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VECTORIAL ELECTRON TRANSFER IN SPATIALLY ORDERED ARRAYS

Progress Report

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Report Narrative:

Progress on "Vectorial Electron Transfer in Spatially Ordered Arrays (DE-DE/FG03-94ER14471 AMD A000), Aug. 1994 - Jan. 1997

by Marye Anne Fox

I. Abstract

With DOE support from August 1994 to August 1997, this project sought to identify methods for controlled placement of light absorbers, relays, and multielectron catalysts at defined sites from a fixed semiconductor or metal surface and, thus, to develop methods for preparing chemically modified photoactive surfaces as artificial photosynthetic units. These designed materials have been evaluated as efficient light collection devices and as substrates for defining the key features that govern the efficiency of long distance electron transfer and energy migration. We have synthesized several different families of integrated chemical systems as soluble arrays, as solid thin films, and as adsorbates on solid electrodes, seeking to establish how spatial definition deriving from covalent attachment to a helical polymer backbone, from self assembly of functionalized tethers on gold or metal oxide surfaces, and from rigid or layered block polymers can lead to controlled electron and energy transfer. We have also conducted physical characterization of semiconductor-containing composites active in controlled interfacial electron transfer, with charge transport in these materials having been evaluated by photophysical and electrochemical methods.

This work has resulted in 26 refereed scientific publications (with 5 more currently in press and 2 under review) and in 23 invited scientific presentations at conferences over the last three years.

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II. Research Results

This report describes progress made in the last three years on projects supported by DOE. The overreaching objectives outlined in the original proposal have largely been achieved: (1) exploration of the possibility of using new families of synthetic polymers in the construction of integrated systems for use in solution and on metal and semiconductor surfaces and (2) achieving an understanding of the photophysical principles controlling vectorial energy and electron migration over distances that are large on a molecular scale. Notable among specific achievements attained in approaching these objectives are: a) the first unambiguous demonstration of the effect of the local electric field on the rates and efficiencies of directional electron transfers in spatially defined media; b) the first use of photophysics to characterize structure in non-linear macromolecular (dendritic) segments; c) the development and testing of an array of new synthetic methods for preparing spatially arranged block polymers bearing optically addressable chromophores; and d) the first example of practical, reversible optical imaging in a two-dimensional self-assembled monolayer. In addition, we have developed methods for controlling macromolecular spatial definition on the nanometer to micrometer scale.

A) Synthesis and Characterization of New Polymeric and Supramolecular Arrays for Directional Electron Transfer

1) Linear Polymers.

Several new families of polymers have been synthesized and shown to have backbone structures that are rigid on typical timescales required for photoinduced electron transfer.¹ These include: a) peptides incorporating attached donor and acceptor groups bound to component non-natural amino acids; b) substituted polynorbornenes prepared by ring-opening metathesis polymerization (ROMP); c) substituted polyisocyanides prepared by nickel-catalyzed polymerization of substituted vinyl monomers, and d) polyacrylates prepared by group transfer polymerization of aryl-substituted acrylates and pentadienoates. This work has provided a library of new synthetic methods useful for preparing spatially arranged block polymers bearing optically addressable chromophores, which we hope to investigate in the next granting period as scaffolds on which one can test the effect of structural variance on the efficiency of intramolecular energy and electron transfer.

a) **Polypeptides.** We have recently prepared alternating AlaAib-peptides bearing donor and acceptor pairs located at the same positions along the peptidic backbone but aligned, respectively, with and against the external macroscopic dipole induced by chain α -

the pyrene-dimethylaniline couple ($\Delta G \approx -0.4$ eV) lies in the normal exothermic region, as confirmed by the variable temperature measurements in THF. The field-induced difference between the driving forces for intramolecular electron transfer in these compounds was also observed by differential pulse voltammetry: the ΔG_{el} of compounds with opposing vectors is 100 mV more negative than in the other set.

The electric field (approximately 10^9 V/m) associated with the permanent dipole of α -helical peptides exerts a profound effect on the rates of intramolecular photoinduced electron transfer between two appended chromophores. The two model peptides **1** and **2** have an identical Ala-Aib backbone and differ only for the position of the donor (N,N-dimethylaniline) and the acceptor (pyrene) groups relative to the electric field generated by the helix. Since the charge separated pair D^+A^- is oriented with the internal electric field in **2** (high-energy state) and against the field in **1** (low-energy state), a more negative driving force and a faster rate are observed for the electron transfer in **1**.

The fluorescence quantum yield of **2** ($\Phi_{f2} = 0.06$) was twice that of **1** ($\Phi_{f1} = 0.03$) in CH_3CN . Time-resolved fluorescence measurements revealed that the fluorescence lifetimes were much shorter in **1** and **2** than in a reference peptide **3** substituted with pyrene only (≈ 300 ns) and that the rate constants for electron transfer in **1** were 5 to 27 times larger than in **2**, depending on the solvent. The biexponential decays of **1** and **2** are likely due to the existence of two (or more) families of ground-state rotational conformers on the time scale of the experiment. Low-temperature measurements in THF showed that the driving force of the electron transfer (≈ -0.4 eV) lies near the normal exothermic region. Differential pulse voltammetry of **1** and **2** showed that the ΔG_{el} of **1** is 100 mV more negative than that of **2**.

When examined by transient absorption spectroscopy, complex decay kinetics were observed for both **1** and **2**, indicating that even these rigid peptides exist in a distribution of conformations.³ This assertion is further supported by single-photon counting measurements, NMR-spectroscopy (COSY, NOESY, and variable temperature 1H -NMR) and extended MM2-force field model calculations. An estimate for the rotational thresholds of the appended chromophores was obtained, and the character of the electronic interaction between the appended chromophores was examined by semiempirical single point calculations. Such calculations show the likely importance of through-bond interactions between the chromophores. The backbone conformational regularities of **1** and **2** are sufficient to establish the previously reported influence of an electrostatic field on photoinduced electron transfer rates, but side chain conformational mobility of **1** and **2** imposes an inherent limitation on achievable experimental differences.

The effect of helix unfolding on the rates of photoinduced electron transfer in model dichromophoric peptides was also investigated.⁴ Upon denaturation by protic solvents (EtOH, MeOH, H₂O, CF₃CH₂OH) or guanidinium, the observed electron transfer rates in **1** and **2** became identical. The helix unfolding was studied by circular dichroism (CD). A second pair of model oligopeptides analogous to **1** and **2** but having L-proline (Pro) instead of α -methylalanine (Aib) incorporated into the backbone, were prepared in order to study unfolded peptides in low dielectric constant solvents. The CD, NMR, and steady-state fluorescence spectra in a variety of solvents establish that one of the chromophores experiences a different local environment in the latter peptides, indicative of a range of different average conformations.

Several families of the same structural type composed alternating L-alanine (Ala) and α -aminoisobutyric acid (Aib) residues with an appended N,N-dimethylanilino, but with a 2-naphthalenyl group replacing the pyrenyl group were also prepared.⁵ Two-dimensional nmr studies show that these peptides exist in MeOH and CDCl₃ as α -helices. As with the pyrenyl peptides, steady state and time-resolved fluorescence measurements show that the distance and dihedral angle between the appended donor and acceptor and the alignment of the vectors for intramolecular charge transfer interaction (from donor to acceptor) with or against that of the helical dipole moment significantly influence the efficiency of photoinduced electronic coupling and, hence, of intramolecular fluorescence quenching.

These studies constitute the first unambiguous demonstration of the effect of the local electric field on the rates and efficiencies of directional electron transfers in spatially defined media .

b) ROMP Polymers. Ring opening metathesis polymerization has been employed as a nearly ideal method for obtaining block copolymers (up to five chemically distinct blocks, so far) with low polydispersity.⁶⁻¹² Chromophores are appended to these groups through an acetal or ketal linkage between a chromophore-labelled aldehyde or ketone and norbornenediol, which is polymerized with a molybdenum amide catalyst. This route opens the strained ring, while retaining a five membered ring along the chains sufficient to mediate conformation interconversion and providing no optical interference by backbone absorption of light. Photophysical studies of the structures of these polymers reveal vectorial photoinduced electron transfer in oligomers containing between two and five discrete blocks, with efficiencies and lifetimes of charge separation dependent on block length, as was projected in the original goals of this proposal. Triplet energy transfer along comparable backbones is comparably efficient.¹¹

A series of homo-, di-, tri- and tetrablock copolymers (MW = 3600 - 28,000) synthesized by ring-opening metathesis polymerization of *exo-cis*-norbornenediol monomer units bearing various aryl chromophores (naphthalene, phenanthrene, anthracene, pyrene,

dimethylaniline, dicyanobenzene, pentamethylbenzene) were examined by steady-state emission.^{6,7} Ketal-appended naphthyl-, phenanthryl-, and anthryl homopolymers show unperturbed monomer emission indicative of a rigid polymer backbone (at least on the timescale of the excited-state lifetimes of the chromophores), whereas acetal-appended naphthyl-, anthryl-, and pyrenyl homopolymers show substantial excimer formation. Molecular modeling of the four possible polymer conformations for both the acetal- and ketal-derived polymers qualitatively explains these differences in their fluorescence emissions. ¹H- and ¹³C-NMR and absorption spectroscopy, as well as retention behavior in gel permeation chromatography (polydispersity indices 1.1-1.4), show this family to exist as rigid, living, well-defined, monodisperse polymers.

Photophysical measurements were used to characterize these well-defined block copolymers⁸ labeled with chromophores and quenchers. Techniques employed in the characterization include: 1) energy migration kinetics in the homopolymers and diblock copolymers; 2) solvent effects (in the series CH₂Cl₂, THF, THF:CH₃CN and CHCl₃) on exciplex emission in diblock copolymers; 3) temperature effects on the fluorescence and phosphorescence of the diblock copolymers; 4) dependence of steady-state and time-resolved emission in a series of triblock copolymers, (dicyanobenzene)₅-(phenanthrene)_n-(dimethylaniline)₅, on relay length (n); and 5) transient absorbance and photoinduced charge separation in the triblock copolymers as a function of relay length. Photoinduced charge separation, lasting 7.2 μs, was achieved in the (dicyanobenzene)₅-(phenanthrene)₁₀-(dimethylaniline)₅ triblock copolymer.

These block copolymers thus represent reasonable models for integrated systems that simultaneously achieve light harvesting^{9,10} and can be used as arrays to promote either singlet or triplet energy transfer.¹¹ For example, the photophysical properties of the analogous homopolymers and block copolymers prepared by ring-opening metathesis

polymerization of norbornenes substituted with benzophenone, naphthalene, and phenanthrene groups have been investigated. When benzophenone is attached to this polynorbornene backbone, its excited state behavior differs from that observed for monomeric benzophenone. A new intramolecular excited state complex can be observed in transient absorption and emission measurements undertaken with the benzophenone-substituted homopolymer. In copolymers bearing benzophenone and naphthalene or phenanthrene substituent blocks, triplet energy transfer from the sensitizer (benzophenone) to the arene is observed. This energy transfer dominates over the intramolecular complexation that characterizes group interactions in the homopolymer.

Similar polynorbornenes substituted with 1-cyano-2-naphthyl and 2,5-dicyanophenyl groups as acceptors, and terminated with a pyrenyl end group, give photoinduced electron transfer upon uv excitation, producing a radical ion pair by single electron oxidation of pyrene and concomitant reduction of the acceptor. In copolymers with one acceptor block, steady state emission reveals extensive pyrenyl fluorescence quenching and parallel exciplex formation between pyrene and the acceptor. With two acceptor blocks, dual exciplex emission is observed, and transient measurements show that the lifetime of the charge-separated state is dependent on the identities of the acceptor(s) and the length of the polymer chain.¹²

c) Polyisocyanates. A more refractory polymer backbone is attained when arene-functionalized polyisocyanates are similarly polymerized into spatially segregated block copolymers,¹³ with kinetic profiles that clearly require "living" oligomers as synthetic intermediates. These in turn permit at-will synthetic manipulation of co-polymer molecular weight and block size.¹⁴ Steady state and time-resolved fluorescence measurements again indicate directional energy migration, this time to an acceptor-quencher interface where electron transfer takes place. As with the other families of polymers, the rigid backbone attained in the polymerization is a key feature if efficient vectorial energy migration is to be observed. Microsecond lifetimes are observed for the radical ion pairs produced by intramolecular photoinduced electron transfer.

Steady-state and time-resolved fluorescence spectroscopy of the homopolymers and di- and triblock copolymers of 2-naphthylethylisocyanide **4**, 9-anthrylethylisocyanide **5**, and 2-phenanthrylethylisocyanide **6** exhibit emission from the isolated chromophores, i.e., naphthyl, anthryl or phenanthryl, upon excitation at 284 or 354 nm.¹³ The absence of excimer emission in the fluorescence spectra of all these homopolymers is indicative of a rigid polymeric backbone. Fluorescence quenching in diblock copolymers containing a dimethylaniline donor block and a naphthalene or anthracene acceptor block as in

copolymers **7** and **8** or triblock copolymer **9** takes place through directional energy migration to the acceptor-quencher interface. The migrating excited state is then quenched at the interface either by photoinduced electron transfer in the anthracene-dimethylaniline diblock copolymer or by exciplex formation in the naphthalene-dimethylaniline diblock copolymer. Upon incorporation of an intervening block derived from pentamethylphenylethylisocyanide, exciplex formation is suppressed in the related triblock copolymer. Transient absorption spectra of this family of di- and triblock copolymers reveal the formation of radical ion pairs, with a lifetime of 1.1 μ s in the anthracene-dimethylaniline diblock copolymer.

- 4: R = 2-naphthyl,
n = 55, 100, 150, or 250
5: R = 9-anthryl, n = 40
6: R = 2-phenanthryl, n = 55

- 7: A = 2-naphthyl,
D = 4-N,N-dimethylanilino,
m = 160, 80, 40, or 20, n = 40;
or m = n = 55
8: A = 9-anthryl,
D = 4-N,N-dimethylanilino,
m = n = 40

- 9: A = 2-naphthyl,
D₁ = pentamethylphenyl,
D₂ = 4-N,N-dimethylanilino,
p = r = 40, q = 20 or 40;
or p = q = r = 100

d) **Polyacrylates.** A new set of block copolymers based on group transfer polymerization of chromophore-laden acrylates and pentadieneoates exhibit interesting photorectification properties.¹⁵ Incorporating closed ring structures within the polymer

backbone confers sufficient structural rigidity that excimer formation can be completely suppressed. Fluorescence quenching experiments have been conducted to show that these new polymers can function as energy funnels, with efficient singlet energy migration taking place intramolecularly by hopping through an energy-graded sequence attached along the rigid macromolecular backbone.

Fluorescence and singlet energy migration can be studied in chromophore-appended polyacrylates in which conformationally restricted ring structures in the polymer backbone prevent excimer formation.¹⁵ Specifically, two substituted α -methylene- γ -butyrolactones (**10a** bearing a naphthyl group and **10b** bearing a phenanthryl group) and a naphthyl-substituted tri(carboxyethyl)-1,6-heptadiene-4-carboxylate (**11**) yield linear polymers with five-membered rings fixed perpendicular to the main chain (poly(**10**)) or cyclopolymers with six-membered rings in the main chain (poly(**2**)) upon radical or group transfer polymerization. 4-Methyl-4-(2-naphthyl)-butyrolactone, 4-methyl-4-(3-phenanthryl)-butyrolactone, and 1-(1-naphthylmethyl)carboxy-1-ethylcarboxycyclohexane were prepared as spectroscopic models for these polymers. No evidence for excimer emission could be seen in poly(**10a**) or poly(**10b**), but poly(**11**) exhibited weak excimer emission. Defects in the polymer structure of poly(**11**) correlate with observed sites for excimer formation. The high efficiency of the observed steady-state fluorescence quenching by CCl_4 demonstrates that singlet energy migration occurs intramolecularly along these polymer chains.

These polyacrylates are structurally complementary to chromophore-laden vinyl polymers prepared earlier in our group.¹⁶ 2-Vinylnaphthalene-(N,N,-dimethylamino)methylstyrene block copolymers were prepared in an assortment of block

lengths, where macromolecular weight was determined by affixing the ratio of monomer-to-initiator. In this series, however, chemical sensitivity of the initiator to contaminants led to a broad range of polydispersities. Even so, it was possible to demonstrate with chromatographically fractionated material that interblock electron transfer, studied by fluorescence quenching, was most efficient in copolymers of approximately equal lengths. Interblock phase separation was significantly influenced by the relative block lengths and by the conformational flexibility of the component chain. The intensities of ground state charge-transfer absorptions in this series of compounds correlated well, for example, with the phase separation required by the photophysical studies.¹⁶

2) Non-linear Macromolecules

a) Dendrimers. A new non-linear architecture has been explored for amplifying vectorial electron transfer into three dimensions in dendrimer segments **15**.¹⁷ By employing chromophore-labeled dendrons as light harvesting antennae, we have been able to show that electronic interaction from a central core can be felt though four intervening groups.^{17,18} The buried radical ion produced by this long-range photoinduced electron transfer has an appreciably longer lifetime (about 1000-fold longer) than the analogously substituted monomeric radical cation produced in solution. We have attributed this effect to physical sequestering of the oppositely charged ions, contrasting with significant long-range electronic coupling on the excited state surface. Continuing work is focussing on the immobilization of these dendrimer fragments onto electrode surfaces, with a goal of exploring the effect of this new semi-spherical architecture as a possible means for efficient light collection and harvesting.

A novel series of dendrimer segments bearing functionalized aryl chromophores **12-15** (such as pyrene and naphthalene) at the periphery has been synthesized using a convergent-growth methodology.¹⁸ Selective excitation of the naphthyl substituted dendrons shows no intramolecular excimer formation, although substantial excimer emission is observed with the pyrenyl substituted dendrons. Fluorescence quantum yields and lifetimes are used to define energy migration through the dendritic backbone. Fluorescence from both the naphthyl monomer and pyrenyl excimer are quenched when a suitable electron donor (e.g., a 3-[dimethylamino]phenoxy group) is covalently attached at the dendron focal point. No sensitized emission from the dendron backbone is observed in the chromophore-labeled dendrons, although the control methyl-capped dendron fluoresces weakly at 310 nm when excited at 284 nm. Absorption and fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes for the chromophore-labeled dendrons are reported. These papers described the first use of photophysics to characterize

structure in non-linear macromolecular (dendritic) segments. First and second generation dendrons can also be modified by complexation with hydrogen bonded partners.

12a R = 2-naphthyl, X = OH

12b R = 2-naphthyl, X = Br

12c R = 2-naphthyl
X = $-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$

12d R = H, X = OH

12e R = H, X = Br

13a R = 2-naphthyl, X = OH

13b R = 2-naphthyl, X = Br

13c R = 1-pyrenyl, X = OH

13d R = 1-pyrenyl, X = Br

14a R = 2-naphthyl, X = OH

14b R = 2-naphthyl, X = Br

14c R = 2-naphthyl
X = $-\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$

14d R = 2-naphthyl
X = 3-(dimethylamino)phenoxy

14e R = H, X = OH

14f R = H, X = Br

14g R = H
X = 3-(dimethylamino)phenoxy-

15a R = 2-naphthyl, X = OH

15b R = 1-pyrenyl, X = OH

15c R = 1-pyrenyl, X = Br

15d R = 1-pyrenyl
X = 3-(dimethylamino)phenoxy

b) Ladderanes. New methods for the synthesis of a series of saturated ladderanes **16**, oligomers of 1,3-cyclobutadiene-1,2-dicarboxylate diesters with pendant 2-naphthyl

16, R- 2-naphthyl

groups, **16**, are described.¹⁹ Absorption and fluorescence spectra provide evidence for ground state through-space interchromophore interaction that becomes stronger with an increasing number of pendant aryl groups. A new fluorescence band ($\lambda_{\text{max}} = 303 \text{ nm}$) observed in the tetramer and pentamer that is blue-shifted from the monomer ($\lambda_{\text{max}} = 335 \text{ nm}$) was assigned as emission from an imperfectly stacked chromophore array. Nonexponential fluorescence decays of all four oligomers, obtained by single photon counting, are accommodated well by conformations attained from a molecular mechanics geometry optimization. In the solid state, the monomeric precursor of the family, tricarbonyl[di-(2-naphthyl)methyl-1,2,3,4- η -1,3-cyclobutadiene-1,2-dicarboxylate]iron exists as highly stable channel solvate under ambient conditions.

3) Liquid Crystals. Previous work in our group has shown that photovoltaic effects can be induced by room temperature irradiation of solid thin films of a highly absorptive, symmetrically substituted zinc porphyrin ordered by slow cooling through a stable liquid crystalline phase. We have now shown that this same phenomenon can be observed in other liquid crystalline compounds, albeit with lower quantum efficiencies.²⁰ We have made progress in correlating the solution phase and solid state absorption characteristics of such materials with the observed photoeffects.

For example, solid state absorption and emission spectra of a family of metallated octakis(β -decoxyethyl) porphyrins exhibit substantial shifts from their solution phase maxima.¹⁹ The efficiency for production of photocurrent upon steady state irradiation of a thin film of the ZnODEP and PdODEP in an indium tin oxide sandwich cell depends on the identity of the metal and does not correlate directly with solution phase oxidation potentials of the series. The rate constants for the production of photocurrent in ZnODEP and PdODEP sandwich photocells under low intensity ($\leq 0.5 \text{ mJ/pulse cm}^2$) irradiation were $k_{\text{app}(1)} = 1.2 \times 10^7 \text{ s}^{-1}$ (pulse = 0.17 mJ/cm^2) and $4.6 \times 10^7 \text{ s}^{-1}$ (pulse = 0.23 mJ/cm^2), respectively, with a second fast, kinetically unresolved component ($k_{\text{app}(2)} > 2 \times 10^8 \text{ s}^{-1}$) being observed at high intensity irradiation ($> 1 \text{ mJ/pulse cm}^2$) in both photocells. The photocurrent decays follow a biexponential rate profile, with fast rate constants of $3.3 \times$

10^5 s^{-1} and $5.9 \times 10^4 \text{ s}^{-1}$ and slower rate constants of $3.7 \times 10^4 \text{ s}^{-1}$ and $8.2 \times 10^3 \text{ s}^{-1}$, respectively. Both appearance and decay kinetics for the observed photocurrents in thin film cells depend on applied bias and on incident excitation energy. Spectra of trapped charges produced by steady state irradiation were reported.

In exploring the spectroscopy of porphyrinic thin films, we have shown that earlier observations concerning spectral shifts induced by comparing solution phase absorption spectra with solid state reflectance spectra in octakis(β -octoxyethyl)metallated porphyrins are general for many related classes of substituted porphyrins, with Soret bands always broadening and shifting blue, while the Q bands shift red and sometimes sharpen. The shift in intensity of the vibrational Q bands relates to solid state polarizability and to observable performance measures of these same molecules as self-organized thin films in photovoltaic devices. Appearance and decay kinetics have been measured for the excited states produced upon visible light excitation of these solid state organic thin films.

In addition, two other families of liquid crystals were prepared and their supramolecular packing characterized. These include a liquid crystalline pyrrole²¹ and 2,3,6,7-tetrakis(alkoxymethyl)tetrathiafulvalenes.²² A pyrrolic analog (4-pyrrole-4'-pentylbiphenyl) of the common liquid crystal 4-cyano-4'-pentylbiphenyl (K-15) exists as a liquid crystal between 200° and 213°C. Attempts to electropolymerize this pyrrole failed,

although the corresponding thiophene, which lacks a stable liquid crystalline phase, electropolymerizes smoothly.²¹

A family of the (alkoxymethyl)tetrathiafulvalenes show melting point behavior typically observed of liquid crystals as a function of appended chain length.²² But again, no evidence for a stable liquid crystalline mesophase could be attained. Although the electrochemical behavior of the family mimicked that of the parent tetrathiafulvalene, its dark conductivity was found to be sensitive to temperature. Short circuit photocurrent observed when members of this family were inserted into an ITO sandwich cell produced charge separation under an applied bias that could be maintained at open circuit for more than about 8 hours.

B) Optical Imaging in Self-Assembled Monolayers on Metals and in Modified Semiconductor Surfaces

Ultraviolet irradiation of self-assembled monolayers of *cis*- and *trans*-4-cyano-4'-(10-thiodecoxy)-stilbene on a polycrystalline gold surface results in visual surface patterning as a consequence of pronounced changes in the surface hydrophobicity induced by end chain alteration accompanying photochemical geometric isomerization.^{23,24} The metal surface influences the efficiency of the photoconversion but does not completely quench excited state reactivity. These studies constitute the first examples of practical, reversible optical imaging in a two-dimensional self-assembled monolayer.

1) Surface Hydrophilicity. Our work in exploring the alteration of normal photochemistry of organic molecules when they are constrained into a self-organized monolayer on a metal electrode has provided a new means for characterizing local order on an appropriate metal surface. Even the observation of net photochemistry on such surfaces was counterintuitive to many theories which predicted rapid and complete excited state quenching by the metallic surface's continuum of states.

Thin-films of *cis*-4-cyano-4'-(10-thiodecoxy)stilbene (**17**) and *trans*-4-cyano-4'-(10-thiodecoxy)stilbene (**18**) on quartz or self-assembled monolayers of these substrates on optically transparent gold undergo photoisomerization and photodimerization reactions when irradiated with >350 nm visible light.²³ The geometric isomerization of the *trans*-isomer has the effect of redirecting the polar cyano group from the external surface into the hydrocarbon-like layer, rendering the exposed surface as much more hydrophobic. As a result, surface hydrophilicity, as measured by variance in the sessile contact angle made upon contact with hexane or water, is proportionately altered.

This work is of importance as a novel optical imaging method as well as a graphic method for characterizing the physical interactions taking place at a solid-liquid or solid-gas interface. By conducting the irradiation in the presence of a filtering mask, well-defined regions of differing hydrophobicity were made visible to the naked eye by cooling the monolayer-coated gold surface in the presence of moist air. The image is permanently recorded and can be read by exposure to water, erased by drying under vacuum, and then reimaged, apparently without surface deterioration, indefinitely. Surface damage can result from abrasive drying of the monolayer-modified surface.

17 R = SH
19 R = SCOCH₃

18 R = SH **20** R = SCOCH₃

A monolayer of **17** on gold blocks the electrochemical oxidation of decamethylferrocene (DMFc) dissolved in CH₃CN in the potential region -0.5 to +0.5 V vs. Ag wire. After scanning between -0.5 and +1.0 V vs. Ag, the monolayer no longer blocks the DMFc oxidation in this solution. Cycling of the potential of monolayers of **17** or **18** on Au in 0.1 M KOH between 0 and -1.2 V vs. Ag results in the reductive stripping of the monolayer from the electrode surface. The cyclic voltammogram of a monolayer of **17** ($\Gamma = 1 \times 10^{-9}$ mol/cm²) has a broad reduction peak, which disappears after the first scan, whereas that of **18** ($\Gamma = 3 \times 10^{-10}$ mol/cm²) has a single, sharp reduction peak, which is persistent upon repeated cycling.

2) Surface Photochromism. The quantum yield for cyclodimerization in a monolayer of **17** is $\Phi = 1 \times 10^{-6}$, whereas those observed in the solid-state thin-films are $\Phi_{\text{cis} \rightarrow \text{trans}} = 4 \times 10^{-3}$ and $\Phi_{\text{cis} \rightarrow \text{dimer}} = 6 \times 10^{-4}$.²⁴ Two photodimers are isolated by irradiation of melts of the derivatives *cis*-4-cyano-4'-(10-thioacetyldecoxy)stilbene (**19**) and *trans*-4-cyano-4'-(10-thioacetyl-decoxy)stilbene (**20**). Irradiation of **19** resulted in photoisomerization to **20** as well as dimerization, as did irradiation of **20**. In a self-assembled monolayer, however, only photodimerization could be observed for **17**, whereas both processes were observed with **18**. The photodimerization removes the conjugated chromophore and induces an appreciable shift in the reflectance absorption and fluorescence spectra for the surface-bound moieties. Because the photodimerization is not reversible, these optical changes effect a permanane write-read sequence. The surface-confined dimer is stable to multiple (at least fifty) optical read-relax cycles although, like the

surface hydrophobicity probes, this surface photochromism is sensitive to surface pressure and abrasive drying.

Extension of this work (see proposal) to appended coumarin and anthracenyl tethered monolayers will provide further illustrations of surface photochromism and a definition of the range across which surface-bound photochromism can be reliably predicted.

C) Long Range Electronic Coupling along Rigid Molecular Backbones. The magnitude of electronic coupling between structurally distinct areas of a multiply functionalized molecule is key to understanding the mode of intramolecular electron transfer and excited state energy migration. A number of low molecular weight model systems were prepared in which intramolecular electronic coupling could be quantitatively assessed. For example, the solution-phase photophysics of several electron transfer donor-donor-acceptor assemblies (**21** – **23**) incorporating *N,N,N',N'*-tetramethyl-*p*-phenylenediamine

(TMPD) derivatized with piperazyl, piperidyl, morpholinyl, and prolinyl groups in the 1- and 4- positions as donor and *N,N*-dimethyl-4-nitroaniline (DMNA), anthraquinone, 3,5-dinitrobenzene, or 2,4-dinitrobenzene as acceptor has been studied.²⁵ In measurements of the model compounds incorporating only the donor moieties, flash photolysis generated the radical cation and lowest lying triplet of TMPD as evidenced by the superposition of their transient absorption spectra.²⁶ Lifetime measurements reveal, as well, a delayed

fluorescence derived from triplet-triplet annihilation. In **22** and **23**, electron transfer from the lowest excited singlet state of TMPD to the various acceptors was established by: (1) steady-state emission measurements where the fluorescence of TMPD was drastically quenched by the acceptor, (2) the transient absorption spectra of the radical cation and radical anion of the donor and acceptor, and (3) a single-exponential decay profile in **22** and **23** superceding the biexponential decay observed in the model donor. We envision extending the methodology for measuring intramolecular electronic coupling by other spectroscopic techniques during subsequent studies.

D) Electron Transfer in Organic-Inorganic Composites.

Our work in preparing organic-inorganic composites as vehicles for studying photoinduced electron transfer and providing access to soluble analogs of semiconductor photocatalyst suspensions has focus on the synthesis of heteropolyoxometallates containing small isolated islands of titania clusters. Both Dawson and Keggin ions **24** have been prepared, but so far disappointingly low levels of photocatalytic activity have been observed. In the course of these exploratory studies, we have begun to develop practical methods for controlling macromolecular spatial definition on the nanometer to micrometer scale, and hence to address the aggregation phenomena and quantum effects that accompany aggregation from single molecules through clusters to bulk materials.

We have also prepared heavily doped TiO₂ electrodes and demonstrated electron mobility in their porous electrode surfaces while operative in a photoelectrochemical cell.²⁷ Work is continuing in an effort to define whether pre-adsorption induced reactivity trends that are analogous to Langmuir-Hinshelwood kinetics typically encountered at photocatalytically active semiconductor interfaces. We have also begun preliminary studies of coated semiconductor particles as key composites for photocatalysis.

The crystal structure of a Ti-substituted Dawson-type polyoxotungstate K₁₉H₉[P₄W₃₂Ti₆O₁₃₂] has been determined in the presence of coordinated oxalate anions. The K⁺ salt is water soluble and the [*n*-Bu₄N]⁺ salt is soluble in acetonitrile and acetone.²⁸ The anion **24** exists as a dimer of two [P₂W₁₆Ti₂O₆₂]¹⁰⁻ units connected via two external TiO₆ octahedra. The photocatalytic activity of the [*n*-Bu₄N]⁺ salt toward the oxidation of cyclohexanol, 1-hexanol, and 2-hexanol gave pseudo first-order rate constants of 0.03 h⁻¹, 0.01 h⁻¹, and 0.01 h⁻¹, respectively. The relative photocatalytic activity for the oxidation of cyclohexanol by (*n*-Bu₄N)₉H₁₉[P₄W₃₂Ti₆O₁₃₂] and various polyoxotungstates of similar structure are compared.

Irradiation with a very high intensity laser pulse (355 nm) induces blue color in TiO₂ powders and films.²⁷ The blue color, which is assigned to the formation of Ti³⁺ in the particle, persists in air for several months. With an increase of the concentration of Ti³⁺ in

a given particle, photocatalytic activity is decreased because of a decrease in the thickness of the space-charge layer as deep Ti^{3+} traps are populated.

Emission quantum yields observed for the dimetallic complexes $[(\text{bpy})_2\text{-Os}^{\text{II}}(\text{tppb})\text{-M}^{\text{II}}(\text{dppb})]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$) **25** and $[(\text{bpy})_2\text{-Os}^{\text{II}}(\text{tppb})\text{-Os}^{\text{II}}(\text{bpy})_2]$ **26** ($\text{bpy} = 2,2'$ -bipyridine; $\text{dppb} = 1,2$ -bis(diphenyl-phosphino)benzene, $\text{tppb} = 1,2,4,5$ -tetrakis(diphenyl-osphino)benzene) reflect substantial intramolecular interaction between the component metal centers.²⁹ The slightly shifted redox potentials and absorption spectra of the dimetallic complexes, in comparison with their monometallic models, $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{dppb})]$ **27** and **28** and $[\text{M}^{\text{II}}(\text{dppb})_2]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$), **29**, are consistent with modest interactions in the ground states of these complexes, as has been observed in the analogous Ni^{II} dimetallic complexes. The quantum yields ($\phi = 0.002 \sim 0.044$) and excited state lifetimes ($\tau = 9 \sim 251$ ns) of the dimetallic complexes $[(\text{bpy})_2\text{-Os}^{\text{II}}(\text{tppb})\text{-M}^{\text{II}}(\text{dppb})]$ ($\text{M} = \text{Ni}$ and Pd) were lower and shorter than those of $[\text{Os}^{\text{II}}(\text{bpy})_2(\text{dppb})]$ ($\phi = 0.049$, $\tau = 270$ ns), as is consistent with quenching of the Os^{II} MLCT state by the second metal center. The apparent intramolecular electron transfer rate constants ($k_{\text{et}} = 3 \times 10^5 \sim 1$

$\times 10^8 \text{ s}^{-1}$) in the excited states of the dimetallic complexes $[(\text{bpy})_2\text{Os}^{\text{II}}(\text{tppb})\text{-M}^{\text{II}}(\text{dppb})]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$) correlate with calculated exothermicities for electron transfer from $^*\text{Os}^{\text{II}}$ to M^{II} ($\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}$).

Intermetallic coupling in the bridged biatallc complexes has been studied by electrochemical and spectroelectrochemical techniques.³⁰ These complexes show minimal cross-ring metal-metal interactions in the ground state, but substantially higher electronic coupling in the excited state. Quantitative description of the sensitivity of electronic coupling to changes in metal or ligand structure are obtained through measurements of the oxidation of the monometallic and bimetallic complexes. The very low conductivities observed in the coordination polymers correlate well with the low intramolecular coupling observed in the bimetallic complexes.

Analogous polymer bound complexes can be shown to be useful in thermal catalysis³¹

of aryl coupling reactions. In particular, polymer-supported analogs of this complex show a higher level of catalytic activity toward carbon-carbon bond formation in a Heck arylation reaction. The polymer-supported Pd(II) complex has a much higher turnover number (by more than an order of magnitude) than either the monomeric complex of Pd(OAc)₂ / PPh₃ at synthetically useful concentrations of reagents. The reaction rate is enhanced by electrochemical pre-reduction of the surface-bound catalyst, presumably because of inhibition of catalyst aggregation in the bound polymer.

E) References

1. Whitesell, J.K.; Chang, H.K.; Fox, M.A.; Galoppini, E.; Watkins, D.M.; Fox, H.; Hong, B. *Pure Appl. Chem.* **1996**, *68*, 1469.
2. Fox, M.A.; Galoppini, E. *J. Am. Chem. Soc.* **1996**, *118*, 2299.
3. Knorr, A.; Galoppini, E.; Fox, M.A. *J. Phys. Org. Chem.* **1996**, in press (invited): "Photoinduced Intramolecular Electron Transfer in Dichromophore-appended α -Helical Peptides: Spectroscopic Properties and Preferred Conformations."
4. Fox, M.A.; Galoppini, E. *J. Am. Chem. Soc.* **1996**, submitted: "Electric Field Effects on Electron Transfer Rates in Dichromophoric Peptides: The Effect of Helix Unfolding."
5. Fox, M.A.; Batchelder, T.L.; Fox, III, R.J.; Meier, M.S. *J. Org Chem.* **1996**, *61*, 4206.
6. Watkins, D.M.; Fox, M.A. *J. Am. Chem. Soc.* **1994**, *116*, 6441.
7. Watkins, D.M.; Fox, M.A. *Macromolecules* **1995**, *28*, 4939.
8. Watkins, D.M.; Fox, M.A. *J. Am. Chem. Soc.* **1996**, *118*, 4344.
9. Watkins, D.M.; Fox, M.A. *Polym. Mater. Encycl.* **1996**, *5*, 3593.
10. Fox, M.A.; Jones, W.; Watkins, D.M. *Chem. & Engin. News*, **1993** (March 15) 38.
11. Fossum, R.D.; Fox, M.A. *J. Am. Chem. Soc.* **1997**, in press: "Intramolecular Complex Formation and Triplet Energy Transfer in Polynorbornenes Incorporating Benzophenone."
12. Fossum, R.D.; Fox, M.A. *J Phys. Chem.* **1997**, submitted: "Dual Exciplex Formation and Photoinduced Electron Transfer in Pyrene End-labeled Polynorbornenes."
13. Hong, B.; Fox, M.A. *Can. J. Chem.* **1995**, *73*, 2101.
14. Hong, B.; Fox, M.A. *Macromolecules* **1994**, *27*, 5311.
15. Fox, H.H.; Fox, M.A. *Macromolecules* **1995**, *28*, 4570.
16. Lin, J.; Fox, M.A. *Macromolecules* **1994**, *27*, 902.

17. Fox, M.A.; Wolf, M.O.; Stewart, G.N. *NATO Adv. Stud. Inst.* **1997**, in press: "Photopatterning to Create New Structures on Surfaces."
18. Stewart, G.N.; Fox, M.A. *J. Am. Chem. Soc.* **1996**, *118*, 4354.
19. Li, W.; Fox, M.A. *J. Amer. Chem. Soc.* **1996**, *118*, 11752.
20. Jones, Jr., W.E.; Melamed, D.; Pan, H.L.; Fox, M.A. *J. Phys. Chem.* **1995**, *99*, 11523.
21. Melamed, D.; Nuckols, C.; Fox, M.A. *Tetrahedron Lett.* **1994**, *35*, 8329.
22. Fox, M.A.; Pan, H.L. *J. Org. Chem.* **1994**, *59*, 6519.
21. Fox, MA.; Wolf, M.O.; Reese, R.S. *NATO Adv. Stud. Inst.* **1996**, 485, 143.
22. Fox, MA.; Wolf, M.O.; Stewart, G.N. *NATO Adv. Stud. Inst.* **1997**, in press.
23. Fox, MA.; Wolf, M.O. *J. Am. Chem. Soc.* **1995**, *117*, 1845.
24. Fox, MA.; Wolf, M.O. *Langmuir*. **1996**, *12*, 955.
25. Pearson, A.J.; Gelormini, A.M.; Fox, M.A.; Watkins, D. *J. Org. Chem.* **1996**, *61*, 1297.
26. Fossum, R.D.; Fox, M.A.; Gelormini, A.M.; Pearson, A.J.J. *Phys. Chem.* **1997**, in press.
27. Torimoto, T.; Fox, III, R.J.; Fox, M.A. *J. Electrochem. Soc.* **1996**, *143*, 3712.
28. Crano, N.J.; Chambers, R.C.; Lynch, V.M.; Fox, M.A. *J. Mol. Catal.* **1997**, in press: "Preparation and Photocatalytic Studies on a Novel Ti-Substituted Polyoxometalate."
29. Wang, P.W.; Fox, M.A. *Inorg. Chem.* **1994**, *33*, 2938.
30. Wang, P.W.; Fox, M.A. *Inorg. Chim. Acta* **1994**, *225*, 15.
31. Wang, P.W.; Fox, M.A. *J. Org. Chem.* **1994**, *59*, 5358.

II. Publications Acknowledging DOE Support in 1994-97

A. Published Scientific Articles

"Synthesis, Characterization, and Photophysics of Photoactive Naphthyl-labeled [n]Ladderanes," Weijin Li and Marye Anne Fox, *J. Amer. Chem. Soc.* **1996**, *118*, 11752.

"Photoinduced Charge Separation and Photophysical Dynamics in Polynorbornene Chromophore- and Quencher-Labeled Block Copolymers," Diana M. Watkins and Marye Anne Fox, *J. Am. Chem. Soc.* **1996**, *118*, 4344.

"Photoelectrochemical Doping of TiO₂ Particles and the Effect of Charge Carrier Density on the Photocatalytic Activity of Microporous Semiconductor Electrode Films," Tsukasa Torimoto, Robert J. Fox, III, and Marye Anne Fox, *J. Electrochem. Soc.* **1996**, *143*, 3712.

"Photochemical and Electrochemical Probes of Structure in Self-Assembled Monolayers," Marye Anne Fox, Michael O Wolf, and R. Scott Reese, *NATO Adv. Stud. Inst.* **1996**, *485*, 143.

"Intramolecular Excited State Electronic Coupling Along an α -Helical Peptide," Traci L. Batchelder, Robert J. Fox, III, Mark S. Meier, and Marye Anne Fox, *J. Org. Chem.* **1996**, *61*, 4206.

"Chromophore-labeled Dendrons as Light Harvesting Antennae," Gina M. Stewart and Marye Anne Fox, *J. Am. Chem. Soc.* **1996**, *118*, 4354.

"Preparation of Functionalized *p*-Phenylenediamine Derivatives Using Arene-Iron Chemistry," Anthony J. Pearson, Ann M. Gelormini, Marye Anne Fox, and Diana Watkins, *J. Org. Chem.* **1996**, *61*, 1297.

"Anisotropic Energy and Electron Migration in Multichromophore-laden Polymers on Metal Surfaces," James K. Whitesell, Hye Kyung Chang, Marye Anne Fox, Elena Galoppini, Diana M. Watkins, Harold Fox, and Bo Hong, *Pure Appl. Chem.* **1996**, *68*, 1469.

"Photoisomerization and Photodimerization in Self-Assembled Monolayers of *cis*- and *trans*-4-cyano-4'-(10-thiodecoxy)stilbene on Gold," Michael O. Wolf and Marye Anne Fox, *Langmuir*. **1996**, *12*, 955.

"Effect of the Electric Field Generated by the Helix Dipole on Photoinduced Intramolecular Electron Transfer in Dichromophoric α -Helical Peptides," Elena Galoppini and Marye Anne Fox, *J. Am. Chem. Soc.* **1996**, *118*, 2299.

"Polymeric Arrays for Directional Energy and Electron Transfer," Marye Anne Fox, *Macromol. Sympos.* **1996**, *101*, 219.

"Light Harvesting Polymers," Diana M. Watkins and Marye Anne Fox, *Polym. Mater. Encyl.* **1996**, *5*, 3593..

"Fluorescence and Singlet Energy Migration in Rationally Designed Acrylate Polymers Bearing Pendant Chromophores," Harold H. Fox and Marye Anne Fox, *Macromolecules* **1995**, 28, 4570.

"Spectroscopy and Time-Resolved Photocurrent Response in Ordered Porphyrin Thin Films," Wayne E. Jones Jr., Dan Melamed, Horng-Long Pan and Marye Anne Fox, *J. Phys. Chem.* **1995**, 99, 11523.

Arene-Functionalized Polyisocyanides: Photophysics of Well-Defined Homopolymers and Block Copolymers for Efficient Light Harvesting," Bo Hong and Marye Anne Fox, *Can. J. Chem.* **1995**, 73, 2101.

"Synthesis and Photophysical Characterization of Aryl-substituted Polynorbornenediol Acetal and Ketal Multiblock Copolymers," Diana M. Watkins and Marye Anne Fox, *Macromolecules* **1995**, 28, 4939.

"Photochemistry and Surface Properties of Self-Assembled Monolayers of *cis*- and *trans*-4-Cyano-4'-(10-thiodecoxy)stilbene on Polycrystalline Gold," Michael O. Wolf and Marye Anne Fox, *J. Am. Chem. Soc.* **1995**, 117, 1845.

"Synthesis and Electrochemistry of a Liquid Crystalline Pyrrole and a Structurally Homologous Thiophene," Dan Melamed, Colin Nuckols, and Marye Anne Fox, *Tetrahedron Lett.* **1994**, 35, 8329.

"Photoinduced Intramolecular Electron Transfer in 1,2,4,5-Tetrakis(diphenylphosphino)benzene-bridged Os^{II}-M^{II} Dimetallic Complexes (M = Ni, Pd, and Pt), " Pei-Wei Wang and Marye Anne Fox, *Inorg. Chem.* **1994**, 34, 36.

"Synthesis and Properties of 2,3,6,7-Tetrakis(alkoxymethyl)tetrathiafulvalenes," Marye Anne Fox and Horng-Long Pan, *J. Org. Chem.* **1994**, 59, 6519.

"A Polymer-Bound Bidentate-Phosphine Palladium Complex as Catalyst for the Heck Reaction," Pei-Wei Wang and Marye Anne Fox, *J. Org. Chem.* **1994**, 59, 5358.

"Arene-Functionalized Polyisocyanides: A Kinetic Study of Polymerization to Prepare Homopolymers and Block Copolymers," Bo Hong and Marye Anne Fox, *Macromolecules* **1994**, 27, 5311.

"Predicting the Effect of Oxidative Doping on the Conductivity of Metal-Tetrakis(dimethyl-phosphino)benzene Coordination Polymers from the Electrochemical Properties of Their Related Bimetallic Complexes," Pei-wei Wang and Marye Anne Fox, *Inorg. Chim. Acta* **1994**, 225, 15.

"Rigid, Well-defined Block Copolymers for Efficient Light Harvesting," Diana M. Watkins and Marye Anne Fox, *J. Am. Chem. Soc.* **1994**, 116, 6441.

"Metal-Metal Interactions in Tetrakis(diphenylphosphino)benzene-bridged Bimetallic Complexes and Their Related Coordination Polymers," Pei-Wei Wang and Marye Anne Fox, *Inorg. Chem.* **1994**, 33, 2938.

"Interblock Electron Transfer in 2-Vinylnaphthalene-N,N-Dimethylaminomethylstyrene Block Copolymers," Jun Lin and Marye Anne Fox, *Macromolecules* **1994**, 27, 902.

B. Scientific Articles Currently in Press (for Which Reprints Are Not Yet Available)

"Photoinduced Intramolecular Electron Transfer in Dichromophore-appended α -Helical Peptides: Spectroscopic Properties and Preferred Conformations," Andreas Knorr, Elena Galoppini, and Marye Anne Fox, *J. Phys. Org. Chem.* **1997**, in press (invited).

"Photoinduced Electron Transfer in Donor-Acceptor Aryl Dyads Based on N,N,N',N'-Tetramethyl-*p*-phenylenediamine as the Donor," Renae D. Fossum, Marye Anne Fox, Ann M. Gelormini, and Anthony J. Pearson, *J. Phys. Chem.* **1997**, in press.

"Preparation and Photocatalytic Studies on a Novel Ti-Substituted Polyoxometalate," Nicholas J. Crano, R. Carlisle Chambers, Vincent M. Lynch, and Marye Anne Fox, *J. Mol. Catal.* **1997**, in press.

"Photopatterning to Create New Structures on Surfaces," Marye Anne Fox, Michael O. Wolf, and Gina M. Stewart, *NATO Adv. Stud. Inst.* **1997**, in press.

"Intramolecular Complex Formation and Triplet Energy Transfer in Polynorbornenes Incorporating Benzophenone," Renae D. Fossum and Marye Anne Fox, *J. Am. Chem. Soc.* **1997**, in press.

C. Papers Submitted for Publication Currently Being Reviewed

"Electric Field Effects on Electron Transfer Rates in Dichromophoric Peptides: The Effect of Helix Unfolding," Marye Anne Fox and Elena Galoppini, *J. Am. Chem. Soc.* **1997**, submitted.

"Dual Exciplex Formation and Photoinduced Electron Transfer in Pyrene End-labelled Polynorbornenes," Renae D. Fossum and Marye Anne Fox, *J. Phys. Chem.* **1997**, submitted.

III. Invited Conference Lectures dealing Wholly or Partially with DOE-Sponsored Research (Mar 1994 - Mar. 1997): Regular University seminar visits are not included.

10th Annual William S. Johnson Symposium in Organic Chemistry, Stanford, CA, Oct. 1996, "Novel Polymer Architectures for Controlling Photoinduced Electron Transfer."

NATO Workshop on Free Radicals in Biology and in the Environment, Bardolino, Lake Garda, Italy, June 1996, "Radical Reactivity Modified by Adsorption onto Surfaces and by Complexation with Metals."

DOE Solar Photochemistry Research Conference, French Lick, IN, June 1996, "Controlling Photoinduced Electron Transfer on α -Helical Peptides and in Self-Assembled Monolayers."

Monsanto Organic Symposium, University of Illinois, Urbana, IL, April 1996, "Anisotropic Electron Transfer in Synthetic Polymers."

NATO Advanced Research Workshop on Physical Supramolecular Chemistry, Miami, Jan 1996, "Photochemical Probes of Structure in Self-Assembled Monolayers."

Symposium on New Directions in Organic Photochemistry, 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 1995, "Photochemistry in a Self-Assembled Monolayer," with M.D. Wolf.

Symposium on Photoactive Macromolecules, 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 1995, "Energy and Electron Migration in Multichromophore Arrays," with G.M. Stewart, D.M. Watkins, H. Fox, and B. Hong.

Symposium of Inorganic Photochemistry, 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 1995, "Surface-Control of the Photocatalytic Redox Reactivity of Heteropolyoxoanions," with C. Chambers and N. Crano.

Robert A. Welch Conference on Nanoparticles, Discussion Leader on Thermodynamics and Supramolecular assemblies, Houston, TX, Oct. 1995.

NATO Conference on Self-Assembled Arrays, Estes Park, CO, Sept. 1995, "Photopatterning to Create New Structures on Surfaces."

3rd International Symposium on Functional Dyes, Santa Cruz, CA, July 1995, "Photophysical Effects of Immobilization of Dyes on Rigid Polymers, with J.K. Whitesell."

19th DOE Conference on Solar Photochemistry, Tamiment, Pa, June 1995, "Photoresponsive Solids and Polymers."

34th National Organic Symposium, Williamsburg, VA, June 1995, "Photosensitive Thin Films and Solids."

30th Euchem Stereochemistry Conference, Bürgenstock, Switzerland, May, 1995, "Synthetic Polymers for Directional Electron Transfer."

Contemporary Inorganic Chemistry: A Symposium in Honor of F.A. Cotton, College Station, TX, Mar 1995, "Directional Electron Transfere in Synthetic Polymers."

7th Winter Conference of the Inter-American Photochemical Society, Clearwater Beach, FL, Jan 1995, "Photoresponsive Surfaces and Polymers", with Michael O. Wolf.

5th Society of Polymer Science, Japan International Polymer Conference, Osaka, Japan, Nov 1994, "Polymeric and Supramolecular Arrays for Directional Energy and Electron Transport over Macroscopic Distances."

Southwest Regional Meeting, American Chemical Society, Fort Worth, TX, Nov. 1994, "Macroscopic Order in Conducting Polymers."

Southwest Catalysis Society, Houston, TX, Nov. 4, 1994, " Photocatalysis as a Probe for Surface-Mediated Reaction Kinetics."

Symposium on Electrochemistry and Novel Materials, 21st Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, MO, Oct. 1994, "Electrochemical Characterization of Low-Dimensional Metal Coordination Polymers and of Photoconductive Liquid Crystals."

International Meeting, European Science Foundation, Ottrott, France, July 1994,
"Nanosized Semiconductor Particles in Zeolites, Porous Glass, and Clay Supports."

18th DOE Solar Photochemistry Research Conference, Lake Tahoe, NV, June 1994,
"Directional Electron Transfer through Macromolecular Arrays."

Plenary lecture, Meeting-in Miniature, Cleveland Section of the American Chemical
Society, Cleveland, OH, Mar. 1994, "Materials for the 21st Century."