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A Transient Lifetime in Photochemistry
An Interview with Anthony Trozzolo

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The Spectrum

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in this issue

focus on

On the cover

Photomicrographs showing the effect of polarized light on the photochromic aziridine crystals. When the plane of polarization is vertical, the crystals with the long vertical axis become blue-colored, whereas the crystals with long horizontal axis remain colorless. When the polarization plane is horizontal, the coloration is reversed as shown in the bottom photo. Photo courtesy of Anthony Trozzolo.

viewpoint

The interview with Tony Trozzolo in this issue is one that should have happened long before this. Tony's role in developing the photosciences as a separate area of research was cemented by his organizing the first Gordon Conference on Organic Photochemistry in 1964. When I saw the picture of the conference attendees (page 5) again I was surprised by how few people I recognized, how big the conference was, and how slender we all were! (I am in row 5 from the top. Nick Turro is in the top row.) More than half the participants were from industry. Who did not attend is almost as interesting as who did. None of the industrial scientists we know today as the "giants of the fledgling areas of photoresists and photopolymerization" attended the conference. I didn't see Lou Minsk, Louis Plambeck, Rolf Dessauer, Edwin Lamb, Leopold Hörner or Chester Carlson on the attendance list.

Lasers were so new that I don't even remember seeing one until after the conference; none of the "laser jocks" of the day showed up. George Porter was there but barely mentioned flash photolysis as I remember, but Ronald Norrish, Günther Schenck, and Theo Förster were not. Each played major roles in research in the photosciences in England and Europe.

Nevertheless, there were many industrial attendees and for good reason. Many industries were exploring the use of the photosciences in processes. And many other industries were exploring new opportunities that used photochemistry. I recall particularly the large groups at the then Union Carbide in Tarrytown, NY, and Charleston, WV. Dave Trecker at Union Carbide contributed a number of new photoinitiators. Dessauer, at DuPont, has already been mentioned. (*The Spectrum*, Vol. 16, Issue 4)

Industrial research has really gone down hill since the halcyon days of the 1960s. Very few companies in the U.S., at least, have anything resembling basic research labs. Bowling Green is near Toledo, OH, which was the original home of many large industries in glass and automobile parts. These industries include Owens Illinois, Owens Corning, Libbey Owens Ford, Champion Spark-plug and Dana Corporation. Each had corporate research efforts when I moved to the area in 1973. None have corporate research efforts now. Two have gone through bankruptcy. One has been taken private and back public. Another was purchased by first an English, and later a Japanese glass firm. The other one evaporated. Owens Illinois, for example, has gone through a series of restructurings and sell-offs. This month it was announced that they were selling their plastics products division. Though the stock is going up, one wonders what—if anything—the company has for sale.

Tony Trozzolo is fond of talking about that first Gordon Conference, and in discussing the many persons that attended it. The attendees came from very different backgrounds. Photochemistry, particularly organic photochemistry, benefited from the physical tools that were just coming to their laboratories like gas chromatography and emission spectroscopy. Physical chemists and theoreticians, on the other hand, benefited from having their explanations needed. The older, dyed in the wool, photochemists like Harry Gunning from Calgary and Robert Livingston from Minnesota delighted in all of the attention the use of light in chemical reactions was receiving. Older physical organic chemists, like Saul Cohen, found the photosciences a way to invigorate their laboratories and provide them younger collaborators.

The photosciences, since those early days, have grown mature in some ways. That old Gordon Conference has gotten a little bit old itself. But the spirit remains, and the excitement abounds every two years when the group of photoscientists that Tony's conference begat, reacquaint for still another session in New Hampshire, Massachusetts or Rhode Island.

D. C. Neckers

special feature

perspective on

a transient lifetime in photochemistry

an interview with Anthony Trozzolo

Anthony Trozzolo is recognized for "outstanding contributions to the science of photochemistry".

The Gregory and Freda Halpern Award in Photochemistry of the New York Academy of Sciences

Courtesy of Anthony Trozzolo

The late Thomas Kuhn, author of that 1962 classic in the philosophy of science, *The Structure of Scientific Revolutions*, argued that science does not advance through a linear accumulation of new knowledge. Instead, it undergoes periodic revolutions—"paradigm shifts," he called them—that abruptly transform scientific inquiry within a particular field.

What fosters these shifts? Many of us have been eyewitnesses to one example. It was the late Richard E. Smalley's skillful use of the forum provided by a Nobel Prize (http://pubs.acs.org/cen/coverstory/84/8441cover.html) to shepheard emergence of nanoscience and nanotechnology as a new scientific discipline. A seminal conference or landmark lecture also may help foster the consolidation of an emerging field of science.

The first Gordon Research Conference on Organic Photochemistry had such an effect, according to some pioneers in this now-robust field. They regard that 1964 conference as *the* seminal event in organic photochemistry's emergence as a self-standing discipline in chemistry. *The Spectrum* is delighted for the opportunity to chat in this edition with the individual who organized and chaired that first conference and played such a memorable role in the maturation of organic photochemistry.

In this interview, however, Anthony M. Trozzolo identifies an earlier conference as the seminal event in organic photochemistry's emergence. Trozzolo's pick is an ACS organic chemistry symposium at Indiana University in which Howard Zimmerman and George Hammond galvanized attendees with interpretations for a variety of organic phototransformations.

Neither of those giants in the field was present at the first Gordon Conference. Trozzolo explains the reason, discusses how photochemistry and its practitioners have changed over the years, describes the evolution of his own research, and offers insights and advice for younger scientists and scientists facing decisions about retirement. Readers will even learn why Trozzolo's most requested talk on the American Chemical Society (ACS) lecture circuit is a "lot of Bologna."

Tony Trozzolo is the Charles L. Huisking Professor Emeritus of Chemistry at the University of Notre Dame. He received his B.S. degree in chemistry from the Illinois Institute of Technology in 1950 and the M.S. and Ph.D. degrees from the University of Chicago in 1957 and 1960, respectively. In 1959, he became a Member of the Technical Staff at the Bell Telephone Laboratories in Murray Hill, New Jersey, where he remained until 1975 when he became the first Huisking Professor at Notre Dame.

Trozzolo's research has focused on the creation and detection of reactive intermediates. The methodology often involves low-temperature photochemistry or solid-state photochemistry. Among the intermediates studied are carbenes, azomethine ylides (from aziridines), carbonyl ylides (from oxiranes), and nitrenes (from azides). The detection techniques include e.p.r. spectroscopy, laser spectroscopy, and optical spectroscopy. Trozzolo also has conducted research in the following fields: photostabilization of polymers, dye lasers, singlet molecular oxygen, charge-transfer complexes, molecular magnets, and superconducting intercalation complexes.

That work resulted in more than 90 research articles and 31 U.S. and foreign patents. Noted as a dynamic lecturer, Tony has delivered over 300 invited lectures at universities, international meetings, ACS symposia, and industrial laboratories. His numerous awards and honors (www.nd.edu/~atrozzol/) include two perhaps unique among photochemical scientists. In 1997, Tony was named "Honorary Citizen" of Castrolibero, Italy, and selected as the first recipient of the Pietro Bucci Prize co-sponsored by the Italian Chemical Society and the University of Calabria. He was also the fourth awardee (after Nick Turro, Orville Chapman, and Howard Zimmerman) of the Gregory and Freda Halpern Award in Photochemistry of the New York Academy of Sciences in 1980.

***The Spectrum:* What led you to organize that first Gordon Research Conference on Organic**

Photochemistry in 1964? Take us back to the early 1960s and describe what was happening in the lab and the marketplace to create the need for such a conference.

Group photo of the 1964 Gordon Conference on Organic Photochemistry.

Courtesy of Gordon Research Conferences

Trozzolo: In 1962, Professor W. George Parks, the Director of the Gordon Research Conferences, published a notice in *Science* soliciting proposals for new Gordon Conferences. I sent in a proposal citing the fact there was no conference being held on a continuing basis on organic photochemistry and that the subject was developing at a very rapid rate. Although the proposal was not acted upon in 1962, a chance meeting at a luncheon (1963 Metro Regional Meeting in Newark) with Cecil L. Brown, who was on the Board of Trustees of the Gordon Conferences, gave me the opportunity to reinforce the case for a conference, and the Gordon Conference on Organic Photochemistry was approved to be held for the first time in 1964 at Tilton School in New Hampshire. Coincidentally, an International Conference on Photochemistry (honoring W. A. Noyes) was held in Rochester in March 1963 and I had the opportunity to meet many of the leading photochemists, such as Ronald Norrish, George Porter, Albert Weller, Egbert Havinga, Gunther Schenck and others. Attendance at this meeting proved invaluable in contacting prospective speakers for the Gordon Conference.

***The Spectrum*: So you assembled the leaders in the field. Who was there?**

Trozzolo: Since this was the first Gordon Conference on Organic Photochemistry, I had the luxury of choosing speakers from the entire field since no one had spoken before. In 1963, photochemistry studies were largely focused on the use of energy transfer in controlling the excited-state chemistry although charge-transfer quenching was being studied by Albert Weller and others. The program of the first Gordon Research Conference was arranged to show this progression. The first speakers—George Porter and N. C. Yang—stressed energy transfer and differences in reactivity of singlet and triplet excited states while the Friday speakers—Sean McGlynn and Albert Weller—concentrated on charge-transfer processes. Other speakers included Orville Chapman, Gary Griffin, Rudolf Wolgast (pinch-hitting for Gunther Schenck), Harry Gunning, James McNesby, Ted Ullman, Robert Livingston, Ed Wasserman, and R. Srinivasan. With this core of thirteen speakers, we had plenty of time for short contributed talks and informal discussion.

***The Spectrum*: How many were in attendance?**

Trozzolo: There were 120 conferees, 73 of whom came from 42 different industrial labs (How times have changed!). Included in the 36 academic conferees (nine of whom were speakers), were three young postdocs from Harvard about to launch brilliant academic careers who drove together to the Conference from Cambridge, namely, Nick Turro, Doug Neckers and Jacques Streith. In later years when I served on the Screening and Scheduling Committee and the Board of Trustees of the Gordon Research Conferences, I always advocated the inclusion of postdocs and even graduate students as participants in the Conferences. Paul Kropp and the late Don Arnold were in industrial labs in 1964, but later, both became academicians and both served as Chairman of the Conference in subsequent years. Other young academicians in attendance included David Hercules, Sally and Frank Mallory, Al Padwa, David Schuster, Peter Borrell, Peter Leermakers, Tony Testa, Colin Steel, and Ron Sauers. In addition to Ed Wasserman, Bell Labs colleagues (who all have played a role in the development of photochemistry) at the Conference included Ed Chandross, Adam Heller, and Larry Snyder.

***The Spectrum*: What did they discuss, what ideas emerged, what do you recall most about the sessions?**

Trozzolo: The topics in the invited talks included: photochemistry of carbonyl compounds, photoisomerizations, photochromism, photolysis of hydrocarbons, epr of triplet ground-state molecules, photoreactions of olefins catalyzed by pi-complexes, charge-transfer in excited states, photocleavage of episulfides, and quenching mechanisms (electron transfer vs. energy transfer). The discussion periods always seemed to go overtime. This was a time for us to get to know each other and to find out what other interesting systems were being studied and what mechanistic concepts were being applied or in need of refinement. My guess is that the impact of the conference was really felt only after we returned to our respective institutions and had time to savor what had transpired in the week at Tilton School.

George Porter and Nick Turro at the 1994 IUPAC Symposium on Photochemistry in Prague when Nick received the Porter Medal.

Courtesy of Anthony Trozzolo

***The Spectrum:* Some of the attendees look back on this conference and say that it was the seminal event that solidified organic photochemistry as a self-standing field in chemistry. Was it the conference content, or the fact that organic photochemistry had reached the point where a Gordon Conference was warranted, or both or what?**

Trozzolo: I am happy to hear that some attendees feel that it was a seminal event, but for me another event took place in 1961 which further increased our interest in photochemistry and its implications in mechanistic organic chemistry. The 19th Organic Chemistry Symposium took place at Indiana University and two of the speakers, Howard Zimmerman and George Hammond, presented their respective studies and interpretations for a variety of organic phototransformations. It was evident that mechanistic organic photochemistry was becoming more rational and excited-state descriptions (largely obtained from the detailed studies of spectroscopists) could be used along with the concept of energy transfer (from photosensitization studies) to explain many photochemical reactions. We had reached a point where it was clear that enough was going on in the field of photochemistry to warrant bringing together that community and the Gordon Conference structure with its great opportunity for informal discussion seemed a natural solution. Professor W. George Parks' *Science* ad mentioned earlier provided the incentive to follow the third line in Rabbi Hillel's dictum: "*If not now, when?*"

***The Spectrum:* Those attendees still remember George Porter's talk. By one account, Porter barely mentioned flash photolysis for which he would win the Nobel Prize a few years later. What do you recall about George Porter's presentation and about George himself?**

Trozzolo: Porter's talk was mainly about the reactivity of excited states of carbonyl compounds and the electronic transitions which created these as well as the differences in reactivity of the singlet and triplet states produced. He had a mechanical model which illustrated the transition and the movement of the electron changing its orbital location. As I mentioned earlier, I had met George Porter on two occasions in 1963, in March at the Noyes Symposium in Rochester, and in July at the 6th International Symposium on Free Radicals held at Cambridge, England. As a pioneer in the technique of matrix-isolation, he was particularly interested in our use of the technique at Bell Labs done in collaboration with Ed Wasserman, Bob Murray, Gerry Smolinsky, and Bill Yager in which the triplet ground-state structure of a variety of carbenes and nitrenes had been determined. I was pleased to learn in early 1964, that he would not only be able to speak at the Conference, but that he was bringing his wife, Stella, and their two young sons, John and Andrew.

***The Spectrum*: Were children allowed on site in those days?**

Trozzolo: At that time, Gordon Conference regulations prevented children under the age of twelve from being housed at the Conference site, and so we arranged for the family to stay at Webster Lodge on Webster Lake just a few miles away from Tilton School. Porter later wrote that it was a great time for the family. In 1967, George and I were both scheduled to present plenary lectures at the 8th International Symposium on Free Radicals in Akademgorodok, Siberia. I was looking forward to seeing him there, because one of his graduate students, Willie Gibbons, had come to Bell Labs to help me elucidate the electronic spectra of aryl carbenes, and we had found a great similarity between our spectra and the spectra of the benzyl radicals which Porter had produced by flash photolysis. Unfortunately, illness kept him from attending. We met periodically at IUPAC symposia, and in 1986, the University of Notre Dame awarded him an honorary Doctor of Science degree.

***The Spectrum*: Was there any sense that George was headed for a Nobel Prize?**

Trozzolo: In 1964, it was clear that matrix-isolation techniques had permitted the characterization of reactive intermediates by stopping them "dead in their tracks" and allowing spectroscopic measurements. Porter and Norrish, in developing flash photolysis, made it possible to generate a large population of the reactive intermediate over a very short time, and thus do spectroscopic measurements on the unencumbered intermediates. It became evident that this would be part of the wave of the future as lasers became available and in 1967, the Fifth Nobel Symposium on "Fast Reactions and Primary Processes in Chemical Kinetics" was held in Sweden featuring Manfred Eigen, Ronald Norrish, and George Porter. The three shared the Nobel Prize in Chemistry that December.

***The Spectrum*: Why were George Hammond and Howard Zimmerman missing from that first conference?**

Trozzolo: One of the first persons that I invited to lecture at that first Gordon Conference was George Hammond. However, just shortly before that time, George had suffered a fainting spell at the 1963 fall ACS meeting in New York and for health reasons did not feel that he could accept. However, he did like the idea of a conference on photochemistry, and having an international perspective, became the organizer of the first IUPAC Symposium on Photochemistry which was held in Strasbourg in 1964. These two series of conferences, along with the International Conference on Photochemistry (organized mainly by physical chemists) and, more recently, the I-APS Conferences, have provided the main forums for the photochemist. I also invited Howard, but George Hammond had invited him to the IUPAC Symposium. My recollection is that Howard also was going to spend some time in Europe visiting friends and former colleagues, thereby conflicting with GRC. I should hasten to add that both George and Howard attended the second Gordon Conference (chaired by the late Orville Chapman) in 1965, and Howard has attended most of the Conferences since 1965.

***The Spectrum*: So you've attended every Gordon Photochemistry Conference since then?**

Trozzolo: No, I missed the 1967 and 1975 Conferences. In 1967, I was invited to present a plenary lecture at the 8th International Symposium on Free Radicals which was being held in Akademgorodok (near Novosibirsk) in Siberia at the same time as the Gordon Conference. It was a great opportunity to visit the "Science City" that I had heard so much about as well as scientists in Moscow and Leningrad. In fact, due to the political situation at that time, it took about three months before I got approval to go from Bell Labs. I missed the 1975 Conference because our move to Notre Dame coincided with the date of the Conference. The 1975 Conference was the last held at Tilton School, as we were moved to the more rustic environment of Proctor Academy for the next eight conferences.

Past chairs and future chair in attendance at the 2005 Gordon Conference on Photochemistry. Standing (left-to-right): Gary Schuster (1989), Paul Kropp (1971), Laren Tolbert (2003), Linda Johnston (2007), David Whitten (1997), and Trozzolo (1964). Seated: Rich Givens (2001), V. Ramamurthy (2005), Kirk Schanze (2005), and Nick Turro (1973).

Courtesy of Dolly Trozzolo

***The Spectrum*: What changes have you noticed in the participants, their presentations, their outlooks as photochemistry matured as a science and younger scientists entered the field?**

Trozzolo: There have been a number of major changes in the Conference since 1964. The biggest change has been the large decrease in industrial conferees so that the last few conferences have only had a handful of industrial participants as compared with 73 at the original Conference. The size of the Conference peaked in 1981 with 145 conferees with the last few conferences averaging slightly above 100. The other major changes, which I consider positives, have been: (1) greater number of foreign conferees (~40%) giving the Conference an international character; (2) greater number of women (The chair of the 2007 Conference is Linda Johnston); and (3) the greater participation by postdocs and graduate students.

With the increased activity in the field of photochemistry, the program has also changed so that from the 13 invited speakers in 1964, we had 34 invited speakers at the 2005 conference, which, in addition, had two poster sessions (posters were not permitted in 1964). The 2005 Conference had a relatively large number of graduate students and postdocs, who as first-time attendees obviously enjoyed the informal interacton with an international group of their peers and affirmed the vitality of the subject. Everyone seemed to participate in the discussions, whether in the lectures or the poster sessions. It is particularly satisfying to me to see the younger scientists of earlier conferences progress in their careers and contribute to the field as photochemistry interacts increasingly with other areas such as materials research, nanotechnology, photobiology, and renewable energy.

***The Spectrum*: You have the reputation as a dynamic, compelling lecturer. Doug Neckers remembers one of your lectures—at the University of Kansas when you were with Bell Labs—despite the passing of almost 40 years. It dealt with azo compound isomerizations. What are the secrets to leaving that kind of impression? What advice can you offer students and younger scientists about delivering an effective talk?**

Trozzolo: I'm flattered that Doug remembers. Actually, the seminar that Doug referred to was in 1963, when he was a graduate student at Kansas and his advisor, Earl Huyser, invited me to give a talk on our recent results on photodecompositions of bis-diazo compounds which produce di-carbenes and intermediates with interesting structures (Since Earl and I both had Wilbert "Bill" Urry as our graduate advisor at the University of Chicago, I can claim Doug as a "scholastic nephew"). How does one give a memorable lecture? I believe that there are several features involved. Since the primary purpose of the lecture is to communicate, it follows that the most important ingredient is content; in other words, have something to say, a story to tell. I have seen talks which were beautiful powerpoint presentations but had little content, and one comes away disappointed.

The second ingredient is to be enthusiastic about having the opportunity to relate your story, particularly when it involves novel and unexpected results. It is also important that you introduce the subject of the talk in a manner in which you and the audience have the same "universe of discourse." Often it is possible to present a talk as a "detective story" with its mystery or unsolved problem; the methodology is introduced, there are a few unexpected turns, and the mystery is solved. Equally important is the effective use of visual aids, whether blackboard, slides, or demonstrations. Ever since my teens, magic has continued to be one of my hobbies, and I believe that performing magic tricks can make you a better lecturer. In one of my lectures on photochromic substances, I produce a poster which appears to be blank. When a "black light" is passed over the poster, the message "It's not magic, it's photochemistry" suddenly appears. It's also the message of Hammond and Zimmerman at the 1961 Organic Symposium and that of the first Gordon Conference in 1964.

Panelists in a seminar, Origins of Photochemistry in Italy, held April 1993 at the Casa Italiana at Columbia University. Left-to-right: Heinz Roth, Maristella Lorch (Director of the Casa Italiana), Angelo Lamola, Nick Turro, and Trozzolo.

Courtesy of Anthony Trozzolo

***The Spectrum*: What first sparked your interest in science during childhood? When did it happen? Were there mentors or role models in elementary school or high school, for instance?**

Trozzolo: My interest in science probably began in the late 1930s when the Museum of Science and Industry opened its west wing. My older brother, Mario, and I spent many

Saturdays visiting the museums of Chicago and what we found particularly appealing about the Museum of Science and Industry (it also was called the Rosenwald Museum) was the "hands-on" exhibits. I liked the colors produced by polarizing filters and wondered how the color was created. There was a "Fire Show" each October which illustrated various forms of combustion, and an exhibit on the hydrolysis of water. I was attracted to chemistry because of its sensual effects such as color changes, white precipitates, crystals of various shapes, etc. Although most of my teachers in both elementary and high school were very dedicated (their early careers began in the Great Depression), several stand out.

My second grade teacher, Miss Margaret Oliphant, taught me the values of good penmanship, neatness, and responsibility. She also double-promoted me into the advanced half of third grade. In high school, I had Mrs. Anatasia Springer for most of my math courses. In addition to being a great teacher of mathematics, she was the faculty sponsor of the Slide Rule and Math Club and when the Club met after school hours, she personally helped me to empirically derive by induction the formulas for permutations and combinations. My Italian teacher, Mrs. Antenisca Nardi, who also had taught my older brothers, strongly encouraged us to continue our education in college, and even visited my parents to stress this point. My chemistry teacher, Francis C. Coulson, reinforced my interest in chemistry. He said (in jest, I assume): "Stay in chemistry, and you'll win a Nobel Prize."

***The Spectrum*: Well, maybe you came closer than you know.**

Trozzolo: The closest that I came to fulfilling that prophesy was when Doug Neckers, my wife and I were in the audience at the Award Ceremony to see Roald Hoffmann and the late Kenichi Fukui receive their Nobel Prize in 1981, but we're still waiting for the phone call from Stockholm.

***The Spectrum*: Did you conduct research as an undergraduate?**

Trozzolo: My undergraduate research advisor at Illinois Tech, Eugene Lieber, provided me with the opportunity to present our results at the September 1949 ACS Meeting in Atlantic City under the title "The Hydroxylamine Number Application to the Identification of Ketones." He was also the one who introduced me to the methodology of doing research. That research also led to my first publication in the June 1950 issue of *Analytical Chemistry*. At the University of Chicago, my advisor, Wilbert H. Urry, convinced me to go back to graduate school in 1956 (even though I was married and had a son) and provided a Union Carbide Fellowship which was specifically given to married students.

At this point, I think that it's important to acknowledge the financial aid which was provided to me both in the form of undergraduate scholarships and Atomic Energy Commission and National Science Foundation Graduate Fellowships as well as the aforementioned Union Carbide Fellowship. Without those sources of support it would have been difficult if not impossible to pursue my studies and research. The presence of role models continued at Bell Labs as we kiddingly referred to our in-house collaborations as "being each other's postdoc." These collaborations widened greatly our research horizons.

***The Spectrum*: Tell us about how you found your way to Bell Labs and then to Notre Dame.**

Trozzolo: My interest in photochemistry actually began as an interest in the spectroscopy of charge-transfer complexes during the three years (1953-56) that I spent at Armour Research Foundation (now IIT Research Institute) working on a variety of contract research projects. I had always had a fascination for generating colors by chemical reactions and the mere mixing of trinitrobenzene and anthracene in solution to generate an orange color provided an excellent example worthy of explanation. The classic Mulliken papers on charge-transfer had just appeared and stimulated many studies in this particular area of research. My interest in solid-state organic chemistry also began during this period under the tutelage of the late Walter McCrone, who was already at that time a microscopist of international repute.

When I returned to the University of Chicago in 1956 to pursue my doctoral research with Professor Wilbert H. Urry, my studies initially concentrated on the photochemical decomposition of diazomethane in polyhalomethanes (a reaction which has had very interesting mechanistic aspects), but ultimately became concerned with bimolecular initiation of free-radical reactions. It was near the end of this period (1958) that I became aware that Bell Laboratories was going to add a few organic chemists to its technical staff in Murray Hill. I was fortunate enough to be one of the five additions in 1959 to join Ed Wasserman (who had arrived a few years earlier from Harvard) in the department headed by Field H. Winslow.

The years that followed were to be scientifically rewarding for each of the six (Ed Chandross, Gerry Smolinsky, Dick (Paul) Story, Bob Murray, Ed Wasserman and me), and later, Heinz Roth, as we launched our individual careers in physical organic chemistry, and in particular, the creation, detection, and characterization of reactive intermediates, such as carbenes, carbocations, and nitrenes. In many of these studies, the photochemical decomposition of a suitable precursor was the preferred method for generating the reactive intermediate. Also, I would be remiss if I did not acknowledge the encouragement of the Bell Labs administration, particularly that of our department head, Field "Stretch" Winslow, a pioneer in polymer chemistry, who became the founding Editor of *Macromolecules* in 1968. Stretch celebrated his 90th birthday last June.

Field (Stretch) Winslow's 80th birthday in 1996. Left-to-right: Trozzolo, Stretch, Ed Chandross, Ed Wasserman, and Gerry Smolinsky.

Courtesy of Anthony Trozzolo

***The Spectrum*: And your path to South Bend, Indiana?**

Trozzolo: The path to Notre Dame probably began (although I didn't realize it at the time) in 1971 when Nick Turro invited Angelo Lamola and me to give his photochemistry course at Columbia since he was going to be on leave (as it turned out, although he was on leave, he stayed at Columbia during this period). It was my first teaching experience since my undergraduate days at Illinois Tech (I had been an AEC and NSF Fellow at Chicago, and these fellowships carried no teaching responsibilities) and I enjoyed it very much except on two occasions. The first exception was when I had to lecture on carbonyl photochemistry with Nick Turro in the front row (he came to all the lectures) and the second was when I had to give a magic show with Koji Nakanishi in the audience. Talk about carrying coals to Newcastle!

In the following year, I was invited to give a series of Peter C. Reilly Lectures at the University of Notre Dame. The title of the series was "Creation and Detection of Excited-State Intermediates" and the lectures dealt with photochromism, singlet oxygen, and dye lasers. Although I had been raised in nearby Chicago and did not leave until the completion of my doctoral research, and had been a life-long Notre Dame football fan, I had never visited the University before my lectures in October 1972. In 1974, I was offered the Huisking Professorship in Chemistry at Notre Dame and a year later in 1975, I joined the Department of Chemistry and became a member of the Radiation Research Laboratory as well. It was not easy to leave Bell Labs' superb research environment and my colleagues there, many of whom had international reputations as outstanding researchers, but in retrospect, it was the right thing to do at that time.

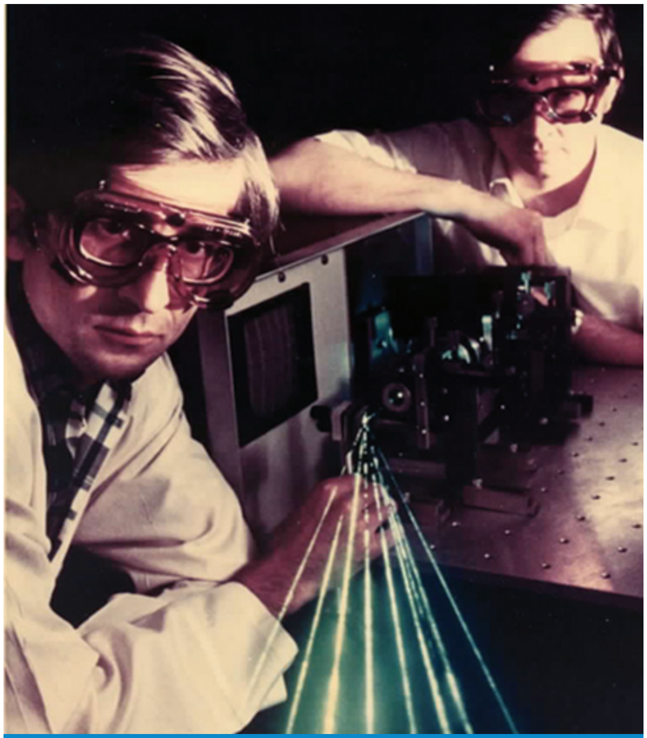
***The Spectrum*: What kept you at Notre Dame?**

Trozzolo: Even before I arrived at Notre Dame, my career began to take on additional facets, involving more administrative functions, such as the Associate Editorship of the *Journal of the American Chemical Society* and the Editorship of *Chemical Reviews* (One can point out that the last three Editors of *Chemical Reviews*, Harold Hart, myself, and the current Editor, Josef Michl, have all had photochemical research interests) and many committee and Board assignments both in the ACS and in the Gordon Research Conferences. Also, being the early occupant of an endowed chair at Notre Dame made me vulnerable to frequent assignments on various committees such as search committees for additional chair positions which were then being established. While these assignments were time-consuming, I felt that I was participating actively in the development of the University.

In addition, the presence of many congenial colleagues, both in the Department and throughout the University, and many excellent students has made the last thirty-one years quite intellectually satisfying and six Notre Dame degrees for my children attest to the nonscientific gratification enjoyed during this period. When our children were undergraduates at Notre Dame, I would often be pleasantly surprised by encountering them on campus on their way to a class (They all lived on campus even though our home was three miles away). But the main reason for remaining is the same as the reason that I came, namely, that as Kingman Brewster, then president of Yale, said in his preface to Father Theodore Hesburgh's book *The Humane Imperative: "Yet because of the religious heritage of the place, Notre Dame is one* *of the few universities I know that reminds the visitor, as well as those who work and study there, that learning at heart is a morally motivated act."*

***The Spectrum*: How did your research interests change over the years?**

Trozzolo: My undergraduate research at IIT involved using the oximation of ketones as an quantitative analytical technique for their identification. At Armour Research Foundation I became interested in microscopic techniques for studying a variety of organic solid-state problems, including charge-transfer complexes. My doctoral research involved thermal bimolecular initiation of free radical reactions. At Bell Labs, the general theme became the creation and detection of reactive intermediates such as carbenes, dicarbenes, ground-state triplet and quintet species, singlet molecular oxygen. The "creation" step usually involved the photolysis of a suitable precursor, and the detection and characterization usually involved a spectroscopic technique such as electron spin resonance, absorption or emission spectroscopy, chemically induced-dynamic nuclear polarization (CIDNP). I also became interested in the oxidative photodegradation of polymers which led to some interesting excursions into photobiology in collaboration with Angelo Lamola and Susan Fahrenholtz.



Exciplex dye laser developed with Charles V. Shank and Andrew Dienes of Bell Labs in 1970. Chuck is changing the wavelength and Andrew is changing the spatial distribution, all happening during the photograph exposure time.

Courtesy of Bell Labs

Another collaboration with Hollis Wickman led (serendipitously) to the synthesis and characterization of the first molecular magnet, the pentacoordinate bis-(N,N-diethyld ithiocarbamato)iron III chloride, which, in addition to its novel magnetic property, had a spin quartet ground state. Collaboration with Chuck Shank and Andrew Dienes led to the "exciplex" laser with very wide tunability range in the visible based on simple notion of differences in pK_a between ground state and excited state of hydroxy-coumarin dyes. One of the interesting features of these studies was that one could time-resolve the stimulated emission from the various excited states and thus get a time-profile of the excited-state proton transfers.

***The Spectrum*: Some of your work was in photochromism?**

Trozzolo: Our interest in photochromism actually was the spin-off of a collaboration with the late Gary Griffin who was interested in the photolysis of oxiranes as a source of carbenes. Low-temperature studies showed that a colored intermediate was being formed in addition to the carbene. It turned out to be the carbonyl ylide.

By turning our attention to aziridines, Thap DoMinh and I were able to generate colored azomethine ylides, which were stable at room temperature for many hours. These turned out to provide for some very useful lecture demonstrations of the ability to control lifetimes of the colored species (azomethine ylide) by making use of substituents, solid-state environment, and, of course, orbital-symmetry conservation rules. At Notre Dame, Tom Leslie was able to get fluid solution lifetimes of the ylides by laser kinetic spectroscopy. Some recent interest has been in the nonlinear optical properties of the photochromic aziridines. Along the way, I managed to do some applied research, usually as the outgrowth of other studies, so that patents have been issued in the area of dye lasers, photochromic lenses, and copper deactivators (to stabilize polyethylene against autooxidation).

***The Spectrum*: How did you become Huisking Professor of Chemistry?**

Trozzolo: When I was first contacted about a position at Notre Dame in 1974, I did not know that it was about an endowed chair. My visit as Reilly Lecturer in 1972 had left a very favorable impression about the hopes and aspirations of the Department of Chemistry. After spending a few days on campus meeting with members of the Department, the Administration, and the Radiation Laboratory, my return home to Murray Hill, New Jersey, was the beginning of an emotional roller-coaster ride for my family and me.

When we finally accepted the Notre Dame offer and made the move in 1975, we were welcomed into the Notre Dame community in grand style. My formal inauguration involved an installation ceremony, inaugural lecture, a Mass honoring Charles and Catherine Huisking, a dinner honoring the Huisking family, and—a football game (Notre Dame vs. Georgia Tech) with 50-yard-line seats. Although we didn't realize it at the time, that game was to become memorialized in the movie "Rudy," as the game in which Rudy Ruettiger, a Notre Dame senior, finally gets to play.

***The Spectrum*: How useful are review articles? Do review articles get enough attention? Should there be more reviews?**

Trozzolo: In 1980, as I began my fourth year as Editor of *Chemical Reviews*, I wrote an editorial in which I pointed out the virtues of the scholarly art of writing review articles, one of which was its value "of integrating and committing to posterity the knowledge and understanding that have been accumulated with much human effort." This rings as true today as it did in 1980, perhaps, even more so. In view of the ever-increasing amount of research studies and publications, there is a continual need to upgrade and organize this new knowledge.

An indication of the stature and usefulness of reviews is provided by recent studies on citation data of publications which shows that review journals have higher impact factors (impact factor is the average number of citations per source item) than other journals and that *Chemical Reviews* consistently has had the highest impact factor of any chemical journal. Whether we need more reviews is answered by saying that we are always in need of good reviews. By that I mean reviews which are comprehensive, but not merely catalogs of data. They need to be critical, with the hope of being seminal in setting new paradigms for the subject. In my short essay at the beginning of the 100th volume of *Chemical Reviews* in 2000, I gave a few examples of reviews published in that journal which have fulfilled those expectations.

***The Spectrum*: Any advice for the sizable number of photochemical scientists who are nearing retirement age? How can they avoid being eclipsed by younger faculty, or make the best decision on whether to retire or work?**

Trozzolo: My advice is aimed at academic scientists since the retirement of industrial scientists in recent years has often been caused by economic factors beyond their control. My advice is this: If you are happy in what you are doing and have the financial support to continue your research, don't retire. If, however, there are certain aspects of your life, people and places to visit, hobbies, etc., that haven't received as much attention during your career as you would like, then retirement has its attraction. For six years after I became emeritus, I was the Assistant Dean of the College of Science and taught a course on "Seeing the Light in Science" which I designed "from scratch." It may be possible to arrange a similar gradual change from a full-time position. I also wouldn't worry about being eclipsed by the younger faculty. It's going to happen, sooner or later. That's actually one of the great satisfactions of the academic career. To see your younger colleagues (whom you had a hand in choosing) succeed in their fields.

***The Spectrum*: What pursuits keep you engaged today?**

Trozzolo: My current activities these days divide up into three groups: institutional, professional, and family. At Notre Dame, I currently serve on the Faculty Senate representing the emeriti faculty. This gives me an opportunity to be "in the loop" regarding University affairs, and to try to insure that the emeriti continue to be regarded as a valuable resource for the University community. I am still actively involved with the ACS Local Section Speaker Service. Of my menu of five different lectures, the one most often chosen by the Sections is: "Origins of Modern Photochemistry in Italy—A Lot of Bologna."

I have continued to be active with the Gordon Research Conferences, attending at least one conference a year since I became emeritus. The year 2006 is a special one for the Conferences, marking their 75th Anniversary. The past year has been eventful for my wife, Dolly, and me as we celebrated an event arranged by our children, our 50th wedding anniversary, and had a new house constructed so that we, in principle, could "down-size." Six months after we moved in, the down-sizing still continues.

***The Spectrum*: Is there any one question you wish we had asked?**

Trozzolo: The question would be: What role did your wife, Dolly, play in your career? And the answer: Dolly has been a constant source of support and encouragement throughout the 51 years of our marriage. From the sacrifices of graduate school when our family was growing and our financial status was barely viable to the absences caused by my increased travel due to professional commitments, she was the mainstay of our family's welfare. Once the children were older, she began to accompany me to meetings and on speaking tours, and has been to so many conferences on photochemistry that she has a pretty good grasp of the vocabulary.


At the 1993 Physical Organic Chemistry Gordon Conference. Left-to-right: Tony, Dolly Trozzolo, and Alex Cruickshank (Director Emeritus of the Gordon Research Conferences).

Courtesy of Anthony Trozzolo

At Gordon Conferences, she urges first-time conferees to "network" and get to know the leaders in the field. Even Alex Cruickshank, long-time Director of the Gordon Conferences, once kidded her about being an honorary conferee. When Father Theodore Hesburgh, while celebrating our 50th Anniversary Mass at Notre Dame last year, was giving his homily about marriage, he mentioned: "The Italians have an expression to define 'love.' It's '*ti voglio bene*' which literally means 'I wish you well'." Dolly has been living that definition and it has reflected on my career.

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assembly of dye aggregates on nucleic acid nanotemplates

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My interest in photochemistry was first engaged by an experiment done as an undergraduate laboratory exercise at the University of Rochester. The experiment involved the photoisomerization of *trans-* to *cis*-stilbene and subsequent photo-oxidation to produce phenanthrene. After a semester spent dealing with oil baths and heating mantles, melting points and chromatography, what a joy it was to use a mercury lamp to drive a chemical reaction, and an HP UV-vis spectrophotometer to monitor the transformation. I suspect that most, if not all, readers of *The Spectrum*, had similar epiphanies that drew them into the wonderful field of photochemistry. The professor who introduced me to photochemistry was David Whitten, who graciously overlooked my mediocre performance in the lecture component of the organic chemistry course he taught and gave me my first research position. The goal of my project was to synthesize various stilbazolium derivatives and study their photochemical dimerization reactions in reversed micelles. Well, this opened a second unforeseen door, namely performing organic chemistry in a solution that contained its own internal structure. Micelles, liposomes, zeolites and clays are all examples of microheterogeneous or organized media and the ability to assemble such structures within a solution offers the opportunity to alter and even control the outcome of a photochemical reaction. The appeal of this notion was reinforced not only by my time spent in the Whitten lab, but also by a sparkling lecture given by Nick Turro at Rochester on the occasion of his receiving the Harrison Howe Award. Turro's talk was the first time I had heard the term "supramolecular" and it seemed to convey something bigger and better than what we were learning in the undergraduate curriculum. I was excited to learn more.

These experiences ultimately led me to pursue my Ph.D. under the guidance of the late David O'Brien at the University of Arizona. O'Brien taught me that supramolecular was not better than molecular, but rather that the two types of synthetic chemistry were complementary. Moreover, if molecular and supramolecular chemistry failed to get you to your destination, maybe a dose of macromolecular chemistry would finish the job. Photochemistry was used to initiate and sustain various polymerization reactions, particularly involving phospholipids that were pre-assembled into bilayer as well as other supramolecular assemblies. Thus, we used molecular chemistry to synthesize polymerizable lipids, supramolecular chemistry to self-assemble the lipids into bilayer or other structures, and finally macromolecular chemistry to either stabilize or destabilize the resulting structure, depending on the goal of the experiments and composition of the materials. In other projects, liposomes were used as nano-concentrators to specifically localize reactants at the bilayer surface or in the hydrophobic interior of the membrane (although we didn't use the prefix "nano" much at that time). Photoinduced electron and energy transfer reactions were studied in these self-assembled systems.[1,2]

After graduation, my path led me to Gary Schuster's lab at the University of Illinois, where we synthesized cationic anthraquinone derivatives that would intercalate into double-helical DNA and upon irradiation, photo-oxidize the DNA bases, ultimately leading to permanent damage at specific sites.[3] Readers will recognize the evolution of this project into the study of electron and hole transport over long distances in DNA to which Schuster's lab has contributed significantly.

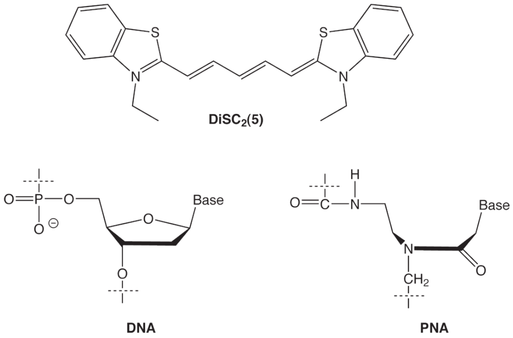
While Schuster and others were investigating photoinduced electron transfer in DNA, chemists, physicists and computer scientists were beginning to use DNA as a construction material for synthesizing elaborate, periodic nanostructures ranging from planar, extended lattices[4] to discrete objects such as tetrahedra,[5] octahedra[6] and even smiley faces (☺)[7]. Arrays consisting of metallic and semiconducting nanoparticles or proteins were assembled using DNA templates.[8] Again, we see the interplay of molecular, supramolecular and macromolecular chemistry in this research. By way of this lengthy introduction, I will now describe a project from my own lab that fits into this context.

DNA-Templated Aggregation of Cyanine Dyes

The binding of organic dye molecules to double-helical DNA has enjoyed a long history. In fact, the ability to stain nuclear material with basic dyes put the "A" (for acid) in "DNA". Today, numerous dyes that either bind to the minor groove of DNA or intercalate into the base pair stack are commercially available and are widely used as fluorescent indicators or stains for DNA. Our interest in the interaction of organic dyes with DNA arose from a desire to develop visible light sensitive photocleavage agents for DNA that could be used in the lab as biological probes and/or in the clinic for photodynamic therapy. This idea was based in large part on work from David O'Brien's lab, showing that cyanine dyes can serve as effective photoinitiators for vinyl polymerizations and that the reaction mechanism likely involves generation of hydroxyl radical from the excited state dye reacting with molecular oxygen.[9] Since hydroxyl radical is an effective DNA cleavage agent, this seemed like a reasonable track to follow.

In our first experiment, a symmetrical cyanine dye, **DiSC$_2$(5)** (Chart 1), was mixed with polymeric DNA having an alternating A-T sequence. A simple UV-vis experiment revealed that the absorption spectrum of the dye shifted hypsochromically by 60 nm (Figure 1A).[10,11] The spectral shift is due to "H"-aggregation of **DiSC$_2$(5)**, promoted by both the hydrophobicity and polarizability of the extended pi system of the dye. While aggregation can be driven by increasing dye concentration or decreasing temperature,[12] we discovered that it could also be promoted by double helical DNA. Thus, the DNA was serving as a template for the assembly of the dye aggregate.

Chart 1. Chemical structures of a cyanine dye, DNA and PNA.



An interesting feature of the DNA-templated aggregate was that the UV-vis spectrum (Figure 1A) was noticeably narrower than the spectrum of the dye in water. This contrasts with dye H-aggregates that form at high concentrations, which typically exhibit very broad absorption spectra, due to the presence of a plethora of structures varying in number of dyes as well as relative orientations of dyes within the aggregate. Evidently, the DNA-templated aggregate has a very well defined structure.

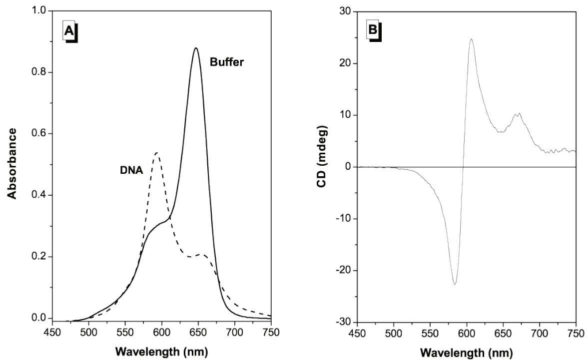


Figure 1. UV-vis (A) and CD (B) spectra for **DiSC$_2$(5)** aggregates assembled on a DNA template.

Spectroscopic experiments were used to identify the DNA binding mode and structure of the aggregated dyes. The sequence dependence of aggregation implicated the minor groove of the DNA as the likely binding site for the dyes, which was later confirmed by NMR experiments.[13] However, the blue shifted absorbance favored binding of the dye as a cofacial dimer rather than a monomer within the groove. Additional dye molecules can also bind as dimers, aligned with other dimers in an end-to-end fashion, leading to a helical aggregate in which the dyes wrap around the minor groove of the DNA template (Figure 2).

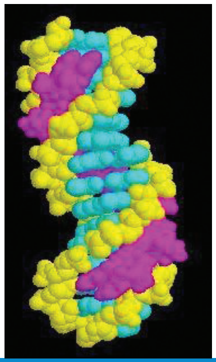


Figure 2. Molecular model illustrating a helical aggregate of three **DiSC$_2$(5)** dimers (purple) assembled in the minor groove of DNA.

The helical structure of the cyanine dye aggregates leads to interesting optical properties. For example, two forms of electronic coupling are observed. First, there is the strong coupling that arises between the two cofacially stacked dye molecules. This leads to splitting of the excited state, where transition to the upper state is allowed, while transition to the lower state is forbidden, thereby accounting for the blue-shifted absorbance spectrum (Figure 3). In addition, a weaker coupling occurs between end-to-end aligned dyes. This coupling is difficult to detect by UV-vis, although low temperature and high dye:DNA ratios promote broadening or even splitting of the absorption band.[14]

The two types of coupling are more evident in the circular dichroism spectra of the dyes. Due to the symmetrical structure of DiSC$_2$(5), no CD signal is observed in solution. However, binding to the chiral DNA template leads to an induced CD spectrum. For DNA templates on which a single, isolated dimer assembles, the CD spectrum is relatively weak and yields a maximum at the same wavelength where the dimer absorbs in the visible. However, end-to-end alignment of multiple dimers leads to the secondary coupling, which is manifested in the CD spectrum as strong exciton splitting that reflects the right-handed helical relationship between the coupled dyes (Figure 1B).

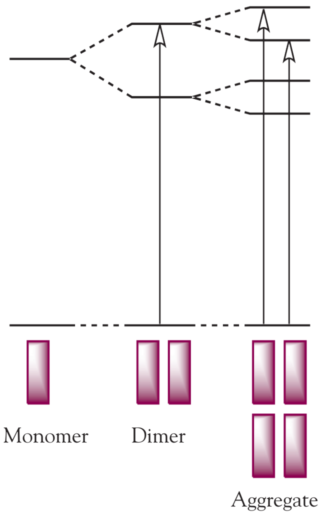


Figure 3. Illustration of excited state energy level splittings and allowed optical transitions for H-aggregated dyes.

Helical Aggregation of Cyanine Dyes on PNA

While the helical dye aggregates assembled on DNA templates have interesting structures and optical properties, they have little applicability. However, we discovered a related phenomenon that led to a simple DNA detection assay. The method involves PNA, a structural homologue of DNA in which the hydrogen bonding purine and pyrimidine bases are attached to a polyamide rather than a polyphosphodiester backbone (Chart 1). The bases in PNA extend from the backbone with the same repeating distance as in DNA allowing complementary PNA and DNA strands to recognize one another and form double-helical complexes in the same way as two complementary DNA strands.[15] However, because of the lack of a negative charge along the PNA backbone, the affinity of PNA for DNA is significantly higher than between two DNA strands. Thus, PNA has been used in a variety of DNA detection schemes.

The minor groove of PNA-DNA duplexes is wider than that of DNA-DNA, but as noted above, there is a lower negative charge density. Thus, it was not clear what dyes like **DiSC$_2$(5)** would do in the presence of PNA-DNA. When the dye was added to a solution containing a 12 base pair PNA-DNA duplex, the color of the solution was purple, in contrast to solutions of the dye alone or with DNA-DNA, where the color is invariably blue.[16] The difference in color arises from the fact that the dye absorption spectrum in the presence of PNA-DNA shifts by 130 nm to the blue, compared with the 60 nm shift observed when the dye binds as a dimer in the minor groove of DNA (Figure 4A). Since the larger shift indicates formation of a more extended aggregate, we proposed assembly of an aggregate based on trimeric units. (The helical structure of the aggregate is evidenced by a strong exciton-split CD spectrum, as shown in Figure 4B.) The hypothesis that the aggregate is templated by the PNA-DNA minor groove was supported by experiments that showed that steric blockage of the major groove did not prevent dye aggregation, but blockage of the minor groove did.[17]

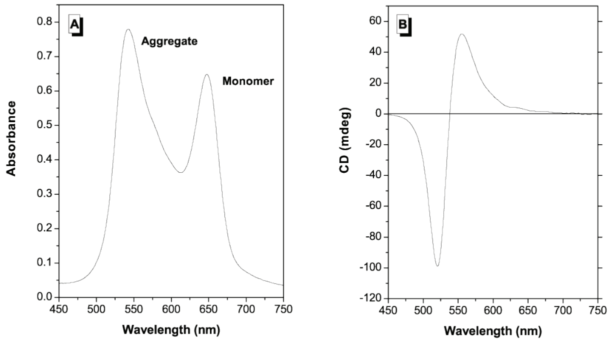


Figure 4. UV-vis (A) and CD (B) spectra for **DiSC$_2$(5)** aggregates assembled on a double-helical PNA-DNA template.

These results demonstrate a simple colorimetric assay for DNA: if a complementary PNA binds to the DNA, then the dye aggregate can assemble and an immediate blue-purple color change is observed. This phenomenon has been the basis for three different assays in which either the visible color change or the induced CD spectrum is used to indicate the presence of the DNA target.[18-20] Sensitivity to single mismatches can be introduced through temperature variation or enzymatic degradation of mismatched duplexes.

DNA-Templated Multichromophore Arrays as Fluorescent Labels

The helical dye aggregates assembled on DNA-DNA and PNA-DNA duplexes exhibit interesting and useful optical shifts and induced CD spectra. However, one troubling feature of these systems is that the dye fluorescence is severely quenched in these aggregates. There is great interest in synthesizing multichromophore arrays for light harvesting and fluorescent labeling applications. The DNA-templated aggregates assembled in the minor groove were appealing for the ability to assemble large numbers of dyes in a small region of space (ca. 2 dyes per 17Å distance along the helix), but the quenched fluorescence precludes their use in fluorescence labeling. An alternative strategy that retains DNA as a template while also hindering dye quenching is to exploit a different binding mode for organic dyes with DNA: intercalation. In this binding mode, the planar chromophore of the dye inserts between adjacent base pairs within the helix. In so doing, the DNA is strongly perturbed because it must get longer and unwind in order to create the intercalation site for the dye. This strongly inhibits binding of another dye at the same site, or even at an adjacent site. Rather, the dyes distribute themselves along the helix at every other site. This allows one to load the DNA helix with a high effective concentration of dye while also keeping the dye molecules at least two base pairs apart (ca. 7 Å), enough to prevent self-quenching. The resulting intercalator arrays will be intensely fluorescent. One can always create even brighter assemblies by increasing the number of base pairs in the DNA template. This could involve making the DNA longer, or resorting to branched structures such as those shown in Figure 5. Since DNA can be readily functionalized with reactive groups for attachment to surfaces or recognition groups for binding to biomolecules, the DNA-dye arrays could be used as labels for tagging other molecules.

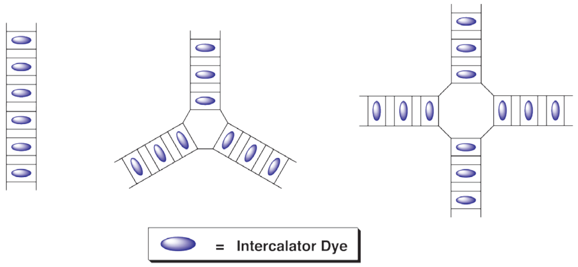


Figure 5. Illustration of DNA-templated arrays of fluorescent intercalator dyes. Branched DNA nanostructures allow a higher density of intercalated dyes to be arrayed.

Conclusion

The assembly of cyanine dye aggregates and arrays on DNA-DNA and PNA-DNA templates blends molecular, supramolecular and macromolecular chemistry. Combining old-school molecular recognition of DNA by minor groove binders and intercalators with modern ideas from the field of DNA nanotechnology allows the efficient synthesis of new materials having a range of UV-visible, CD and fluorescence characteristics. It is hard to believe that 20 years have passed since Dave Whitten first introduced me to photochemistry and supramolecular assemblies.

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the (photo)chemistry of anthocyanins

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Anthocyanins (from the Greek words for flower, *anthos*, and blue, *kyanos*) constitute the major red and purple pigments in terrestrial plants,[1,2] where they concentrate in vacuoles in the cells of fruits, flowers and leaves (Figure 1). In flowers, anthocyanins attract insect pollinators, while in certain carnivorous plants they attract insect prey. Light-sensitive seedlings or plants subjected to excessive doses of light often respond by synthesizing anthocyanins, presumably to protect the photosynthetic apparatus from the excess incident radiation and photooxidative stress.[3,4]

Figure 1. Typical anthocyanin colors in fruit (grapes, strawberries), leaves (poinsettia) and flowers (blue hydrangea; red roses).

Anthocyanins are omnipresent in our diet, have little or no known toxicity and are usually quite water-soluble, making them particularly attractive as natural substitutes for synthetic pigments and antioxidants.[1,2] However, in aqueous solution, most anthocyanins lose their color rather rapidly at pH > 3. Thus, widespread practical application of anthocyanins as coloring agents will require novel strategies for stabilizing their color at near-neutral pH, which in turn requires a deeper understanding of the chemical and photochemical reactivity of anthocyanins.

The basic chromophore of anthocyanins is the 7-hydroxyflavylium ion (Chart 1). Naturally-occurring anthocyanins typically have hydroxyl substituents at positions 3 (always glycosylated, necessary for thermal stability) and 5 (occasionally glycosylated) as well. The phenyl- or B-ring usually has one or more hydroxy or methoxy substituents.[1,2] Some of the most common natural anthocyanins are indicated in Chart 2. The colors of natural and synthetic anthocyanins range from yellow to purple (every color except green has been observed) and depend on the substitution in the B-ring, the local pH, the state of aggregation of the anthocyanin or the occurrence of complexation by organic molecules or, particularly in the case of blue colors, by metal cations as well.[5,6] Although many hundreds of anthocyanin structures have been reported in the literature, these differ primarily in the nature of the sugars present in the glycosylated portions.

Chart 1. The 7-Hydroxy-flavylium Ion

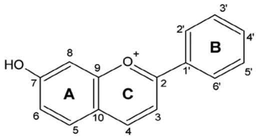
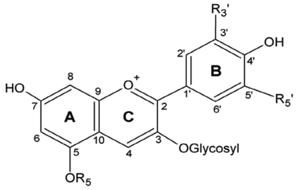
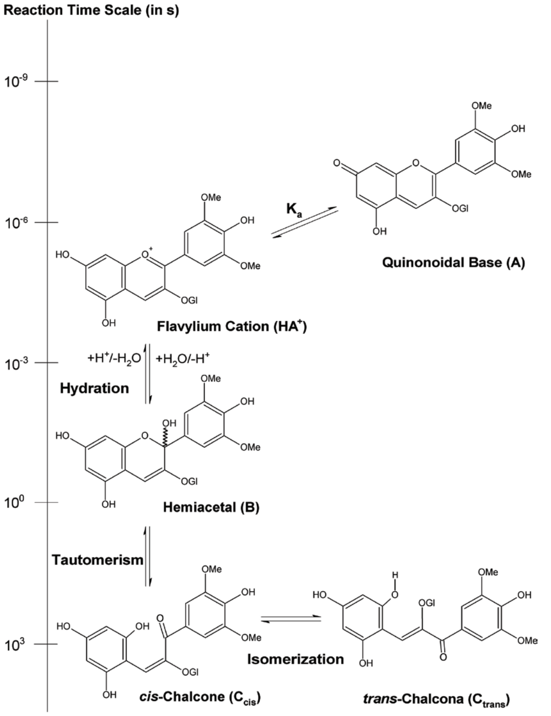


Chart 2. Some of the More Common Naturally-Occurring Anthocyanins



malvin: R_3', R_5' = OCH_3 ; R_5 = Glycosyl
oenin: R_3', R_5' = OCH_3 ; R_5 = H
pelargonin: R_3', R_5' = H ; R_5 = Glycosyl
peonin: R_3' = OCH_3 ; R_5' = H ; R_5 = Glycosyl
cyanin: R_3' = OH ; R_5' = H ; R_5 = Glycosyl
delfinin: R_3', R_5' = OH ; R_5 = Glycosyl

Rationalization of the chemical and photochemical properties of anthocyanins is quite complex. In the ground state, natural anthocyanins can exist in acidic aqueous solution (pH < 7) in at least five different forms that are coupled to each other via pH-dependent equilibria[1,2,7] (Scheme 1), while in basic solution this number can increase due to additional deprotonation equilibria. At pH < 3, the dominant form is the red or purple flavylium cation (**AH^+**). **AH^+** is a weak acid (pK_a of the 7-hydroxy group in the range of 4-5) that deprotonates to the blue quinonoidal base **A**. However, flavylium cations are subject to attack at C-2 by nucleophiles such as water. Thus, at pH > 3, addition of water to form the colorless or pale yellow hemiacetal (**B**) is often more favorable, leading to loss of the color. Tautomerism of the hemiacetal gives the cis-chalcone (**C_{cis}**), followed by slow isomerization to the trans-chalcone (**C_{trans}**). At neutral pH, the dominant form of anthocyanins is typically the hemiacetal (**B**), in equilibrium with minor amounts of the isomeric chalcones (**C_{cis}** and **C_{trans}**). In the first excited singlet state, 7-hydroxyflavylium ions are superphotoacids ($pK_a^* < 0$)[8], transferring a proton to water in about 6-20 ps, and the chalcones can undergo photoisomerization and, as a consequence, exhibit photochromism.[9]



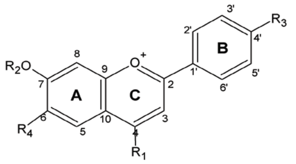
Scheme 1. Chemical transformations of oenin, a typical anthocyanin, in aqueous solution.

Background for the Brazil-Portugal Collaboration

When we began our collaborative studies six years ago, several aspects of anthocyanin (photo)chemistry were completely open questions. Although the ground-state prototropic reactions of the flavylium cation can affect anthocyanin color, the proton transfer dynamics had not been determined for any of the natural or synthetic anthocyanins. There had been very few systematic studies of the excited-state deactivation mechanisms and the possible fate of the solar radiation absorbed in vivo and in vitro by anthocyanins was completely unknown. Although free anthocyanins generally begin to lose their color at pH > 2.5-3 in aqueous solution due to the onset of the hydration and tautomerization processes indicated in Scheme 1, evolution has developed strategies for stabilizing the red color of anthocyanins at pH values around 4-5 (the pH of plant cell vacuoles in which anthocyanins are located in vivo). In these vacuoles, complexation of the flavylium cation by colorless "copigment" molecule such as hydroxylated benzoic and cinnamic acids, hydroxyflavones, and other polyphenols prevents color bleaching by stabilizing the flavylium cation with respect to the uncolored hemiacetal and chalcone forms.[10] The driving force for this phenomenon, commonly referred to as "copigmentation", was generally assumed to be a hydrophobic effect, perhaps combined with hydrogen bonding interactions.

A key feature of our studies has been the use of model synthetic anthocyanins (Chart 3) in which part of the reactivity has been blocked or in which the charge or hydrophobicity has been altered. Examples of the former include the 4-methyl-7-hydroxyflavylium ion (**HMF**), in which hydration is disfavored, allowing studies of the prototropic reactivity in the absence of the other ground-state multiequilibria, and the 4-methyl-7-methoxy-flavylium ion (**MMF**), in which the the prototropic equilibrium is blocked (Figure 2). Examples of the latter include 7-hydroxyflavylium-4-carboxylic acid (**CHMF**),[11,12] which is cationic at low pH

Chart 3. Synthetic Anthocyanin Probes



HMF: $R_1 = CH_3$; $R_2,R_3,R_4 = H$
MMF: $R_1,R_2 = CH_3$; $R_3,R_4 = H$
DHF: $R_3 = OH$; $R_1,R_2,R_4 = H$
CHMF: $R_1 = CO_2H$; $R_2,R_3,R_4 = H$
HHMF: $R_1 = CH_3$; $R_4 =$ n-Hexyl, $R_2,R_3 = H$

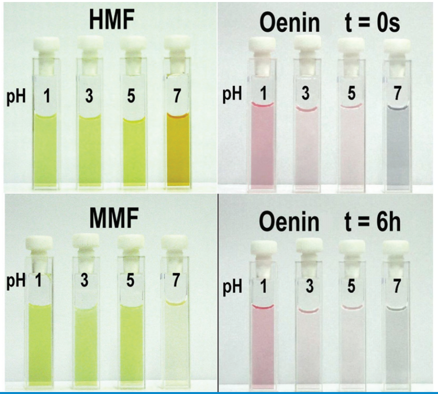


Figure 2. pH-Dependent color of aqueous solutions of **HMF** ($pK_a = 4.4$; predominantly **HA+** at pH 1-3 and **A** at pH 7), **MMF** (no deprotonation, hydration at pH 7) and **Oenin** immediately after preparation ($pK_a = 3.7$; predominantly **HA+** at pH 1, **A** at pH 7) and after equilibration for 6h in the dark (bleaching due to hydration, tautomerism and isomerization at pH > 2.5).

(pK_1 = 0.73), zwitterionic at intermediate acidic pHs (pK_2 = 4.84) and anionic at neutral pH, and water-insoluble anthocyanins with pendent aliphatic chains[13] such as the 6-(n-hexyl)-7-hydroxy-4-methyl-flavylium ion (**HHMF**). When a simple compound that undergoes all of the (photo)chemical reactivity characteristic of natural anthocyanins is required, the 4',7-dihydroxyflavylium ion (**DHF**) is a convenient choice. In most cases, the methodology developed with these synthetic analogs has been extended to representative natural anthocyanins.

Ground and Excited State Proton-Transfer Dynamics in Aqueous Solution

Excitation of synthetic anthocyanin analogs such as **HMF** and **DHF** in aqueous solution results in ultrafast adiabatic excited-state proton transfer (ESPT) to water in 6-10 ps to produce the excited base form (**A***), which then decays to its ground state in about 100-200 ps.[8] Since both the excited state proton transfer from the excited acid **AH⁺*** and the subsequent decay of **A*** to its ground state are very fast, nanosecond laser flash photolysis can be employed to perturb the ground-state acid-base equilibrium and the deprotonation (k_d) and reprotonation (k_p) rate constants determined by following the relaxation back to equilibrium as a function of pH.[14] Since $k_{obs} = k_d + k_p[H^+]$, where k_{obs} is the reciprocal of the lifetime of the excess **A** produced by the laser pulse, a plot of k_{obs} vs. $[H^+]$ furnishes both the protonation (slope) and deprotonation (intercept) rate constants (Figure 3). In addition, the fact that $pK_a = \log (k_p/k_d)$ provides a check on the values and a more precise value of k_d when the pK_a is known independently. Interestingly, the values of k_p and k_d could also be readily determined for several natural anthocyanins by this method.[7,15] Because the perturbation of the ground-state acid-base equilibrium by the laser pulse is a direct consequence of excited-state proton transfer, this constituted the first evidence, albeit indirect, for the occurrence of excited-state proton transfer in these naturally occurring anthocyanins.

Diglycosylated anthocyanins such as malvin, cyanin and pelargonin are only weakly fluorescent, while monoglycosylated anthocyanins are practically non-fluorescent. Careful picosecond time-resolved fluorescence measurements[15] confirmed the occurrence of ultrafast (6-20 ps) adiabatic ESPT from **AH⁺*** to water of several weakly-fluorescent natural anthocyanins. Comparison of the fluorescence lifetimes of the **AH⁺*** form of anthocyanins (6-20 ps) with that of **MMF** (4.7 ns), in which proton transfer is blocked, clearly shows that highly efficient ESPT is the predominant process (>99%) responsible for the weak fluorescence of the flavylium cation form of anthocyanins. This process is highly efficient as an energy-wasting mechanism and probably serves to protect free **AH⁺*** from photodegradation and from intersystem crossing to the triplet state (that might potentially sensitize the formation of singlet oxygen).

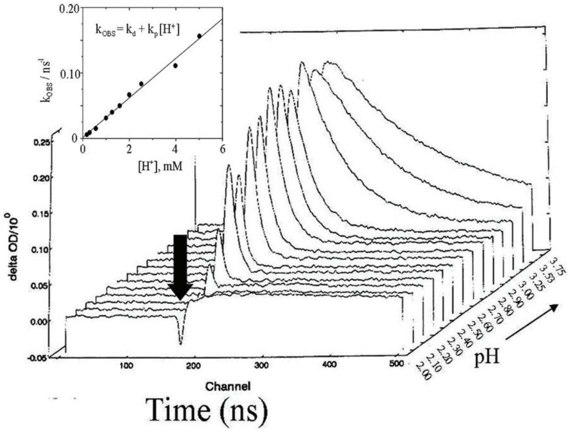
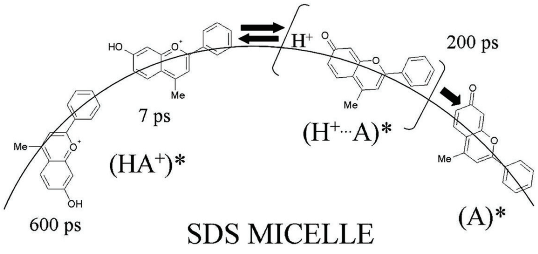


Figure 3. Laser flash photolysis perturbation of the ground state acid-base equilibrium of **HMF** as a function of solution pH (from pH 2.00-3.75); 5 ns pulse at 355 nm from a Nd-YAG laser at the arrow, absorbance of **A** monitored at 410 nm. The variation of the observed rate constant for decay **A** with $[H^+]$ is shown in the inset. Below pH 2.2, reprotonation occurs during the laser pulse.

Proton-Transfer Dynamics at Micelle Surfaces

Micelles influence the local pH[16,17] and the relative stabilities of the various forms of the anthocyanin, resulting in shifts in the pK_as and in the pH-dependent speciation (relative proportions of **AH⁺**, **A**, **B** and the chalcones).[7,18] Employing the laser flash photolysis perturbation technique, the protonation and deprotonation rates of anthocyanins can also be determined at micelle surfaces.[7,12,18] Reprotonation is diffusion-controlled and involves encounter of **A** with a proton arriving from the aqueous phase. The rates of both deprotonation and hydration are much slower (by about 20-40-fold) in aqueous micellar solution of the anionic detergent sodium dodecyl sulfate (SDS) than in water, suggesting a specific stabilization of **AH⁺** by the anionic micellar environment. Conversely, inclusion of the anthocyanin in cationic hexadecyltrimethyl ammonium chloride (CTAC) micelles results in a slight destabilization of the **AH⁺** form and, in the case of **HMF**, induces hydration and tautomerism not observed in water.[18]

Synthetic anthocyanins, in particular water-insoluble anthocyanins with hydrophobic side chains, have proven to be excellent probes of proton transfer dynamics at the surface of detergent micelles.[19,20] In bulk aqueous solution,[8] the kinetics of ESPT are straightforward with only two kinetically and spectrally resolved species present, AH^{+*} and A^*. In contrast, studies of **HMF** in SDS and of the micelle-anchored probe **HHMF** in SDS and CTAC micelles have shown that four kinetically resolvable species are present: two distinct populations of AH^{+*} and two distinct populations of A^* (Scheme 2). One of the populations of AH^{+*} is coupled to A^* via ESPT, while the other (much longer lived) corresponds to AH^{+*} molecules that are oriented at the micelle surface in such a way as to inhibit the normal ultrafast ESPT. The two populations of A^* are the initially formed geminate proton-anthocyanin base pair ($H^+\bullet\bullet\bullet A^*$), which can either decay by efficient geminate reprotonation back to the acid or, upon proton escape, become free A^*.

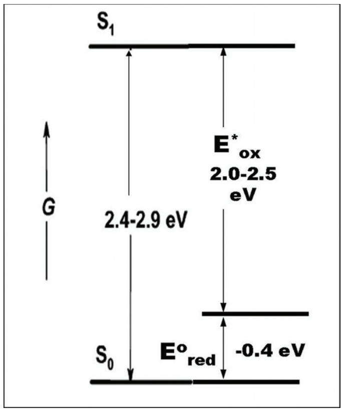


Scheme 2. ESPT dynamics of **HMF** at the anionic SDS micellar surface.

Copigmentation and the Excited-State Redox Properties of Anthocyanins

Steady state fluorescence studies showed that the excited singlet state of **MMF** is efficiently quenched by typical copigment molecules. The quenching is static in nature and a consequence of the presence of ground state MMA-copigment complexes. Consequently, fluorescence quenching provides a convenient and straightforward method for determination of the equilibrium constants, K_{cop}, for complex formation or copigmentation.[10,21] As expected for a process dominated by charge-transfer interactions, the log K_{cop}, values for a variety of anthocyanin-copigment pairs correlate linearly with the redox properties of the copigment (ionization potential, IP) and the anthocyanin (electron affinity, EA). Thus, although there may be additional stabilization of the anthocyanin-copigment complex by other factors, charge transfer from the copigment to the anthocyanin makes a significant contribution to the stability of anthocyanin-copigment complexes and must clearly be taken into account in any analysis of the copigmentation of anthocyanins by colorless organic molecules.

Charge-transfer complexation of the anthocyanins in vivo has important consequences for color intensification or copigmentation and for the photochemical stability of anthocyanins. From the standpoint of color stabilization, charge transfer to the anthocyanin should decrease the positive charge at carbon 2 of the flavylium cation, resulting in a reduction in the equilibrium constant for hydration. Thus, charge transfer nicely rationalizes the inhibition of the hydration of the flavylium ion upon complexation with the copigment. The HA^+ form of anthocyanins is quite easily reduced[10,21,22] and, hence, in the excited state, the cationic form of anthocyanins turns out to be a superb electron acceptor[10,21] (Scheme 3). From the standpoint of photostability, efficient static quenching of the excited state of anthocyanin-copigment complexes via exergonic excited state electron transfer (ESET) followed by fast back transfer to give the ground state of the complex provides a highly efficient energy-wasting mechanism for copigmented anthocyanins that protects them from photodegradation.



Scheme 3. Excited singlet state redox properties of the AH^+ form of synthetic anthocyanins. Excitation energies are in the range of 2.4-2.9 eV and reduction potentials typically ca. -0.4 V.

Other Photoprocesses of Anthocyanins

No consideration of the photochemistry of anthocyanins would be complete without mention of their photochromic properties.[9,11] There are two important photochemical processes that can cause anthocyanin color changes: (1) *cis-trans* photoisomerization of the chalcones (C_{cis} and C_{trans}) and (2) photocatalyzed ring closure of the cis-chalcone to the hemiacetal (**B**) followed by acid-catalyzed loss of water to give AH^+. In the dark, the photogenerated AH^+ then reverts thermally back to the equilibrium mixture of AH^+, **B**, C_{cis} and C_{trans}.

Concluding Remarks

In the last few years, we have made substantial progress in understanding important aspects of the complex chemistry and photochemistry of anthocyanins. We now understand many of the factors that affect the ground state equilibria of anthocyanins and can manipulate these equilibria (and hence anthocyanin color) in micellar media by appropriate choice of the detergent. We have characterized the dynamics of proton transfer in solution and at the surface of micelles and have demonstrated the importance of charge-transfer interactions in anthocyanin-copigment complexes. ESPT and ESET have been shown to be the major energy wasting processes via which uncomplexed and complexed anthocyanins, respectively, convert the absorbed incident radiation into heat without suffering photochemical reaction. Studies in progress are directed towards the elucidation of the properties of the excited triplet state of flavylium ions in which proton transfer has been blocked, such as **MMF**, as triplet sensitizers and as electron acceptors.

Acknowledgments

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mono- and oligo-ruthenium(II) complexes of tridentate ligands

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One of the biggest challenges facing humanity is the ever-growing demand for energy, particularly as the world's population should rise to near 10 billion by 2050.[1] One could then ask: Will there be enough energy available to power the Earth, even at today's level of energy consumption? Oil, gas, coal, and nuclear energy are non-renewable resources that may not last into the next century, however, alternative forms of energy, for example, wind and solar energy, are renewable and have the potential to power humanity for centuries to come.[2] Although direct conversion of wind and solar energy into electricity is a very promising avenue of research, its conversion into chemical energy could address important issues such as how to store energy without significant losses. The advent of effective fuel cell technologies based on hydrogen also leads to the question of how to produce large quantities of hydrogen without making use of non-renewable resources. Thus, the production of hydrogen by way of solar energy conversion appears to be an effective means to meet some of the world's future energy needs.[1]

Although research into the photo-generation of hydrogen expanded rapidly in the 1970s due to increasing oil prices, there had been a lull in research as oil prices dropped over the 1980s and 1990s. The recent sustained increase in the price of oil over the last five or so years has reinvigorated the field as has an increased understanding of how Nature produces chemical energy. Many researchers are inspired by the natural photosynthetic systems found in green plants and bacteria, which produce vast quantities of chemical energy from sunlight everyday. These natural systems are highly evolved and complex to the point where one could only dream of duplicating their structure,[3] however, with proper design principles, one might aspire to duplicate their function.[4]

In an artificial photosynthetic system (APS), the secondary chromophores (the equivalents of carotenoids and chlorophylls in natural systems) would be synthetic molecules combined in a fashion to create a gradient in their excited-state energies (Fig. 1). The energy transfer (ET) component of an APS allows energy to be funneled down to a primary chromophore, the natural equivalent of which is P680, the special pair, found in Photosystem II. In the electron transfer (eT) component of an APS, the primary chromophore transfers an electron to an electron acceptor, which would relay the electron to a redox catalyst. Regeneration of the oxidized primary chromophore by a suitable electron donor (in the best case scenario H_2O) would allow a second excitation of the primary chromophore. Following the transfer of another electron to the redox catalyst, H_2 could then be produced from H^+. In natural systems a similar series of electron transfer reactions eventually leads to the production of ATP which fuels the conversion of CO_2 into glucose.

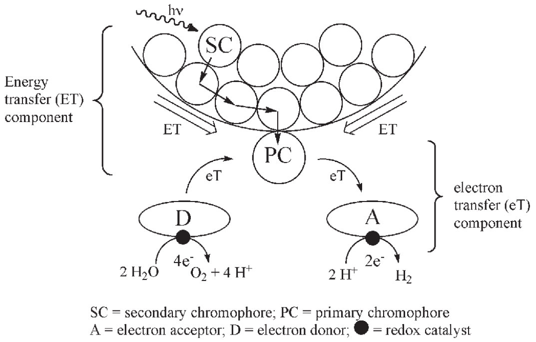


Figure 1. Energy transfer (ET) and electron transfer (eT) components of an artificial photosynthetic system (APS): Energy transfer from the secondary chromophores to the primary chromophore leads to electron transfer and the production of H_2 by way of a redox catalyst.

My group's research in this area has focused on the primary chromophore and its incorporation into multinuclear arrays, the energy transfer component indicated in Figure 1. Multinuclear complexes composed of tris-bidentate complexes of Ru(II) (e.g., $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine)) had previously been shown to transfer energy among the component parts depending on the choice of metal ion incorporated into the array.[5] One drawback of the $Ru(bpy)_3^{2+}$ motif, however, is that the Λ and Δ enantiomers of the monometallic unit will lead to diastereomeric complexes in its polynuclear assembly. Although enantiopurification techniques have been developed to address this challenge,[6] we wanted to investigate the use of Ru(II) complexes of tridentate ligands as achiral equivalents to $Ru(bpy)_3^{2+}$. This approach is not new,[7] but it was shown quite early on that the $Ru(tpy)_2^{2+}$ motif (tpy = 2,2':6',2"-terpyridine) was not too promising a candidate due to its short MLCT (metal-to-ligand charge-transfer) excited-state lifetime at room temperature (r.t.) and that the $Ir(tpy)_2^{2+}$ motif would fare better.[8] The principal deactivation pathway for the Ru(II) complexes of tridentate ligands is through thermal population of metal-centred (MC) states from MLCT states, followed by ready non-radiative deactivation back to the ground state (Fig. 2).[9] There were, however, interesting reports of prolonged excited-state lifetimes at r.t. for the Ru(II) complexes of tpy and related tridentate ligands that showed promise for further design enhancements of the ligands bound to the Ru(II) centre.[10] Several design approaches were developed to increase the energy separation between the MC and MLCT states by: i) lowering the energy of the MLCT state,[9a] and ii) by raising the energy of the MC state,[11] and more recently, iii) a combination of the i) and ii).[12]

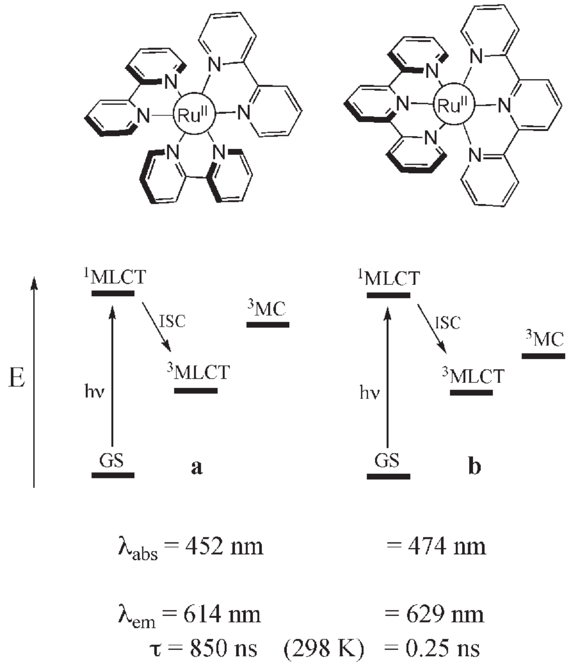


Figure 2. The different excited-state lifetimes of a) Ru(bpy)$_3^{2+}$ and b) Ru(tpy)$_2^{2+}$.

Our own approach has been to lower the energy of the MLCT state while avoiding non-radiative deactivation according to the energy-gap law. In this approach, we chose to incorporate an aromatic ring off the back of tpy in order to increase electron delocalization in the excited state, a very promising approach that was previously used for Ru(bpy)$_3^{2+}$ with phenyl-substituted bpy and tpy (Fig. 3a, **1** with R=H).[13] In order to assure ourselves that the rings were coplanar, we introduced 1,3-diazines (pyrimidines) substituted in the 2-position, so as to remove the unfavourable H-H repulsion between the aromatic group and the tpy (cf. biphenyl twist) and to introduce favourable C-H to N hydrogen bonding (Fig. 3b, **2** with R=H). This approach lead to an increase in the r.t. excited-state lifetime from 1 ns to 8 ns, in complexes Ru(**1**)$_2^{2+}$ and Ru(**2**)$_2^{2+}$, respectively.[14] Further substitution on the pyrimidine ring *para* to the tpy led to increased excited-state lifetimes (up to 200 ns for Ru(**2**)$_2^{2+}$, R = CN in Fig. 3b, an 800-fold increase over Ru(tpy)$_2^{2+}$) as shown in Table 1. The excited-state lifetimes increased due to a lower energy MLCT state (Ru(**2**)$_2^{2+}$, R = CN emits at 713 nm), in contrast to the energy gap law. This is further exemplified by Ru(**1**)$_2^{2+}$ emitting at 700 nm (Fig. 3a, R = H), yet having a very short luminescence lifetime (1 ns). We attribute this to the increase in electron delocalization in our family of complexes[15] which leads to less distortion in the excited state and more similarity to the Franck-Condon state.[16] As a consequence, as the energy of the excited state is lowered, there is less overlap direct with the ground state, and a longer lifetime results.

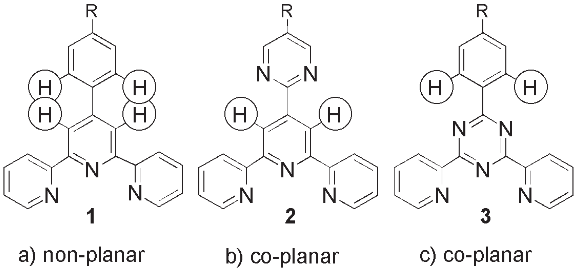


Figure 3. Tridentate ligands functionalized with pendant aromatic groups in order to increase electron delocalization in the acceptor orbital of the ligand.

Table 1. Room-temperature luminescence lifetimes for (R-pm-tpy)Ru(tpy)$^{2+}$ complexes.[a,b]

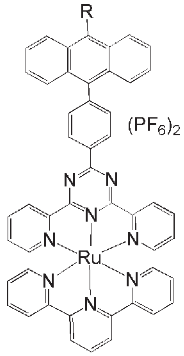
R group	Lifetime (τ), ns	λ_{max} em., nm
H	8	675
Ph	15	680
Cl	21	684
Pm	43	690
CN	200	713

a) for the various R groups of complex **2** in Figure 3;
b) in acetonitrile.

With these promising results in hand, we looked at the possibility of increasing the excited-state lifetimes even more by using the "energy reservoirs" described by Ford and Rogers.[17] In this approach, the non-emitting triplet state of an organic polyaromatic ring is equilibrated with the ^{3}MLCT state to generate bichromophoric complexes. Thus, pyrene appended to Ru(bpy)$_3^{2+}$ leads to a bichromophoric complex with a prolonged excited-state lifetime. In our complexes, the triplet state of pyrene would be too high in energy, whereas, the anthracene triplet would be of appropriate energy. Indeed, the excited-state lifetimes of Ru(**2**)$_2^{2+}$-type complexes could be prolonged to 1800 ns with appended anthracene units, a 7200-fold increase, and a lifetime superior to that of Ru(bpy)$_3^{2+}$ itself.[18] A long-range bichromophoric effect could also be demonstrated whereby the anthracene was not connected to the ligand generating the MLCT state.[19]

Although these ligands and their Ru(II) complexes proved very promising for our next step, the assembly of polynuclear arrays, their synthesis was still a multistep process and we wanted to develop methodology to afford readily synthesized ligands. So instead of appending a pyrimidine off the back of tpy, we chose to introduce the two additional N atoms into the central pyridine of tpy and to append a simple phenyl group off of the triazine core (Fig. 2, **3**).[20] With these new tridentate ligands, we were able to produce Ru(II) complexes with prolonged luminescence lifetimes, albeit with not as great an effect as the Ru(**2**)$_2^{2+}$-type complexes (From Fig. 2, Ru(tpy)(**3**)$^{2+}$: R = H; λmax = 740 nm, τ = 9 ns; R = Br; λmax = 739 nm, τ = 12 ns). Although it is tempting to state that the energy gap law is getting the best of us, as triazines are weaker donors than pyridines, the MC states would not be as high in energy as in Ru(tpy)$_2^{2+}$, which would lead to increased deactivation by thermal population of the MC state. This is also supported by the fact that most derivatives of Ru(**3**)$_2^{2+}$ are not emissive at r.t.[21]

Appending anthracene to these complexes did not increase the excited-state lifetimes of the complexes as it did for Ru(**2**)$_2^{2+}$-type complexes as the ^{3}An state now lies higher in energy than the ^{3}MLCT state of the Ru(tpy)(**3**)$^{2+}$ complexes (Fig. 4, **4** : R = H; λmax = 735 nm, τ = 13 ns). In this case, we decided to modify the energy of the ^{3}An and not the ^{3}MLCT, and so as bromo-anthracene has a lower triplet excited state energy than anthracene, the bichromophoric effect can be used to increase the excited-state lifetime of this complex to a small extent (Fig. 4, **5** : R = Br; λmax = 738 nm, τ = 54 ns).[22]



R = H, **4**
R = Br, **5**

Figure 4. Anthracene (**4**) and bromo-anthracene (**5**) functionalized Ru(II) complexes of triazine-based ligands.

We then moved to build up polynuclear arrays with our new complexes using the well-known chemistry of tetracarboxylate metal dimers.[23] Thus, the Ru(II) complexes of *p*-carboxy-phenyl functionalized tpy can displace the acetates from Rh$_2$(OAc)$_4$ to give mono-, di- (*cis* and *trans*), and tri-substituted Rh-Rh dimers, the ratio of which depends on the stoichiometry of the reagents (Fig. 5).[24] The X-ray crystal structure of the *trans* bis-Ru(II) complex shows that the two Ru(tpy)$_2$ centres are well separated and that the Rh-Rh-dimer core is intact, with a distance of 2.6 nm between the Ru(II) centres.[24] All of the complexes are, however, non-emissive at r.t. as Rh-Rh dimer has a non-emissive triplet state at lower energy than the ^{3}MLCT state of the Ru(II) complexes. Incorporation of triazine-based ligands into the periphery of the assembly leads to r.t. emission from the ^{3}MLCT, suggesting that the non-emissive triplet of the Rh-Rh dimer does not lie low enough in energy to deactivate the Ru(tpy)(**3**)$^{2+}$ MLCT by energy transfer.[25]

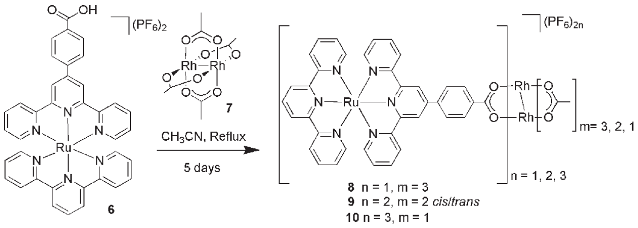


Figure 5. The synthesis of oligonuclear complexes from metal-metal dimers.

We are now poised to build up even larger polynuclear arrays using this metal-metal dimer approach. A more promising avenue of research may be to replace the remaining acetates in structures such as that found in Figure 5 with electron donors and acceptors in order to create charge separated states over fairly large distances. The incorporation of redox catalysts into our assemblies remains to be done, however, we are looking forward to the challenge of creating catalytic systems for the photo-generation of H_2 from H_2O.

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go out to all of our collaborators, in particular Sebastiano Campagna and Frédérique Loiseau.

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Changing Trends in Doctoral Degrees in the United States

Which of these universities sent the most undergraduates on to a doctorate in science or engineering during the 20th Century? Duke University, Johns Hopkins University, the University of Nebraska, Virginia Tech, the University of Iowa, or Oberlin College in Ohio?

Despite an enrollment substantially smaller (3,000 at present) than those giant institutions, Oberlin College provided the baccalaureate origins of more science and engineering doctorates over an 80-year period (nearly 2,800).

That's one of the surprises in a new National Science Foundation (NSF) report documenting trends and patterns in the rapid growth and changing demographics of doctoral education in the United States. Entitled *U.S. Doctorates in the 20th Century*, it tells who is educated and where.

The report (http://www.nsf.gov/statistics/nsf06319) also describes the complex changes taking place in the pursuit of doctoral degrees, especially in new interdisciplinary fields. For example, five of the eight leading doctorate-granting universities from 1920-1999 were Midwest-based, Big Ten schools. Prior to that period, the majority of doctorate-granting institutions were East Coast institutions. "The report shows how much has changed in doctoral education in just 25 years," said Susan T. Hill, director of the Doctorate Data Project in NSF's Division of Science Resources Statistics.

"For one thing, nearly two-thirds of all doctorates awarded in this country occurred in the last 25 years of the 20th century. Second, the United States has become an educator of the world, expanding its role in providing doctorates to foreign-born and U.S. students. Third, the U.S. system reveals a great flexibility in opening varied pathways for Ph.D. recipients into career opportunities both in and outside their fields. This has increased U.S. innovation, competitiveness and leadership in many fields."

A new National Science Foundation report reveals the growing number of women and foreign nationals who pursued U.S. doctorates in the 20th century, among a range of other trends and patterns.

Courtesy of Argonne National Laboratory

A few highlights of the NSF report:

Changes in demographics

Men received 73 percent of all doctorates awarded in the 20th century, but in the 1990s, women made significant gains, receiving over 40 percent of all doctorates. Foreign nationals held less than 10 percent of all doctorates before 1960 but received more than a third of all science and engineering (S&E) doctorates by 1999, and 17 percent of non-S&E doctorates.

New pathways to doctoral degrees

Two-year colleges vastly increased their role in educating those who go on to pursue a Ph.D. In the century's final five years, 1995-1999, one-fifth of all American Indians/Alaska Natives who received doctorates attended two-year colleges. One-sixth of all Hispanic Ph.D. recipients also reported having attended two-year colleges. From 1995-1999, almost a third of African-American Ph.D. recipients reported receiving an undergraduate degree from a Historically Black College or University (HBCU).

Increasing indebtedness

In 1999, for the first time, more than half of all graduating doctorates reported debt from their undergraduate and graduate education. In non-S&E fields, doctorates owing more than $20,000 from education loans quadrupled between the late 1980s and late 1990s. The corresponding percentage for science and engineering doctorates owing more than $20,000 was also significant, more than doubling during the same period.

"The report is an essential reference for understanding how the nation's educational system evolved," Hill said. "It's an indispensable starting point for those who plan the next steps we take in this remarkable enterprise. The increasing reliance on loans to support doctoral study is a trend we should follow as students from lower income groups make decisions on whether or not to seek advanced degrees."

Digital Imaging Technology Helps Preserve Ancient Hindu Text

Digital image processing and analysis can be extremely important tools for the restoration of old works of art, books, and manuscripts. These projects forge collaborations between scientists and artists.

One of the newest and most unusual involved a collaboration of scientists and philosophers who used imaging technologies to digitally restore a 700-year-old palm-leaf manuscript containing the essence of Hindu philosophy.

P. R. Mukund and Roger Easton, of the Rochester Institute of Technology, headed the effort to digitally preserve a collection of 36 original Hindu writings known as the Sarvamoola granthas that date to the 13th and 14th centuries.

Centuries of inappropriate storage techniques, botched preservation efforts, and degradation have left the Sanskrit document difficult to handle and to read. Each leaf of the manuscript measures 26 inches long and two inches wide, and is bound together with braided cord threaded through two holes. Heavy wooden covers sandwich the 340 palm leaves, cracked and chipped at the edges.

Each palm leaf of the sacred Hindu manuscript, the Sarvamoola granthas, was captured in multiple sections, processed and digitally stitched together. The top image shows the condition of an original leaf from the text, stitched together but unprocessed. The bottom image shows a stitched and processed page after applying modern imaging technologies. Images were taken with a Sensys scientific digital camera and an infrared filter.

Courtesy of Roger Easton, Rochester Institute of Technology, and Keith Knox, Boeing LTS

"It is literally crumbling to dust," said Mukund. "The book will never be opened again unless there is a compelling reason to do so, because every time they do, they lose some. After this, there won't be a need to open the book."

Mukund, who studies and teaches Hindu philosophy, learned about the document through his spiritual teacher in India. He then enlisted RIT colleague Easton, who imaged the Dead Sea Scrolls and is currently working on the Archimedes Palimpsest—a famed medieval parchment manuscript that contains treatises by Archimedes. Easton brought in Keith Knox, an imaging senior scientist at Boeing LTS, as a consultant. Mukund added Ajay Pasupuleti, a doctoral candidate in microsystems at RIT to complete the team.

The scientists imaged the document during a visit to India, using a scientific digital camera and an infrared filter to enhance the contrast between the ink and the palm leaf. Images of each palm leaf, back and front, were captured in eight to 10 sections, processed and digitally stitched together. The scientists ran the 7,900 total images through various image-processing algorithms using Adobe Photoshop and Knox's own custom software.

"This is a very significant application of the same types of tools that we have used on the Archimedes Palimpsest," Easton said. "Not incidentally, this also has been one of the most enjoyable projects in my career, since the results will be of great interest to a large number of people in India."

The processed images of the document will be stored in a variety of media formats, including electronically, in published books and on silicon wafers for long-term preservation. Etching the sacred writings on silicon wafers involves a process called aluminum metallization. It transfers an image to a wafer by creating a negative of the image and depositing metal on the silicon surface.

Each wafer can hold the image of three leaves. More than 100 wafers will be needed to store the entire manuscript. As an archival material, silicon wafers are both fire- and waterproof, and readable with the use of a magnifying glass.

Champion Buys Kodak Photochemicals

Champion Chemtech Ltd., of Mississauga, Ontario, Canada in September agreed to buy Eastman Kodak Co.'s photochemical business for an undisclosed sum. The unit produced photochemicals used by photo processors to develop film and print photographs.

Earlier in 2006, Champion similarly purchased a Kodak facility in Chalon, France. Kodak also is closing part of its Kodak Park synthetic chemicals manufacturing facility, which made other chemicals.

The moves were part of Kodak's effort to downsize its traditional photographic operations while transforming the company to focus more on digital imaging. The step will involve elimination of about 27,000 jobs by the end of 2007.

In-situ Photopolymerization Could Simplify Manufacture of Display Devices

A new technique for creating vertical alignment among liquid crystal molecules could lead to less expensive flexible displays and a better understanding of the factors that govern operation of those popular liquid crystal display (LCD) systems.

Liquid crystals are a key component of displays, including those in laptop computers and flat panel televisions. Controlled by a network of transistors, the liquid crystals change their optical characteristics in response to electrical signals to create the text and images we see.

LCDs remain costly because manufacturing processes are complex, requiring multiple steps that can introduce defects. Among the steps is the application of a polymer film—the so-called alignment layer—to the two pieces of glass between which the liquid crystals operate. The film, which must be rubbed after being coated on the glass, anchors the crystals with a fixed alignment. The process of rubbing to create the necessary alignment can damage some of the transistors and introduce dust, producing defects that can reduce the manufacturing yield of the panels.

Researchers at the Georgia Institute of Technology now have found a way to eliminate the polymer rubbing step by adding side chains to the polymer molecules. Instead of rubbing, they use the in-situ photopolymerization of alkyl acrylate monomers in the presence of nematic liquid crystals to provide a cellular matrix of liquid crystalline droplets in which the chemical structure of the encapsulating polymer controls the liquid crystal alignment.

"Small changes in the chemical nature of the polymer will change the alignment of the molecules at surfaces," said Mohan Srinivasarao, who described the self-aligning of liquid crystals at the 232nd national meeting of the American Chemical Society in San Francisco. "It turns out that this can be done over a fairly large area, and it is reproducible. This would be an alternative way to create the alignment that is needed in these devices."

Srinivasarao and colleagues used the technique and a nematic material with negative dielectric anisotropy to fabricate highly flexible liquid crystal devices that have high contrast and fast response times—without using an alignment layer. Control is obtained by variation of the alkyl side chains and through copolymerization of two dissimilar monofunctional acrylates.

Beyond simplifying the fabrication process and potentially increasing device yield, the technique also offers other advantages. Because devices are based on vertical alignment of the liquid crystals, their "off" state can be made completely dark. In addition, the liquid crystals provide strong binding between the two substrate surfaces, making the resulting display less sensitive to mechanical deformations and pressure—ideal for flexible displays that lack the structure provided by glass plates.

Why CEO Compensation Does Matter

Conventional wisdom is that overpaying a chief executive officer (CEO) in a large company doesn't matter because the company can easily absorb what seems like a single isolated extravagance.

New research by executive compensation scholars, however, has concluded that CEO pay has direct consequences for compensation at lower employee levels. Believed to be the comprehensive study of its kind to be conducted, it analyzed data from more than 120 firms over a five-year period.

Entitled "Overpaid CEOs and Underpaid Managers: Fairness and Executive Compensation," it was done by researchers from Rutgers University, Stanford University, and the Pennsylvania State University. It was published in the September/October 2006 issue of *Organization Science*.

Researchers concluded that when a CEO is overpaid by 64 percent, individuals in his/her company at Level 2 (chief operating officer or chief financial officer, for instance) are overpaid by 26 percent. Individuals at Level 5 (division general managers), in turn, are overpaid by 12 percent.

"Given the large sums paid to some senior executives, the total cost for overpayment could be a big number—and, in some cases, significantly affect shareholder returns," said Charles O'Reilly, a co-author of the study who is with the Stanford Graduate School of Business.

Top echelon pay also impacts subordinate turnover. The study found that CEOs serve as a key referent for employees in determining whether their own pay is fair. Simply put, if the CEO is overpaid, subordinates are more likely to leave.

"CEO compensation impacts employee retention more than we realized," said lead author James B. Wade, of Rutgers University. "Our research found that CEO overpayment is related to turnover, which can have important long-term consequences. It is quite possible that those most likely to leave because of perceived unfairness are precisely those employees coming up in the organization that would eventually rise to the top management team level."

Atmospheric Photochemistry: New Role for Winds

Winds circling high above the far Northern Hemisphere have a much greater impact on upper stratospheric ozone levels than previously thought, a new University of Colorado at Boulder study reports.

Cora Randall and colleagues found that the winds allowed near-record amounts of ozone-destroying nitrogen oxide gases (NO_x) to descend some 30 miles to the top of Earth's stratosphere in March 2006.

Because NO_x destroys ozone, which heats up the stratosphere by absorbing ultraviolet radiation, the naturally occurring gases could trigger atmospheric changes that could have unanticipated climate consequences, she said.

In February 2006, winds in the polar upper stratospheric vortex—a massive winter low-pressure system that confines air over the Arctic region—sped up to rival the strongest such winds on record, Randall said. The only time more NO_x was observed in the upper stratosphere was in the winter of 2003-04, when huge solar storms bombarded the region with energetic particles, triggering up to a 60 percent reduction in ozone molecules, said Randall.

"We knew strong winds would lead to more NO_x in the stratosphere if there were solar storms," said Randall. "But seeing that much NO_x come down into the stratosphere when the sun was essentially quiet was amazing."

The upper stratosphere is several miles higher than the ozone hole region, which forms in the lower stratosphere due to emissions of chlorine, bromine and other gases over the decades. Because there is significantly less ozone in the upper stratosphere, the ozone-destroying NO_x gases are unlikely to cause immediate health threats, such as increases in skin cancer, she said.

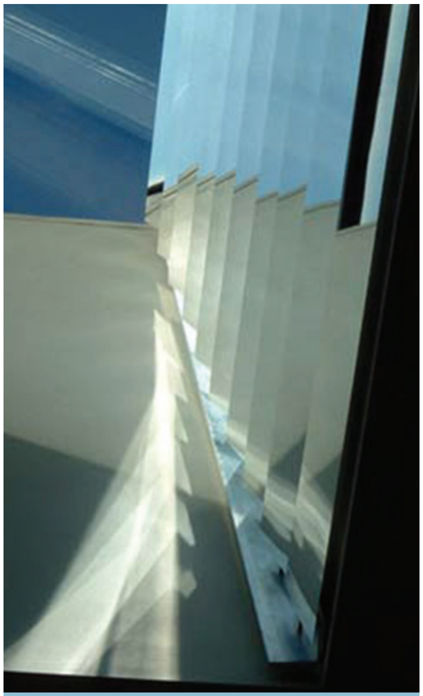
But the destructive NO_x gases—created above the stratosphere when sunlight or energetic particles break apart oxygen and nitrogen molecules—appear to be important players in controlling the temperature of Earth's middle atmosphere, Randall said.

"If human-induced climate change leads to changes in the strength of the polar vortex, which is what scientists predict, we'll likely see changes in the amount of NO_x descending into the stratosphere. "If that happens, more stratospheric NO_x might become the rule rather than the exception."

More Effective Use of Light in Architecture

What is light? To photochemical scientists, photons of just the right energy are a means for exciting atoms, making or breaking chemical bonds, driving and controlling chemical reactions. To architects, light is a means to reveal spaces and volumes as human beings interact with their environment.

So said Marilyne Andersen, an architect who is with the Massachusetts Institute of Technology's Building Technology Program, which is seeking better ways of incorporating natural light into building design. The research takes into consideration the many positive effects of natural light, including the considerable financial savings in energy bills and the overall effects natural light has on well-being, as well as the challenges that natural light presents.



Detail of a skylight designed to redirect and optimize daylight in Marilyne Andersen's MIT office. The assembly includes aluminum slats of varying inclination angles that maximize daylight penetration into the office space while avoiding reflections on the computer screen—and creating interesting visual effects.

Courtesy of Marilyne Andersen

In a recent lecture, Andersen explained that using as much natural light in buildings as possible has many advantages over using artificial lights—if its penetration is appropriately controlled.

Andersen cited studies in which natural light seemed to improve productivity in the workplace, and may have significant health benefits in terms of regulating human circadian rhythms. Although the studies are still at an early stage, Andersen did say that researchers know that natural light is "part of our biological needs. Intuitively, we prefer daylight to electric light."

In a typical building, lighting accounts for 25-40 percent of energy consumption. By allowing more natural light to penetrate and controlling both its light and heat components, the financial savings could be considerable, Andersen said. In addition to its health and financial benefits, natural light also provides an almost "perfect white light" that has a number of visual benefits. Best of all, natural light is of course, plentiful and free.

Andersen acknowledged that natural lighting can be difficult to utilize. Architects must cope with glare, overheating, variability and privacy issues (resulting from use of transparent construction materials). Andersen and her students have been working on ways to decrease the negative aspects of using natural light while taking full advantage of the positive.

The New Windows Vista

Windows Vista, the new operating system from Microsoft, will become widely available early in 2007.

Available in five different editions, Vista includes multiple advanced features, including a stunning new user interface with 3-D animations, transparencies, and other eye candy.