

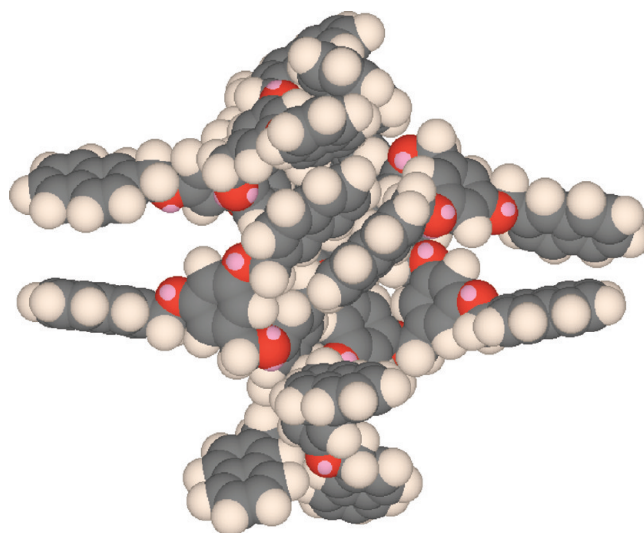
## A Perspective on Organic Chemistry: Physical Organic Chemistry

Marye Anne Fox\*

*Department of Chemistry and Biochemistry, University of California at San Diego, 9500 Gilman Drive,  
La Jolla, California 92003-0005*

*mafox@ucsd.edu*

*Received August 9, 2009*



A physical organic chemist wants to understand the detailed sequence of bond makings and bond breakings by which new or well-known reactions take place, i.e., the reaction mechanism, and to identify any metastable intermediates involved. The ultimate goal of such studies is to predict, and hope to control, chemical reactivity by determining how molecular structure and the immediate local environment affect a reaction of probative interest. Physical organic chemistry, in turn, provides structural insight, upon which others significantly depend for making new materials and for predicting and understanding new chemical and biochemical processes. I was fortunate in my own research to be able to study photocatalysis and photoinduced electron transfer as unifying themes that underlined our most significant work.

A physical organic chemist looks like a different animal to different observers. To a synthetic organic chemist, a physical organic chemist appears to be a physical chemist, using instrumentation to measure properties of readily available, often structurally simple compounds with unusual covalent structures or orbital properties. To a physical chemist, s/he appears to make interesting, structurally designed molecules, whose structural complexity provides unique opportunities to test theoretical postulates. Both are right: a physical organic chemist makes and measures molecules. S/he also wants to understand the detailed sequence of bond makings and bond breakings by which new or well-known reactions take place, i.e., the reaction mechanism, and to identify any metastable intermediates involved.

The ultimate goal of such studies is to predict, and hope to control, chemical reactivity by determining how molecular structure and the immediate local environment affect a reaction of probative interest. A subset of this goal is to define how catalysts function, whether the catalyst is a complexing metal, a hydrogen-bound noncovalent complex, or an enzyme. In many ways, physical organic chemistry can therefore be viewed as an exciting intellectual challenge and therefore as a highly rewarding exercise. Physical organic chemistry, in turn, provides structural insight, upon which others significantly depend for making new materials and for predicting and understanding new chemical and biochemical processes.

I was fortunate in my own research to be able to study photocatalysis and photoinduced electron transfer as unifying

themes that underlined our most significant work. This approach allowed us to investigate structure and reactivity at a sophisticated level and to probe how ground and excited state mechanisms differ.

Although mechanistic photochemistry was being aggressively pursued at the time by three major groups (Howard Zimmerman's at Wisconsin, George Hammond's at Caltech, and Nick Turro's at Columbia), all three (and members of these and other research groups spun from them) were personally supportive of my proposed ventures into reactions on photochemically activated surfaces. This professional kindness was available to many young photochemists, who in turn felt real comradery with the established groups. Howard went so far as to treat me as a "chemical grandchild" in that two of my research mentors had worked as his students. I fondly remember late, late night discussions at Gordon conferences in New England, at January meetings in Florida of the Interamerican Photochemical Society, and at IUPAC Photochemistry gatherings in Europe for over two decades, addressing both chemical details and philosophy of science, and providing a safe home to propose wild, new ideas.

### Preparation for an Academic Career in Physical Organic Chemistry: Undergraduate Research

As a student, I had an excellent series of research experiences that led me to start my own career in physical organic chemistry. My first serious jump into that pool was a summer project sponsored by the National Science Foundation as an REU (Research Experience for Undergraduates) with Professor A.J. Kresge at the Illinois Institute of Technology. We looked at the kinetics of vinyl ether hydrolysis induced by Brønsted and Lewis acids, showing the contributions of general and specific acid catalysis. That work led to my first *JACS* paper, for work performed as an undergraduate.<sup>1</sup>

Besides finishing a B.S. in Chemistry, I also completed the classes needed for Ohio secondary teacher certification in chemistry and mathematics. Although at the time I thought these education courses, including student teaching in a suburban public school in suburban Cleveland, to be mere formalities, they later helped me to appreciate the wisdom and hard work required for excellent classroom instruction. In particular, I came to respect the ways great teachers must keep current in their discipline, while remaining compassionate toward the quite time-consuming needs of the students. I also learned how clear, high expectations for strong performance by the students were essential to the success of the individual: this is a life-long goal.

### Graduate School: M.S. Studies

Knowing that I would have to move with my first husband, John Fox, when he finished his last year of medical school, I decided to first pursue a masters degree and therefore I took up a kinetic study of benzalazine with Roger Binkley at Cleveland State University, which used a variety of physical tools to establish excited state mechanisms.<sup>2</sup> I loved the cleanness of activating a molecule by exposure to light, rather than with another reagent. I was quite convinced of the beauty and utility of photochemistry. The project worked so well that I was able to complete a masters degree in 9 months, so I could get a job teaching chemistry at Cuyahoga Community College, an institution best known

for its campus river, which was so polluted, when I worked there, that it caught fire.

These studies took place soon after Dr. Martin Luther King, Jr. was assassinated, and I felt compelled to make a personal contribution to the effort for social and racial equality in the only way I knew, i.e., teaching secondary math and science in an essentially all-minority school in East Cleveland. I taught math to graduating seniors three days a week as a substitute teacher (as much as was possible, given that I had TA obligations as well), in a classroom that would otherwise have had no teacher. So I was called a "permanent substitute". A large tarpaulin was being used partially to compensate for a charred wall, the school having been partially burned in the riots following King's murder.

I seemed to be the only white teacher in the school. On the first day, I turned in a form declaring completion of my substitute assignment: the principal did not recognize the form because to his recollection no "outside" teacher had ever before lasted through a whole day.

Eventually, students and faculty grew to trust me and I them. "Senior math" turned out to be a class focusing on the addition of two digit plus two digit numbers, e.g.,  $17 + 22 = ?$ . Understandably, the students were bored. I was very proud that at year's end the students could fill out income tax returns, and for their final exams, they did just that at a neighborhood church. I was delighted that several of my students graduated from high school and went on to community college, apparently without math anxiety.

The experience made a lasting impression, one I feel to this day. In large part, it accounts for the passion with which I have pursued inclusion of women and minorities in science and engineering. I had seen first-hand the extraordinary effort required to compensate for low expectations, and how important a single dedicated teacher can be in helping such students to think about scientific careers. Every academic chemist ought to experience the joy of turning around a nonachiever.

### Graduate School: Pursuing a Ph.D.

Accompanying John Fox to his choice for a medical residency, I hoped to teach again when we settled in Hanover, NH, but no positions were available. I then turned to Dartmouth and had the good fortune to be admitted to David Lemal's research group. My first project, preparation and characterization of a highly strained perfluorinated tetrahydropyridane, did not yield product, but it taught me a valuable lesson. The decision-making exercised in choosing when to persist and when to move on in a chemical project is of enormous subsequent value, whether inside or outside science. Later, I learned from Bob Ingraham, then CEO of Glaxo-Smith-Kline, that sometimes it is highly useful to "fail fast".

Having failed on my first synthetic venture, I quickly finished two photochemical projects<sup>3,4</sup> involving the photo-rearrangement of chlorinated arenes. I was able to formulate mechanism and to trap highly strained intermediates encountered in the valence isomeric interconversion of halogenated arenes, pyrazines, pyridazines, and pyrimidines. These and related investigations gave me a good basis for my dissertation.

The best part of my graduate studies, however, was active mentoring by Lemal, enabling me to finish my graduate work in three years so I could move on with my husband and small son. Part of that mentoring was his willingness to work

at my side, on occasion overnight, so I could continue to progress while still taking care of my very premature baby during the day. His commitment was extraordinary, really. And quite atypical, I later learned. The other part of mentoring that made the Dartmouth program so unique was the active involvement by the faculty from other disciplines: Gordon Gribble, Tom Spencer, Chuck Braun, and Walter Stockmeyer seemed always to be looking over my shoulder, positively, throughout my entire graduate school experience, especially the Wednesday evening seminars that seemed to end quickly, but in fact lasted 3–4 h. They were also enormously helpful in advising me after the graduate school years were ended.

Perhaps the most important career advice came from Lemal, who by his healthy lifestyle and devotion to family at the same time he maintained a razor-sharp focus on science, convinced me that professional and personal lives could be balanced. As a small tribute to those who mentored me, I have hung in my office a copy of an exercise I did in kindergarten in 1952 while learning to print the letter “W”. The letter grade is faded, but the key point is not. It says: You must wish and work, a sentiment that captures what Dave Lemal taught me. Perhaps it was expected then that without even a change in expression, he automatically approved time off for taking care of my newborn son.

### Postdoctoral Experience

In July 1974, again accompanying a husband who had been drafted and assigned to Andrews AFB, I easily found a postdoctoral position at the Naval Research Lab synthesizing a range of organofluorine compounds. Unfortunately, then-President Nixon imposed a hard freeze on all new governmental positions just before I was to start. After waiting for three months, I decided to look elsewhere. I'll always be grateful that Stuart Staley at the University of Maryland was so supportive in helping me rapidly qualify for an NSF postdoctoral fellowship in the RANN (Research Applied to National Needs) program.

My photochemical experience helped me quickly to produce a fluorescence detector for a high pressure liquid chromatograph,<sup>5</sup> which was used for a project on monitoring air quality, based on observing chemical kinetics of reactions on the surfaces of aerosols.<sup>6</sup> Staley was kind enough to allow me to work independently as well on several of his projects.<sup>7</sup> Three months after I started at Maryland, the hiring freeze was lifted and my job offer at NRL was reinstated. I am sure I would have enjoyed the NRL, but I declined, choosing instead to seek an academic job. I had taught in junior high, high school, a community college, and in a research university and still loved teaching and did not want to give it up.

It seems ironic that the direction of my career toward academia was, unknowingly, determined by Richard Nixon.

### Beginning an Independent Academic Career

Upon completion of John's military service, we could move anywhere so the decision on location was mine. I chose to accept a position as an assistant professor at the University of Texas at Austin: I consider this decision one of the most important ones I ever made and one I would never regret. Although there was only one woman (Joanne Ravel) on the 50-some faculty in Austin, I was dazzled by the possibility of collaborating with Allen Bard, Roland Petit, and Michael Dewar,

along with a strong group of organic colleagues just hired as assistant professors. I also had the chance as an assistant professor to meet frequently and informally with several academic giants: Norman Hackerman, Karl Folkers, and Albert Noyes.



Michael Dewar and George Olah at Marye Anne Fox's house, Reaction Mechanisms Conference, Austin, Texas.

My start-up package, a total of \$35K, was a departmental record at the time, and several colleagues promised I could also use their instrumentation. The Center for Fast Kinetics Research (CFKR) would make it possible to follow sub-nanosecond-lived transients, which was then state-of-the-art. Eligibility for support from the Robert A. Welch Foundation, which would provide seed-funding for new ideas, was a strong competitive advantage available only to Texas faculty. Support from the Welch Foundation was one of the principal reasons I decided to accept the UT offer. Now serving on the Welch scientific advisory board, I can see the profound effect of the Foundation in stimulating highly creative work of others in Texas.



Norm Hackerman, Marye Anne Fox, Yuan T. Lee, and Joseph Goldstein at a Welch Foundation banquet, October 2005.

As a woman and a mother, I also felt welcome in the department and in the university. UT-Austin's president was a woman (Lorene Rogers), and only later did I learn that her appointment had been in Home Economics, not Biochemistry, the field in which she trained, because she was not welcomed in the latter department.

When I interviewed in the spring of 1976, at age 28, I recall stating that efficient solar energy conversion would likely be a key "grand challenge," one that was of high priority to the health of the planet. This term had been used by those who were then predicting supercomputing to be a grand challenge, when applied to astrophysics, astronomy, chemical reaction pathways, etc. It is amusing to note that just within the last years the National Academy of Engineering asserted that "making solar energy economical" is indeed listed as 1 of 14 global grand challenges.

### Choosing a Chemical Niche: Photoexcitation of Arenes and Anions (Early 1970s)

The approach I wanted to take was to discover and characterize compounds whose absorption maxima had been shifted to the visible or infrared region of the spectrum in order to overlap more consistently with the solar spectrum. Photolysis might then initiate electron transfer, which in turn would be expressed as photovoltage, photocurrent, or energy storage within strained compounds or redox products. I had two general goals: (1) discovering new reactions initiated by photoinduced electron transfer from stable anions, metal complexes, or dyes<sup>8</sup> and (2) finding a way to improve the efficiency of solar-driven water splitting on photoexcited semiconductor surfaces, a reaction that had recently been discovered by Fujishima and Honda at the University of Tokyo.<sup>9</sup> Both areas used the techniques of photochemistry and electrochemistry to define new reaction pathways useful in structural chemistry and in catalysis.

Although these reactions are quite focused in scope, they were easily extended to include how other reactions can take place in nonhomogeneous media, as well as how local environmental control can affect chemical reactivity. These areas are of sufficient general chemical interest to the physical organic community to have attracted continuing support throughout my academic career, even to the present day, from the Department of Energy and, until recently, from the NSF.

I began my independent work armed with an unusually broad set of experiences: synthesis, from simple molecules through seemingly impossible ones; kinetics, from laser flash photolysis and pulse radiolysis through stopped flow methods to sequential product isolation; electrochemistry, using cyclic voltammetry and redox-based synthesis; emission and absorption spectroscopy; and environmental sampling. Given that I had taught chemistry or math at every level: in middle school and high school; in wealthy and poor districts; in a community college; as a teaching assistant; and as a university lecturer, I felt ready to be on my own. I was anxious to begin teaching and to start my independent research career.

### Building a Research Group

I was fortunate to recruit three graduate students my first year, and then two or three in each succeeding year. Upon adding a couple postdoctoral fellows, this produced a good

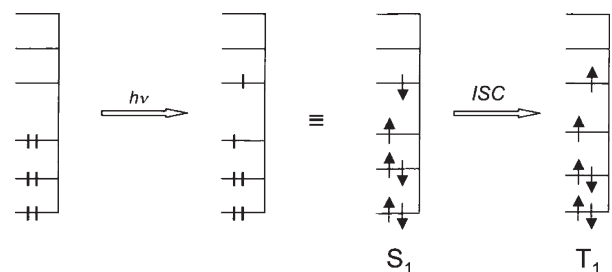


FIGURE 1. Photochemistry: activation by absorption of a photon.

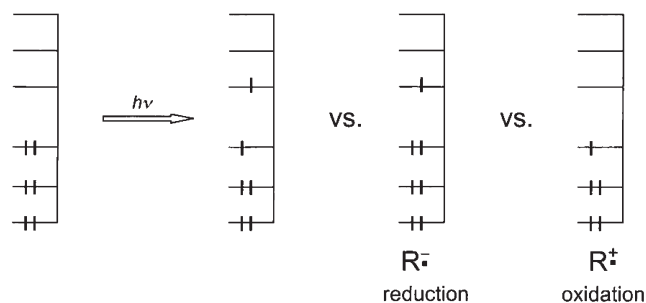


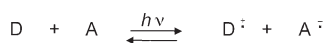
FIGURE 2. Orbital vacancies in excited states and radical ions.

size research group at steady state: small enough to avoid being unwieldy, but large enough so that someone was making good progress every week. Philosophically, I have always believed that each student should have his/her own scientific problem that may be related to general research goals, but distinct. This helped to keep morale and excitement high and encouraged cooperation, rather than competition, within the research group.

### Organic Photochemistry and Semiconductor-Mediated Photocatalysis (Late 1970s)

I began by asking my students to start on photochemical and electrochemical problems that would illustrate the relationship between photoexcitation and enhanced redox reactivity. A highly simplified representation of orbital structure in ground and excited states is shown in Figure 1. Here, absorption of a photon promotes an electron from the highest occupied molecular orbital (HOMO) of the ground state to the corresponding lowest unoccupied molecular orbital (LUMO). If the initially formed singlet undergoes a spin flip, the corresponding triplet is produced. By using flash photolysis, one could determine spectra and rate constants for the formation and decay of each of these transients or those related by electron transfer.

It is interesting to compare orbital occupancy of these excited states with the corresponding oxidized and reduced radical ions in Figure 2 that depicts one single configuration (for simplicity). Notice that the HOMO of the excited state is isoenergetic (in this highly simplified model) with that of the radical anion and that the excited state LUMO is isoenergetic, to the first order, with that of the radical cation were it not for the presence of an additional vacancy in what would have been a frontier orbital. A simple inference, then, is that excited states might react through similar pathways to those followed by singly oxidized or reduced congeners. There is, in other words, a strong connection between



- Energetics
- Separation
- Chemical Composition of Intervening Tether
- Superexchange
- Reorganization Energy
- Solvation
- Kinetics of Back Electron Transfer

**FIGURE 3.** Control elements in photoinduced electron transfer.

organic electrochemistry that produces oxidized or reduced reactive intermediates and photoexcitation that produces a comparable shuffling of filled and empty orbitals.

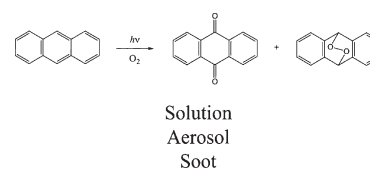
In particular, photoinduced electron transfer reactions constitute a unifying theme for many different areas of science, including that most vital of all chemical reactions, photosynthesis. As shown in Figure 3, the exchange of an electron or hole can be influenced by a large array of controlling factors, both for unbound donor D and acceptor A pairs and for those connected by a tether of varying chemical composition. This slide presents as well a unifying theme for those working in our research group and for varied collaborations cited within the four volume series we edited with Michel Chanon.<sup>10</sup>

Enveloped within this theme, our group went on to study a wide range of fascinating materials and reaction pathways. These included investigations of photogalvanic cells,<sup>11</sup> orbital topology in conjugated anions,<sup>12</sup> photochemical formation of reactive intermediates<sup>13</sup> and donor–acceptor pairs,<sup>14</sup> carbanion photolysis,<sup>15</sup> theoretical studies of photochemical electron ejection,<sup>16</sup> redox photochromism,<sup>17</sup> and dye sensitization of electrodes via charge injection.<sup>18</sup> I am quite pleased to see these topics, which we studied in the late 1970s into the early 1980s, are again being studied widely as relevant to devising practical sources of alternative energy.

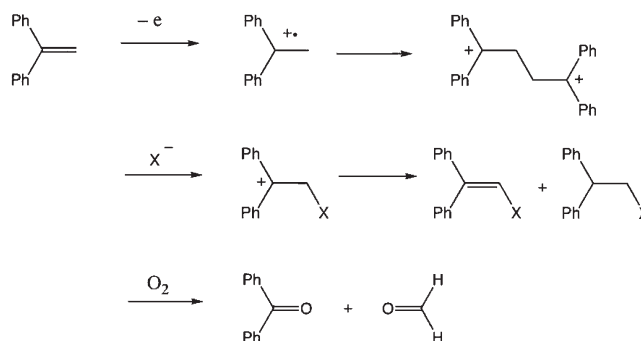
### Photochemistry in Nonhomogeneous Environments (Early 1980s)

We became particularly interested in photoinduced electron transfers that took place across interfaces, specifically on a solid electrode surface in contact with a gaseous stream or a liquid solution containing an oxidizable substrate.<sup>19</sup> The idea focused on interfacial transfer of electrons and holes achieving long-lived charge separation. If the reverse electron transfer to re-form the ground state were suppressed, these oxidized and reduced radical anions (or chemical intermediates derived from them) could be physically separated by migrating along the well-defined surface. By controlling the nature of the surface, it became possible thereby to control predictable redox chemistry.<sup>19</sup>

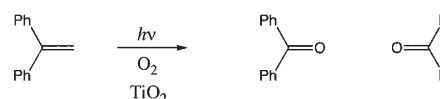
We already knew that yields of competing oxidation products varied radically, depending on whether the photo-reactions were to take place in solution, in the gas phase, or as an adsorbate on soot or an oxide aerosol (Figure 4).<sup>6</sup> One can further show that shifts in the ratio of observed products mirror that which takes place upon electrochemical oxidation if the local environment is modified (Figure 5). Thus, oxidative trapping of the singly oxidized intermediate from the electrochemical oxidation of 1,1-diphenylethylene on an inert metal electrode gives mixtures dominated by dimer if the reaction is conducted as a highly concentrated electrolyte solution, chloride adduct if a salt electrolyte is employed, and



**FIGURE 4.** Surface alteration of excited states partitioning.



**FIGURE 5.** Local environmental control of chemical oxidation pathway.



**FIGURE 6.** Photocatalytic oxidative cleavage.

an oxidative cleavage product if the solution is aerated. The product mixture is as expected for a radical cation that migrates to the electrochemical double layer, where it is chemically trapped.

A much cleaner reaction ensues if the same substrate is oxidized as an acetonitrile solution in contact with  $\text{TiO}_2$  particles suspended in the same solution (Figure 6). I can still remember how excited the group was when we first saw evidence that photocatalytic oxidative cleavage of diphenylethylene to benzophenone was quantitative,<sup>20</sup> and that the quantum efficiency of the cleavage could be improved by attaching cation-stabilizing groups at the para-position of either ring.<sup>21</sup> Flash photolysis of such a suspension shows independent verification of surface-bound cation radicals as key intermediates.<sup>22</sup> We were thrilled to demonstrate that we could use standard tools, and newly invented ones, to define reaction mechanisms on irradiated surfaces. This was an ultimate “green” reaction, using ambient air as the source of oxygen and simply filtering the product away from a catalyst that could be reused many times!

It is now well-understood that the mechanism of this conversion is as outlined in Figure 7. Thus, band gap irradiation produces a surface-accessible valence band hole and a conduction band electron, either of which, or both, can be trapped by interfacial charge transfer to or from an adsorbate of interest. Trapping of the photoinduced electron–hole pair determines the quantum efficiency of this photocatalytic step. The adsorbed intermediate is then trapped by adsorbed  $\text{O}_2$ . The resulting intermediate closes to a dioxetane cation radical, reductive cleavage of which is driven energetically by the formation of two carbonyl groups.

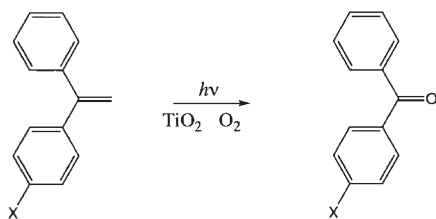


FIGURE 7. Mechanism of photocatalytic oxidative cleavage.

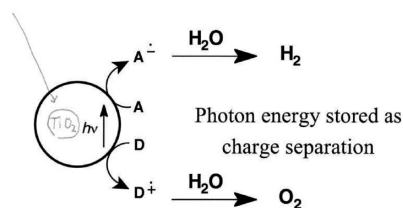


FIGURE 8. Charge separation on an illuminated semiconductor surface.

Restoration of charge neutrality takes the semiconductor back to its original structure, ready for another cycle. Indeed, product formation has taken place in such systems without any loss of metal oxide catalyst. In water, charge trapping is accomplished mostly via a surface-bound hydroxyl radical, a species of very high nondiscriminate reactivity.

This process requires continuing photoexcitation at a wavelength greater than the semiconductor band gap, and the surface-controlled reaction can properly be defined as photocatalytic. When the semiconductor particle is  $\text{TiO}_2$  (or any other wide band gap semiconductor) and the coadsorbates are oxygen and the oxidizable reactant, the surface-bound hole is sufficiently energetic to oxidize virtually any organic molecule that bears either a heteroatom or any conjugation. This method for controlled oxidation is often called organic photocatalysis or organic photoelectrochemistry, a central theme of much of our experimental work. Our most prolific work has involved the definition of other controlling factors that affect parallel reactions of a range of organic substrates.

This work is also closely aligned with photocatalytic water splitting, shown in Figure 8, and with continued oxidation to achieve full mineralization of pollutants and other waste products. The former has been extensively investigated as one of the “Holy Grails” of photocatalysis,<sup>23</sup> and the latter is the basis for a number of technologically important products, e.g., self-cleaning windows, antibacterial hospital wall coatings, and containment of oil spills, among others.<sup>24</sup> A third approach, first employed successfully by Graetzel and his co-workers, uses adsorbed dyes on mesoscopic metal oxide supports to sensitize redox transformations,<sup>25</sup> with high photon-to-current efficiency.

Photochemical water splitting is more complex than the diphenylethylene oxidation shown above. Although both reactions start in the same way through formation of an electron–hole pair, energetic factors mitigate against water acting as an electron donor, and the conversion of  $\text{H}_2\text{O}$  to  $\text{O}_2$  is a four-electron process. The semiconductor surface cannot efficiently assemble four holes at a given irradiation site. Moreover, desorption of hydrogen and oxygen gases requires specific metallic catalysts that lack a sufficiently high turnover number to justify their high cost.<sup>37</sup>

Many oxidative transformations have been accomplished on irradiated suspensions of  $\text{TiO}_2$ ,<sup>24a</sup> the least expensive and most stable of large band gap metal oxide semiconductors. The throughput required for  $\text{TiO}_2$ -mediated destruction of toxic materials and of organic pollutants, however, is very high. Development of methods for practical environmental detoxification will necessitate the full attention of talented engineers in order to improve quantum yields for a fluidized bed requiring ultraviolet irradiation.<sup>24b</sup>

Dye-sensitized mesoscopic solar cells<sup>25</sup> that aim to produce photocurrent are much improved over attempts at photosensitization several decades ago when low surface area supports were investigated.<sup>17,18</sup> They still require better absorptive overlap in the region of the incident solar spectrum, as well as improved stability of the dyes and supports for practical long-term photosensitization.

### The Difficult Challenge of Balancing Career and Marriage

This work began drawing national and international attention, and I began being invited to give many departmental seminars both in the U.S. and abroad. And I also started being invited to many national and international conferences, often as a plenary speaker. Such meetings, in turn, led to a variety of fascinating international collaborations, which demanded even further time away from home.

At one point in the mid-eighties, so as to reserve time for my children, I was booking three to four years in advance for visiting lectures. Once in Switzerland, a session chairman made a mistake, calling me to the podium instead of Jean-Marie Lehn, as scheduled. When I started by saying that I was not Professor Lehn, Jean-Marie jokingly called from the audience that I could deliver his talk as well as he.

All of this was taking place with a husband and three children in Austin, none of whom could travel with me, with John having a thriving medical practice and the boys needing to be in school. One day when I returned to resume teaching, it became obvious that John Fox and I had grown apart irreconcilably. Having both agreed that the boys came first, I bought a house just three blocks from his so our children could still have a mother and father, an arrangement that, judging from their own professional and private successes, worked acceptably well. I also promised not to move away from Texas until the youngest son, Matthew, finished high school in Austin.

Having amicably settled into this new arrangement, I threw myself even more intensively into my work and to time spent with my three sons.

### Platforms for Long-Range Electron Transfer (Mid–Late 1990s)

This continued focus on work led our research group to explore a much wider range of systems dependent on photo-induced electron transfer. In order to understand more fully the factors that govern photocatalysis on irradiated semiconductor surfaces, we designed new systems that covalently bind an emissive substrate, a donor, or an acceptor at a solid metal interface.

The simplest systems are those in which an end-functionalized alkane is introduced as a self-assembled monolayer on a planar metal surface.<sup>26</sup> The tight packing attained in these thin films will minimize conformational irregularities and will fix the distance between the metallic support and the

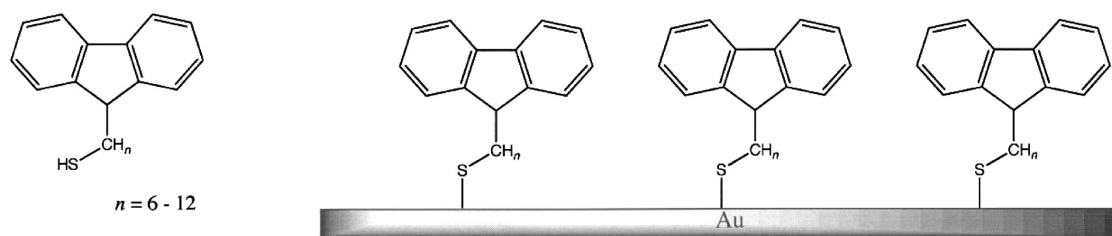


FIGURE 9. Tight packing in an arene-terminated self-assembled monolayer.

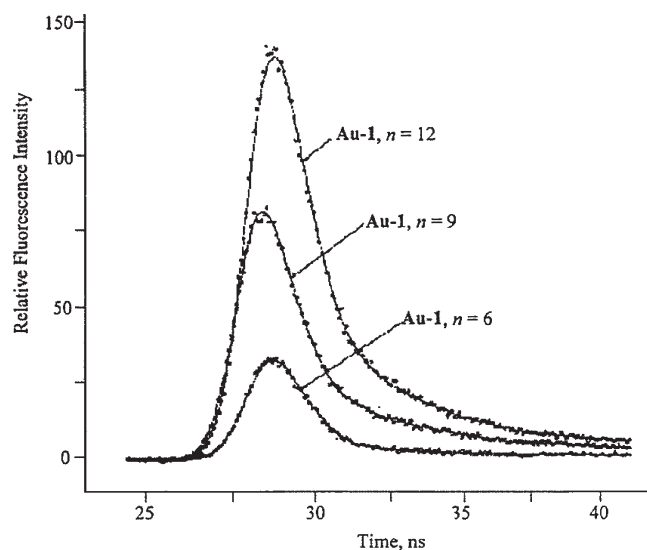


FIGURE 10. Chain-length-dependent emission in an arene-terminated thin film on gold.

emissive arene for each chain length. Shown in Figure 9 are a series of substituted fluorenes, differing only in the length of the alkyl sulfide that binds the emissive arene to freshly deposited gold films.<sup>27</sup>

The corresponding emission intensities for each member of the series, when bound to gold through a gold–sulfur linkage, are observed to increase upon increasing the length of the intervening hydrocarbon linkage (Figure 10). The weaker emission correlates with a shortened lifetime attained by enhanced through-bond quenching by the gold support. This through-bond coupling includes contributions from higher energy states, thus providing a superexchange mechanism. The larger the number of weakly coupling states, the slower will be the rate of distance-dependent through-bond excited state quenching.

Donor/acceptor pairs coupled via through-bond interactions should also depend on the chemical composition of the tether and on the magnitude of the chain dipole (Figure 3). Peptides and nucleic acid represent two such families of biological interest, and saturated and unsaturated hydrocarbons represent another, with profound implications for material science and coatings.

A simplified example of a peptide-connected donor–acceptor pair is shown as Figure 11. Here, a polyaniline chain of up to four units proved to be sufficiently soluble in convenient solvent to be N-capped by a 2-naphthylcarboxamido group and C-capped by a 1-aminobiphenyl group. The naphthyl group can then act as an electron acceptor and the biphenyl as an electron donor, as Closs and Miller have

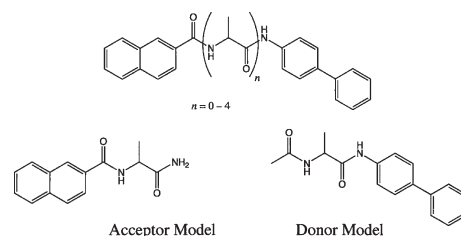


FIGURE 11. Peptide scaffolds between donors and acceptors.

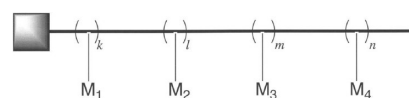


FIGURE 12. Gradients for directional electron or energy transfer.

elegantly shown for the analogous species dissolved in glasses or homogeneous solution.<sup>28</sup>

The scientific question we wished to address is whether a simple polypeptide chain wrapped to a rigid helical conformation with an associated macroscopic dipole moment (from the C- to the N-terminus) can affect the rates of forward and back electron transfer.<sup>29</sup> Unfortunately, our first attempt with the polyaniline system shown in Figure 11 failed to yield the desired helical conformation because of limited solubility during synthesis. If the alanine unit is replaced by aibn (an  $\alpha$ -methylated alanine), the solubility problem becomes moot and a [3,10] helical conformation is attained with donor/acceptor pairs capping both ends.<sup>30</sup>

With a chain of at least six (aibn)s, photoinduced electron transfer rates established by flash photolysis, with and against the dipole, are differentiated by more than an order of magnitude, depending on solvent. Both forward and reverse electron transfer are so affected.<sup>31</sup> Thus, the chemical composition of the intervening scaffold and environmental control is a highly significant design feature for electron-transfer-induced reactivity. This work required expertise in multiple subareas, and I found a perfect expert collaborator at the other end of the corridor in Welch Hall at UT-Austin. Jim Whitesell is a chemist whose creativity has long been insufficiently appreciated by the chemistry community, in my opinion. A short list of areas for which he provided early seminal contributions include total synthesis,<sup>32</sup> demonstration of asymmetric induction with a C<sub>2</sub> chiral ligand,<sup>33</sup> long-range orientation of peptides on surfaces<sup>34</sup> with profound implications for nonlinear optics,<sup>35</sup> chiral structural analysis by <sup>13</sup>C NMR,<sup>36</sup> kinetics of homo-chiral and heterochiral polymerization,<sup>37</sup> first principles of crystal engineering,<sup>38</sup> and the NEER Principle (nonequilibration of excited state rotamers).<sup>39</sup>

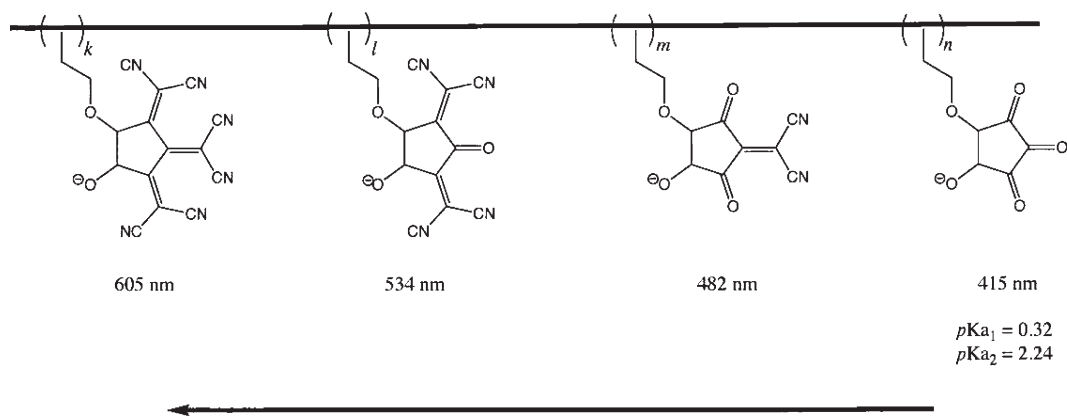


FIGURE 13. Vectorial energy transfer: a requirement for artificial light harvesting.

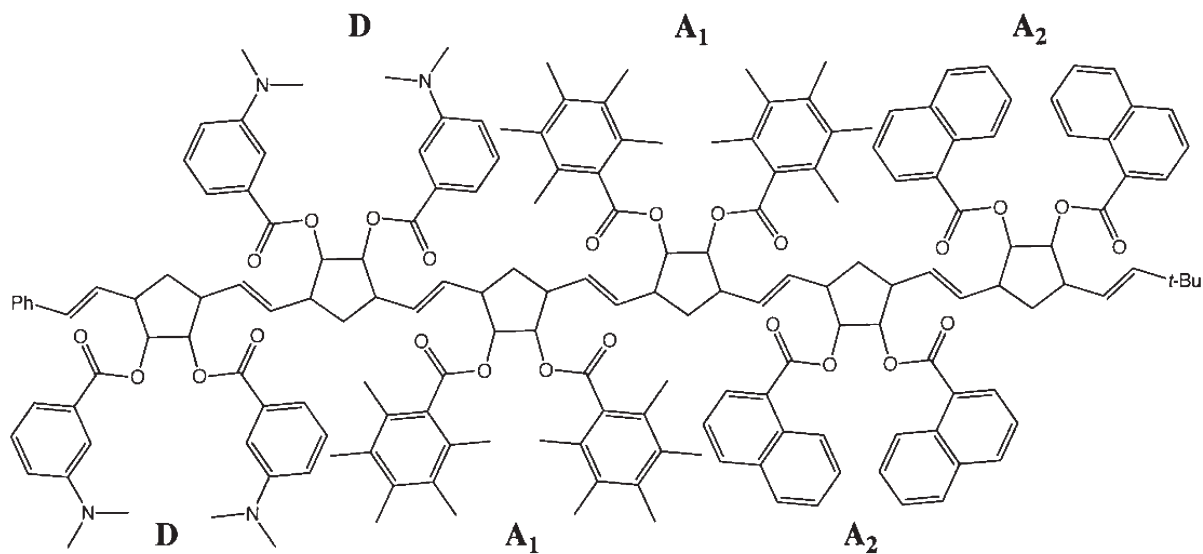


FIGURE 14. Polymeric triblock directional system.

With such a background, he seemed to be an ideal collaborator for the research directions we wished to pursue and an ideal co-author for the organic text I had long wanted to write. This turned out to be correct, and 20 years later, we look back on over 30 papers published together. We married in 1990, making me the eighth member of my research group to have married a fellow chemist.

Jim has two sons; I have three. I can still hear my friends Mary and Michael Dewar admonishing us, as we considered getting married—"Five, Marye Anne! Count them!" We married (and collaborated) anyway.

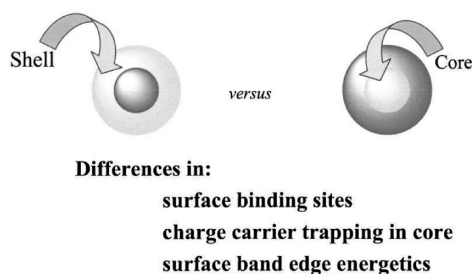
#### Multistep Vectorial Energy and Electron Transfer (Mid 1990s)

As we continued our work on photocatalysis, we realized the need to incorporate the control elements of Figure 3 into our designed integrated systems. We formed a group sponsored by the Gas Research Institute to explore such arrays. (It also provided a vehicle to work more closely with Allen Bard, whom I regard as a creative genius.) We chose to address how variable energy differences could influence the observed rates of forward and back electron transfer. We then sought to design arrays that could facilitate multiple hops directed along an energetic gradient.

We began by addressing the challenge of fully exploiting electron transfer while suppressing back electron transfer (charge recombination) in multicomponent systems. The initially formed charge-separated pair, however, can resist charge recombination if a second charge trap is placed adjacent to the first. The concept is illustrated in Figure 12, where  $M_x$  refers to a set of substrates similar in structure, but differing in singlet or triplet energy or redox potential. If the components can be arranged so as to develop an optical or redox gradient, additive effects can be attained in dyads, triads, tetrads, etc.<sup>40</sup> And by blocking back electron transfer in the photogenerated radical ion pair, the efficiency of light harvesting can be improved.<sup>41</sup> Understanding these optical effects became a goal, with direct relevance to accurate descriptions of biomimetic arrays. This was particularly important if the goal is to devise systems that resemble photosynthesis or other light-sensitive biological arrays.

Consider the specific example shown in Figure 13, in which a family of croconate anions are modified by one, two, or three condensations to produce the corresponding dicyanoethylene condensation products.<sup>42</sup> The transition energies are red-shifted along the series, as shown in the shifts of the absorption maxima as wavelengths listed below each structure in Figure 13.





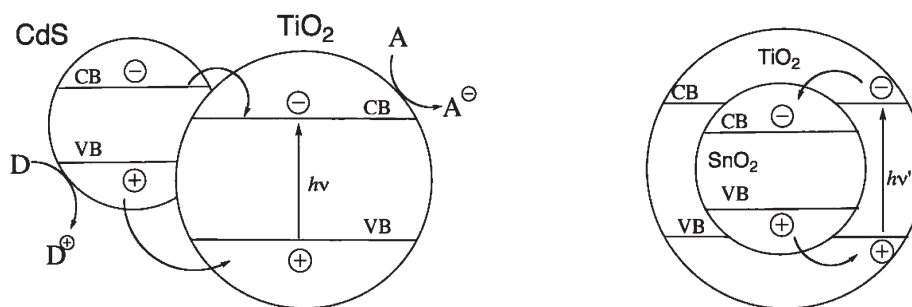
**FIGURE 15.** Surface differentiation in shell–core clusters.

If these dyes are attached as polymer blocks rigidly positioned in the correct energetic order by sequential introduction of monomer during the synthetic polymerization, vectorial energy transfer will become possible. When random energy walks within a block are accompanied by migration across each of the block polymer interfaces, energy (or electrochemical potential) will funnel to the lowest level position along the polymer chain. This sequence is then repeated for each chromophore pair until the lowest energy excited state is populated. That is, photoexcitation at any absorbed wavelength will initiate directional, thermodynamically controlled, energy transfer on either the singlet or triplet excited state manifold, with energy and electron transfer proceeding from the higher energy excited state donor to the lower lying acceptor.

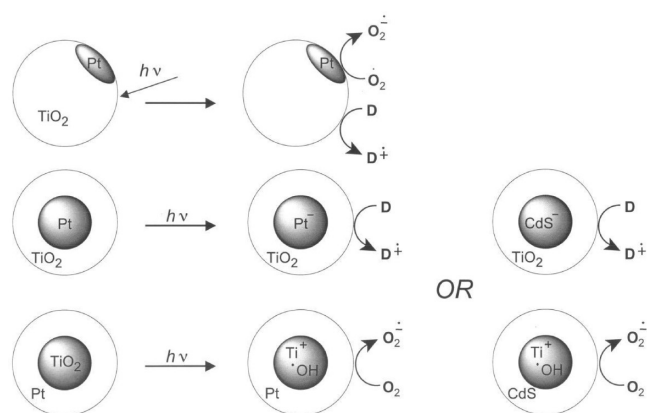
Irrespective of the excitation wavelength or the spatial constraints of the position of the incident light, the imposed energy gradient will permit energy transfer to proceed only in one direction, i.e., from the right to the left as shown. If the ends of the polymer can be distinguished, for example, by anchoring one end to a metal electrode surface, charge containment effects can be optimized (Figure 13).

Macroscopic directionality, parallel to that achieved by this solution phase method, is achieved by sequential polymer growth from a solid surface. By introducing singly labeled monomers in proper sequence to a living polymer chain, an ordered polymer can be attained, as in Figure 14. This approach thus produces energetically ordered polymeric thin films arranged by increasing or decreasing wavelength maxima, or by increasing or decreasing redox potential. By switching the order of addition of monomer, a gradient to or from the poised electrode can be attained.<sup>43</sup>

The resulting coated electrode is an interesting component for the integrated systems likely to be needed for next-generation solar cells, i.e., energy ordered thin layers on metal electrodes. These polymeric arrays in which either



**FIGURE 16.** Multiple electron hops on composite semiconductor particles.



**FIGURE 17.** Interface geometry in isomeric catalysts.

energy or electron transfer takes place directionally are also biomimetic,<sup>44</sup> by analogy to the multichromophoric aggregates encountered within the light-harvesting units of phycobilisomes or other light concentrators<sup>45</sup> and the repeated electron hops induced by photoexcitation of the membrane-bound special pair of substituted porphyrins within the reaction center in bacterial photosynthesis.<sup>46</sup>

Light harvesting on purely synthetic arrays, achieved through multichromophoric excitation and followed by multiple nonrandom hops toward an ultimate target, is therefore a fundamental area ripe for further investigation. By employing monomers bound to  $\pi$ -stacked metalated porphyrins,<sup>47</sup> polycyclic arenes, substituted benzenes, and substituted anilines,<sup>43</sup> our group has reduced this concept to practice (see Figure 14).<sup>48</sup> These studies are relevant not only to biology<sup>49</sup> but also to materials chemistry, e.g., for such areas as field-effect transistors, wires, photodiodes, and flexible plastic conductors.<sup>50</sup> These studies illustrate the possibility of developing linear and planar electron transfers, i.e., one- and two-dimensional, respectively.

#### Shell–Core Clusters (Mid-to-Late 1990s)

Inherently, the ordered systems discussed above were designed as electron donor/acceptor pairs with different degrees of conformational freedom. Thus, two general local environments were explored: (1) homogeneous solutions or (2) thin films either physisorbed to semiconductor surfaces or chemically bound to a planar face of a metallic crystal. A third option is to examine the properties of nanomaterials entirely coated by another of different chemical composition, shown in Figure 15 as shell–core clusters.

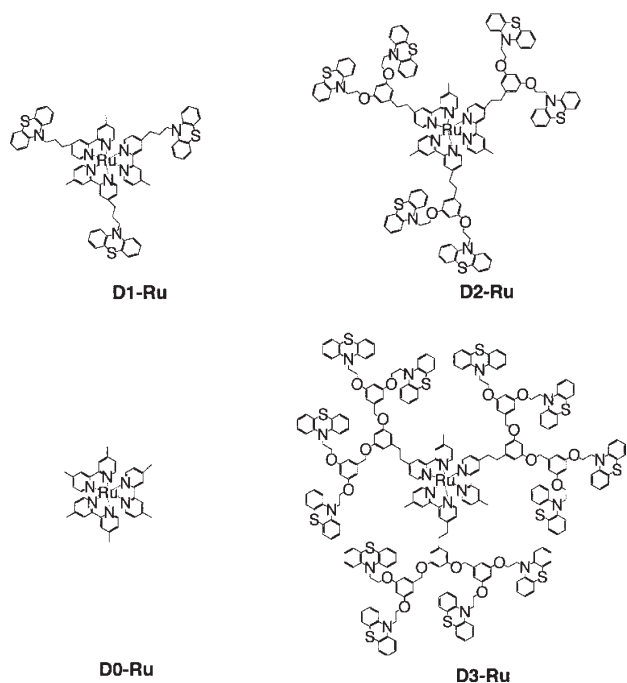


FIGURE 18. Four generations of ruthenium core dendrimers.

The particles may have identical overall chemical composition, but quite different exposure to reagents present in a contacting solution. The composition of such coated particles may be purely organic but with components of variable polarity and hydrophilicity/hydrophobicity, organic–inorganic composites, or purely inorganic materials with different crystal lattice packings. Physical properties also differ as a function of surface binding, carrier trapping within the core, and Fermi level pinning of band edges.<sup>51</sup>

Semiconductor shell–core composites function by interfacial electron transfer analogous to photocatalytic production of an electron–hole pair (Figure 8) or the multiple electron hops intrinsic to photochemical vectorial transfer in light harvesting (Figure 13). Thus, the coated particles shown in Figure 16 have the additional experimental parameter of selective excitation of one semiconductor in the presence of another (CdS on the left structure or TiO<sub>2</sub> on the right structure) and the option for multiple hops to surface sites for a desired reaction.<sup>52</sup>

Similarly, controlled catalysis results from deposition of key gas-evolving catalysts at the site where interface geometry, as would be helpful in pursuing water splitting or other chemical storage options derived from solar energy conversion (Figure 17). Indeed, many recent advances have relied on multiple electron hops for efficient chemical conversions.<sup>53</sup>

### Energy and Electron Migration in Photoresponsive Dendrimers (Early 2000s)

Structural complexity associated with shell–core clusters is also encountered within families of dendrimers. Like the shell–core clusters, succeeding generations of dendrimers provide a core reagent bound to branched coupling compounds. Shown in Figure 18 are four generations of dendrimers based on Ru(bpy)<sub>3</sub>, an inorganic compound employed effectively in inorganic solar energy conversion, modified by attachment at the periphery of multiple dye units (here, phenothiazine<sup>54</sup>). Recent advances in synthesis<sup>55</sup> have made access to these and analogous materials readily available to synthetic chemists, and hence they constitute an expanded class of compounds of interest to photochemists.<sup>56</sup>

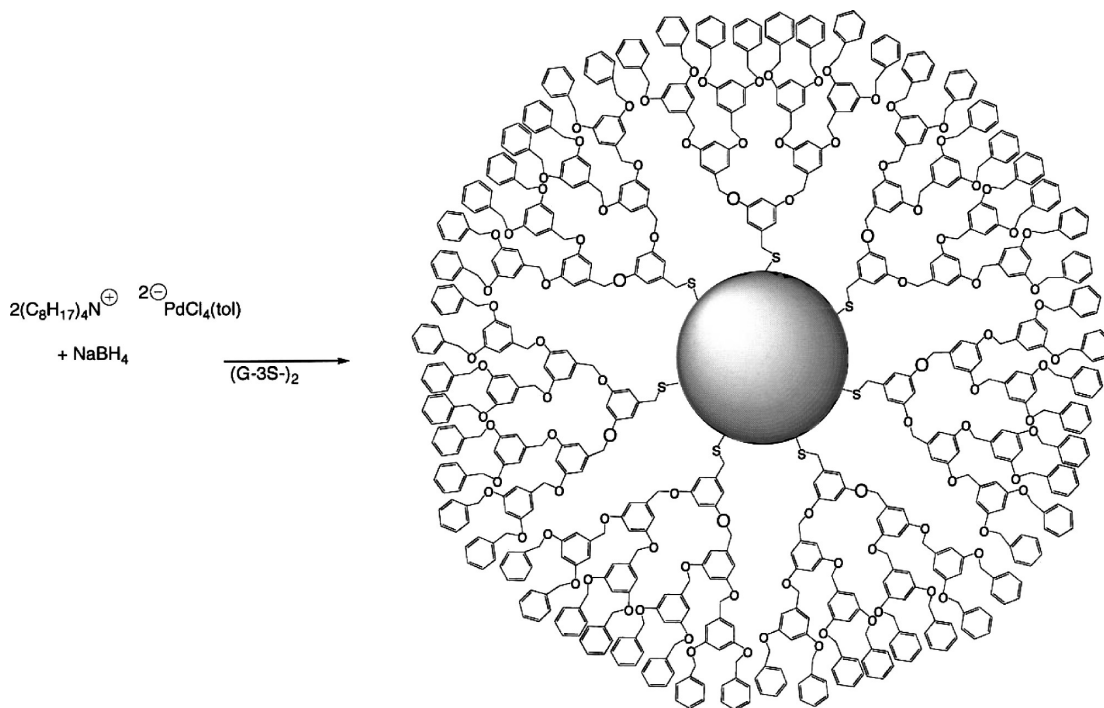


FIGURE 19. Controlled catalysis by dendrimeric coating of a palladium nanocluster.

It is important to recognize, as was the case with adsorbates moving on and off the surface of a illuminated semiconductor surface, that coating of particles with dendrimeric segments can also provide a method to control access to catalytically active metal clusters. For a palladium particle capped by a dendrimer to monolayer coverage (Figure 19), reagent motion to and from the surface of the catalyst is possible through the illustrated pores. In both the Heck reaction and the Suzuki reaction, chemical yields are higher with the dendrimeric coated cluster than with the bare metal itself. The functionalized catalyst also exhibited improved turnover number and turnover frequency, while inhibiting precipitation of the expensive platinum catalyst.<sup>57</sup>

### Transition to Management/Administration (1990s to 2000s)

My current appointment at UC San Diego is as Chancellor and Distinguished Professor. My time commitment to the Chancellor's Office is substantial, and I am only able to remain active in research because my colleague (and husband) Jim Whitesell has been willing to provide assistance and frequent oversight to the postdoctoral fellows who work on the scientific problems outlined above.

It is not surprising therefore that people often ask me why I moved away from full-time research when the research was going so well and was so personally rewarding. They also frequently ask me to tell how such a shift took place.

Recall that one of the major reasons I chose to join the faculty in Austin was to interact with several world-class scientists. I had indeed had the chance to co-teach Advanced Electrochemistry with Al Bard, Advanced Molecular Orbital Theory with Michael Dewar, and a freshman seminar with Norman Hackerman. In all cases, I learned far more science than I contributed.

I am grateful that I learned nuances about science policy from the best—Frank Rhodes, president emeritus of Cornell; Jim Duderstadt, president emeritus of the University of Michigan; Neal Lane, then director of the National Science Foundation; Dick Atkinson, president emeritus of the University of California; and most of all, Norman Hackerman, president emeritus of Rice and the University of Texas. They showed me practical means for supporting science and emphasized the importance of public understanding of science. I remember them fondly as great friends.

Even while I was still untenured, Norm Hackerman arranged for me to be nominated to serve on a Commission on Physical Science, Mathematics, and Applications at the National Academy of Sciences. At the Academy, I later served on the Council and on the Governing Board and I chaired such divergent groups as the Government—University—Industry Research Roundtable, a study on the use of taggants in explosives in response to the Oklahoma City bomb, cyber-infrastructure, methods to encourage women and minorities to pursue science and mathematics, and a study on evaluating the quality of undergraduate science teaching, all while working with world experts.



Signing the members' book, National Academy of Sciences, with Secretary Peter Raven, Washington, DC.

Soon thereafter, I was honored to be appointed to the Waggoner Regents Chair in Chemistry at Texas. Possibly because there were so few women recognized at that level at that time, I was quickly asked to serve during the next two decades on an advisory panel for almost every federal agency that supported scientific research.

A successful term in those positions led to an appointment to the National Science Board, after Senate confirmation, where I was privileged to chair Programs and Plans and then later to serve as Vice Chair. I learned a great deal about the infrastructure for national and international science, as well as the investment required for quality K-12 science education. I was pleased to make the case for the need for investment in the social sciences, and I was asked frequently to testify to Congress on the importance of enhanced funding at NSF. My term on the NSB overlapped with Al Cotton's, and I was fortunate indeed to be the recipient of his candid advice, mentoring, and friendship, which I consider to be among the most valuable of my career. His style may have been gruff, but in Cotton, I found a man with a soft heart who truly cared deeply about science, his students, and the value of education. My term also overlapped with Dick Zare's, who always provided creative ways of looking at challenges: one cannot but learn a lot from him.



Swearing in at National Science Board with Mary Good, Chair.



Inaugural Cotton Medal Symposium, College Station, Texas, with John Fackler and Al Cotton.



Testifying at House Science Committee with Representative Bob Ethridge (D-NC).

In parallel in Austin, I had become the Director of the Center for Fast Kinetics Research, a facility that my research group used extensively. I was also being pressured to become department chair, which I steadfastly refused. But when Robert Berdahl became President and announced he would appoint a Vice President for Research, I became more interested in an administrative position. When he promised that I could continue my research quarter time and would have wide freedom in building some exciting new institutes and improving technology transfer procedures, I decided to accept. This was in spite of never having been a department chair, dean, or provost. Norman Hackerman advised me strongly NOT to close my laboratory, as an administrator's credibility with the faculty rests in being able to remain aligned with academic values and to maintain one's scholarly interests. Absolutely excellent advice, especially if you can identify a willing and able collaborator.

My background came from DC experience and from the management skills I gained by serving on several corporate board. My interest in administration is parallel to what drove me in Chemistry: the urge to build, whether molecules or institutions.

While I served as Vice President for Research at UT-Austin, I was able to reconstruct research finance so that indirect costs were returned to the college level. I also headed an initiative (Project DISC) to examine information technology as a tool for achieving the academic mission, including online instruction, and as a platform for new interdisciplinary degrees, e.g., Ph.D. in digital finance and a M.S. in commercialization of technology. We were pleased as well to form an important Research liaison with the new Sematech and to support the creation of several industrial affiliate programs.

George W. Bush was then Governor of Texas, and it was natural that he should consult the UT vice president for research about science and mathematics, for K-12 education and how science affects emerging industries, especially computer technologies and biotechnology. I was pleased to serve on his Texas advisory board, where he was always interested in data-driven decisions.

When Bush became president, he nominated me, with concurrence of the Senate, to the President's Council of Advisors on Science and Technology (PCAST), where I chaired a study on broadband infrastructure, which I am told was used extensively within the administration. Not all topics so examined by PCAST were comparably treated, as the President's focus seemed to narrow to the execution of the wars and the prevention of world terrorism.

Although I loved my job at UT, other opportunities began to present themselves. For example, opportunities for commercialization of university intellectual property were quite limited in Texas at that time. Given the chance to promote commercialization of university intellectual property by developing 1000 green-field acres at North Carolina State University, I jumped into the role of Chancellor. In my six-year stay, the Centennial Campus supported 62 start-ups, founded a technology-based magnet middle school, and constructed a training facility for those seeking to enter the biotechnology market. The quality of life improved through major upgrades of athletics facilities, including an on-campus golf course, several academic buildings, and an Alumni center. The Trustees graciously named the Fox Undergraduate Science Laboratory in recognition of this work.

And who can resist the lure of UC San Diego, where in five years we have constructed 2 M square feet of assignable space with a value of \$1.6 B, completed a \$1 B Capital Campaign, and provided a home to a new Nobel Laureate (Roger Tsien) who wanted only a 24 h parking spot as his "reward"?

After 17 years in senior administration (five years as Vice President for Research at Texas, six years as Chancellor at North Carolina State University, and going into my sixth year a Chancellor at the University of California San Diego), it is a decision I have only infrequently regretted. At the same time, I have tried hard to support actively the students and postdocs who work at the bench to provide new chemical data and insight, sometimes a difficult task, made possible only by the Whitesell collaboration.

### Concluding Remarks

My professional life has been a celebration of several areas of physical organic chemistry, which I believe has transcended its traditional boundaries to be required for advancement of biological and materials chemistry,<sup>57</sup> specifically by building on fundamentals of nanoscience<sup>58</sup> and photoinduced electron transfer.<sup>59</sup> It has provided me with an intellectually stimulating environment that would have been possible only with the collaboration of an exceedingly talented group of over 150 individuals. I'm proud, indeed, that so many of my co-workers have themselves had productive careers in physical organic chemistry, broadly conceived. Together they taught me more than I deemed possible.

I am particularly pleased, on behalf of those with whom I have worked closely over the years, that the American Chemical Society has acknowledged our integrated contributions to chemistry and science policy in selecting me in 2004 to receive the 2005 Charles Lathrop Parsons Award (for outstanding public service).

I'm also grateful for financial support from a long list of granting agencies, especially the National Science Foundation and the Office of Basic Energy Science at the Department of Energy. And I also appreciate the opportunity to serve/have served on Committees of the American Chemical Society and on the governing or advisory boards of the Robert A. Welch Foundation, the Camille and Henry Dreyfus Foundation, the Burroughs-Welcome Foundation, and the Gordon Research Conferences.

Finally, I acknowledge the generous tolerance of my family, with whom we've achieved a workable balance between time spent on science and with Jim, our sons, and grandchildren. Without their good spirit, Jim and I would be successful in neither lab nor home.

### References

- (1) Kresge, A. J.; Chen, H. L.; Chiang, Y.; Fox, M. A.; Sagatys, D. S.; Murrill, E. *J. Am. Chem. Soc.* **1971**, *93*, 413.
- (2) Fox, M. A.; Binkley, R. W. *Tetrahedron Lett.* **1970**, 5257.
- (3) Fox, M. A.; Nichols, W. C.; Lemal, D. M. *J. Am. Chem. Soc.* **1973**, *95*, 8164.
- (4) Fox, M. A.; Lemal, D. M.; Johnson, D. W.; Hohman, J. R. *J. Org. Chem.* **1982**, *47*, 398.
- (5) Fox, M. A.; Staley, S. W. *Anal. Chem.* **1976**, *48*, 992.
- (6) Fox, M. A.; Olive, S. *Science* **1979**, *205*, 582.
- (7) For example, see: (a) Staley, S. W.; Fox, M. A.; Hirzel, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3910. (b) Staley, S. W.; Fox, M. A.; Cairncross, A. *J. Am. Chem. Soc.* **1977**, *99*, 4524. (c) Staley, S. W.; Linkowski, G. E.; Fox, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4818.
- (8) Fox, M. A. *Chem. Rev.* **1979**, *79*, 253.
- (9) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
- (10) (a) Fox, M. A.; Chanon, M., Eds. *Photoinduced Electron Transfer*; Elsevier: Amsterdam, 1988; Vols. I–IV. (b) Fox, M. A. *Chem. Rev.* **1992**, *92*, 365.
- (11) Fox, M. A.; Kabir-ud-Din. *J. Phys. Chem.* **1979**, *83*, 1800.
- (12) Fox, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 4008.
- (13) Fox, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 5339.
- (14) Fox, M. A.; Singletary, N. J. *Tetrahedron Lett.* **1979**, 2189.
- (15) (a) Fox, M. A.; Singletary, N. J. *Solar Energy* **1980**, *25*, 229. (b) Fox, M. A.; Singletary, N. J. *J. Org. Chem.* **1982**, *47*, 3412.
- (16) Fox, M. A.; Dewar, M. J. S.; Nelson, D. J. *J. Organomet. Chem.* **1980**, *185*, 157.
- (17) Fox, M. A.; Voynick, T. A. *J. Org. Chem.* **1981**, *46*, 1235.
- (18) (a) Fox, M. A.; Nobs, F. J.; Voynick, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 4029. (b) Fox, M. A.; Nobs, F. J.; Voynick, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 4036.
- (19) Fox, M. A. *Acc. Chem. Res.* **1983**, *16*, 314.
- (20) Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 6757.
- (21) Fox, M. A.; Chen, C. C. *Tetrahedron Lett.* **1983**, *24*, 547.
- (22) Fox, M. A.; Lindig, B. A.; Chen, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 5828.
- (23) (a) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, *28*, 141. (b) Rajeshwar, K. *J. Appl. Electrochem.* **2007**, *37*, 765.
- (24) (a) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341. (b) Fox, M. A. *Chemtech* **1992**, *11*, 680. (c) Frank, N. S.; Bard, A. J. *J. Phys. Chem.* **1977**, *81*, 1481. (d) Fujishima, A.; Rao, T. N.; Tryk, D. A. *J. Phys. Chem. C* **2000**, *1*, 1.
- (25) (a) O'Regan, B.; Graetzel, M. *Nature* **1991**, *355*, 737. (b) Graetzel, M. *Nature* **2001**, *414*, 338. (c) Hagfeldt, A.; Graetzel, M. *Chem. Rev.* **1995**, *95*, 49.
- (26) (a) Bain, C. D.; Whitesides, G. M. *Science* **1988**, *240*, 62. (b) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Anstutz, A. *Science* **1997**, *276*, 384.
- (27) (a) Kittredge, K. W.; Fox, M. A.; Whitesell, J. K. *J. Phys. Chem. B* **2001**, *105*, 10594. (b) Fox, M. A.; Wooten, M. D. *Langmuir* **1997**, *13*, 7099. (c) Fox, M. A.; Kittredge, K. W. *Langmuir* **1998**, *14*, 816.
- (28) Dance, Z. E. X.; Ahrens, M. J.; Vega, A. M.; Ricks, A. B.; McCamant, D. W.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 830.
- (29) (a) Knorr, A.; Galoppini, E.; Fox, M. A. *J. Phys. Org. Chem.* **1997**, *10*, 475. (b) Batchelder, T. L.; Fox, R. J., III; Meier, M. S.; Fox, M. A. *J. Org. Chem.* **1996**, *61*, 4206.
- (30) (a) Meier, M. S.; Fox, M. A.; Miller, J. R. *J. Org. Chem.* **1991**, *56*, 5360. (b) Fox, M. A. *J. Peptide Sci.* **2002**, *8*, L-18.
- (31) Fox, M. A.; Gallopini, E. *J. Am. Chem. Soc.* **1997**, *119*, 5277.
- (32) Whitesell, J. K.; Minton, M. A. *J. Am. Chem. Soc.* **1986**, *106*, 6802.
- (33) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
- (34) Whitesell, J. K.; Chang, H. K. *Science* **1993**, *261*, 73.
- (35) Whitesell, J. K.; Chang, H. K. *Angew. Chem.* **1994**, *33*, 871.
- (36) Whitesell, J. K.; Lacour, T.; Lovell, R. L.; Pojman, J.; Ryan, P.; Nosaka, Y. N. *J. Am. Chem. Soc.* **1988**, *110*, 991.
- (37) Whitesell, J. K.; Pojman, J. *Chem. Mater.* **1990**, *2*, 248.
- (38) Whitesell, J. K.; Davis, R. E.; Wong, M. S.; Chang, N. L. *J. Am. Chem. Soc.* **1994**, *111*, 523.
- (39) Whitesell, J. K.; Minton, M. A.; Tran, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 1473.
- (40) For example, see: Fossum, R. D.; Fox, M. A.; Gelormini, A. M.; Pearson, A. J. *J. Phys. Chem. B* **1997**, *101*, 2526.
- (41) (a) Stewart, G. N.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354. (b) Ghaddar, T. H.; Wishart, J. F.; Kirby, J. L.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 12832.
- (42) (a) Fox, M. A.; Kamat, P. V.; Fatiadi, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 1191. (b) Fox, M. A.; Kamat, P. V. *J. Photochem.* **1984**, *24*, 284.
- (43) (a) Fossum, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 1197. (b) Watkins, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4344. (c) Watkins, D. M.; Fox, M. A. *Macromolecules* **1995**, *28*, 4939.
- (44) Gust, D.; Moore, T. A.; Moore, A. *Acc. Chem. Res.* **2001**, *34*, 40.
- (45) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (b) Kanan, M. V.; Nocera, D. G. *Science* **2005**, *307*, 397. (c) Kohi, S. W.; Weiner, L.; Konstantinovski, L.; Shimon, L. J.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74.
- (46) Eisenberg, R. *Science* **2009**, *324*, 44.
- (47) (a) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1990**, *94*, 158. (b) Jones, W. E.; Melamed, D.; Pan, H. L.; Fox, M. A. *J. Phys. Chem.* **1995**, *99*, 11523. (c) Schouten, P. G.; Warman, J. M.; Pan, H. L.; Fox, M. A. *Nature* **1991**, *353*, 476.
- (48) Fox, M. A. *Acc. Chem. Res.* **1999**, *32*, 201.
- (49) (a) Grinstaff, M. W.; Meyers, S. R. *J. Am. Chem. Soc.* **2008**, *130*, 14444–14445. (b) MacDiarmid, J. A.; Brahmabhatt, H. *Nat. Biotechnol.* **2009**, *27*, 643–651.
- (50) (a) Liscio, A.; DeLuca, G.; Nolde, F.; Palermo, V.; Muellen, K.; Samori, P. *J. Am. Chem. Soc.* **2007**, *130*, 780. (b) Peng, H. *J. Am. Chem. Soc.* **2007**, *130*, 42. (c) Yasutomi, S.; Morita, T.; Imanishi, Y.; Kimura, K. *Science* **2004**, *304*, 1944. (d) Lee, M. R.; Eckert, R. D.; Forberich, K.; Dennier, G.; Brabec, C. J.; Gaudiana, R. A. *Science* **2009**, *324*, 232. (e) LeMieux, M. C.; Roberts, M. I.; Barman, S.; Jin, Y. W.; Kim, J. M.; Bao, Z. *Science* **2008**, *321*, 101. (f) Moore, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 12201.
- (51) (a) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 14168. (b) Canepa, M.; Fox, M. A.; Whitesell, J. K. *Photochem. Photobiol.* **2003**, *2*, 1177.
- (52) Kamat, P. V. *J. Phys. Chem.* **2008**, *112*, 1021.
- (53) Brown, P.; Kamat, P. V. *J. Am. Chem. Soc.* **2008**, *130*, 8890.
- (54) (a) Stewart, G. M.; Fox, M. A. *J. Amer. Chem.* **1996**, *118*, 4354. (b) Stewart, G. M.; Fox, M. A. *Chem. Mater.* **1997**, *10*, 860.
- (55) Frechet, J. M. J. *Science* **1994**, *263*, 1710.
- (56) (a) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 6491. (b) Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. *Nano Lett.* **2003**, *3*, 1757.
- (57) Fox, M. A. *Pure Appl. Chem.* **1997**, *69*, 235.
- (58) Odom, T. W.; Pileni, M. P. *Acc. Chem. Res.* **2008**, *41*, 1565.
- (59) Fox, M. A. *Photochem. Photobiol.* **1987**, *45*, 58.