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NEW ARCHITECTURES FOR INTEGRATED PHOTOELECTROCHEMICAL
SYSTEMS

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FINAL REPORT ON: "NEW ARCHITECTURES FOR INTEGRATED PHOTOELECTROCHEMICAL SYSTEMS"

Marye Anne Fox

During the three year grant period, significant progress has been made toward the accomplishment of each of the goals outlined in the original proposal. The budget proposed for the project was also expended fully, as originally projected.

In accord with these objectives, we have prepared an array of new macromolecules and supramolecular aggregates in which a light-sensitive organic group initiates long range photoinduced electron transfer in this designed heterogeneous environment. In doing so, we have developed several new synthetic methodologies for accurate spatial definition of these polymeric arrays on a nanometer to micrometer scale. We have used these integrated materials to define the photophysical principles that control vectorial energy and electron migration over distances that are large compared with the dimensions of most small molecules. By attaching these same molecules to the surface of a metal or semiconductor electrode, we have obtained chemically modified surfaces that function as efficient vehicles for conversion of incident photons to chemical or electrical energy. Thus, we have investigated: 1) the synthesis and characterization of new polymeric and supramolecular arrays for directional electron transfer; 2) new techniques for optical imaging in self-assembled monolayers on metals (mostly gold); and 3) fundamental principles that govern long range electronic coupling along rigid molecular backbones.

Toward the first objective, several families of rigid linear polymers have been prepared to which pendant chromophores are attached. These include oligonucleotides, peptides, ring-opening metathesis polymers (ROMP) derived from substituted polynorbornenes, group transfer polymers, and ladderanes. For example, as many as five blocks of definable length have been included in low polydispersity copolymers. We have also continued our work in synthesizing spherical, layered dendrimers in order to compare electron transfer events taking place in two and three dimensions. We have been particularly interested in how the polymer backbone affects intramolecular orbital coupling and how conformational and field effects can influence the efficiency and direction of electron transfer.

With Professor J.K. Whitesell, we have explored the use of self-assembled monolayers (SAMs) as vehicles for high resolution imaging and information recording on metal surfaces. After demonstrating proof-of-concept that photochemical activity can be observed in SAMs, we have shown that surface energy, as expressed by differential recognition of hydrophobic or hydrophilic molecules, can be altered by photochemical geometric isomerization that leads to monolayer reordering that affects exposure of hydrogen bonding groups. Permanent optical imaging can be attained by photocycloaddition reactions on light-sensitive molecules included within a SAM. With some appended chromophores, this imaging is indelible, whereas with others reversible read-write sequences have been shown to be possible. Reversion can be accomplished either with wavelength-specific photoactivation or by thermal activation of the reversion. We continue our efforts to better define those factors that limit the reversibility through multiple read-write cycles.

Finally, we have employed these arrays to uncover fundamental interactions that influence the efficiency of the forward and back electron transfers that take place in organic arrays and in organic-inorganic composites. Thus, electrochemical cells have been constructed that employ several families of interesting materials as key light-

absorbing components. For example, the structural variance of a family of porphyrins that form stacked liquid crystals have been compared with analogs that do not aggregate into a stable mesophase. The effect of the highly exoergic driving forces on the rates of electron transfer between donor and acceptor groups in model dyads has been investigated, and the influence of a superimposed electric field on the direction and efficiency of electron transfer has been assessed. Similar structural variance has been studied to understand the efficiency as redox photocatalysts, both as dissolved species useful as models for nanoscopic clusters and as ordered arrays appended to a metal oxide semiconductor electrode.

We include with this report a reprint of an invited review article ("Fundamentals in the Design of Molecular Electronic Devices: Long Range Charge Carrier Transport and Electronic Coupling," Marye Anne Fox, *Accts. Chem. Res.* 1999, 32, 201.) that summarizes selected highlights of the progress made toward the general principles being pursued during the last three years.

Specific conclusions reached in each of our published studies follow:

"Photophysical Quenching and Photocurrent Effects Mediated by Guanine in Pyrene End-labeled Oligonucleotides," Eran Zahavy, Scott Reese, and Marye Anne Fox, *J. Biol. Chem. Lumines. Spectr.* 2000, 15, 75.

Luminescence is found to be a sensitive probe of local environment when an oligonucleotide is attached to a smooth gold surface and terminated by a highly fluorescent pyrenyl group. The efficiency of fluorescence quenching depends on the length and chemical composition of the oligonucleotide. It is also found that complementary base pairing can take place in this self-assembled surface, making fluorescence measurements an effective sensor for highly complementary oligonucleotide fragments. The mechanism of fluorescence quenching is likely to involve hole hopping from guanine to guanine either in the connecting chain or in the complementary double strand oligonucleotide pair.

"Photoreactivity of Self-assembled Monolayers of Azobenzene or Stilbene Derivatives Capped on Colloidal Gold Clusters," Jian Zhang, James K. Whitesell, and Marye Anne Fox, *Chem. Mater.* 2001, 13, 2323.

Azobenzene groups appended at the end of an alkyl thiol chain constrained to the surface of a gold nanocluster of narrow spatial dispersity produces a shell-core nanocomposite, one of the first with an inorganic core and an organic shell. Because π stacking of the arenes is weak, little further aggregation of the nanoparticles was observed. Photo-induced geometric isomerization from the trans- isomer to the cis- isomer took place with high quantum efficiency. Although this same conversion takes place in solution or in an organized layer on the gold cluster, higher conversions are observed in the former. The observed quantum yields for isomerization were affected by the length of the alkyl linker because of distance-dependent through-bond quenching by the metallic core.

"Competitive Photochemical Reactivity in a Self-Assembled Monolayer on a Colloidal Gold Cluster," Jun Hu, Fang Liu, Jian Zhang, Kevin Kittredge, James K. Whitesell, and Marye Anne Fox, *J. Am. Chem. Soc.* 2001, 123, 1464.

The surface composition of a shell-core cluster produced by depositing a self-assembled monolayer of an aryl-terminated alkyl chain containing a photocleavable group on a pre-formed gold nanocluster can be easily manipulated by controlled ultraviolet photolysis. Although weak nearest-neighbor interactions between substituted stilbenes are observed, photoinduced geometric isomerization was easily monitored, with lower yields of product being attained from photodimerization. Strong coupling between

the singlet and triplet manifolds on the excited state surface made selective activation of the photocleavable nitrobenzoate inefficient.

"The Effect of the Spacer Chain Length on the Fluorescence Intensity of 9-Alkylfluorenyl Thiol Self-assembled Monolayers on Gold," Kevin Kittredge, James K. Whitesell, and Marye Anne Fox, *Proc. DOE Solar Photochem. Res. Conf.* 2001, 22, 115.

Long chain alkyl fluorenes could be attached to an evaporated gold surface when the alkyl chain is ω -terminated with an amine, a thiol, or a disulfide group. When dense packing of the self-assembled monolayer was attained, the fluorescence efficiency of the attached arene was found to depend sensitively on the chain length of the linker group, rather than on the chemical composition of the surface binding functional group. A detailed mechanistic formulation of the observed kinetics reveals that conformational regularity (and decreased degrees of conformational freedom) are required in order to sort the effect of distance on long range energy and electron transfer within these pre-arranged assemblies.

"A Convenient Trimethylsilylthioxy-Dehalogenation Reaction for the preparation of Functionalized thiols," Jun Hu and Marye Anne Fox, *J. Org. Chem.* 1999, 64, 4959.

One of the major limitations currently facing those who propose to develop complex arrays on the surfaces of metal electrodes is the necessity to synthesize and purify the requisite α,ω -functionalized molecules before attempting the anchoring step. In this work, we describe a new synthetic method for the *in situ* generation of self-assembled monolayers of highly functionalized thiolates on noble metals. We have demonstrated that alkyl halides or alkyl tosylates can be used directly, upon treatment with tetrabutylammonium trimethylsilylthiolate, a reagent which is itself generated *in situ* from two commercially available reagents, tetrabutylammonium fluoride and hexamethyldisilathiane.

Although the formation of defect-free monolayers by this technique requires a somewhat longer annealing time (a few hours), subsequent experiments have shown that the method has high utility for producing defect-free monolayers from thiols that are inherently unstable or light sensitive, since the steady state concentration of the depositing thiol is low at all times. Thus, judicious control of the surface deposition rate can be attained by variance of kinetic parameters, i.e., temperature and/or concentration, permitting a facile new method for producing highly organized, completely blocking monolayers from several much more accessible functional groups. Even multiply functionalized groups, such as one target of interest for its photochemical properties that bear an ester, a nitro group, and an isomerizable aryl moiety, can be thus employed.

"Fundamentals in the Design of Molecular Electronic Devices: Long Range Charge Carrier Transport and Electronic Coupling," Marye Anne Fox, *Accts. Chem. Res.* 1999, 32, 201.

The design features required for practical implementation of optoelectronic or photonic devices are highlighted in this invited review article. Because nearly all such devices rely on the interplay between spatial organization at the molecular level and the efficiency and directionality of electron transfer or electronic coupling between interactive groups, chromophore positioning in molecules of defined molecular weight, but with variant chemical compositions, is particularly important. Several examples elaborated here describe our synthetic approaches to several families of rigid macromolecules with defined positions for absorptive groups. These model systems are then evaluated for initiation of photoinduced electron transfer and how the efficiency of this process is influenced by through bond coupling and local electric field effects.

"Photophysical Quenching Mediated by Guanine Groups in Pyrenyl-N-alkylbutanoamide End-labeled Oligonucleotides," Eran Zahavy and Marye Anne Fox, *J. Phys. Chem. B*, 1999, 103, 9321.

A synthetic method was developed for preparing pyrenebutanoic acid end-labeled oligonucleotides. This approach allowed for easy variation in the composition of the main chain, and hence the specification of the separation between guanine units on the single chain or complementary chain. The methodology also permitted pairing with duplexes in which a donor is affixed to one end and an acceptor (or other functionality) to the other end. For example, lifetimes for the pyrenyl group could be established by fluorescence measurements in Pyrene-NH(CH₂)₆-5'-A₁₀-3' which lacks a guanine group, in the analogous duplex Pyrene-NH(CH₂)₆-5'-A₁₀-3'-T₁₀-5', and in analogous systems in which one of the adenine units is replaced by a guanine at a variable distance from the pyrene group. It also permitted the introduction of multiple guanine groups, as a means for search for multiple hops between the several closely spaced guanine groups along the oligonucleotide chains.

Duplex formation was established by circular dichroism and nuclear magnetic resonance measurements. Fluorescence quenching was observed whether the guanine quencher was located along the same strand to which the pyrenyl group was attached or along the complement, suggesting strong interaction through covalent bonds and through hydrogen bonds in the duplexes. Because helix conformational effects are significant, and quenching contributions from vibronically coupled internal conversion shows only very weak structural dependence on the position of guanine. The observed quenching rates were found to depend only very weakly on distance, with a non-monotonic fall-off of electron transfer being observed along the series of progressively further spaced guanines. This non-linearity implies conformational complexity and weaker quenching by one of the other component amino acids, likely thymine. Variation of the length of the polymethylene spacer caused differential interaction of the pyrenyl group with the duplex, presumably because of lowered conformational flexibility in the shorter chain.

"Spectral and Cyclic Voltammetric Characterization of Self-assembled Monolayers on Gold of Pyrene End-labeled Oligonucleotide Duplexes," R. Scott Reese and Marye Anne Fox, *Can. J. Chem.* 1999, 77, 1077.

The oligonucleotide single strands and duplexes prepared in the previous study were modified by end-attachment of a short alkyl thiol chain, permitting deposition as a self-assembled monolayer onto a freshly prepared flat gold surface. The oligonucleotide duplexes were anchored either by depositing a thiol-terminated single oligonucleotide strand by *in situ* self-assembly, followed by exposure to the complementary oligonucleotide, or by direct assembly of a preformed- oligonucleotide-complement duplex. The deposition process could be monitored by following off-angle fluorescence intensity from the modified surface or by observing the blocking behavior of the thin film toward electroactive couples dispersed in a contacting electrolyte solution.

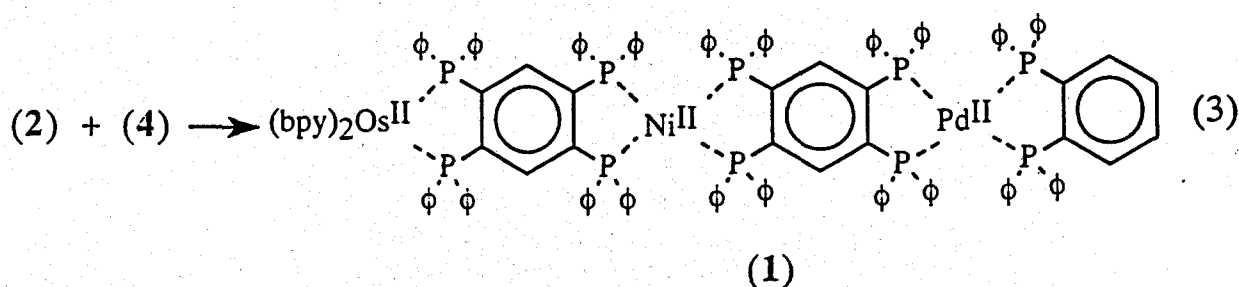
Because the probe oligonucleotide also bore a light-absorptive sensitizer (pyrene), the resulting thin film was photoresponsive, although with a current flow of the opposite direction from that predicted from a normal photoelectrochemical sensitization effect. Surface emission measurements show no evidence for intermolecular pyrene aggregation on the electrochemically blocking surfaces. Thus, the strong electronic coupling made possible through the linked oligonucleotides strongly perturbs surface photoeffects.

"Self-Assembled Monolayers on Gold of Thiols Incorporating Conjugated Terminal Groups," R. Scott Reese and Marye Anne Fox, *J. Phys. Chem.* 1998, 102, 9820.

Three arene groups of varying π -conjugation length were attached through nucleophilic substitution to the 6-position of 1-thiyl-6-bromo-hexane, and the resulting α,ω -functionalized groups were anchored to a polycrystalline gold surface, forming densely packed electrochemically passivated monolayers. Infrared spectroscopy and ellipsometry measurements of the monolayer indicate that the aryl components are roughly perpendicular to the gold surface in the highly oriented monolayer, likely because of strong attractive interactions between the neighboring π -systems. This interpretation is also consistent with pronounced red-shifts in the emission spectra of the attached molecules. These stacking interaction thus dominate over the crystal packing forces of the hexyl chains, which have been suggested as important factors for understanding local organization in self-assembled monolayers of hexanethiols.

"An OsII-NiII-PdII Trimetallic Complex as an Electro-Switchable-Photoinduced-Electron-Transfer Device," Eran Zahavy and Marye Anne Fox *Chemistry-Europe J.* 1998, 4, 1647.

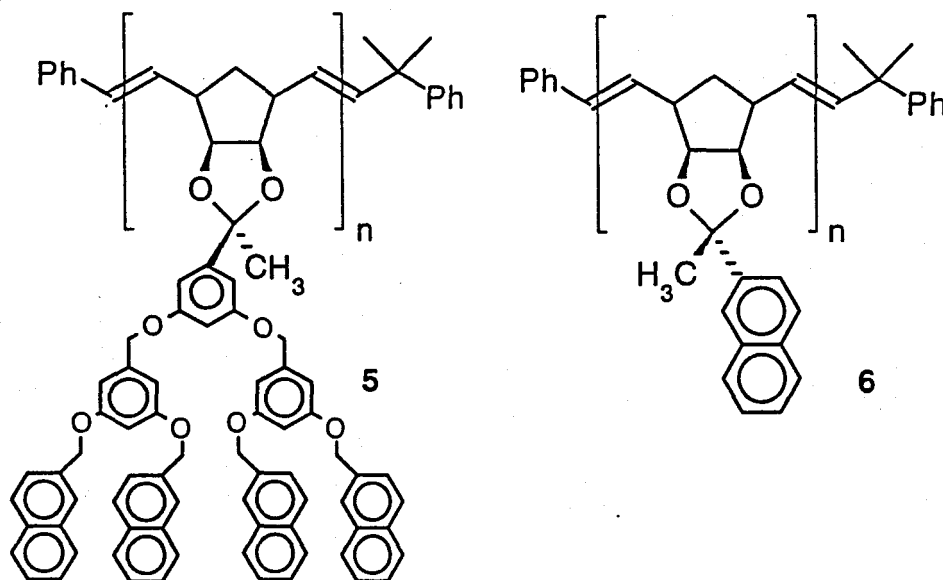
A complex bearing a sequence of redox-active metal coordination sites (Os^{II} - Ni^{II} - Pd^{II} **1** and an analogous bimetallic complex (Os^{II} - Ni^{II}) functions as an Electro-Switchable-Photoinduced-Electron-Transfer (ESPET) molecular device, in which the Os^{II} center is the light harvesting component, the Pd^{II} site is the electron acceptor, and the Ni^{II} site serves as the electroswitchable intervening spacer. The Ni^{II} center can be reduced selectively, permitting regulation of the photoinduced-electron-transfer from the excited Os^{II} site to the Pd^{II} . In their oxidized forms, both complexes show transient biexponential emission decays with the short-lived component assigned to oxidative quenching of $^*\text{Os}^{\text{II}}$ by Ni^{II} and the long-lived (minor) component assigned to the unquenched $^*\text{Os}^{\text{II}}$ site. In the electroreduced form, the bimetallic complex **2** shows suppressed oxidative quenching by the Ni^{II} site and an extended localized emission lifetime. In the trimetallic complex, the electroreduction enables direct oxidative quenching by the Pd^{II} site. The direct oxidation by Ni^{II} was significantly reduced (from 90% to 50%) and the lifetime of the excited Os^{II} site was extended.



"Dendrimer-Linear Polymer Hybrids through ROMP," Gina M. Stewart and Marye Anne Fox, *Chem. Mater.* 1998, 10, 860.

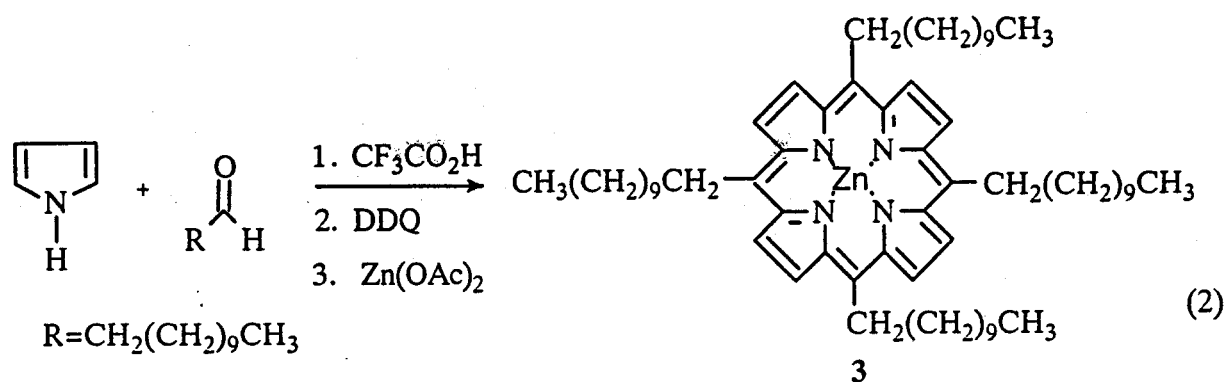
By employing ring-opening metathesis polymerization of a dye-labeled dendron segment bearing a polymerizable side chain, a linear polymer hybrid in which second- and third-generation dendrimers provide a high density of optical chromophores has been

obtained. There is substantial excimer emission in the resulting hybrid polymer, and further study is needed to differentiate intramolecular and intermolecular interactions. The resulting polymers exhibit high solubility in conventional organic solvents and can be cast as films that show promising optical effects deriving from the unusual architecture of the hybrid macromolecule.



"The Effect of Structural Variation on Photocurrent Efficiency in Alkyl-Substituted Porphyrin Solid State Thin Layer Photocells," Marye Anne Fox, Jennifer R. Vincent, Dan Melamed, Tsukasa Torimoto, Chong-yang Liu, and Allen J. Bard, *Chem. Mater.* 1998, 10, 1771.

Three structurally variant alkyl-substituted porphyrins (Zn (II) 2,3,7,8,12,13,17,18-octakis-*n*-decylporphyrin, M(II), *meso*-5,10,15,20-tetrakis-*n*-(undecyl)porphyrin, M = Co, Cu, Pd, and Zn), and Zn (II), and *meso*-5,10,15,20-tetrakis-*n*-(phenoxynonyl)porphyrin were found to exist as photoconductive insulators and produce significant short circuit photocurrent and open circuit photopotential when irradiated as solid thin films in an ITO sandwich cell. Liquid crystalline phase stability, the identity of the inserted metal, and the nature of its supramolecular packing all influence the observed photoelectrochemical response. One porphyrin, which has a stable liquid crystalline phase, produces higher steady state photocurrents than do the corresponding *meso*-substituted porphyrins, although liquid crystallinity is not an absolute requirement for observation of a photoresponse. Among porphyrin family shown, the zinc complex gave the highest steady state photocurrent. When a phenyl ring orthogonal to the porphyrinic plane was present, the observed photovoltaic response was significantly diminished, probably because of difficulties in achieving effective close packing.



"Synthesis and Photophysical Characterization of Group Transfer Polymers with Pendent Aryl Chromophores," Marye Anne Fox and Heike W. Thompson, *Macromolecules* 1998, 30, 7391.

In most vinyl polymers, energy migration is suppressed because excimer traps localize and dissipated the excitation energy. Naphthalene- and pyrene-labeled polymers prepared by group transfer polymerization of methyl 2-(2-naphthyl)acrylate, methyl 2-(1-pyrenyl)acrylate, and ethyl 5-(2-naphthyl)pentadienoate and ethyl 5-(2-naphthyl)hexadienoate, respectively, were studied as probes for backbone conformational rigidity. Various arenes were attached as covalent bonded groups appended to the polymer backbone containing π -bonds or rigid small rings.

Excimer formation was observed in the steady-state fluorescence spectra, and the observation of biexponential decay of time-resolved fluorescence indicates two distinct environments for excimer formation. These, in turn, point to substantial conformational flexibility in the polymer backbone.

DOE-SPONSORED PUBLICATIONS 1998-2001

- "Photophysical Quenching and Photocurrent Effects Mediated by Guanine in Pyrene End-labeled Oligonucleotides," Eran Zahavy, Scott Reese, and Marye Anne Fox, *J. Biol. Chem. Lumines. Spectr.* **2000**, *15*, 75.
- "Photoreactivity of Self-assembled Monolayers of Azobenzene or Stilbene Derivatives Capped on Colloidal Gold Clusters," Jian Zhang, James K. Whitesell, and Marye Anne Fox, *Chem. Mater.* **2001**, *13*, 2323.
- "Competitive Photochemical Reactivity in a Self-Assembled Monolayer on a Colloidal Gold Cluster," Jun Hu, Fang Liu, Jian Zhang, Kevin Kittredge, James K. Whitesell, and Marye Anne Fox, *J. Am. Chem. Soc.* **2001**, *123*, 1464.
- "The Effect of the Spacer Chain Length on the Fluorescence Intensity of 9-Alkylfluorenyl Thiol Self-assembled Monolayers on Gold," Kevin Kittredge, James K. Whitesell, and Marye Anne Fox, *Proc. DOE Solar Photochem. Res. Conf.* **2001**, *22*, 115.
- "A Convenient Trimethylsilylthioxy-Dehalogenation Reaction for the preparation of Functionalized thiols," Jun Hu and Marye Anne Fox, *J. Org. Chem.* **1999**, *64*, 4959.
- "Fundamentals in the Design of Molecular Electronic Devices: Long Range Charge Carrier Transport and Electronic Coupling," Marye Anne Fox, *Accts. Chem. Res.* **1999**, *32*, 201.
- "Spectral and Cyclic Voltametric Characterization of Self-assembled Monolayers on Gold of Pyrene End-labeled Oligonucleotide Duplexes," R. Scott Reese and Marye Anne Fox, *Can. J. Chem.* **1999**, *77*, 1077.
- "Photophysical Quenching Mediated by Guanine Groups in Pyrenyl-N-alkylbutanoamide End-labeled Oligonucleotides," Eran Zahavy and Marye Anne Fox, *J. Phys. Chem. B*, **1999**, *103*, 9321.
- "Photophysical Quenching by Guanine in Pyrene End-labeled Oligonucleotides," Marye Anne Fox, James K. Whitesell, and Eran Zahavy, *Proc. DOE Solar Photochem. Res. Conf.* **1999**, *23*, 129.
- "Self-Assembled Monolayers on Gold of Thiols Incorporating Conjugated Terminal Groups," R. Scott Reese and Marye Anne Fox, *J. Phys. Chem.* **1998**, *102*, 9820.
- "An Os^{II}-Ni^{II}-Pd^{II} Trimetallic Complex as an Electro-Switchable-Photoinduced -Electron-Transfer Device," Eran Zahavy and Marye Anne Fox *Chemistry-Europe J.* **1998**, *4*, 1647.
- "Dendrimer-Linear Polymer Hybrids through ROMP," Gina M. Stewart and Marye Anne Fox, *Chem. Mater.* **1998**, *10*, 860.
- "Guanine-Mediated Photoinduced Electron Transfer in Pyrene End-Labeled Oligonucleotides," Marye Anne Fox and Eran Zahavy, *Proc. DOE Solar Photochem. Res. Conf.* **1998**, *22*, 115.

"The Effect of Structural Variation on Photocurrent Efficiency in Alkyl-substituted Porphyrin Solid State Thin Layer Photocells," Marye Anne Fox, Jennifer R. Vincent, Dan Melamed, Tsukasa Torimoto, Chong-yang Liu, and Allen J. Bard, *Chem. Mater.* 1998, 10, 1771.

"Synthesis and Photophysical Characterization of Group Transfer Polymers with Pendent Aryl Chromophores," Marye Anne Fox and Heike W. Thompson, *Macromolecules* 1998, 30, 7391.

**INVITED PROFESSIONAL LECTURES DEALING WITH DOE-
SPONSORED WORK (1998-2001)**

- XXIth IUPAC Meeting on Photochemistry, Moscow, July 2001, "Optoelectronic Interactions in Organized Media."
- Gordon Research Conference, July 2001, "Modification of Photoreactivity by Constraint within a Self-Assembled Monolayer."
- Department of Energy Solar Photochemistry Research Conference, Lake Tahoe, CA, June 2001, "The Effect of the Spacer Chain Length on the Fluorescence Intensity of 9-Alkylfluorenyl Thiol Self-assembled Monolayers on Gold," with Kevin Kittredge and James K. Whitesell.
- American Chemical Society Pan American Chemical Conference, San Juan, Puerto Rico, July, 2000, "Controlling Two- and Three-Dimensional Photochemistry in Self-assembled Monolayers."
- XXV International Symposium on Macrocyclic Chemistry, Scotland, July 2000, "Photoswitchable Ditopic Receptors: Synthesis, Cation-induced Self-assembly into Dimeric Complexes and Stereospecific [2+2]-photocycloaddition of Multiphotochromic 15-crown-5 ethers of Quinoline," with E.N. Andrioukhina, O.A. Fedorova, E.N. Ushakov, A.V. Buevich, M.V. Alfimov, B. Eliasson, U.G. Edlund, J.K. Whitesell, and S. Gromov.
- 13th International Conference on the Photochemical Conversion and Storage of Solar Energy, IPS 2000, July 2000, Aspen, CO, with J.K. Whitesell, J. Hu, F. Liu, K. Kittredge, and J. Zhang, "Contrasting Photoreactivity in Self-assembled Monolayers on Planar Gold Surfaces and as Shells on Colloidal Gold Clusters."
- IXth International Symposium on Luminescence Spectrometry, Montpellier, France, May 2000, with Eran Zahavy and Scott Reese, presented by Dr. Zahavy, "Photophysical Quenching and Photocurrent Effects Mediated by Guanine in Pyrene End-labeled Oligonucleotides".
- Global Salute to Polymers, American Chemical Society RTP Polymer Group, Cary, NC, Oct. 1999, "Electron Transfer in Asymmetric Polymers."
- 37th IUPAC Congress/ 27th GDCh General Meeting, Berlin, Aug. 1999, "Controlling Two- and Three- Dimensional Photochemistry in Self-assembled Monolayers."
- Fourth International Conference on Materials Chemistry, Trinity College, Dublin, Ireland, July 1999, "Shell-Core Nanoparticles."
- 54th Pacific Northwest Regional American Chemical Society Meeting, Portland, OR, June 1999, "Photochemistry in Self-Assembled Monolayers."
- International Symposium on Fast Visualization of Microstructures, Austin, TX, April 1999, "Pulse Radiolysis and Laser Flash Photolysis as Techniques for Characterizing Local Aggregates."

Student Affiliates, American Chemical Society, Raleigh, NC, Nov. 1998, "Designed Materials for Vectorial Electron Transfer."

Molecular and Supramolecular Photochemistry Symposium, American Chemical Society National Meeting, Boston, MA, August 1998, "Photoelectrochemistry of Polymer-Metal Oxide Composites and Liquid Crystals," with Weijin Li, Luis Otero, Hiroyuki Osora, and Julie Teetsov.

Symposium on Nanoscaled Materials, American Chemical Society National Meeting, Boston, MA, August 1998, "Dendrimer Shell-Core Nanoclusters," with Robert L. Abdon.

XVII IUPAC Symposium on Photochemistry, July 1998, Sitges, Spain, "Controlling Long Range Electronic Interactions."

Symposium on Nanomaterials, American Chemical Society National meeting, Dallas, TX, Mar 1998, "Imaging with Chromophore-modified Self Assembled Monolayers" with James K. Whitesell, Andrew McKerrow, Weijin Li, and Marilyn Wooton.

Maria Goeppert Mayer Symposium, University of California at San Diego, March 1998, "Controlling Long Distance Electronic Interactions in Oriented Peptides and Self-Assembled Monolayers."

First Internet Conference on Photochemistry (Internet Journal of Science: <http://www.netsci-journal.com>) "Photosensitization of Nanocrystalline TiO_2 Film Electrodes by a $\text{Ru}(\text{bpy})_3^{2+}$ -Labeled Polyimide," with Hiroyuki Osora and Weijin Li.

"Towards the Second Century of Carbocation Chemistry," a Symposium at the Fifth Chemical Congress of North America, Cancun, Nov 1997, "Long-lived Cation Radicals Produced by Photoinduced Electron Transfer."

Symposium on Supramolecular Structures: Characterization and Physical Aspects, Fifth Chemical Congress of North America, Cancun, Nov 1997, "Perturbation of Excited State Reactivity by Covalent Attachment of Photoactive Molecules to Metal or Semiconductor Surfaces."

American Chemical Society National meeting, Las Vegas, NV, Sept. 1997, Eminent Scientist Lecture: "Bridging the Gap: From Molecules to Materials."

V Encuentro Latinoamericano de Fotoquímica y Fotobiología, Los Cocos, Cordoba, Argentina, Sept. 1997, "Photosensitization of Thin SnO_2 Nanocrystalline Semiconductor Film Electrodes with Metalloporphyrins and Alkyl-substituted Metalloporphyrins," with Luis Otero.

Eight International Conference on Organized Molecular Films, Asilomar, CA August 1997, "Fluorescence Probes for Chemical Reactivity at the Interface of a Self-Assembled Monolayer," with Weijin Li, Marilyn Wooton, Andrew McKerrow, and James K. Whitesell.

Royal Netherlands Academy of Arts and Science, Amsterdam, April 1997, Symposium on Smart Materials, "Synthetic Architectures for Controlled Electron Transfer."