1 of 1

Photochemical Approaches to Conversion of Light to Electricity or Fuel

Progress Report on Research and Request for Continuation Support

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Report for the Period 12/01/92-11/30/93

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Progress Report

Progress on DOE-supported research conducted during the period 12/01/92-11/30/93 is highlighted in this report. Details of research accomplishments are found in publications citing support from the DOE and in forthcoming articles. A list of these research articles appears at the end of this Progress Report. The overall aim of the research is to expand the understanding of photochemical and photophysical processes for the purpose of contributing to the knowledge base needed to ultimately develop photochemical systems for the conversion of light to electricity or fuel.

Orientation of Multi-Component Redox Polymers on Surfaces. Control of the primary structure of multi-component redox polymers is possible using ring opening metathesis polymerization (ROMP). Thus, it is possible to prepare polyblock polymers where each block is comprised of redox-active monomers with a particular formal potential. The blocks can be ordered to achieve an arrangement such that their formal potentials are ordered to effect unidirectional (vectorial) charge transport from block to block. An example of the diversity of redox units that can be built in to a polymer via ROMP is illustrated by I. A

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variety of polyblock redox polymers have now been prepared via ROMP. Studies of charge transfer in such systems has already yielded some interesting results (*vide infra*).

A key to exploiting the polyblock redox materials in devices for demonstration of vectorial electron transfer is the ability to control another aspect of primary structure, namely the point of attachment of the polymer to a conducting surface. Oriented multi-component redox molecules on a conductor allows investigation of their vectorial electron transport properties. Research has now shown that it is possible to "kill" the living polymer with an aldehyde functionalized with a group that yields a polyblock redox polymer with a terminal group effective in attaching the polymer to a surface, as illustrated in Scheme I. The details of the chemistry for introducing the terminal group and for

Scheme I. Strategy for Linking Polymers to a Surface Via Terminal Group

proving its efficacy in binding the molecule on a surface are provided in our article entitled "Surface Attachment of Well-Defined Redox-Active Polymers and Block Polymers via Terminal Functional Groups" by D. Albagli, G. C. Bazan, R. R. Schrock, and M. S. Wrighton (*J. Am. Chem. Soc.*, **1993**, 115, 7328-7334).

In the coming grant period we anticipate preparing relatively high molecular weight polymers for the purpose of studying vectorial electron transport from

block to block in electrode-confined polymers. None of the polymers prepared to date exhibits vectorial electron transport, presumably because all redox active sites are electrode accessible in the low molecular weight materials prepared to date.

Excited State Electron Transport in Multi-Component Molecules Prepared via ROMP. ROMP has been used to prepare multi-component redox active molecules terminating in a derivative of $[(\text{pyridine})\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})]^+$ with blocks from monomers containing a phenothiazine derivative, a derivative of N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD), or combinations of these. The lowest excited state of the Re moiety is a Re to 2,2'-biquinoline charge transfer state that is luminescent in fluid solution at room temperature, and this lowest excited state is known to be quenched by electron transfer from donors such as phenothiazine and TMPD. Examples of the new molecules prepared via ROMP are illustrated by II-IV

The exciting finding is that the redox groups in the multi-component molecules (both the phenothiazine and the TMPD) is that photoexcitation of the terminal Re moiety results in excited state electron transfer from the donor (phenothiazine or TMPD) to the Re center, as detected by transient absorption spectroscopy following laser flash photolysis to excite the Re moiety. The radical cation of phenothiazine and TMPD have characteristic visible absorptions, and

these provide evidence that charge separation can occur following photoexcitation of the Re moiety of II-IV.

Now research will focus on determining whether a cascade of electron transfer events can occur in the multi-component molecules in the following sequence: (1) photoexcitation of the Re center, (2) electron transfer from phenothiazine to the excited Re center, and (3) electron transfer from the TMPD center to the phenothiazine radical cation. This sequence of events has been detected for the three components dissolved in fluid solution, Figure 1.

An encouraging finding is that the lifetime of the charge separated state in the Re-phenothiazine and Re-TMPD systems can apparently be lengthened by placing hydrocarbon blocks between the Re moiety and the donor (phenothiazine or TMPD) block. A more complete study of the lifetime of the charge separated state and factors influencing it will be undertaken in the next period of the DOE grant.

Molecular Materials for Solid State Photovoltaics. In the progress report of last year, sexithiophene has been reported to serve as the active material (light absorber/charge separation) in a simple solid state device consisting of sexithiophene sandwiched between two metals of dissimilar work function, e.g. Pt and Al. Work continues on this system, with an emphasis on understanding the poor fill factors associated with the device. It is now believed that the Al contact is a contributor to some difficulties, but it is also evident that poor electron mobility is a contributor to poor performance. Evidence that poor electron mobility is a problem is that the performance depends on the side of the device exposed to the light, with superior performance for irradiation through the Al contact. This means that photoexcited electrons have a shorter distance to travel to reach the Al contact than when the excitation is through the contact that collects the photogenerated holes. In the coming year derivatives of

Figure 1. Transient spectra at various times following laser flash photolysis of $[(\text{pyridine-4-carboxaldehyde})\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})]^+$ in the presence of 10 mM N-methylphenothiazine and 0.01 mM TMPD in $\text{CH}_3\text{CN}/0.1 \text{ M } [(n\text{-Bu}_4)\text{N}]\text{PF}_6$ showing first electron transfer quenching of the excited Re species by phenothiazine to yield initially the phenothiazine radical cation (top frame) followed by electron transfer from TMPD to the phenothiazine radical cation to yield TMPD^+ (middle frame). Eventually, at long times the TMPD^+ back reacts with the reduced Re species to regenerate the original solution (bottom frame).

sexithiophene will be prepared with the aim of improving carrier mobilities. Additionally, study of liquid junction devices (replacing the Al contact with a solvent/electrolyte/redox couple combination) will be undertaken.

Publications Citing DOE Support

"Surface Attachment of Well-Define Redox-Active Polymers and Block Polymers via Terminal Functional Groups", D. Albagli, G. C. Bazan, R. R. Schrock, M. S. Wrighton, *J. Am. Chem. Soc.*, **1993**, *115*, 7328-7334.

"Inter- and Intramolecular Quenching of the Singlet Excited State of Porphyrins by Ferrocene", R. Giasson, E. J. Lee, M. S. Wrighton, *J. Phys. Chem.*, **1993**, *97*, 2596-2601.

"Comparison of Diffusion Coefficients of Electroactive Species in Aqueous Fluid 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*, 2732-2739.

"Hydrophobic Effects in Surface-Confined Decaalkylferrocene Redox Polymers", D. A. Albagli, M. S. Wrighton, *Langmuir*, **1993**, *9*, 1893-1897.

"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**, *97*, 6060-6065.

"Intermolecular and Intramolecular Excited State Electron Transfer Involving Electrode-Confined Rhenium Carbonyl Complexes: Toward Molecule-Based Systems for Light Absorption, Charge Separation, and Optical Energy Conversion", C. S. Christ, Jr., J. Yu, X. Zhao, G. T. R. Palmore, M. S. Wrighton, *Inorg. Chem.*, **1992**, 31, 4439-4440.

"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. A. Albagli, G. C. Bazan, R. R. Schrock, M. S. Wrighton, *J. Phys. Chem.*, **1993**, 97, 0000. [In press]

"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*, submitted.

"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.*, submitted.

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