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VECTORIAL ELECTRON TRANSFER IN SPATIALLY ORDERED ARRAYS

Progress Report

Jan. 1991 – Jan. 1994

Marye Anne Fox

Department of Chemistry

University of Texas at Austin

Austin, TX 78721

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Report Narrative: Progress on "Vectorial Electron Transfer in Spatially Ordered Arrays (DE-FG05-85ER13387), Jan 1991-Jan. 1994

A. Research Results

Significant progress has been made toward each of the objectives described in the original research proposal. This program seeks to identify methods for rapid, controlled placement of light absorbers, relays, and multi-electron catalysts at defined sites with respect to a semiconductor or metal surface and thus to develop methods for preparing chemically modified photoactive surfaces as artificial photosynthetic units.¹⁻⁴ We have begun to synthesize integrated chemical systems on solid electrodes in which spatial definition derives from covalent attachment to a helical polymer backbone, from self assembly of functionalized tethers on gold or metal oxide surfaces, and from layered block polymers. We have also developed methods to synthesize and physically characterize semiconductor-containing composites capable of controlling interfacial electron transfer and have investigated photophysical characteristics of specific low molecular weight models for these semiconductor clusters. Electron and energy transport in these materials are being evaluated by photophysical and electrochemical methodologies.

Progress has been made in four areas: a) the synthesis of new materials for directional electron transfer; b) the preparation and characterization of anisotropic composites containing organic and inorganic components; c) the elaboration of mechanisms of electrocatalysis; and d) the development of new methods for surface modification of metals and semiconductors.

Toward the first objective, several novel classes of materials have been prepared: molecules capable of forming macroscopic charge transfer complexes with potential as organic metals, liquid crystals, coordination polymeric semiconductors, dimensionally controlled conducting organic polymers, and block copolymers. A new series of tetrathiafulvalene derivatives **1** have been prepared which exhibit interesting magnetic

$R = C_nH_{2n+1}$, $n = 1, 3, 5, 6, 7, 8, 10, 12, 14$

1

2

properties and which can function as photoelectrets.⁵ As in the liquid crystals prepared in earlier years of this program, these solid state materials show appreciable persistent polarization under irradiation. The mechanism of charge transport has been investigated in symmetrically substituted liquid crystalline porphyrins **2** by microwave conductivity,⁶ showing that order near the phase transitions can be exploited in the construction of a photoresponsive solid state device.

A family of newly prepared organometallic coordination polymers **3** show light

3

responsiveness and activity as semiconductors.⁷ Spectroelectrochemical techniques have been employed to characterize electronic coupling and persistent conductivity changes in the dark and upon irradiation for oxidatively⁸ and reductively⁹ doped coordination polymers containing nickel, palladium, and platinum tetraphosphino-ligated complexes.

Conductivity has also been measured in a series of anisotropically graded conducting organic polymers. The control of the oxidative potential employed during their formation permitted preparation of lamellar anisotropic arrays **4** of polypyrrole when

4

deposited from micellar solution¹⁰ or in the presence of an oriented liquid crystalline electrolyte.¹¹ Similarly, chronoamperometry was used to predict the spatial distribution of monomer units in a graded conductive pyrrole / thiophene copolymer.¹²

A comparison of these macroscopically graded materials with microscopic analogs formed by functionalization along an oligopeptide backbone is anticipated. The initial work has defined solubility limitations for polyalanines **5** and has shown that electron transfer

rate studies can be used as sensitive probes for conformational folding in complex molecules.¹³ Synthetic work has continued in preparing a series of modest length peptides (10 – 26 units) which can be conformationally held in a helical conformation. The inclusion of aminoisobutyric acid units as alternating groups with functionalized alanines 6

has solved the solubility problem, permitting the formation of a [3,10] helix, as established by nmr and circular dichroism measurements. The synthetic methods used provide sufficient flexibility to place the donor and acceptor groups at variable positions along the chain, both with and against the dipole moment gradient enforced by the network of hydrogen bonds responsible for helix formation.^{3,14} Rate measurements now being conducted will specify unambiguously the magnitude of the through-bond coupling of a hydrogen bond, a value which has only been indirectly estimated through rough models in biologically relevant work.

We have also prepared several new classes of block copolymers. By using anionic polymerization methods, block copolymers 7 containing variable lengths of poly-2-vinylnaphthalene and poly-*p*-N,N-dimethylmethylstyrene have been prepared.¹⁵ The

efficiency of fluorescence quenching of the naphthyl excimer by the appended amino group correlates with the appearance of charged radical ions in the transient absorption spectrum. Conformational folding of the flexible polymer backbone permits strong through-space interaction of the donor-acceptor pairs in oligomeric models containing about twenty monomer units. The importance of this folding diminishes as the length of the polymer is increased, with phase-separation providing discrete regions for each of the blocks in the higher molecular weight homologs. The intermediate weight oligomers can

be induced to open to an extended conformation by including the oligomer within a polymeric micelle.

Synthetic work has also progressed in developing new methodologies for block polymerization. Both ring-opening metathesis polymerization¹ and group transfer polymerization¹⁶ methods are being pursued. Both organic and inorganic electron transfer relays are being incorporated into these new composite polymers. Work toward identification of the factors controlling the migration of excitons and electrons over macroscopically measurable distances is proceeding for a series of di- and tri-block copolymers **8**.

8

Work toward the second objective has focussed on synthetic work undertaken to construct organic / inorganic composites which show special reactivity deriving from their controlled environment. In addition to addressing the influence of an inert support¹⁷ or a non-homogeneous medium¹⁸ on the attainable chemistry evolving at an irradiated semiconductor surface, this work has led to the preparation of quantized CdS clusters in micelles,¹⁹ of composites **9** in which a sensitizer initiates electron transfer over long

9

distances to a RuO₂ cluster capable of gas evolution,²⁰ and of a coupled porphyrin-spacer-viologen supermolecule **10** in which conformational equilibration can be controlled by

10

ZnP: R = H

dispersion within an inverse micelle.²¹ Theoretical work describing electron and energy migration in composite micelles has also been completed.²²

The third objective, the search for new redox-activated catalysts, has been pursued in three directions. The effect of substitution on the electronic properties of a family of tetraphenylethylenes has revealed that multiple electron transfer catalysis can result from the twisting induced in the parent by single electron oxidation or reduction.²³ The synthetic utility of bis(dialkylphosphino)benzene nickel (0) as a catalyst for electrochemical coupling of aryl and vinyl halides has been elaborated,²⁴ with mechanistic details of the catalysis found to be dependent on the alkyl substitution pattern.²⁵ The search for new redox-activated catalysts has led us to investigate redox reactions induced by complex bases and reducing agents. This class of compound relies on aggregative activation for the high reactivity observed. We have determined that a reversible Ni(0) complex is involved in these reagents,²⁶ whose activity can be mimicked on modified electrode surfaces.

Finally, progress continues in exploring new methods for characterizing chemically modified surfaces. A digital simulation method for describing corrosion and aging of semiconductor surfaces has been described.²⁷ Photoresponsiveness of semiconductor surfaces modified by attachment of polymeric complexants²⁸ or photosensitizers²⁹ or by exposure to water³⁰ has been investigated and the use of such modified surfaces in photoelectrochemical cells has been described. A mechanistic investigation of charge injection from visible light-absorbing anions and dianions into semiconductor electrodes in photogalvanic cells, as supported in earlier DOE grants, has also appeared.³¹

A new thrust in surface modification by binding of self assembled monolayers to metal electrode surfaces has been begun.³² Our previous success in preparing self-assembled monolayers based on gold-thiol interactions³³ has been elaborated with electrochemical probes for intramonolayer interactions and for cross-membrane energy and electron transfer.³⁴ Specifically, such studies have shown that defect populations can be kinetically differentiated and that exchange reactions permit selective spatial functionalization at defect sites that remain stationary on common laboratory exchange-time scales. In an extension of this electrochemical characterization, our current studies focus on the preparation of thioalkylpyrenes and thioalkylperylene of varying chain lengths and the use of photophysical techniques for the characterization of their architectural assembly on metallic (gold, silver, and copper) or semiconductor (indium tin oxide) surfaces.

References

1. Watkins, D.M.; Fox, M.A. *J. Am. Chem. Soc.* **1993**, submitted.
2. Fox, M.A.; Jones, W.; Watkins, D.M. *Chem. Engin. News* **1993**, Mar. 15, 1993, 38.

3. Fox, M.A. *Accts. Chem. Res.* **1992**, *25*, 569.
4. Watkins, D.M.; Fox, M.A. *Adv. Chem. Ser.* **1994**, in press.
5. Fox, M.A.; Pan, H.-L. *Proc. SPIE* **1991**, *1436*, 2.
6. Schouten, P.G.; Warman, J.M.; Fox, M.A.; Pan, H.-L. *Nature* **1991**, *353*, 736.
7. Fox, M.A.; Chandler, D.A. *Adv. Mater.* **1991**, *3*, 381.
8. Wang, P.W.; Fox, M.A. *Inorg. Chim. Acta* **1994**, submitted.
9. Wang, P.W.; Fox, M.A. *Inorg. Chem.* **1993**, submitted.
10. Collard, D.M.; Fox, M.A. *J. Am. Chem. Soc.* **1991**, *113*, 9414.
11. Torres, W.; Fox, M.A. *Chem. Mater.* **1992**, *4*, 146.
12. Torres, W.; Fox, M.A. *Chem. Mater.* **1992**, *4*, 583.
13. Meier, M.S.; Fox, M.A.; Miller, J.R. *J. Org. Chem.* **1991**, *56*, 5380.
14. Fox, M.A.; Batchelder, T., unpublished work.
15. Fox, M.A.; Lin, J. *Macromol.* **1994**, in press.
16. Fox, M.A.; Thompson, H., unpublished work.
17. Fox, M.A. *Res. Chem. Intermed.* **1991**, *15*, 153.
18. Fox, M.A. *Top. Curr. Chem.* **1991**, *159*, 68.
19. Barzykin, A.V.; Fox, M.A. *Isr. J. Chem.* **1993**, *33*, 21.
20. Resch, U.; Fox, M.A. *J. Phys. Chem.* **1991**, *95*, 6169.
21. Resch, U.; Hubig, S.; Fox, M.A. *Langmuir* **1991**, *7*, 2923.
22. Barzykin, A.V.; Barzykina, N.V.; Fox, M.A. *Chem. Phys.* **1992**, *163*, 1.
23. Muzyka, J.; Fox, M.A. *J. Org. Chem.* **1991**, *56*, 4549.
24. Fox, M.A.; Chandler, D.A.; Lee, C.-J. *J. Org. Chem.* **1991**, *56*, 3246.
25. Fox, M.A.; Chandler, D.A.; Kyba, E.P. *J. Coord. Chem.* **1992**, *25*, 1.
26. Fox, M.A.; Merkert, J.R.; Caubere, P. *New J. Chem.* **1994**, in press.
27. Fox, M.A.; Perone, S.P.; Kiwiet, N.J.; Fox, M.A. *J. Electroanal. Chem.* **1991**, *313*, 61.
28. Fox, M.A.; Chandler, D.A., *Macromol.* **1991**, *24*, 4626.
29. Fox, M.A.; Britt, P.F. *New J. Chem.* **1992**, *16*, 113.
30. Anpo, M.; Chiba, K.; Tomonari, M.; Coluccia, S.; Che, M.; Fox, M.A. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 543.
31. Fox, M.A.; Campbell, K.A.; Hurst, J.R.; Maldonado, R.; Echegoyen, L.; Soulen, R.L. *J. Org. Chem.* **1992**, *57*, 3728.
32. Collard, D.M.; Fox, M.A. *Proc. 15th DOE Solar Photochem. Res. Conf.* **1991**, 197.
33. Creager, S.E.; Collard, D.M.; Fox, M.A. *Langmuir* **1990**, *6*, 1617.
34. Collard, D.M.; Fox, M.A. *Langmuir*, **1991**, *7*, 1192.

B. Papers currently being considered for publication that acknowledge DOE support (Abstracts of each are attached in Appendix I.):

"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, submitted.

"Rigid, Well-defined Block Copolymers for Efficient Light Harvesting," Diana M. Watkins and Marye Anne Fox, *J. Am. Chem. Soc.* 1993, submitted.

"Metal-Metal Interactions in Tetrakis(diphenylphosphino)benzene-bridged Bimetallic Complexes and Their Related Coordination Polymers," Pei-Wei Wang and Marye Anne Fox, *Inorg. Chem.* 1993, submitted.

C. List of Publications for the Past Three Years (1991-93), including those in press, that acknowledge DOE support (Abstracts of each are listed in the attached Appendix):

(Where available, reprints not submitted with earlier progress reports are included separately.)

"Light Harvesting Polymers," Diana M. Watkins and Marye Anne Fox, *Adv. Chem. Ser.* 1994, in press.

"Interblock Electron Transfer in 2-Vinylnaphthalene-N,N-Dimethaminomethylstyrene Block Copolymers," Jun Lin and Marye Anne Fox, *Macromol.* 1994, in press.

"A Picosecond Study of the Photophysics of CdS Clusters Grown in Situ in Reversed Micelles," A.V. Barzykin and Marye Anne Fox, *Isr. J. Chem.* 1993, 33, 21.

"Graded Spatial Distribution in Conducting Co-polymers of Pyrrole and Thiophene," Walter Torres and Marye Anne Fox, *Chem. Mater.* 1992, 4, 146.

"Covalently-linked Cyclooctatetraenyl Dianions as Sensitizers in Photoelectrochemical Cells," Marye Anne Fox, Kay A. Campbell, John R. Hurst, Rene Maldonado, Luis Echegoyen, and Robert L. Soulen, *J. Org. Chem.* 1992, 57, 3728.

"Influence of Steric Bulk on the Relative Stability and Interchangeability of the Various Oxidation States for Nickel Complexed with 1,2-bis(dialkylphosphino) benzene," Marye Anne Fox, Daniel A. Chandler, and Evan P. Kyba, *J. Coord. Chem.* 1992, 25, 1.

"Photosensitization of Semiconductor Electrodes by Adsorbed Polymeric Thin Films," Marye Anne Fox and Phillip F. Britt, *New J. Chem.* 1992, 16, 113.

"Polymeric and Supramolecular Arrays for Directional Energy and Electron Transport over Macroscopic Distances," Marye Anne Fox, *Accts. Chem. Res.* 1992, 25, 569.

"Electronic Excitation Transport and Trapping in Micellar Systems: Monte Carlo Simulations and Density Expansion Approximation," A.V. Barzykin, N.S. Barzykina, and M.A. Fox, *Chem. Phys.* 1992, 163, 1.

"Electrosynthesis of Polypyrrole in a Nematic Liquid Crystal," Walter Torres and Marye Anne Fox, *Chem. Mater.* **1992**, *4*, 583.

"A Lamellar Conducting Polymer by Self-Assembly of an Electropolymerizable Monomer," David M. Collard and Marye Anne Fox, *J. Am. Chem. Soc.* **1991**, *113*, 9414.

"Peptide Conformational Distributions as Studied by Electron Transfer Kinetics," Mark S. Meier, Marye Anne Fox, and John R. Miller, *J. Org. Chem.* **1991**, *56*, 5380.

"Charge Separation in Functionalized Tetrathiafulvalene Derivatives," Marye Anne Fox and Horng-Long Pan, *Proceedings, SPIE-The International Society for Optical Engineering*, **1991**, *1436*, 2.

"Semiconductor Particles Included within Supports," Marye Anne Fox, *Res. Chem. Intermed.* **1991**, *15*, 153.

"Influence of Linking Alkyl Chain Length on Intramolecular Photoinduced Electron Transfer in Bipyridine-Linked Porphyrin-RuO₂ Clusters," Ute Resch and Marye Anne Fox, *J. Phys. Chem.* **1991**, *95*, 6169.

"The Effect of Substituents on the Electrochemistry of Substituted Tetraphenylethylenes," Jennifer Muzyka and Marye Anne Fox, *J. Org. Chem.* **1991**, *56*, 4549.

"Photoinduced Electron Transfer from a Surfactant Zinc Porphyrin to Dialkylviologens in Water-in-oil Microemulsions. Effect of Interfacial Charge," Ute Resch, Stephan Hubig, and Marye Anne Fox, *Langmuir* **1991**, *7*, 2923.

"The Use of Electroactive Thiols to Study the Formation and Exchange of Alkanethiol Monolayers on Gold," David M. Collard and Marye Anne Fox, *Langmuir* **1991**, *7*, 1192.

"Photocatalysis on Native and Platinum-Loaded TiO₂ and ZnO. Origin of Different Reactivities on Wet and Dry Metal Oxides," Masakazu Anpo, Katsuichi Chiba, Masanori Tomonari, Salvatore Coluccia, Michel Che, and Marye Anne Fox, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 543.

"Synthesis and Electrochemical Activity of Nickel Phosphine Complexes and Polymers Bound to Electrode Surfaces," Marye Anne Fox, Daniel A. Chandler, and Pei-wei Wang, *Macromol.* **1991**, *24*, 4626.

"A Semiconductive Nickel-Phosphine Coordination Polymer," Marye Anne Fox and Daniel A. Chandler, *Adv. Mater.* **1991**, *3*, 381.

"Digital Simulation of the Laser-Induced Open Circuit Photovoltage at the Semiconductor-Electrolyte Interface," John M. Martin, Sam P. Perone, N.J. Kiwiet, and Marye Anne Fox, *J. Electroanal. Chem.* **1991**, *313*, 61.

"Photoinduced Electron Transfer in Arranged Media," Marye Anne Fox, *Top. Curr. Chem.* **1991**, *159*, 68.

"Electrocatalytic Coupling of Aryl Halides with 1,2-Bis(di-2-propylphosphino)benzene Nickel (0)," Marye Anne Fox, Daniel A. Chandler, and Chang-jin Lee, *J. Org. Chem.* **1991**, *56*, 3246.

D. Invited Lectures on DOE-Supported Work Presented at Scientific Meetings (1991-1993)

"Interblock Charge Transfer in 2-Vinylnaphthalene -N,N,-Dimethylaminomethylstyrene Block Copolymers," Marye Anne Fox and Jun Lin, *Proc. DOE Solar Photochem. Res. Conf. 1993*, in press.

"Anisotropic Conduction in Synthetic Thin Films," Marye Anne Fox, David Collard, Walter Torres, and Horng-long Pan, *Proc. DOE Solar Photochem. Res. Conf. 1992*, 16, 119.

"Vectorial Electron Transfer Mediation: Electrochemical Characterization of Self-Assembled Functionalized Redox-Active Monolayers on Gold," David M. Collard and Marye Anne Fox, *Proc. 15th DOE Solar Photochem. Res. Conf. 1991*, 197.

Southwest Regional Award, 49th Southwest Regional American Chemical Society Meeting, Austin, Oct. 1993, "Dimensionally Controlled Electron Transfer"

NATO Advanced Research Workshop on Photoinduced Electron Transfer Reactions, Praia da Falesia, Portugal, Sept. 1993, "Photoinduced Electron Transfer in Three-Dimensionally Controlled Polymers."

Third International Congress of Polymer Photochemistry, Sestri Levante, Italy, Sept. 1993, "The Conductive Properties of Columnarly Stacked Porphyrins and Phthalocyanines Studied by Time-Resolved Microwave Conductivity," with P.G. Schouten, J. Warman, and H-L. Pan.

XVIth International Conference on Photochemistry, Vancouver, British Columbia, Canada, Aug. 1993, "Controlling Electron Transfer in Macromolecular Media."

Gordon Research Conference on Supramolecules and Assemblies, Henniker, New Hampshire, July 1993, "Three Dimensional Arrays for Controlled Electron Transfer."

Symposium on Electron Transfer in Organic Colloidal Systems II, 183rd Meeting of the Electrochemical Society and Joint Meeting with the Electrochemical Society of Japan, Honolulu, May 1993, "Electron Transfer in Micelle-dispersed 2-Vinylnaphthalene - p-Vinyl-N,N-dimethylbenzylamine Block Copolymers," with Jun Lin.

Special Colloquium on Women in Science, Florida State University, Tallahassee, Feb. 1993, "Designed Materials for Controlled Electron Transfer."

Texas Conference on Spectroscopy and Photochemistry, Center for Fast Kinetics Research, Austin, Feb. 1993, "Directional Electron Transfer."

East Texas Section, American Chemical Society, Houston, Jan. 1993, "Designing Molecular Electronic Devices."

IUPAC Conference on Physical Organic Chemistry, Aug. 1992, Ithaca, NY, "Three Dimensionally Ordered Materials for Controlled Electron Transfer."

Kendall Award Symposium, American Chemical Society National Meeting, San Francisco, April, 1992, "Photophysical Probes for Structure in Reversed Micelles," with A. Barzykin.

American Chemical Society Division of Chemical Education Symposium on Electron Transfer Processes in Inorganic, Organic, and Biochemical Systems," American Chemical Society National Meeting, San Francisco, April, 1992, "Dimensionally Controlled Electron Transfer from Photoexcited Organic Donors."

Gordon Research Conference, Electrochemistry, Ventura, CA, Jan. 1992, "Polymeric Arrays for Catalytic Redox Chemistry".

Symposium on Electrochemistry in Microheterogeneous Fluids, Fourth Chemical Congress of North America, New York, Aug. 1991, "Photoinduced Electron Transfer in a Composite Surfactant Porphyrin - Metal Oxide Cluster," with U. Resch.

Symposium on Photosensitive Metal-Organic Systems: Mechanistic Principles and Recent Applications, Fourth Chemical Congress of North America, New York, Aug. 1991, "Molecular Models for Semiconductor Particles: Luminescence Studies of Inorganic Clusters," with T. Türk, A. Vogler.

1991 International Symposium on Organic Reactions, Kyoto, Japan, Aug. 1991, "Synthesis of Spatially Ordered Electron Relays: Charge Transfer in Layered Conducting Polymers, Conducting Co-Polymers, and Redox-active Functionalized Alkylthiols on Gold."

Sandbjerg Meeting on Organic Electrochemistry, Soc. Chimica Scandinavica, Sandbjerg, Denmark, June 1991, "Electrocatalytic Coupling of Aryl and Vinyl Halides by Monomeric and Polymeric Bisphosphinobenzene Nickel (0)."

Third Annual Symposium on Organic Chemistry, Western New York Section of the American Chemical Society and Occidental Chemical Corporation, June 1991, "Controlling Electron Transfer in Organic Media."

Symposium on Photochemistry and Photoelectrochemistry of Organic and Inorganic Molecular Thin Films, International Society for Optical Engineering, Los Angeles, Jan. 1991, "Charge Separation in Functionalized Tetrathiafulvalene Derivatives."

E. Appendix: Abstracts of All Papers (Submitted, In Press, and Published) from Jan. 1991 - Jan 1994 that Acknowledge Support from this Grant

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

Abstract. Intermetallic electronic coupling in 1,2,4,5-tetrakis(dimethylphosphino)-benzene bridged bimetallic Ni, Pd, and Pt complexes has been studied by electrochemical and spectroelectrochemical methods. These bimetallic complexes show minimal cross-ring metal-metal interactions. The observed oxidation potential for the monometallic Ni^{II} complex is similar to that of its bimolecular analog, but substantial shifts from the monometallic complexes are observed for the Pd^{II} and Pt^{II} complexes. The very low conductivities observed in the metal-phosphine coordination polymers ($\text{M} = \text{Ni}^{\text{II}}$, Pd^{II} , and Pt^{II}) and their partially-oxidized (p-doped) analogs are consistent with the minimal coupling observed in the bimetallic complexes.

"Rigid, Well-defined Block Copolymers for Efficient Light Harvesting," Diana M. Watkins and Marye Anne Fox, *J. Am. Chem. Soc.* 1993, submitted.

Abstract. Light-harvesting polynorbornene homopolymers and block copolymers bearing appended aryl chromophores, with and without attached quenchers, exhibit steady-state fluorescence spectra indicative of isolated absorbing units. The lack of excimer emission in any of these monodisperse homopolymers is indicative of a rigid polymer chain. Enhanced intramolecular fluorescence quenching of the naphthalene emission in the naphthalene-dimethylaniline diblock copolymer takes place through vectorial energy migration to the interface. A statistical mechanical analysis of energy hopping to the interface (where quenching takes place) suggests that optimal design of block length for energy migration over long distances depends on excited state lifetime, driving force for electron transfer quenching, and polymer rigidity.

"Metal-Metal Interactions in Tetrakis(diphenylphosphino)benzene-bridged Bimetallic Complexes and Their Related Coordination Polymers," Pei-Wei Wang and Marye Anne Fox, *Inorg. Chem.* 1993, submitted.

Abstract. Electrochemical, electron paramagnetic resonance, and spectroelectrochemical methods have been used to probe electronic coupling through a 1,2,4,5-tetrakis(diphenylphosphino)benzene bridging ligand connecting metal centers in several Ni, Pd, and Pt-containing dimetallic complexes. These dimetallated complexes showed weak intervalence charge transfer (IT) bands and slightly shifted redox potentials in comparison with their monometallic models. A Marcus-Hush analysis of the energies of the IT bands for the electrochemically generated mixed-valence heterodimetallic complexes ($\text{Ni}^0\text{-Pd}^{\text{II}}$ and $\text{Ni}^0\text{-Pt}^{\text{II}}$, respectively) established the magnitude of intermetallic electronic coupling. The weak thermal coupling observed in these dimetallated complexes is consistent with the very low conductivities (10^{-8} - $10^{-10} \Omega^{-1} \text{ cm}^{-1}$) observed in the polymeric analogs of these complexes; namely, the newly prepared metal coordination polymers ($\text{M} = \text{Ni}^{\text{II}}$, Pd^{II} , and Pt^{II}) with 1,2,4,5-tetrakis(diphenylphosphino)benzene.

"Light Harvesting Polymers," Diana M. Watkins and Marye Anne Fox, *Adv. Chem. Ser.* 1994, in press.

Abstract. Organized polymeric assemblies are being investigated for the unique functional properties induced by the absorption of light. These arrays, bearing pendant photoactive groups in their excited states, are useful for such diverse functions as solar energy conversion, photoconductivity, optical storage, and others once thought to be attainable only in nature and in small-scale electronic devices. The successful design and synthesis of such polymers relies on the judicious assembly of functional components in an organized array. Light-induced electron and energy transfers that occur in these arrays constitute the fundamental events that are discussed in detail in this chapter.

"Interblock Electron Transfer in 2-Vinylnaphthalene-*N,N*-Dimethaminomethylstyrene Block Copolymers," Jun Lin and Marye Anne Fox, *Macromol.* 1994, in press.

ABSTRACT: 2-Vinylnaphthalene-((*N,N*-dimethylamino)methyl)styrene block copolymers (1) of variable block lengths constituted from two monomers with substantially different redox potentials were prepared by anionic polymerization. Interblock electron transfer studied by fluorescence quenching was most efficient in block copolymers with approximately equal individual block lengths. Copolymers with very different lengths for the individual blocks exhibited substantially lower quenching efficiencies, probably because of interblock phase separation, as suggested by phase-dispersal studies. The intensities of the observed ground-state charge-transfer absorptions in these block copolymers correlate with the degree of phase separation.

"A Picosecond Study of the Photophysics of CdS Clusters Grown in Situ in Reversed Micelles," A.V. Barzykin and Marye Anne Fox, *Isr. J. Chem.* 1993, 33, 21.

Abstract. A study of the dynamics of the electronic states of CdS semiconductor clusters grown in situ in reversed micelles via picosecond pump-probe technique reveals efficient transient bleaching of the excitonic absorption. This effect is attributable mainly to hole localization near the trapped electron, with no evidence of electron ejection (forming a solvated electron) detectable despite the apparent proximity of the cluster to the included water pool. Bleaching efficiency is cluster-size dependent, and recovery kinetics are governed by the nature of the particle surface. Similar decay behavior is observed in cluster fluorescence. Generally, the decay is characterized by two components, the faster attributed to recombination of a mobile, detrapped electron with a trapped hole, and the slower to an exchange interaction between trapped carriers.

"Graded Spatial Distribution in Conducting Co-polymers of Pyrrole and Thiophene," Walter Torres and Marye Anne Fox, *Chem. Mater.* 1992, 4, 146.

Random and spatially graded copolymers of pyrrole and thiophene formed at fixed concentrations of monomer under potentiostatic control are characterized by X-ray photoelectron spectroscopy and electroanalytical techniques. Unlike previously described copolymers composed of discrete bilayers of polypyrrole and polythiophene, neither the random nor spatially graded copolymers exhibited appreciable long-term charge rectification.

"Covalently-linked Cyclooctatetraenyl Dianions as Sensitizers in Photoelectrochemical Cells," Marye Anne Fox, Kay A. Campbell, John R. Hurst, Rene Maldonado, Luis Echegoyen, and Robert L. Soulen, *J. Org. Chem.* 1992, 57, 3728.

In order to explore whether this photoresponse, i.e., the critical disproportionation, might be improved by constraining two such sensitizer units to a single molecule, we have examined the electroreduction of a series of covalently bridged bis(cyclooctatetraenyls) 2-4⁸ to determine whether this hydrocarbon link would permit significant perturbation of their electrochemical behavior. We then compare the utility of their dianions with those of 1, bis(cyclooctatetraenyl) 5,⁹ and perfluorotetrakis(cyclobutacyclooctatetraene) 6¹⁰ as sensitizers in photoelectrochemical cells.

"Influence of Steric Bulk on the Relative Stability and Interchangeability of the Various Oxidation States for Nickel Complexed with 1,2-bis(dialkylphosphino) benzene," Marye Anne Fox, Daniel A. Chandler, and Evan P. Kyba, *J. Coord. Chem.* **1992**, *25*, 1.

The reduction potentials and electrochemical reversibilities of a series of nickel complexes of 1,2-bis(dialkylphosphino)benzene are sensitive to the steric bulk of the alkyl substituents. With very large ligands, electroreduction is accompanied by rapid secondary chemical reaction, and spectroscopic evidence for the intermediacy of a coordinatively unsaturated species is presented. The potentials required for electrooxidation of these complexes are shifted to more positive potentials by increasing bulk of the alkyl substituents on the bisphosphino ligands.

"Photosensitization of Semiconductor Electrodes by Adsorbed Polymeric Thin Films," Marye Anne Fox and Phillip F. Britt, *New J. Chem.* **1992**, *16*, 113.

ABSTRACT. — Photosensitization of current production in a photoelectrochemical cell equipped with metal oxide semiconductor electrodes modified by adsorbed poly-(10-substituted-2-(9-anthryl)ethyl methacrylates) **1** has been examined. Irradiation of a polymer-coated SnO_2 electrode ($\lambda > 330 \text{ nm}$) generated a photocurrent 40 times larger than irradiation of a bare SnO_2 electrode, with the coated electrodes exhibiting action spectra which parallel the absorption profiles of the polymers. Optimal conditions for photosensitized current generation were obtained on an indium tin oxide electrode coated with poly-(10-*n*-butyl-2-(9-anthryl)ethyl methacrylate) **1-Bu** immersed in an aqueous solution of benzoquinone/hydroquinone (0.02 M) at pH 8.5. Increasing steric bulk of the substituent at the 10-position of the anthryl group decreased the attainable polymer-sensitized photocurrent.

"Polymeric and Supramolecular Arrays for Directional Energy and Electron Transport over Macroscopic Distances," Marye Anne Fox, *Accs. Chem. Res.* **1992**, *25*, 569.

Photoinduced electron transfer,¹ one of the simplest conceivable molecular transformations, has profound consequence on reactivity, converting an electron-rich donor molecule D to an electrophilic cation radical and an electron-deficient molecule A to a nucleophilic anion radical (eq 1).

"Electronic Excitation Transport and Trapping in Micellar Systems: Monte Carlo Simulations and Density Expansion Approximation," A.V. Barzykin, N.S. Barzykina, and M.A. Fox, *Chem. Phys.* **1992**, *163*, 1.

A theoretical treatment of electronic energy transport and trapping in a finite volume is presented by taking, as a typical example, an ensemble of chromophores solubilized in a spherical micelle. A truncated power series expansion in the chromophore density is used to calculate the configurational average of $G^S(t)$, the probability that an initially excited donor molecule is still excited, and $G^D(t)$, the probability of finding an excitation in the sub-ensemble of donors at time t , which are directly related to experimental observables. A detailed analysis of the problem via a Monte Carlo simulation is carried out for different occupation numbers of donor and trap molecules in a micelle, and for different ratios of the micelle radius to the Förster radius. The density expansion, as checked against the numerical results, provides a quite reasonable approximation, especially at short times and low chromophore concentrations. The difference in energy transfer dynamics between a finite and infinite volume system is described. The theory developed can be useful for probing structural details of microdisperse systems via time-resolved fluorescence measurements.

"Electrosynthesis of Polypyrrole in a Nematic Liquid Crystal," Walter Torres and Marye Anne Fox, *Chem. Mater.* **1992**, *4*, 583.

Pyrrole was anodically polymerized on platinum and indium-tin oxide electrodes in the nematic liquid crystal 4-cyano-4'-pentylbiphenyl containing an electrolyte. The nematic mixture was oriented with respect to the opposite working and counterelectrodes, which were separated by a 13- μm spacer, by previous silanization of the electrodes or by applying a sufficiently high electric field. Orientation of the nematic polymerization mixture induces shifts in the voltammetric peaks and the absorption spectral bands of the resulting films to more negative potentials and higher wavelengths, respectively. Some anisotropic conductivity was attained in films prepared in an oriented nematic environment. However, measurements along and across the film surface showed only small conductivity differences, and no evidence for crystallinity was obtained.

"A Lamellar Conducting Polymer by Self-Assembly of an Electropolymerizable Monomer," David M. Collard and Marye Anne Fox, *J. Am. Chem. Soc.* **1991**, *113*, 9414.

The formation of this head-to-head bilayer type assembly by polymerization of pyrrole-containing surfactants from micellar solutions implies that assembly of the monomers, or growing polymer chain, at the electrode (i.e., as a hemimicelle) predominates over the head-first delivery of the surfactant to the electrode by the micelle. The homopolymers assemble into a layered morphology, producing a film which is highly ordered relative to other poly(heterocycles). This method can be used without the need for an ordered supporting medium, and with the distinct advantage of operational simplicity over the use of the Langmuir-Blodgett technique for the deposition of such materials.

"Peptide Conformational Distributions as Studied by Electron Transfer Kinetics," Mark S. Meier, Marye Anne Fox, and John R. Miller, *J. Org. Chem.* **1991**, *56*, 5380.

The preparation and electron-transfer (ET) behavior of a homologous series of alanine oligomers bearing naphthoyl groups at the N-termini and biphenylamide groups at the C-termini is described. Electron pulse radiolysis was used to generate the corresponding radical anions, and the rates of ET were monitored at 700 nm (decay of donor) and at 500 nm (growth of acceptor). Several systems displayed ET decays too fast to measure ($k_a > 10^{10}$), and in the others multiexponential decay kinetics were observed. The ET decay of dipeptide 3 could be fit to two exponential described by rate constants of 5.2×10^8 (22%) and 5.6×10^9 s⁻¹ (78%). In the longer peptides, the fit of the rate constants (and their relative contributions to total intensity) becomes less well-defined, suggesting additional conformational diversity.

"Charge Separation in Functionalized Tetrathiafulvalene Derivatives," Marye Anne Fox and Horng-Long Pan, *Proceedings, SPIE-The International Society for Optical Engineering*, **1991**, *1436*, 2.

The synthesis of a family of symmetrical derivatives of tetrathiafulvalene bearing long chain ether groups is discussed. A comparison will be made between this family of compounds and those obtained with symmetrically substituted zinc octakis(alkoxyethyl)porphyrins, which have been shown to exhibit unusual photoeffects when dispersed as liquid crystals in symmetrical cells consisting of indium tin oxide electrodes as windows.

"Semiconductor Particles Included within Supports," Marye Anne Fox, *Res. Chem. Intermed.* **1991**, *15*, 153.

Irradiated semiconductor surfaces have been recognized within the last several years as important catalysts for driving photoinduced electron transfer reactions [1]. By dispersing a semiconductor within a support which is itself inert to the reaction conditions, chemical selectivity is altered by influencing the kinetics for these charge transfers. Furthermore, integrated systems consisting of several components acting in a synergistic way can improve the efficiency of charge separation and, hence, of the desired photoreactivity [2]. We briefly overview in this article some of the recent investigations which have employed semiconductor photocatalysts in or on photoinactive supports.

"Influence of Linking Alkyl Chain Length on Intramolecular Photoinduced Electron Transfer in Bipyridine-Linked Porphyrin-RuO₂ Clusters," Ute Resch and Marye Anne Fox, *J. Phys. Chem.* 1991, 95, 6169.

In a series of covalently linked *meso*-tris(octyloxyphenyl)porphyrin-RuO₂ composite clusters, the efficiency of photoinduced intramolecular electron transfer from the porphyrin to the covalently attached RuO₂ cluster depends on the length of the alkyl chain $-(CH_2)_n-$, $n = 1, 4-7$ separating the surfactant-like porphyrin from the bipyridine ligating site. The broadening of the porphyrin Soret band and the observation of two distinct triplet-state lifetimes upon complexation to RuO₂ are best interpreted as arising from at least two distinct sets of conformers: (1) a family of folded conformers in which RuO₂ is complexed to the porphyrin π -electron system and (2) a family of more extended (noncomplexed) conformers. The complexed conformers exhibit broadened absorption spectra, decreased fluorescence quantum yields, and diminished triplet-state lifetimes compared to the noncomplexed conformers. Axial ligation of the zinc porphyrin to pyridine reduces intramolecular complexation between the porphyrin π -electron system and the RuO₂ cluster in ZnPB_nR, resulting in unperturbed (narrow) absorption spectra, diminished fluorescence quenching, and a strong diminution of the relative amplitude of the short-lived porphyrin triplet state.

"The Effect of Substituents on the Electrochemistry of Substituted Tetraphenylethylenes," Jennifer Muzyka and Marye Anne Fox, *J. Org. Chem.* 1991, 56, 4549.

The oxidation and reduction potentials for pairs of electron-rich and -poor 1, Tables I and II, indicate that complete ground-state equilibration to form a dication-dianion pair would be endothermic, as is consistent with the absence of CT bands. Although this contrasting behavior is at least partially thermodynamic, it may also in fact derive from the kinetic retardation for electron transfer in these systems imposed by a requisite geometry change^{18,28} encountered in either the two-electron oxidation or reduction or the difficulty of permitting strong electronic interaction between two substrates twisted from planarity

"Photoinduced Electron Transfer from a Surfactant Zinc Porphyrin to Dialkylviologens in Water-in-oil Microemulsions. Effect of Interfacial Charge," Ute Resch, Stephan Hubig, and Marye Anne Fox, *Langmuir* 1991, 7, 2923.

Photoinduced electron transfer from the excited triplet state of a water-insoluble neutral zinc porphyrin to the dicationic dimethyl- and dioctylviologens has been investigated in homogeneous solution and in both anionic and cationic water-in-oil microemulsions. The rate constants of forward electron transfer depend on both the environment and the alkyl chain length of the viologen. The back electron transfer rate constants are much less sensitive to the medium and independent of viologen type. In the cationic microemulsion, a plot of the observed first-order quenching rate constant vs viologen concentration shows two linear regions with considerably different slopes for dimethylviologen, but only a single linear region for the more hydrophobic dioctylviologen. The location of dioctylviologen in the cationic microemulsion seems to be controlled by hydrophobic-hydrophilic rather than electrostatic interactions. For the more hydrophilic dimethylviologen, electrostatic interactions with the positively charged surfactant molecules at the interface may be more important.

"The Use of Electroactive Thiols to Study the Formation and Exchange of Alkanethiol Monolayers on Gold," David M. Collard and Marye Anne Fox, *Langmuir* 1991, 7, 1192.

Treatment of mixed monolayers of hexadecanethiol and 16-(ferrocenylcarbonyloxy)hexadecanethiol on gold with solutions of alkanethiols results in the replacement of approximately one-third of the electroactive thiol. This exchange can be monitored by integration of the cyclic voltammetric wave. If this exchange is carried out with a second electroactive thiol, the signal from this species indicates adsorption, and diminution of the original signal represents desorption during exchange. Subsequent treatment of the three-component monolayer with a nonelectroactive thiol results in loss of the signal from the second electroactive species without loss of the original species. These results are consistent with exchange of thiols from defect sites, which are immobile over extended periods.

"Photocatalysis on Native and Platinum-Loaded TiO₂ and ZnO. Origin of Different Reactivities on Wet and Dry Metal Oxides," Masakazu Anpo, Katsuichi Chiba, Masanori Tomonari, Salvatore Coluccia, Michel Che, and Marye Anne Fox, *Bull. Chem. Soc. Jpn.* 1991, 64, 543.

"Synthesis and Electrochemical Activity of Nickel Phosphine Complexes and Polymers Bound to Electrode Surfaces," Marye Anne Fox, Daniel A. Chandler, and Pei-wei Wang, *Macromol.* 1991, 24, 4626.

ABSTRACT: More favorable electroactivity (in the reductive electrocatalytic coupling of aryl halides) is observed for adsorbed polymeric nickel phosphine complexes than with their covalently anchored monomeric nickel analogues. Syntheses of the relevant ligands are described and methodology for formation of polyvinylbenzyl chloride bearing pendant bisphosphinobenzene groups and polymers with bisphosphinobenzene incorporated into the backbone is discussed. The electrochemical activities of these ligands and their coordinated nickel complexes provide useful probes for the characterization of the chemically modified electrode surfaces.

"A Semiconductive Nickel-Phosphine Coordination Polymer," Marye Anne Fox and Daniel A. Chandler, *Adv. Mater.* 1991, 3, 381.

We report herein our investigation of some materials properties of 1, which was prepared by coordination polymerization with a new polyphosphino ligand 1,2,4,5-tetrakis(dimethylphosphino)benzene 3, together with a brief comparison of its electrochemistry with that of monometallic (2) and bimetallic (6) models of the polymer.

"Digital Simulation of the Laser-Induced Open Circuit Photovoltage at the Semiconductor-Electrolyte Interface," John M. Martin, Sam P. Perone, N.J. Kiwiet, and Marye Anne Fox, *J. Electroanal. Chem.* 1991, 313, 61.

The finite difference method is used to simulate digitally the transient laser-induced open circuit photovoltage at the semiconductor/solution interface. Factors influencing the response are characterized in the presence and absence of charge transfer. These factors include minority carrier lifetime, initial potential, intensity, donor density, and mobility. Electron-hole separation produces an initial rapid excursion towards the flatband condition. The subsequent relaxation is dominated by charge redistribution and recombination. Charge transfer also affects relaxation, resulting in a further increase in open-circuit photovoltage. The simulation results are in excellent agreement with experimental observations.

"Photoinduced Electron Transfer in Arranged Media," Marye Anne Fox, *Top. Curr. Chem.* 1991, 159, 68.

A kinetic scheme can be written, Scheme 1, in which the rates of back electron transfer from the contact, solvent-separated, and free ions must each be individually considered. Clearly, the greater the tendency of a given solvent to separate the ions, the less significant will be the electrostatic interaction between them, and the greater tendency to suppress back electron transfer for a period sufficiently long to allow radical ion chemistry to ensue. A major concern of this article will be in defining the efficacy of supramolecular assemblies which create inhomogeneous arrays to control the secondary chemistry of radical ions formed via photoinduced electron transfer.

"Electrocatalytic Coupling of Aryl Halides with 1,2-Bis(di-2-propylphosphino)benzene Nickel (0)," Marye Anne Fox, Daniel A. Chandler, and Chang-jin Lee, *J. Org. Chem.* **1991**, *56*, 3246.

Dibromo- and dichloro(1,2-bis(di-2-propylphosphino)benzene)nickel(II) is compared with tetrakis(tri-phenylphosphino)nickel(II) as an electrocatalyst for the reductive coupling of aryl halides. In many of the reactions examined, dehalogenation of the substrate predominated over coupling; however, preparative yields of biphenyls as high as 96% can be obtained with aryl chlorides and 2 mol % of the title catalyst in polar, coordinating solvents. Experimental factors governing the efficiency of these reactions are discussed, and possible mechanisms for coupling and catalyst deactivation are considered. Much better selectivity for aryl chlorides is attained in electroreductive couplings catalyzed by the title compound, whereas electrocatalysis with $(\text{Ph}_3\text{P})_4\text{NiCl}_2$ allows for selective intra- and intermolecular coupling at aryl bromide and vinyl chloride sites. Modest yields of cyclization products can be attained with either electrocatalyst in the presence of appropriately functionalized aryl or vinyl halides.

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