DOE/ER/13914--1

Photochemical Approaches to Conversion of

Light to Electricity or Fuel

Final Report

for Period April 1, 1991-April 30, 1995

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June, 1998

Prepared for

The U. S. Department of Energy
Agreement No. DE-FG02-88ER13914

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Abstract

Research supported by the Department of Energy focused on the development of molecular and semiconductor based approaches to the conversion of light to electricity or fuels. Studies of molecular systems included the preparation and characterization of new molecules which could serve as light absorbers and/or as elements that bring about charge separation following photoexcitation. Ring-opening metathesis polymerization, in particular, was demonstrated to be useful in preparing new functional polymers of importance in developing fundamental understanding of the excited state dynamics of multicomponent polymers for light absorption and charge separation. Charge separation and ultimate collection is essential to the development of efficient systems for the conversion of light to electricity or fuel. Molecular materials such as poly(p-phenyleneethynylene)s represent possible semiconductor photovoltaic materials that can be both efficient and low cost. Study of the optical and electrical characteristics and excited state behavior of such new materials contributed to an understanding of the design parameters needed for efficient photovoltaic devices based on such materials. Approaches to functionalization of electrode, including photoelectrode, surfaces for the purpose of improving interface energetics and kinetics in photoelectrochemical devices show that a wide range of molecular chemistry can be applied to tailoring the properties of electrode/electrolyte interfaces.

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Research Highlights

New Polymers. Two classes of new polymers were prepared and characterized: one class is a set of materials prepared by ring-opening metathesis polymerization which was established to be a method for the preparation of polymers having interesting redox, optical, and surface-attachment functionality and the second are the poly-*p*-phenyleneethynylenes which when properly derivatized can be solubilized and studied and manipulated. These new materials offer illustrations of the opportunity to "engineer" the properties of molecular materials for optimization of properties for use in photochemical approaches to energy conversion.

A number of research publications citing DoE support have appeared documenting the research findings. Some of the highlights of the findings are given here with reference to the publication number given in the list that follow the Research Highlights section.

For the poly-*p*-phenyleneethynylenes (publications #2-6) we found:

- Highly luminescent materials in solution and in the solid state;
- Relatively high conductivity upon oxidation in the solid state; and
- The high conductivity implies good carrier mobility, suggesting that photovoltaic effects would be seen in the solid state, provided carriers can be

photogenerated. Preliminary, but unpublished findings suggested the possibility of introducing functional groups (e.g. terminal *p*-nitrophenyl) that would lead to charge transfer quenching of the (luminescent) excited state to create delocalized carriers.

For new polymers formed by ring-opening metathesis polymerization (publications #10 and 11) we found:

- The synthetic methodology can be useful to prepare well-defined, multi-block polymers which include a variety of redox active and light-absorbing centers;
- It is possible to order the redox centers using the "living" polymerization method, allowing control of the sequence of redox centers and chromophores. The method allows the incorporation of a terminal group in the polymer that can be useful in attaching the resulting polymer to a surface in an oriented fashion; and
- Polymers prepared allow study of the fundamentals of excited state, intramolecular electron transfer over potentially long distances.

Viologen/Quinone Systems and Molecular Rectification. Unidirectional charge transfer is essential in efficient photochemical energy conversion based on excited state electron transfer. A variety of viologen/quinone systems have been demonstrated to exhibit charge trapping when confined to electrode surfaces, as described in publications #1 and 13. Basically, the demonstration is that the viologen centers of a viologen/quinone polymer can effect the mediated reduction of the quinone at potentials where the viologen is electrochemically reducible. However, once reduced the quinone centers are electrochemically inaccessible, even at potentials very positive of the potential thermodynamically required to effect oxidation (charge removal) of the reduced quinone center. Such charge trapping provides an

example of "molecular rectification" . The charge can be chemically released using appropriate mediators.

Modification of Photoelectrode Materials With Molecular Reagents. CdX (X=S, Se), Si and MS₂ (M= Mo, W) electrodes can be modified with molecular reagents as detailed in publications #8,9, 12 and 16. The important conclusion is that the properties of the photoelectrodes can be altered in purposeful ways by using molecular materials. Perhaps most interesting among the several results in the ability to see selective interaction of certain molecular reagents with the different crystal faces of CdX electrodes. Developing a better understanding of the effects of such chemistry on interfacial electron transfer rates and energetics remains an important objective in such research.

Novel Electrolyte Media for Electrochemical Devices. Fluid solutions are sometimes viewed as problematic in photoelectrochemical energy conversion devices. Our research has demonstrated that polyacrylate gels (publication #14) are viable electrolyte media. In particular, the gels appear to have high ionic conductivity and relatively large, electroactive species have diffusion coefficients in the gel which are similar to the values in aqueous (fluid) electrolytes.

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Publications Stemming from DoE Research

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1. "pH-Dependent Rectification in Redox Polymers: Characterization of Electrode-Confined Siloxane Polymers Containing Naphthoquinone and Benzylviologen Subunits", G. T. R. Palmore, D. K. Smith, M. S. Wrighton, *J. Phys. Chem. B*, **1997**, 101, 2437.
 2. "Effect of the Solid State Structure on the Third-Order Nonlinear Optical Response of Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s", *J. Phys. Chem.*, **1996**, 100, 18931.
 3. "Solid State Structure and Photoluminescence Properties of Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s", C. Weder, M. J. Wagner, M. S. Wrighton, *Mat. Res. Soc. Symp. Proc.*, **1996**, 413, 77 (Materials Research Society).
 4. "Efficient Solid-State Photoluminescence in New Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s", C. Weder, M. S. Wrighton, *Macromolecules*, **1996**, 29, 5157.
 5. "Fluorescence Studies of Poly(*p*-phenyleneethynylene)s: The Effect of Anthracene Substitution", T. M. Swager, C. J. Gil, M. S. Wrighton, *J. Phys. Chem.*, **1995**, 99, 4886.
 6. "Solid State Ordering and Potential Dependence of the Conductivity in Poly(2,5-dialkoxy-*p*-phenyleneethynylene)", *Chem. Mater.*, **1995**, 7, 418.
 7. "Charge-Transfer-to-Solvent Photochemistry of Electrode-Confined Ferrocene- and Cobaltocene-Based Polymers: Photoelectrochemical Reduction of Halocarbons", H. B. Tatistcheff, L. F. Hancock, M. S. Wrighton, *J. Phys. Chem.*, **1995**, 99, 7689.
 8. "Flat Band Potential Measurements of Naked and Viologen-Modified n-WS₂ Electrodes in Aqueous Iodide and Triiodide Solutions", J. Huang, M. S. Wrighton, *J. Phys. Chem.*, **1994**, 98, 9097.
 9. "Surface Modification of n-MoS₂ Electrodes with a Viologen-Based Redox Polymer: Persistent Attachment of a Polysiloxane via a Thin SnO₂ Adhesion Layer", J. Huang, M. S. Wrighton, *Langmuir*, **1993**, 9, 3284.

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10. "New Functional Polymers Prepared by Ring-Opening Metathesis Polymerization: Study of the Quenching of Luminescence of Pyrene End Groups by Ferrocene or Phenothiazine Centers in the Polymers", D. Albagli, G. C. Bazan, R. R. Schrock, M. S. Wrighton, *J. Phys. Chem.*, **1993**, *97*, 10211.
11. "Surface Attachment of Well-Defined Redox-Active Polymers and Block Polymers via Terminal Functional Groups", D. Albagli, G. C. Bazan, R. R. Schrock, *J. Am. Chem. Soc.*, **1993**, *115*, 7328.
12. "Hydrophobic Effects in Surface-Confined Decaalkylferrocene Redox Polymers", D. Albagli, M. S. Wrighton, *Langmuir*, **1993**, *9*, 1893.
13. Charge Trapping by Anionic Quinones Electrostatically Bound to a Highly Charged Cationic Quinone-Viologen Polymer or a Cationic Poly(3-viologen-thiophene)", C. T. Hable, R. M. Crooks, J. R. Valentine, R. Giasson, M. S. Wrighton, *J. Phys. Chem.*, **1993**, *9*, 1517.
14. Comparison of Diffusion Coefficients of Electroactive Species in Aqueous Fluid Solution Electrolytes and Polyacrylate Gels: Step-Generation-Collection Diffusion Measurements and Operation of Electrochemical Devices", H. B. Tatistcheff, I. Fritsch-Faules, M. S. Wrighton, *J. Phys. Chem.*, **1993**, *97*, 2732.
15. "Inter- and Intramolecular Quenching of the Singlet Excited State of Porphyrins by Ferrocene", R. Giasson, E. J. Lee, X. Zhao, M. S. Wrighton, *J. Phys. Chem.*, **1993**, *97*, 2596.
16. "Face-Specific Interactions of Anionic Sulfur-donors with Oriented Crystals of (001) CdX (X = Se, S) and Correlation with Electrochemical Properties", J. J. Hickman, M. S. Wrighton, *J. Am. Chem. Soc.*, **1991**, *113*, 4440