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Foreword

This special issue commemorates a special event. It provides opportunity and motivation to reflect on the changes that have occurred in photochemical science during the lifetimes of many of us. It is appropriate that we use the occasion to especially honor six people who have made enormous contributions to evolution of the field as we now know it. We need not go back to the year they were born, which was also the year that I graduated from high school, to appreciate the magnitude of the change during recent decades. That sense is well conveyed by returning to 1959, the year that Nick Turro entered Caltech as a graduate student.

At that time we were considered pioneers, real frontiersmen, because a few years earlier we, meaning Bill Baker, Bill Moore, and I, had started measuring quantum yields of photochemical reactions in solution, had thought a little about the results, and published some of our ideas. Of course, we did not discover the triplet states of organic molecules. That had been done by Mike Kasha in his graduate work with G. N. Lewis at Berkeley. A generation of physical chemists—Noyes, Steacle, Leighton, and Burton to name a few—had recognized and exploited the fact that the slow emission, called phosphorescence, of simple ketones in the vapor phase comes from triplet states. George Porter had just begun to identify some of the long-lived transients which he saw in flash photolysis of solutions as triplets.

Our working equipment was, by today's standards, incredibly primitive. However, we were one of the few (perhaps the only) "organic" laboratories in the world to have an optical bench with light-collimating lenses, solution filters, and a calibrated thermopile.

A number of labs, including ours, went to work studying the scope and mechanisms of photoreactions in solution. It was exciting to be able to speak with some confidence of the reactions of excited singlet and triplet states, what they might and might not do, and something of the kinetics of reactions and various decay paths. We could talk sagely about various quenching processes, energy transfers, $n\pi^*$ and $\pi\pi^*$ states, etc. We now know that some of our assumptions and conclusions were imperfect, but we made great progress. Those of us working with organic molecules began to realize that the voluminous work that had been accumulated by scientists developing silver halide photography contained concepts, especially photoinduced electron transfers, and had considerable relevance to our work. [Unfortunately, the suggestions which Gerald Oster had been making concerning photoinduced electron transfer had been largely ignored.]

We made tremendous progress in the 1960s, but we left many questions, some of which we had not even thought of asking, unanswered. This is not a historical piece. However, comparison of where we were then with where the science is now shows that a good deal of ground has been traversed. The many papers in this symposium give a picture of where we are today. Photochemistry is spread over the entire map of physical science. The field of life science, especially medicine, is permeated with photochemical science. The same is true of materials science.

Our capability to do things has been marvelously enhanced. Lasers had not even been invented in the early 1960s. At that time we were pleased to monitor transients produced by light absorption on the millisecond time scale. Today, a number of laboratories are working in the femtosecond domain. It is interesting that in at least some of the labs where lifetimes are routinely measured in picoseconds or less, there is no longer any equipment with which one can do millisecond kinetics. Similar evidence of change was brought to my attention a few years ago when I was working with Dick Weiss and his group at Georgetown University. We wanted to do experiments for which a nitrogen laser would have been an ideal light source. Fifteen years earlier the giant nitrogen laser was a workhorse in many laboratories doing research in spectroscopy and photochemistry. However, I could not locate one by calling all of the labs that I could think of within a 50 mile radius of Washington, DC. I suddenly realized that time and photochemistry were marching on.

I have looked especially at what the crop of *young* people turning sixty this year are doing at this time. They have traversed the ground from then to now and in doing so have been among the leaders who have moved photochemical science. After beginning at rather similar places, they have spread in different ways. There are those who have expanded themselves broadly and those who have penetrated ever more deeply in one direction. Superficial observers might see the latter as stuck in muddy ruts, yet they keep coming up with gold in the form of new science.

Peter Wagner and Jack Saltiel are two who have studied basically similar systems throughout their careers to probe ever more deeply the microphysical behavior of excited states. Wagner has used ketone photochemistry to establish time scales for intramolecular action ranging from times required for conformational adjustment of molecules to establishment of internal charge transfer interactions. He, along with Yang and Scaiano, has taught us a great deal by study of the biradicals produced by ketone undergoing the Yang (or Norrish Type II) reaction.

Saltiel began his photochemical career studying photoisomerization of the stilbenes and has never stopped. He has mapped the excited state energy surfaces for stilbenes and related compounds, and the times required to explore them, in remarkable detail by using photochemistry, spectroscopy, and shrewdly chosen structural changes. For example, his study of *cis*-1-(2-anthryl)-2-phenylethylene has allowed him to document (1) adiabatic isomerization, (2) conformer control of intramolecular electronic interactions, and (3) quantum chain processes. In a related study of the 1,6-diphenyl-1,3,5-hexatrienes, he also found a quantum chain process similar to those recently reported by Arai and Tokumaru.

Two who have chosen paths rather different from those of their photochemical peers are Liu and Neckers. Liu has worked primarily with the photochemistry of the retinoids and carotenoids, conjugated polyunsaturated, natural substances which play crucial roles in human physiological action. The materials, especially the retinoids, because of their role in vision, have been studied extensively by flash kinetic spectroscopy. Liu has chosen a unique role to amplifying our knowledge of their photochemistry. He and his co-workers have synthesized many of the geometric isomers of the natural materials and studied their spectra and photochemistry. The results have provided insight into the excited state processes in the compounds which could not have been gained by study only of the natural compounds or their readily available chemical relatives. A crowning jewel of this work is their discovery of a new class of compounds, the spiralenes, in which suitably placed, sterically demanding substituents force a lower homologue of β-carotene in spiral configuration. In this configuration C=C bonds are held in a configuration appropriate for excitonic interaction

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giving rise to what Liu calls “secondary orbital” interactions. (Whitten might call the interactions “excitonic”).

Neckers did not begin his research in photochemistry by studying spectra and measuring quantum yields. He looked for ways to use in polymer science what the rest of us were doing and has done so with remarkable success. He first made and used polymeric photosensitizers and then went on to develop photoinduced polymerization. His stock in trade has become use of photoinduced electron transfer to initiate acrylate polymerization. His group has learned more than some people thought they ever wanted to know about the excited states of dyes as electron donors or acceptors, and gone on to use that knowledge to produce remarkable new polymer science. They have pushed the wavelength for photoinitiation into the near-infrared region of the spectrum and have discovered simple fluorescence probes to monitor the state of cure of cross-linked polymers. Neckers has also participated in development of commercial applications of his chemistry, most spectacularly in employing computerized data from CAT scans to create three-dimensional models of internal structures in the human body. If you want a replica of your skull or heart, see Neckers.

Turro and Whitten have cast their nets broadly and both continue to come up with bumper catches of new science. It is noteworthy that both have in recent years come to work extensively with aggregates. It is significant that leaders in photochemistry are taking steps on the path from chemists’ traditional province of molecular science to the supramolecular domain of materials science.

Whitten began his postdoctoral research by using comparison with photochemistry to adduce molecular mechanisms of reactions initiated in solutions by γ-rays. However, at the same time he and Bill Stephenson discovered and investigated the quenching of fluorescence of aromatic hydrocarbons by conjugated dienes. That process cannot be attributed simply to electronic energy transfer, the process which had then come to be our first recourse in accounting for quenching of excited states. Much of Whitten’s research since that time has, in one way or another, related to excited states interactions in bimolecular or polymolecular systems.

He was one of the first to thoroughly document the fact that many quenching process involved electron transfer which often escaped detection because rapid reverse transfer to generate molecules in their ground states occurred at rates faster than diffusive separation of the reaction partners. One such example was quenching of the emission from the ruthenium tris(bipyridyl) cation by trinitrobenzene. Flash spectroscopy showed the transient appearance of the TNB anion radical. In that case the products of the transfer were a negative ion and a triply charged cation so there was a substantial electrostatic barrier to separation.

Whitten was one of the first to understand the complexity of photoluminescence quenching. Energy transfer and electron transfer are two, now obvious, mechanisms but there are other ways in which quencher and quenchee can form hybrid excited states which undergo rapid nonradiative decay. David Whitten has probably contributed more than anybody else to documentation of the complexities. He has employed a remarkable arsenal of tools in the work; in a recent publication he cites the use of “micro-calorimetry, dynamic light scattering, cryo-transmission electron microscopy, and reagent entrapment.” He has also made use of photochemistry and classical spectroscopy.

Much of his work has involved assembling systems for study in configurations which they are unlikely to find in bimolecular encounter in isotropic solutions. Langmuir–Blodgett films and vesicles formed by fatty acids and amphiphilic phospholipids have been most frequently used. Experimental methods have been absorption and emission spectroscopy in both classical and flash kinetic modes. Most recently, the group has used experience with simpler systems to diagnose structures of dimers and higher aggregates. For example, amphiphilic monosquaraines and bis(squaraines) form a number of structures having very spectra and excited state lifetimes. Since in most cases symmetry precludes permanent electrical polarization of the ground states, binding energies in aggregates are attributed to exciton coupling. The results shed important light on the nature of such forces which are responsible for long-known phenomena such as the stacking of dyes in solution.

One of Whitten’s major contributions was organization of the Center for Photoinduced Electron Transfer at the University of Rochester, one of the most successful of the Science and Technology Centers sponsored by the National Science Foundation in recent years.

Turro’s first work in photochemistry was made in my laboratory at Caltech. He and the late Peter Leemakers carried out the first *designed* photosensitized reactions based on intermolecular transfer of triplet excitation energy. During a two-week period they discovered both photolysis of ethyl pyruvate and isomerization of conjugated dienes sensitized by benzophenone. Turro has never slackened his pace after that rapid beginning; nor has he ceased to seek genuinely new knowledge. In the modest space appropriately allowable for a Foreword it is not possible to even skim the cream from the flood of new science in his 600+ papers. He discovered the chemiluminescence of 1,2-dioxetanes which are so energy rich that their thermal decomposition produces excited states of ketones. A number of applications for the process have been found, including use to provide the readout in highly successful new clinical assays. He has made and interpreted telling observations about many of the processes by which excited molecules seek to divest their excess energy—radiative and nonradiative decay, chemical reactions, classical and nonclassical energy transfer, etc. Some of the most brilliant of these studies describe *and put to use* the effects of magnetic fields, both external and provided by nuclei, the reactive molecules on photoreactions. An example acceleration of the triplet → singlet process in radical pairs by ^{13}C nuclei. Perhaps the most comprehensive work has involved photochemistry and spectroscopy of molecules in environments which in some way restrict their motion. Included are silica surfaces, crystalline zeolites, the cavities of cyclodextrin complexes and, most recently, the molecular tentacles of starburst dendrimers.

One of the reasons for Turro’s productivity is the ease with which he works with others. In a quick count I found 28 senior scientists with whom he has co-authored articles, and there are probably more. I am one who believes that active collaboration does more than fervid competition to advance the science. The two editions of Turro’s *Molecular Photochemistry* were obviously written to inform, rather than impress, and are still another way in which he has enriched the science.

These six scientists have taken rather different paths and, because they have done so, have done far more to enrich the science than if they had become enmeshed in fervid competition in which all did essentially the same things. I am both proud and humble because of my own close association with each of them. Three (Turro, Liu, and Saltiel) were students in my group at CalTech. Two (Wagner and Whitten) spent time with me as postdoctoral fellows. The sixth, Doug Neckers, was never a member of a group which I directed, but for the past ten years it has been my good fortune to be a regular visitor in his laboratory at Bowling Green. I have not only enjoyed the associations but I have also learned more than they will ever know from each of them.

Dr. George S. Hammond