency and, therefore, low photocurrents. Electron transfer to the redox electrolyte (I_3^-/I^-) rather than into the TiO_2 conduction band is a competing process (dark current) that results in lower photovoltages, and that has been observed in aggregates. Finally, excess of dye molecules stacked together may act as an optical filter.

Strategies to Prevent Aggregation

Over the past decade several strategies to prevent aggregation on TiO_2 have been developed. These range from simple methods, such as the use of coadsorbates, to separate the dye molecules, to more complex approaches including the development of molecular hosts that encapsulate individual dye molecules. These approaches, summarized in Figure 2, are listed in order of increasing complexity in this review. For each strategy, we have selected a few, representative examples, and included promising work in progress.

In general each of these strategies influences the sensitization process in more than one way, since any kind of structural or surface modification designed to separate the dye introduces other variables. For instance, acidic coadsorbates,[24] can shift the semiconductor conduction band edge position (the conduction band edge shifts by 59 mV/pH unit). Bulky substituents on the chromophoric unit often lead to improved solubility. Coadsorbates have a shielding effect on the electrolyte, decreasing competing dark currents.[24,27]

Encapsulation in cages results in dramatic differences in the injection and recombination processes, altering the mechanism of interfacial electron transfer, and slowing dramatically the charge recombination rates.[28]

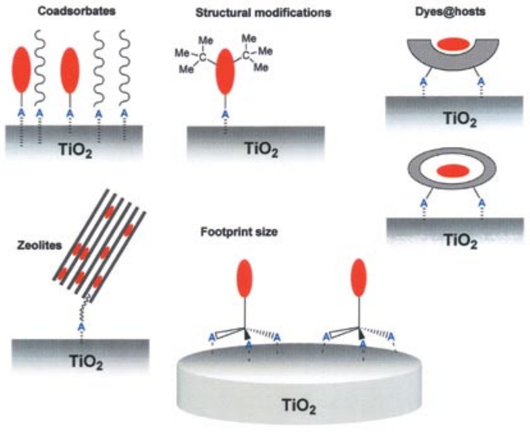


Figure 2. Common strategies employed to avoid aggregation of dyes on TiO_2.

Coadsorbates

Fatty acid, or carboxylic acids with lipidic substituents, have been used for many years as coadsorbates to “dilute” dye molecules on the surface of the semiconductor. Examples include myristic acid, hexadecylmalonic acid (HDMA), chenodeoxycholic acid (CDCA) and deoxycholic acid (Figure 3). Deoxycholic acid and the structurally similar CDCA, with a large, and rigid, lipophilic steroid framework are among the most effective coadsorbates.

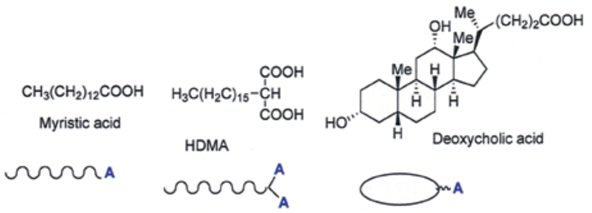


Figure 3. Structures of fatty acids and lipids employed as coadsorbates.

The use of fatty acids as coadsorbants often resulted in higher photocurrents and photovoltages. The improvement in photocurrent has been attributed not only to the suppression of aggregates, and the inhibition of quenching processes due to energy transfer,[14] but also to a positive shift of the conduction band edge due to the binding of an acidic adsorbate.[24] Furthermore, the lipophilic coadsorbant coats the surface, acting as a shield for the electrolyte. The “shield effect” inhibits the recombination between e^-/TiO_2 and I_3^-, thereby suppressing dark currents and increasing photovoltages.[24,27] Similar effects were observed when 4-^{t}*Bu*-pyridine or other pyridine derivatives have been used to shield the surface.[29, 30]

Structural modifications

A classical method to avoid dye aggregation, employed for decades in solutions as well as at interfaces, is to add directly on the chromophore bulky substituents (typically saturated alkyl chains in the case of organic aromatics). In this way the formation of dimers or excimers is avoided without significantly changing the photophysical properties of the chromophoric unit. An additional benefit of this method is that alkyl substituents often increase the solubility of otherwise insoluble materials. An example of this strategy are the t-butyl-modified perylene chromophores (**I** in Figure 4) developed and studied by Willig and coworkers.[25]

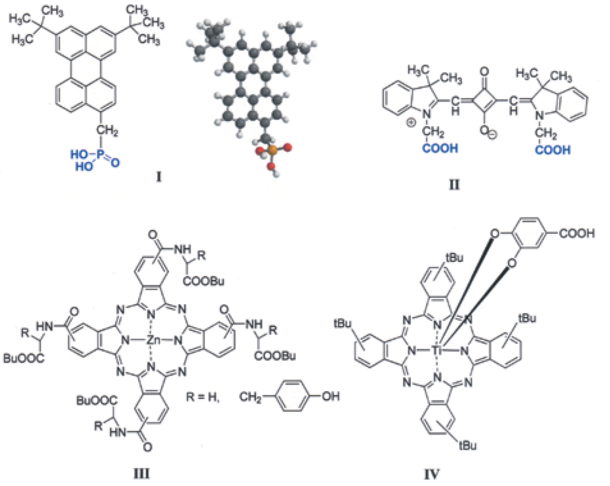


Figure 4. Examples of dyes substituted with substituents that inhibit aggregation by steric effect.

The comparative study of efficiencies of symmetrical and unsymmetrical squaraine dyes in DSSCs showed that their light harvesting efficiencies was correlated not only to symmetry effects, but also to differences in aggregation, as efficiencies decreased upon formation of dimers.[22] Simple methyl groups on the squaraine framework could break the aggregates (**II** in Figure 4). Phthalocyanines substituted with glycine or tyrosine improved solubilities and decreased aggregation due to steric effects,[14] while axial ligation to a titanium metal center in phthalocyanines prevented stacking (**III** and **IV**, respectively, Figure 4).[14,31] The substituent approach is conceptually simple and can be realized for most dyes. The synthetic effort, however, is significantly increased in some cases and the structural modification, must be adapted for different dye molecules. This can become a disadvantage when performing a systematic study of a series of dyes.

Footprints

Tripodal linkers with three COOR binding groups have been used by Galoppini and coworkers to attach Ru(II) complexes and organic dyes to the surface of semiconductors.[32-34] These dye-linker-anchor system allows controlling the distance and orientation of dyes on the semiconductor surface, serving as models for fundamental interfacial electron transfer studies. The possibility of using the footprint size of tripodal linkers to avoid chromophores aggregation is now being explored.[35, 36] This approach is attractive because it should allow more control over the distribution of the dyes on the surface than the use of a coadsorbant, and a same linker can be used to anchor a variety of chromophores, without the need to modify each chromophoric unit with bulky groups. The tripod having adamantane as the core (Ad-Tripod) has a footprint of ~ 53 Å^2 spanned by the three *p*-carboxy-phenyl arms and the Si-Tripod has a footprint of ~190 Å^2 spanned by the three *p*-carboxyphenyl-4-ethynylphenyl arms, Figure 5.

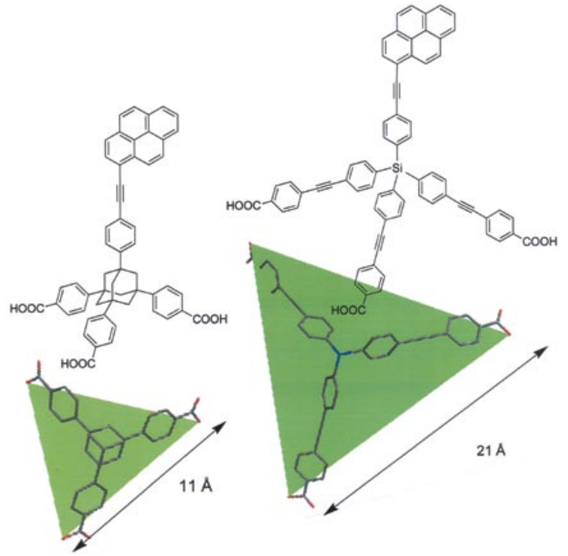


Figure 5. Tripodal pyrene derivatives (Ad-tripod and Si-Tripod) and comparison of the respective footprints.

The photo luminescence emission spectrum of the Ad-Tripod bound to ZrO_2 (an insulator) was observed as a function of surface coverage. Preliminary data suggest that at low surface coverages, the pyrene monomer emission is characteristic, and with further increases in surface coverage, there is a substantial increase in monomer fluorescence intensity, along with a slight increase in the excimer emission. The phenomenon of aggregation seems to be almost independent of surface coverage and cannot be completely eliminated by the tripodal footprint. Experiments aimed to determine the origin of this effect and studies on the influence of footprint size on aggregation are in progress with the silicon tripod.

"Molecular insulation": dyes@hosts

A clever strategy involves the "molecular insulation" of each single dye molecule (guest) by encapsulation in a host molecule, and attachment of the resulting 1:1 host-guest complex to the surface.[28] A Cram-type hemicarcerand[37] and α-, β- or γ-cyclodextrins[38] are the first examples of this approach (Figure 6 and 7, respectively). In these cases, supramolecular encapsulation not only prevented the self-aggregation of dye molecules, but also allowed the immobilization of a lipophilic chromophore on a hydrophilic semiconductor surface by using a water-soluble host with multiple anchoring groups that bind to the surface (OH groups in the case of cyclodextrins and COOH groups in the case of the hemicarcerand). The host molecules used in these studies do not absorb in the visible region of the spectrum, effectively acting as transparent containers.

Electron injection from supramolecular host-guest assemblies into TiO_2 nanoparticles (diluted colloidal solutions) was recently demonstrated by Piotrowiak and coworkers using a hemicarcerand substituted with eight COOH groups and having ~200 Å^3 internal volume.[37] The water soluble host encapsulated azulene, which is lipophilic, and bound it to the surface of a TiO_2 nanoparticle (azulene@host/TiO_2, Figure 6). The electron injection into TiO_2 following photoexcitation of azulene resulted in fluorescence quenching and the formation of the encapsulated azulene radical cation (azulene$^{+\cdot}$@host/TiO_2/e^-). The formation of this species was confirmed by nanosecond transient absorption measurements. Encapsulation within the hemicarcerand slowed down the charge recombination process by *three orders of magnitude* (τ = 44 ns), and the recombination kinetics was fit by a single exponential, while azulene directly attached to the surface through a COOH group exhibited inhomogeneous charge recombination on the ps time scale (τ_1 = 5 ps; τ_1 = 53 ps for 1-carboxyazulene). This was in contrast with any other recombination processes on TiO_2 which show complex multiexponential behavior.

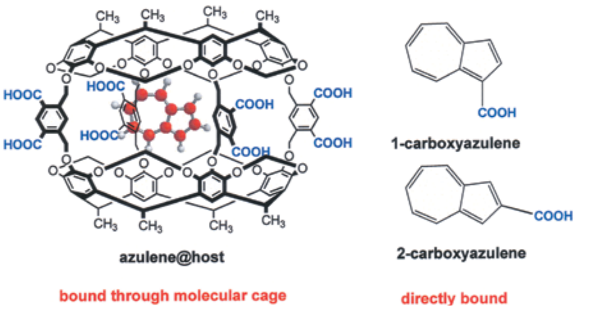


Figure 6. The hemicarcerand decks to TiO_2 nanoparticles through the COOH groups.

The encapsulation of dyes using cyclodextrins has been studied by several groups, because of the accessibility of the CD hosts, which are commercially available, and their availability in different sizes (α, β and γ). As in the case of dye@hemicarcerand, the CD hosts lead to a "molecular insulation" effect. An example is the work by Durrant and coworkers,[28] with CD-threaded sensitizer dye rotaxanes. These dyes, when bound to TiO_2 (either directly through a sulfonate linkage or as host-guest complexes through the CD–OH groups), resulted in a long-lived photogenerated charge separation. The interfacial charge transfer kinetics was monitored by using microsecond-millisecond transient-absorption spectroscopy and it was observed that for the dye bound through a CD (Figure 7), the recombination dynamics were slower than that of the directly bound dye. This slow charge recombination kinetics was attributed to a larger physical separation between the dye cation and the TiO_2 surface.

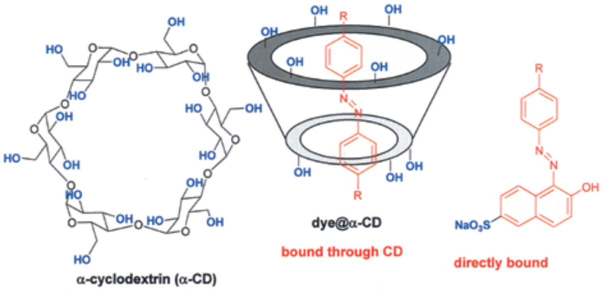


Figure 7. Example of a cyclodextrin employed to act as host for azobenzene dyes. The dye@CD binds to TiO_2 through the OH groups. A comparison was made with an azobenzene directly bound through a sulfonate group.

In conclusion, the immobilization on the TiO_2 surface of lipophilic dyes that are encapsulated in polar hosts dramatically alters the mechanisms of interfacial electron transfer processes, and has several important consequences. The dye is "insulated" from the unhomogeneity of the complex surface of the films (where solvent, water, electrolytes are bound or physisorbed) and which is one of the factors often invoked to explain the complexity of the injection/recombination kinetic processes. Also, charge recombination between the injected electron and the dye radical cation is slowed. This is important, because charge recombination processes, often a significant competing process with small organic dyes, are undesirable for DSSCs. One aspect that deserves to be studied is whether DSSCs devices prepared from organic dyes encapsulated in a host are more stable, as the reactive intermediates (azulene$^{+\cdot}$, for instance) are protected by the host molecule.

Zeolites

One of the most promising and innovative strategies along this line, but with additional complexity, involves encapsulation of organic dyes in zeolites.[39] Calzaferri and coworkers have filled Zeolite L crystals having parallel and cylindrical channels with organic dye molecules, Figure 8.[40]

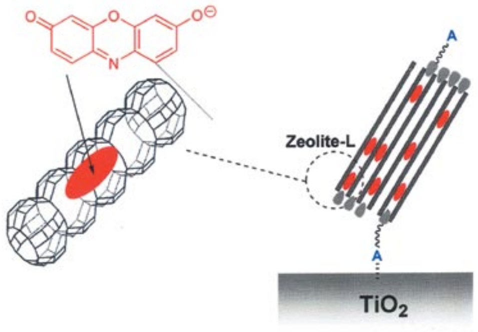


Figure 8. Representation of a dye-loaded Zeolite L crystal bound to TiO_2 film surface.

This strategy avoids face-to-face aggregation and provides a good control over the organization of multiple layers of dyes. The scope of this work goes beyond the control of aggregation phenomena, as the dye-zeolite assemblies form a new kind of light harvesting antennas. Dyes used in this study included oxazines, perylenes, fluorenones, stilbenes, azobenzenes and other molecules that fit into the Zeolite L channels (free diameter of ~ 12.6 Å).

The insertion of the dye molecules in the channels was controlled by diffusion, so that layers of different chromophores (donors and acceptors) intercalate in the crystals. "Stopcock" molecules were used to close the channels ends and "stopcock" molecules capped with functional groups will allow to covalently attach the filled zeolite crystals to the surface of a semiconductor, although this last important step is still under development, Figure 8. Clearly, the capability to properly bind and orient the antennas on the semiconductor to form an interface is a crucial requirement for future applications.

Conclusions

Many future devices, including solar cells, will consist of organic dye molecules interfaced with semiconductor nanoparticles. One of the factors that result in lower efficiencies is the formation of aggregates. We have presented and discussed some of the strategies created to prevent this phenomenon. Over the years, the strategies have become more complex and imaginative. This tendency is reflected in all aspects of semiconductor nanoparticles functionalization, demonstrating the importance of molecular design and the need for highly interdisciplinary research in the field of photovoltaics.

Acknowledgement

Elena Galoppini is grateful to the NSF-NIRT Program (Grant 0303829) for funding.

References

1. Kalyanasundaram, K.; Grätzel, M. *Coord. Chem. Rev.* **1998**, *177*, 347-414.
2. Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33*, 269-277.
3. Odobel, F.; Blart, E.; Lagrée, M.; Villieras, M.; Boujtita, H.; El Murr, N.; Caramori, S.; Bignozzi, C. A. *J. Mater. Chem.* **2003**, *13*, 502-510.
4. Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *Chem. Commun.* **2001**, 6, 569-570.
5. Hara, K.; Dan-oh, Y.; Kasada, C.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Langmuir* **2004**, *20*, 4205-4210.
6. Wang, Z. S.; Hara, K.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Arakawa, H.; Sugihara, H. *J. Phys. Chem. B* **2005**, *109*, 3907-3914.
7. Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 4490-4493.
8. Tian, H.; Liu, P. H.; Zhu, W.; Gao, E.; Wu, D. J.; Cai, S. *J. Mater. Chem.* **2000**, *10*, 2708-2715.
9. Tian, H.; Liu, P. H.; Meng, F. S.; Gao, E.; Cai, S. *Synth. Met.* **2001**, *121*, 1557-1558.
10. Khazraji, A. C.; Hotchandani, S.; Das, S.; Kamat, P. V. *J. Phys. Chem. B* **1999**, *103*, 4693-4700.
11. Nazeeruddin, M. K.; Humphry-Baker, R.; Grätzel, M.; Wohrle, D.; Schnurpfeil, G.; Schneider, G.; Hirth, A.; Trombach, N. *J. Porphyrins Phthalocyanines*, **1999**, *3*, 230-237.
12. Nazeeruddin, M. K.; Humphry-Baker, R.; Grätzel, M.; Murrer, B. A. *Chem. Commun* **1998**, 6, 719-720.
13. He, J.; Hagfeldt, A.; Lindquist, S. E. *Langmuir* **2001**, *17*, 2743-2747.
14. He, J.; Benkö, G.; Korodi, F.; Polívka, T.; Lomoth, R.; Åkermark, B.; Sun, L.; Hagfeldt, A.; Sundström, V. *J. Am. Chem. Soc.* **2002**, *124*, 4922-4932.
15. Ramakrishna, G.; Ghosh, H. N.; *J. Phys. Chem. B* **2001**, *105*, 7000-7008.
16. Matsumura, M.; Mitsuda, K.; Yoshizawa, N.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 692-695.
17. Sayama, K.; Sugino, M.; Sugihara, H.; Abe, Y.; Arakawa, H. *Chem. Lett.* **1998**, 8, 753-754.
18. Guo, M.; Diao, P.; Ren, Y. J.; Meng, F.; Tian, H.; Cai, S. M. *Sol. Energy Mater. Sol. Cells* **2005**, 88, 23-35.
19. Wang, Z. S.; Li, F. Y.; Huang, C. H.; Wang, L.; Wei, M.; Jin, L. P.; Li, N. Q. *J. Phys. Chem. B* **2000**, *104*, 9676-9682.
20. Wang, Z.; Huang, Y.; Huang, C.; Zheng, J.; Cheng, H.; Tian, S. *Synth. Met.* **2000**, *114*, 201-207.
21. Wang, Z. S.; Li, F. Y.; Huang, C. H. *J. Phys. Chem. B* **2001**, *105*, 9210-9217.
22. Alex, S.; Santhosh, U.; Das, S. *J. Photochem. Photobiol. A* **2005**, *172*, 63-71.
23. Hara, K.; Kurashige, M.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *New. J. Chem.* **2003**, *27*, 783-785.
24. Kay, A.; Grätzel, M.; *J. Phys. Chem.* **1993**, 97, 6272-6277.
25. Burfeindt, B.; Hannappel, T.; Storck, W.; Willig, F. *J. Phys. Chem.* **1996**, *100*, 16463-16465.
26. Yamada, Y.; Amao, Y. *Langmuir* **2005**, *21*, 3008-3012.
27. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Charvet, R.; Humphry-Baker, R.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 14336-14341.
28. Haque, S. A.; Park, J. S.; Srinivasarao, M.; Durrant, J. R. *Adv. Mater.* **2004**, *16*, 1177-1181.

29. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382-6390.
30. Huang, S. Y.; Schlichthörl, G.; Nozik, A. J.; Grätzel, M.; Frank, A. J. *J. Phys. Chem.* **1997**, *101*, 2576-2582.
31. Palomares, E.; Martínez-Díaz, M. V.; Haque, S. A.; Torres, T.; Durrant, J. R. *Chem. Commun.* **2004**, *18*, 2112-2113.
32. Galoppini, E.; Guo, W.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2001**, *123*, 4342-4343.
33. Galoppini, E.; Guo, W.; Zhang, W.; Hoertz, P. G.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 7801-7811.
34. Piotrowiak, P.; Galoppini, E.; Wei, Q.; Meyer, G. J.; Wiewiór, P. *J. Am. Chem. Soc.* **2003**, *125*, 5278-5279.
35. Liu, A. Synthesis of Si based Tripodal TiO_2 Sensitizers with a large footprint. M.S. Thesis, Rutgers University, Newark, NJ, Sep 2003.
36. Thyagarajan, S.; Carlisle, R. A.; Meyer, G. J.; Galoppini, E., manuscript in preparation.
37. Pagba, C.; Zordan, G.; Galoppini, E; Piatnitski, E. L.; Hore, S.; Deshayes, K.; Piotrowiak, P. *J. Am. Chem. Soc.* **2004**, *126*, 9888-9889.
38. Anderson, S.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1310-1313.
39. Calzaferri, G.; Huber, S.; Maas, H.; Minkowski, C. *Angew. Chem. Int. Ed.* **2003**, *42*, 3732-3758.
40. Brühwiler, D.; Gfeller, N.; Calzaferri, G. *J. Phys. Chem. B* **1998**, *102*, 2923 – 2929.

About the Authors

Elena Galoppini received the Laurea in Chimica from the Università degli Studi di Pisa, Pisa, Italy, in 1989 and her Ph.D. from the University of Chicago in 1994 under the guidance of Philip E. Eaton. She was a postdoc at the University of Texas at Austin with Marye Anne Fox, where she studied the influence of the α-helix dipole of oligopeptides substituted with electron donor–acceptor pairs on intramolecular electron transfer rates. She is currently an Associate Professor in the Chemistry Department at Rutgers University/Newark. Her research focuses on functionalization of semiconductor nanoparticles. She can be reached by e-mail: galoppin@andromeda.rutgers.edu.

Sujatha Thyagarajan received her Masters in Chemistry from Madras Christian College, University of Madras, India in 1997 and is currently a graduate student in the laboratory of Galoppini. Her research focuses on the development and applications of novel linkers with a large footprint for the sensitization of semiconductor nanoparticles.

The Spectrum Goes Electronic

Beginning with the Spring, 2006 issue *The Spectrum* will be available only in an electronic format.

We are in the process of compiling a database of email addresses so we can notify all of our subscribers when each issue of *The Spectrum* is available.

To remain a subscriber, please send your email address to:

photochemical@listproc.bgsu.edu

Please send any questions or comments to Pat Green, editor.

pat.green1@sbcglobal.net

FELs For Photochemistry/ Photobiology

A new laser with "unparalleled" applications in photochemistry, photobiology, materials science, and high sensitivity spectroscopy has won a coveted R&D 100 Award, *R&D Magazine*'s picks for the 100 most technologically significant new products of 2005.

Called the Tunable Energy Recovered High Power Infrared Free-Electron Laser (FEL), it was developed at the Department of Energy (DOE) Thomas Jefferson National Accelerator Facility in Newport News, VA. A number of other institutions are installing versions of the device for research and other applications.

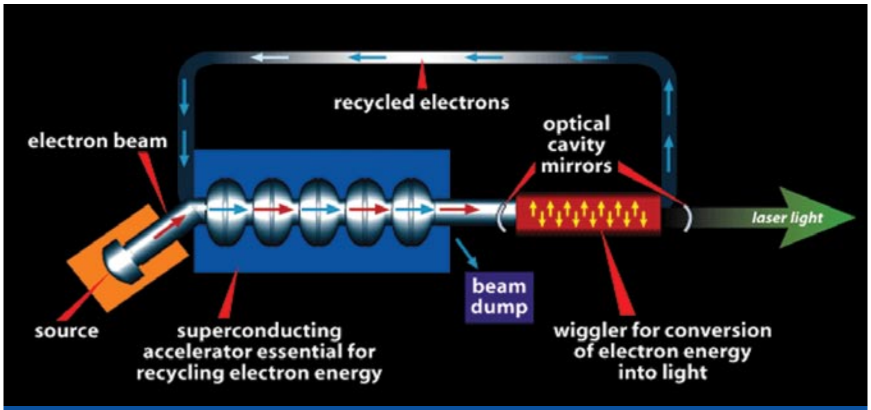
"We're looking for products and processes that can change people's lives for the better, improve the standard of living for large numbers of people, save lives, promote good health, and clean up the environment," said the editors of *R&D Magazine*. It began handing out the awards in 1963.

The Jefferson Lab FEL, funded mainly by the Department of the Navy's Office of Naval Research, may substantially expand use of high-output lasers in research and industry. Materials processing with lasers, for instance, is a $1-billion-year industry.

Applications are limited, however, by the availability of cost effective high power lasers. The new FEL technology is economical enough to expand uses of production lasers and open new applications that were never considered in the past because of the high costs.

FELs provide intense, powerful beams of laser light that can be tuned to a precise wavelength. They absorb and release energy at any wavelength, because the electrons are freed of atoms. This key feature enables the FEL to be controlled more precisely than conventional lasers to produce intense powerful light in brief bursts with extreme precision.

Since it requires no lasing medium in the cavity, a FEL can operate at very high power levels without the usual cavity heating problems.



Free Electron Laser Baser Basics

Electrons are released from the source at the lower left, and are accelerated in a superconducting linear accelerator (linac). After emerging from the linac, the electrons pass into a laser cavity which has a wiggler at its center. This wiggler causes the electrons to oscillate and emit light which is captured in the cavity, and used to induce new electrons to emit even more light. After exiting the optical cavity the electrons then travel around the loop at the top and back into the linac. Here they give up most of their energy to a new batch of electrons, making the process highly efficient.

Courtesy of Jefferson Lab

The Jefferson Lab FEL is based on an energy-recovered linac (see graphic), which makes the process highly efficient.

FELs cost less and are more versatile for high-volume materials processing than other manufacturing tools. FELs based on Jefferson Lab's superconducting electron-accelerating technology are being developed to process plastics, synthetic fibers, advanced materials, and metals as well as components for electronics, microtechnology, and nanotechnology.

Prospective products include durable, yet attractive polymer fabrics for clothing and carpeting; cheap, easily recyclable beverage and food packaging; corrosion-resistant metals with increased toughness; mechanical and optical components with precisely micromachined features; microcircuitry; and electronics for harsh conditions.

Lasers already are used, for instance, in processing polyester fabric, to produce a texture, feel, and appearance more like natural fibers. Development of an industrial-scale FEL for high-volume surface treatment will result in substantial improvement, the lab said.

FELs also can be used to fabricate three-dimensional mechanical structures with dimensions as small as a micron, one ten-thousandth of a centimeter, and with features that are smaller still. Applications include ultrahigh-density CD ROM technology and improved micro-optical devices.

German Ultraviolet FEL

German Chancellor Gerhard Schröder in August dedicated the world's first free-electron laser (FEL) for the short-wavelength range of ultraviolet radiation. The Vacuum Ultraviolet (VUV) FEL is located at the DESY facility in Hamburg.

"The VUV-FEL at DESY is the worldwide first," said DESY Research Director Jochen Schneider. "It generates especially intense and extremely short flashes of laser light that open up completely new insights into the nanoworld. Using the VUV-FEL, scientists can for instance film chemical reactions. The unique radiation enables ground-breaking experiments in fields such as cluster physics, solid state physics, surface physics, plasma research and molecular biology."

About 200 scientists from a dozen countries have signed on for research projects with the device.

Schneider said the VUV-FEL peak brilliance surpasses that of the most modern synchrotron radiation sources by a factor of ten million. In addition, its radiation is coherent, and its wavelength is tunable within the range from 6 to 30 nanometers. The radiation pulses are extremely short—10 to 50 femtoseconds. That will allow scientists to directly observe the formation of chemical bonds or the processes that occur during magnetic data storage.

Titan's Photochemical Smile?

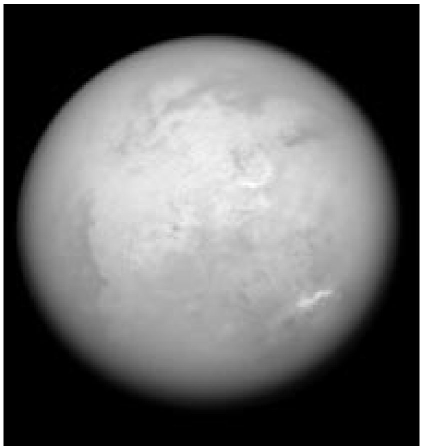
With a little imagination, you can see a strange smile on the surface of Titan, Saturn's largest moon.

New images taken during the Cassini-Huygens mission clearly show an unusually bright area, which astronomers have named "Xanadu." A project of NASA and the European Space Agency, the spacecraft arrived at Saturn in July 2004. The Huygens probe landed on Titan in January. Cassini is still in operation.

To the southwest is a peculiar semicircular line, which imaging scientists are calling "The Smile." It is the brightest spot on Titan's surface.

About 345 miles long, the feature is apparent at both visible and infrared wavelengths.

Titan's atmospheric photochemistry figures into NASA's tentative explanation. At the landing site of the Huygens probe, brighter regions corresponded to icy upland areas, while the darker regions were lowlands with a higher proportion of the organic photochemical byproducts.



Titan's Big Smile

The Smile is a peculiar semi-circular feature seen on Titan during Cassini's recent pass near Saturn's largest moon. The 345-mile Smile is the brightest spot on Titan's surface and may correspond to icy upland areas.

Courtesy of NASA

Its thick atmosphere is rich in organic compounds, formed from methane photolysis. With sunlight continuously destroying methane, astronomers do not know where Titan gets new methane to refresh its atmosphere.

On Earth, life itself refreshes the methane supply. Methane is a by-product of the metabolism of microbes in peat bogs, rice fields, and ruminant animals.

Titan, however, seems too hostile —too cold with no liquid water—for life.

With the Smile's exact nature still a mystery, scientists will continue to gather data from future flybys during Cassini's planned four-year mission.

New Target for Photodynamic Therapy

Helicobacter pylori (*H. pylori*), the bacterium that causes stomach ulcers and chronic gastritis, accumulates photoactive porphyrins and is killed by visible light, researchers from Massachusetts and Minnesota have reported.

Among the world's most common infectious agents, *H. pylori* colonizes the stomachs of 50-90% of the world's population. It causes chronic gastritis and gastric ulcers. The microbe also has been implicated in the development of stomach cancer.

Once acquired, *H. pylori* can persist for life, causing frequent stomach problems. Antibiotic therapy is the treatment of choice in developed countries, and highly effective. However, alternative treatments are needed.

Antibiotic treatment fails in about 20% of patients in developed countries, some *H. pylori* strains are antibiotic-resistant, and often is unavailable or too costly in poorer countries.

In the study, various strains of *H. pylori* were cultured and found to produce porphyrins, naturally occurring compounds that cause photosensitivity. When the cultures were exposed to visible broadband light, results showed both virulent and drug-resistant strains of *H. pylori* were killed. Blue/violet light was the most effective.

"We have shown that all tested strains of *H. pylori* naturally accumulate a mixture of PPIX and CP (porphyrins) that can sensitize the bacteria to killing by visible light, particularly blue light," the researchers reported. "This finding suggests that a novel phototherapy approach may be applied in the human stomach to eliminate *H. pylori* infection."

The full study appears in the July 2005 issue of the journal *Antimicrobial Agents and Chemotherapy*.

Charging Electrons

Photoinduced electron transfer is a fundamental step in photochemical reactions, including those underlying photosynthesis and commercially important processes like photography, xerography, and photolithography.

Exactly how long does it take an electron to travel from one atom to the next?

A research team from Germany and Spain has reported a measurement in the attosecond range. One attosecond is about 0.000000000000000001 seconds.

Studying the dynamics of electrons in sulfur atoms deposited on ruthenium surfaces, they found that electrons jump from the sulfur to the ruthenium in about 320 attoseconds—320 quintillionths of a second.

Alexander Föhlsich, of the University of Hamburg in Germany headed the research group, with a "core-hole clock" to time electrons. Researchers beamed x-rays at the sulfur, exciting an electron near the atom's center so that it jumped, leaving an empty "core-hole" in its place.

The electron then moves onto the ruthenium metal in less time than it takes for the hole to be filled by another electron. That process, called "hole decay," or the "natural lifetime" of the hole, is known to take 500 attoseconds. Föhlisch said the measurement began the instant the core hole was created and stopped when the core hole was filled by another electron.

Föhlisch believes the research will enable studies of electrodynamics on the attosecond scale. The core-hole method may be especially useful in studying spin-dependent electron-transfer, using circularly polarized light to create electrons in different spin states.

Knowledge of how electrons move will be a crucial step for developing spintronic computing, where information is stored in spin state of electrons. The study appeared in the July 21 edition of *Nature*.

World "First" in Electronic Paper

Fujitsu Laboratories Ltd. early in 2006 plans to begin test marketing a product that represents a major step toward practical electronic paper.

E-paper is the dream material that's thin and lightweight like paper, and flexible enough to roll up into a cylinder. Text and images written on it can be viewed in bright sunlight. Unlike paper, however, a sheet of the material can be written on and erased countless times—electronically—and used for everything from books to roll-up TV screens that can be carried from room to room.

Fujitsu claims it has developed the world's first film substrate-based bendable color electronic paper with an image memory function.

E-Paper Bends Without Distortion

World's first film substrate-based bendable color electronic paper with image memory function, shown being bent without causing distortion to the image.

Courtesy of Fujitsu Laboratories Ltd.

The material displays vivid color images that resist distortion even when the screen is bent, and features an image memory function that enables continuous display of the same image without the need for electricity.

With very low power consumption needed to change screen images, it is ideal for displaying information or advertisements in public especially on columns and other curved surfaces, Fujitsu said. The firm terms it "a type of new electronic media that can be handled as easily as paper."

Numerous electronic paper R&D efforts are underway, Fujitsu acknowledged. "However, thus far there had been no color electronic paper available that uses flexible film substrate capable of being bent without affecting the screen image and which features a memory function."

Key features include:

- No electricity required for continuous display, minimal power consumption when changing screen image.
- An image memory function that enables continuous display of the same image even when electricity is turned off therefore no electricity is required for continuous display.
- Screen image can be changed using minimal electricity consumption equivalent to the weak radio waves used in contactless IC cards.
- Energy consumption only one one-hundredth to one ten-thousandth of conventional display technologies.

Made with proprietary Fujitsu technology, it includes three displaying layers—red, blue, and green. Since no color filters or polarizing layers are required, it features color that is significantly more vivid than conventional reflective-type LCDs.

Phototherapy for Cancer

Stanford University scientists have reported a new technique that combines carbon nanotubes and laser illumination to selectively kill cancer cells in laboratory experiments but leaves healthy ones unharmed.

"One of the longstanding problems in medicine is how to cure cancer without harming normal body tissue," says Hongjie Dai, a chemist who co-authored the study. "Standard chemotherapy destroys cancer cells and normal cells alike. That's why patients often lose their hair and suffer numerous other side effects. For us, the Holy Grail would be finding a way to selectively kill cancer cells and not damage healthy ones."

Dai and his colleagues took advantage of carbon nanotubes' ability to absorb near-infrared light. It excites electrons in the nanotubes, and they release excess energy in the form of heat.

In the experiment, researchers coated nanotubes with folate in order to assure that the nanotubes targeted malignant cells but not normal ones. The surface of cancer cells has unusually large numbers of folate receptors. The folate-coated nanotubes thus were attracted to cancer cells, and poured in through the receptors.

When hit with a laser beam, the cells containing nanotubes were quickly destroyed by the heat, while cells without nanotubes showed no ill effects. The laser beam can be delivered externally, or internally via a fiber optic device, said Dai.

"It's actually quite simple and amazing," Dai observed. "We're using an intrinsic property of nanotubes to develop a weapon that kills cancer."

The group is now experimenting with better ways of targeting nanotubes. One involves coating nanotubes with an antibody that attaches to specific sites on cancer cells.

Rice University scientists have conducted similar experiments on mice with cancerous tumors. Instead of carbon nanotubes, the Rice team injected the tumors with gold-coated nanoshells and exposed the animals to near-infrared light for several minutes. The tumors disappeared within 10 days without damaging any healthy tissue.

A full report on the study appeared in the August 1 online edition of the *Proceedings of the National Academy of Sciences*.

New Chemical Bonding Centers

The National Science Foundation (NSF) has selected Harry B. Gray (featured in *The Spectrum*'s spring edition) and colleagues from the California Institute of Technology and the Massachusetts Institute of Technology for funding in three new Chemical Bonding Centers (CBCs).

CBCs are multi-faceted research teams intended to tackle a "big problem" in chemistry, in an atmosphere that's flexible, tolerant of risk and open to thinking far outside the box.

Gray, who is with the Caltech team, and colleagues will search for efficient, economical ways to store solar energy in the form of chemical bonds. That advance is critical for using sunlight as a renewable source of fuel and chemical feedstocks, NSF noted.

Researchers will focus on getting sunlight to split water into its higher energy building blocks, hydrogen and oxygen. They will also work to raise public awareness about the importance of renewable energy, and the scientific challenges required to address it.

"The aim of the awards is to encourage very talented people to attack major problems that would engage the public and have a long-term societal benefit—and be something they are not already doing," said Philip B. Shevlin, one of the NSF program officers who manages the CBC program.

Other new centers will be at Columbia University and the University of California at Irvine.

Caltech Chemical Bonds

This is the type of DNA-based walking machine that will be explored at the new CBC Center for Molecular Cybernetics. The particular walker shown here was actually demonstrated in 2004 by Caltech chemists Jong-Shik Shin and Niles A. Pierce. All the various DNA strands involved in its operation are synthesized artificially. Rising in a vertical double helix are the orange and black strands that form the body and legs of the walker itself. Along the bottom is the multicolored spiral of a DNA-based "track," which also carries a series of green, purple, red and blue "attachment" strands. The motion of the walker is powered by two types of free-floating "fuel" strands, colored yellow and pink, which alternately come in, intertwine with the appropriate leg and attachment strand, and then detach to allow the walker to take the next stride.

Courtesy of Niles A. Pierce, California Institute of Technology

Funded through NSF's Division of Chemistry, each award provides $1.5 million to the center over a three-year period. At the end of that time, those centers showing high potential will be eligible to continue their work with a Phase II award, which will provide $2 million to $3 million per year for up to five years. These awards are also potentially renewable for an additional five years.

University of California at Irvine chemist Shaul Mukamel heads the second new CDC team, which includes the University of California-Santa Barbara. They will use both theory and experiments to probe the real-time inner workings of molecules at single-atom resolution. The goal is to illuminate elementary chemical events such as the gain and loss of an electron from a single molecule; the making and breaking of chemical bonds; and the transport of charge among molecules.

The new CBC Center for Molecular Cybernetics, headed by Columbia University's Milan N. Stojanovic, will have eight principal investigators from seven institutions. They are Columbia; Boston University; Caltech; the Universities of Michigan, Chicago, and New Mexico; and the Hospital for Special Surgery in New York City.

Their goal: To make synthetic molecular machines powered by chemical bond transformation. The group will synthesize chemical structures having two or more protruding appendages of DNA, each able to grab onto or let go of a surface in response to an external stimulus.

Microdisplacement Printing

Pennsylvania State University scientists reported a new technique called microdisplacement printing that may have applications in the highly precise placement of molecules during fabrication of nanoscale components for electronic and sensing devices.

The technique is based on microcontact printing, a simple and widely used method of fabricating chemical patterns that does not require clean rooms. Both methods involve "inking" a patterned rubber-like stamp with a solution of molecules, then applying the inked stamp to a surface. "Microdisplacement gives us more control over the precision with which the patterns are placed and retained, and also allows us to use a wider range of molecules," said Paul S. Weiss, who led the team.

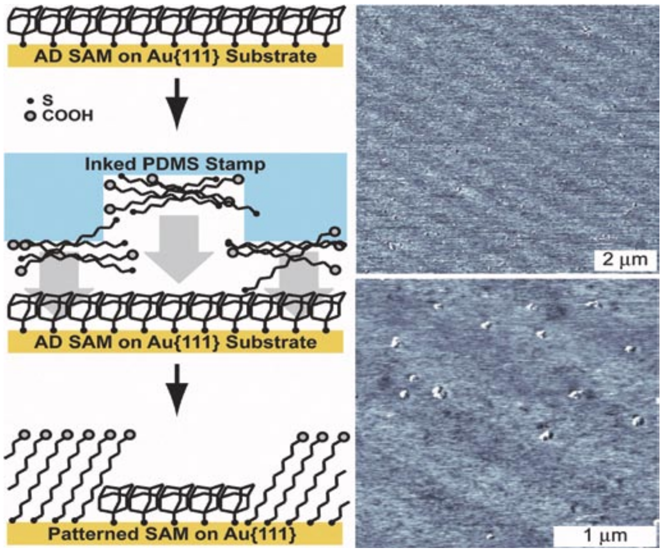
One limitation of microcontact printing is that its precision is limited at the edges of a stamped pattern by the tendency of the applied molecules to skitter across the stamped surface. It can blur the applied pattern.

Microdisplacement printing technique solves the problem by applying a self-assembled-monolayer film of spherical adamantanethiolate molecules to keep the stamped molecules in place on the surface. "We specifically engineered the adamantanethiolate molecule to have a very weak chemical bond with the surface so that it would detach easily when bumped by a stronger-bonding molecule," Weiss explained.

The molecules inked on the stamp replace the adamantanethiolate molecules wherever they touch the monolayer film, but the surrounding molecules in the film remain attached to the surface to prevent the applied molecules from wandering.

"Microdisplacement printing uses many of the same procedures as microcontact printing except one first prepares the substrate by coating it with a self-assembled monolayer of adamantanethiolate, which is inexpensive and easy to apply," Weiss said.

Weiss and colleagues described the technique in the September 14 issue of *Nano Letters*.



New Printing Technology

In microdisplacement printing, a weakly bound film is displaced by contact stamping with molecules that bind more strongly to the substrate. This process leaves a patterned film with regions of strongly bound molecules (where the weakly bound molecules were displaced) and regions of the remaining weakly bound molecules. Left, a schematic of the microdisplacement printing process, using a 1-admantanethiolate self-assembled monolayer as the weakly bound film and 11-mercaptoundecanoic acid as the displacing ink molecules on a striped stamp. Right, lateral force microscopy images of a sample made by the microdisplacement printing. The higher friction (shown as light) stripes are the ink. The lower friction (shown as dark) stripes are the remaining, undisplaced 1-adamantanethiolate regions.

Courtesy of Penn State

Center for Photochemical Sciences at Bowling Green State University Seeks Contributions for Outreach Efforts

The art of photoscience, or understanding matter through the use of light, is all about the possibilities one can imagine when looking at the sun. Scientists in this field study the nature and properties of new materials created when objects or chemical systems absorb light. The breadth and potential of the photosciences span from our fingertips to complex products and processes. The ability to direct and target light has applications in surface imaging when taking a photograph or making a Xerox copy, therapeutic drug monitoring for immunodiagnostics, rapid prototyping and process control, or the use of lasers to initiate chemical reactions. Other industrial applicability areas include hardware for the communications industry (fiber optics, silicon wafers, computer chips), digital printing and printing plates, and energy curable paints and varnishes. The development of filters for color liquid crystals, photo coating and photo printing have led to a number of environmentally friendly products such as solvent-less inks. But most importantly in the current context of a probable energy crisis, the photosciences promise technologies for solar energy conversion and alternative energy sources. What is, what isn't, what might be and how to find ways to use sunlight for more of our energy needs are questions photoscientists can answer.

The impact of Bowling Green State University's Center for Photochemical Sciences in Northwest Ohio, regionally and internationally in the last twenty years is unquestionable. As George Hammond once said, "The Center for Photochemical Sciences is a unique organization that has achieved world-class status. It has had remarkable success not only in producing outstanding research in photochemistry but also in bringing the results of that work to valuable applications." The Center research is important not only to peers in the scientific community, to whom the Center is thankful for the recognition it has received, but also to the general public and even the local academic communities who hardly understand what the photosciences are. But the Center's impact extends beyond science into understanding communities, cultures and nations. Above and beyond its science, the strange diversity of the Center's makeup has generated a cultural explosion in Bowling Green that has not subsided 20 years after the Center's birth, which indeed demonstrates that science knows no borders.

One of the Center's purposes is to expand the synergism of research, teaching and applications in the photochemical sciences by serving as a clearinghouse for the dissemination of information. The Center has started an aggressive outreach campaign to educate the community about the photosciences and raise public awareness to issues such as sustainability, alternative energy sources, preservation and replacement of scarce resources, and advanced approaches to medical diagnostics and therapy.

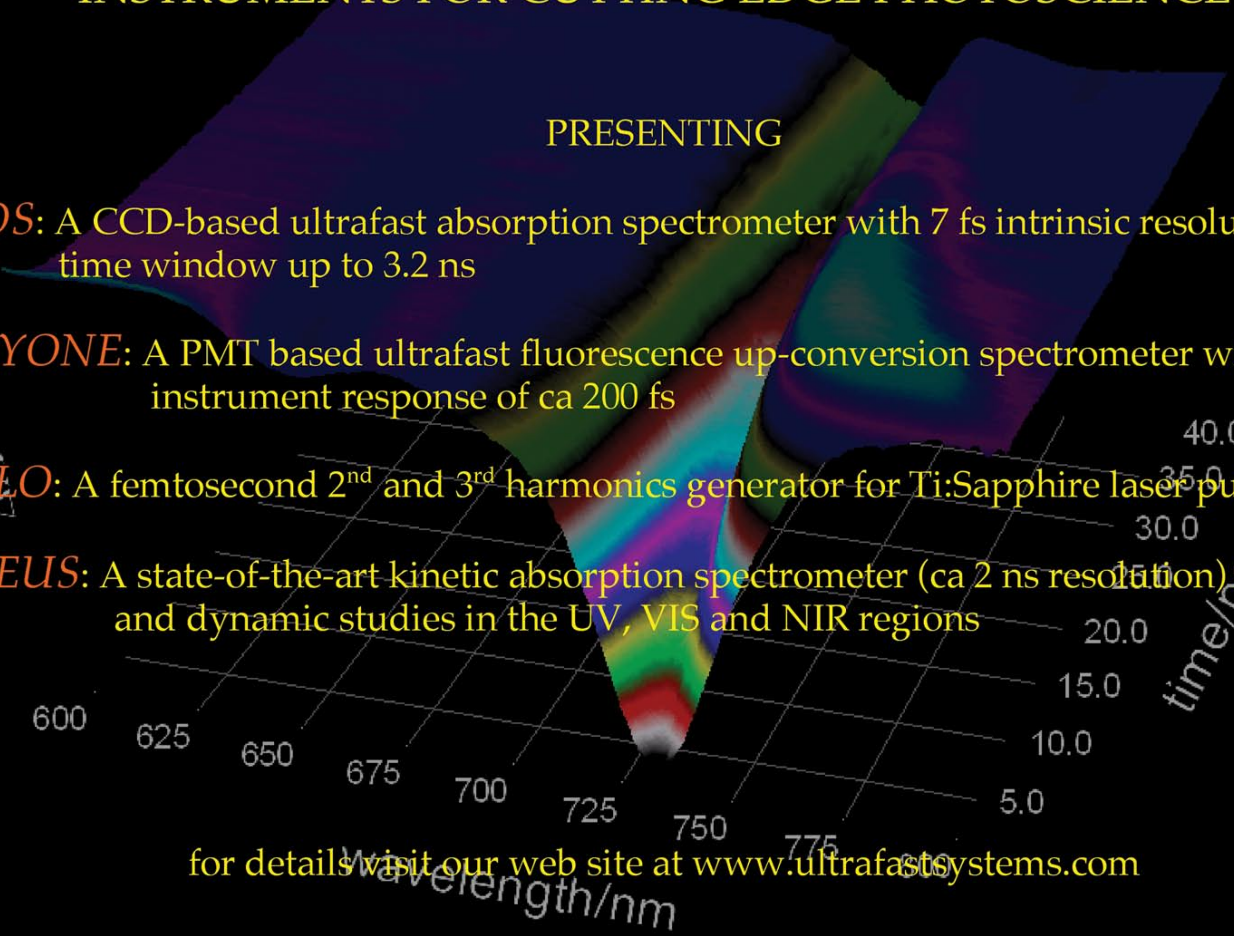
As one knows, talking to non-scientists about what we do and making it be music to their ears is not an easy task. Some scientists as those at the University of Hawaii thought of having top-notch faculty hold lunchtime lectures for the local business community, as mentioned in the last issue of *The Spectrum*. They used flashy lecture titles as attention grabbers, like "Mummy Talks: The Egyptian Mummy Project," "Princess Di of the North" or "Can Dogs See Ghosts?" to gather crowds for an Egyptology or a chemistry lecture. Others, including Center scientists, have created print materials and images that cross the line between science and art, in an effort to convey the excitement of (photo) science to a broad audience.

The Wright Capital Project, renamed the Wright Photoscience Laboratory, has enabled many initiatives that educate the community about the photosciences. This state funded program is part of the Third Frontier Project initiated by Governor Bob Taft in 2002 to "support world-class research, commercialization, training, and information technology infrastructure designed to accelerate company growth and job creation throughout Ohio." Some of the Center's related efforts include an updated professional website with added features (http://www.bgsu.edu/departments/photochem); multiple presentations to the BGSU Foundation Board, administration and academics, campus-wide research conferences; informative brochures and promotional materials; educational DVDs; local magazine interviews; involvement with WBGU public TV station for the creation of a mini-series of photoscience related infomercials; booth displays and participation at nation-wide professional meetings; and sponsorship of professional forums with an applied research focus.

A recently launched Center Outreach website targets high school students, teachers and educators, undergraduate students and the general public. We invite you to visit:

http://www.photochembgsu.com) and tell us how to improve and enhance it.

Please send us your stories, anecdotes, photos, or videos, which have light as the central theme. We welcome your comments and contributions and would love to hear from you!



40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
time/ps
600
625
650
675
700
725
750
775
Wavelength/nm

Center for Photochemical Sciences
Bowling Green State University
Bowling Green, Ohio 43403

NonProfit Organization
U.S. Postage Paid
Bowling Green, OH
Permit #1