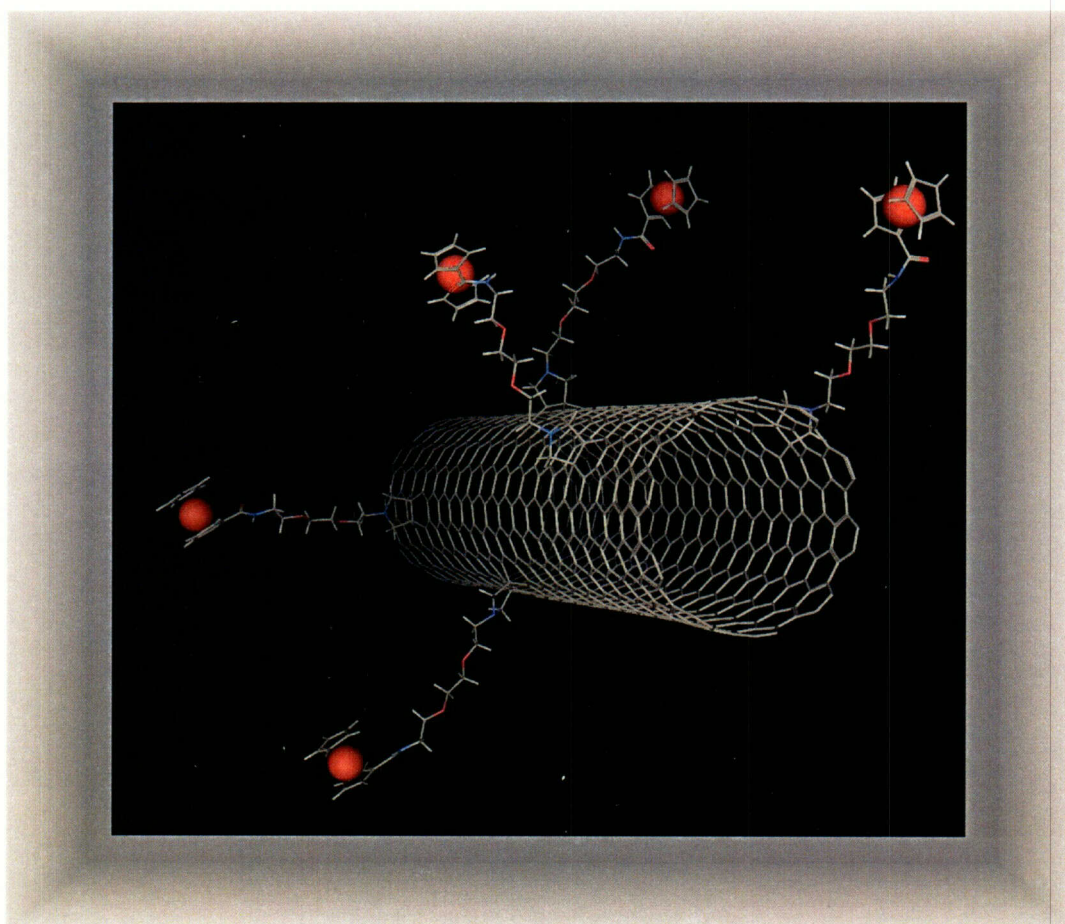


Proceedings of the
Twenty-Seventh
DOE Solar Photochemistry
Research Conference



Sponsored by:
Chemical Sciences, Geosciences and Biosciences Division
Office of Basic Energy Sciences
U.S. Department of Energy

Held at:
Airlie Conference Center
Warrenton, Virginia
June 6 - 9, 2004

Cover Graphics

The figure on the cover portrays a single wall carbon nanotube (SWNT)–ferrocene (Fc) conjugate as a novel donor-acceptor nanohybrid. Photoexcitation of the SWNT band gap is followed by a rapid intraensemble charge separation, which yields a long-lived charge-separated (SWNT)^{•-}-(Fc)^{•+} state (i.e., lifetime of 1110 ± 100 ns). The presence of SWNT^{•-}, detected by laser flash photolysis, has been confirmed by time-resolved pulse radiolysis and steady-state bulk electrolysis. (Dirk Guldi, Notre Dame Radiation Laboratory)

FOREWORD

The 27th Department of Energy Solar Photochemistry Research Conference, sponsored by the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences, is being held June 6-9, 2004, at the Airlie Conference Center, in Warrenton, Virginia. These proceedings include the meeting agenda, abstracts of the formal presentations and posters presented at the conference, and an address list for the 85 participants.

The Solar Photochemistry Research Conference brings together grantees and contractors of the Chemical Sciences, Geosciences and Biosciences Division who are engaged in fundamental research on solar photochemical energy conversion. The meeting provides a forum for exchange of new information and ideas, identification of needs and opportunities, and fosters collaboration among investigators. The synergy that has been achieved by this group of investigators is a major strength of the program. The research seeks to mimic key aspects of photosynthesis - antenna, reaction center, catalytic cycles, and product separation - in conversion of light energy to chemical energy for production of alcohol fuels from carbon dioxide, hydrogen from water, ammonia from atmospheric nitrogen, or other needed chemicals at lower cost by using sunlight as the energy source. Of interest in regard to solar water splitting, the President's FY 2005 Budget to Congress requests support for fundamental research in the Office of Basic Energy Sciences to help overcome key technology hurdles in the President's Hydrogen Fuel Initiative. A solicitation for research proposals (Program Notice DE-FG01-04ER04-20, Basic Research for the Hydrogen Fuel Initiative) has been issued which includes Solar Hydrogen Production as one of five focus areas.

Our special guest plenary lecturer is Professor Petra Fromme of Arizona State University, who will present fascinating X-ray crystallographic structures of Photosystems I and II. The topical sessions that follow feature presentations on photosynthesis and additional photosynthetic architectures; biomimetic light-harvesting arrays; organic semiconductors; nanohybrid assemblies; photoelectrochemistry; and the characterization and reactions of excited state metal complexes.

I would like to express my sincere appreciation to Sophia Kitts of the Oak Ridge Institute for Science and Education for preparation of this volume with short lead time, and to Kathy Neumann and the staff at the Airlie Conference Center for their warm hospitality. To the 17-year Brood X cicadas, timed for this meeting, we welcomed the opportunity to meet you and to hear your song. To all the participants who have contributed to the success of the program, I am grateful, particularly the speakers, poster presenters, and all who have instilled an atmosphere of intellectual inquiry and excitement to this conference.

Mary E. Gress
Chemical Sciences, Geosciences and
Biosciences Division
Office of Basic Energy Sciences

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Program

27th DOE SOLAR PHOTOCHEMISTRY RESEARCH CONFERENCE

June 6-9, 2004

Airlie Conference Center
Warrenton, Virginia

PROGRAM

Sunday, June 6

- 4:00 - 9:00 p.m. Registration, Garden Room
5:00-11:00 p.m. Reception, Roof Terrace
6:30 – 8:00 p.m. Buffet Dinner, Airlie Dining Room

Monday Morning, June 7

SESSION I

Plenary Session

Mary E. Gress, Chairman

- 7:30 a.m. Breakfast, Airlie Dining Room
- 8:30 a.m. Opening Remarks
Mary E. Gress, U.S. Department of Energy
- 8:45 a.m. **Plenary Lecture.** Structure and Function of Photosystems I and II
Petra Fromme, Arizona State University
- 9:45 a.m. Coffee Break

SESSION II

Photosynthesis and Photosynthetic Architectures

James R. Norris, Jr., Chairman

- 10:15 a.m. Factors That Tune Electron Transfer in Photosynthetic Reaction Centers
Marion C. Thurnauer, Argonne National Laboratory
- 10:45 a.m. Magnetic Resonance and Electron Transfer Studies of Carotenoids
Lowell D. Kispert, University of Alabama
- 11:15 a.m. Resolving Conformational Envelopes of Designed Photosynthetic Architectures
David M. Tiede, Argonne National Laboratory
- 11:55 a.m. Lunch, Airlie Dining Room

Monday Afternoon, June 7

SESSION III
Biomimetic Light-Harvesting and Organic Semiconductors
Kirk S. Schanze, Chairman

- 1:15 p.m. Towards the Rational Design of Synthetic Light-Harvesting Arrays
Jonathan S. Lindsey, North Carolina State University
- 1:45 p.m. Energy and Electron Transfer in Nonconjugated Dendrimers
S. Thayumanavan, University of Massachusetts, Amherst
- 2:15 p.m. Break
- 2:35 p.m. Synthesis, Characterization, and Catalytic Applications of Organic-Inorganic Shell-Core Composites
Marye Anne Fox, North Carolina State University
- 3:05 p.m. Towards a Unified Treatment of Electronic Processes in Organic Semiconductors
Brian A. Gregg, National Renewable Energy Laboratory

Monday Evening, June 7

- 5:30 p.m. Social Hour, Roof Terrace
6:30 p.m. Dinner, Airlie Dining Room

SESSION IV

- 7:30 p.m. Posters (Odd numbers), Jefferson Room
Light Refreshments on Roof Terrace

Tuesday Morning, June 8

SESSION V
Nanohybrid Assemblies for Solar Photoconversion
Tijana Rajh, Chairman

- 7:30 a.m. Breakfast
- 8:30 a.m. Mimicking Bacterial Photosynthetic Function
Devens Gust, Arizona State University
- 9:00 a.m. A Photoactive Lipid Membrane Coupled to a Planar Semiconductor through a Conducting Polymer
S. Scott Saavedra, Neal R. Armstrong, University of Arizona

- 9:45 a.m. Fundamental Studies of Light-Induced Charge Transfer, Energy Transfer, and Energy Conversion with Supramolecular Systems
Joseph T. Hupp, Northwestern University
- 10:15 a.m. Coffee Break
- 10:45 a.m. Integrating Single Wall Carbon Nanotubes into Donor-Acceptor Nanohybrids
Dirk M. Guldi, Radiation Laboratory, University of Notre Dame
- 11:15 a.m. Photochemical Properties of Nanoscale Assemblies of Linked Semiconductor Quantum Dots and Single Wall Carbon Nanotubes
Michael J. Heben, National Renewable Energy Laboratory
- 11:45 a.m. Understanding Nanoscale Quantum Dot Chemistry: Interactions with Proteins
Michael E. Himmel, National Renewable Energy Laboratory

Tuesday Afternoon, June 8

- 12:15 p.m. Lunch
- 1:30 p.m. Depart for Luray Caverns

Tuesday Evening, June 8

- 5:30 p.m. Social Hour, Pavilion
- 6:30 p.m. Cookout, Pavilion

SESSION VI

- 8:00 p.m. Posters (Even numbers)
Light Refreshments on Roof Terrace

Wednesday Morning, June 9

SESSION VII

Semiconductor Nanoparticle-Based Energy Conversion

Nathan S. Lewis, Chairman

- 7:30 a.m. Breakfast
- 8:30 a.m. Computational Studies of Biomolecule Interactions with Titanium Oxide Nanoparticles
Peter Zapol, Argonne National Laboratory
- 9:00 a.m. Studies of Spectral Sensitization of Anatase (101) Single Crystal Electrodes Using Carboxylated Cyanine Dye
Bruce A. Parkinson, Colorado State University

- 9:30 a.m. Unique Approaches to Solar Photon Conversion Based on Semiconductor Nanostructures and Novel Molecular Chromophores; Dynamics of Electron Relaxation, Interfacial Charge Transfer, and Carrier Multiplication
Arthur J. Nozik, National Renewable Energy Laboratory
- 10:00 a.m. Coffee Break
- 10:20 a.m. Theoretical Studies of Electron Transfer and Optical Spectroscopy in Complex Molecules
Richard A. Friesner, Columbia University
- 10:50 a.m. Spectroscopy and Dynamics of GaSe and InSe Nanoparticles and Nanoparticle Aggregates
David F. Kelley, University of California, Merced
- 11:20 a.m. Photocatalysis and Photoelectrochemistry Using Inorganic Colloids and Nanocrystals
Thomas E. Mallouk, Pennsylvania State University
- 11:50 a.m. Lunch, Airlie Dining Room

Wednesday Afternoon, June 9

SESSION VIII
Characterization and Reactions of Excited States

James K. McCusker, Chairman

- 1:10 p.m. Time-Resolved X-Ray Diffraction and the Structures of Excited States of Molecular Complexes
Philip Coppens, State University of New York at Buffalo
- 1:40 p.m. Designing Ligands to Promote Photooxidation of a Ru(II) Aqua Complex as a First Step in Water Decomposition
Randolph P. Thummel, University of Houston
- 2:10 p.m. Photoinduced Chemical Reactions of Metal Complexes: M-M Bond Formation/Cleavage and Small Molecule Activation
Etsuko Fujita, Brookhaven National Laboratory
- 2:40 p.m. Bimetallic Redox Sites for Photochemical CO₂ Splitting in Mesoporous Silicates
Heinz Frei, Lawrence Berkeley National Laboratory
- 3:10 p.m. Closing Remarks
Mary E. Gress, U.S. Department of Energy

Session I

Plenary Session

STRUCTURE AND FUNCTION OF PHOTOSYSTEMS I AND II

HongQi Yu¹, Ingo Gortjohann¹, Yana Bukman¹, Craig Yolley¹, Devendra K. Chauhan,
Alexander Melkozernov and Petra Fromme¹

¹ Department of Chemistry and Biochemistry, Arizona State University, PO Box 871604,
Tempe, AZ 85287-1604

Energy for all higher life on earth is supplied by oxygenic photosynthesis, which is the main biological process on earth that converts the light energy from the sun into chemical energy. The primary step in this energy conversion, the light-induced charge separation, is catalyzed by two distinct, membrane intrinsic protein complexes, photosystems I and II.

Photosystem I of cyanobacteria consists of 12 protein subunits, to which more than 100 cofactors are non-covalently bound: one functional unit of Photosystem I contains 96 Chlorophyll *a* molecules, 22 carotenoids, 3 Fe₄S₄-clusters and 2 phylloquinones that perform the complex function of light harvesting and charge separation. Photosystem I exists as a trimer in the cyanobacterial membrane, with a molecular mass of more than 1,000,000 Da. The X-ray structure of photosystem I at a resolution of 2.5 Å [1] showed the location of the individual subunits and cofactors and provided new information on the protein-cofactor interactions. Recently, the structural model of plant PS I was determined by BenShem et al. [2] shining light into the similarities and differences between the plant and cyanobacterial Photosystem I. In the talk, biochemical data and results of biophysical investigations are discussed with respect to the X-ray crystallographic structures of PS I in order to discuss the following open problems in Photosystem I:

- a) Interaction of Photosystem I with the soluble electron carriers ferredoxin and cytochrome *c6*/plastocyanin
- b) Function of the antenna system in Photosystem I
- c) Interaction of Photosystem I with its peripheral antenna systems

Increasing knowledge on the structure and function of Photosystem II has been accumulated during the last three years by X-ray structure analysis of cyanobacterial Photosystem II at 3.8 Å [3], 3.7 Å [4], 3.6 Å [5], and 3.5 Å [6] resolution. The structures will be compared and discussed in respect to the function of Photosystem II with special focus on the oxygen-evolving complex. In the last part of the talk, the structures of Photosystem I and II will be compared and discussed in respect to the evolution of the Photosystem I and II.

- [1] Jordan, P., Fromme, P., Witt, H.T., O. Klukas, Saenger, W. and Krauß, N. (2001) *Nature* 411, 909-917 Three-dimensional structure of cyanobacterial Photosystem I at 2.5 Å resolution
- [2] Ben-Shem A, Frolow F, Nelson N (2003) Crystal structure of plant photosystem I. *Nature* 426: 630-635
- [3] Zouni A, Witt HT, Kern J, Fromme P, Krauss N, Saenger W, Orth P (2001) Crystal structure of photosystem II from *Synechococcus elongatus* at 3.8 Å resolution. *Nature* 409: 739-743
- [4] Kamiya N, Shen JR (2003) Crystal structure of oxygen-evolving photosystem II from *Thermosynechococcus vulcanus* at 3.7-Å resolution. *Proc Natl Acad Sci U S A* 100: 98-103
- [5] Fromme P, Kern J, Loll B, Biesiadka J, Saenger W, Witt HT, Krauss N, Zouni A (2002) Functional implications on the mechanism of the function of photosystem II including water oxidation based on the structure of photosystem II. *Philos Trans R Soc Lond B Biol Sci* 357: 1337-1344; discussion 1344-1335, 1367
- [6] Ferreira KN, Iverson TM, Maghlaoui K, Barber J, Iwata S (2004) Architecture of the photosynthetic oxygen-evolving center. *Science* 303: 1831-1838

Session II

***Photosynthesis and Photosynthetic
Architectures***

FACTORS THAT TUNE ELECTRON TRANSFER IN PHOTOSYNTHETIC REACTION CENTERS

M. C. Thurnauer, L. M. Utschig, D. M. Tiede, S. L. Schlesselman,
A. M. Wagner, O. G. Poluektov

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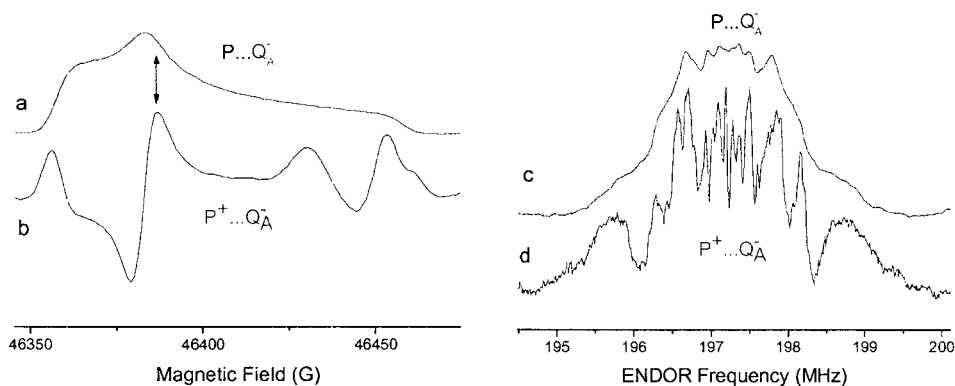
Photosynthetic reaction center (RC) proteins are the premier systems for resolving fundamental mechanisms responsible for highly efficient photochemical energy conversion. Crystal structures of the RCs from purple photosynthetic bacteria (PB), and photosystems I and II (PSI, PSII) of cyanobacteria and higher plants reveal their striking similarities with respect to the organization of the cofactors that participate in the important charge separation. Although all three systems share common structural features, the mechanisms involved in electron transfer are necessarily optimized differently, in order to accommodate varied “functional” roles. Thus, our recent work focuses on understanding how the local protein environment and conformational dynamics may influence the electron transfer processes. We have developed new approaches to monitor electron transfer pathways, local structural changes that accompany charge separation, and the effect of the protein on electronic structure. This work takes advantage of our capabilities in multifrequency (including high magnetic field (HF)) electron paramagnetic resonance (EPR) coupled with our ability to prepare specialized RC proteins.

Mapping electron transfer pathways. The common fundamental structural and energetic requirements for efficient charge separation in photosynthetic RCs are clearly evident from time-resolved (TR) EPR studies. TR-EPR spectra of the transient charge separated state P^+Q^- , where P is a chlorophyll species and Q a quinone, exhibits electron spin polarization (ESP) as a result of being a spin correlated radical pair (SCRCP) formed by photo-initiated sequential electron transfer steps. ESP is sensitive to the magnetic resonance parameters and interactions between photochemically oxidized and reduced species. In this context, the photosynthetic RCs provide a fascinating test-bed for development of advanced theoretical and experimental approaches in magnetic resonance which yield new insights into the charge separation process.

A new phenomenon, associated with the SCRCP nature of $P^+Q_A^-$ (Q_A is the first quinone acceptor), formed in PB RCs was observed. This phenomenon is manifest when TR electron nuclear double resonance (ENDOR) spectra of RC proteins are recorded at HF EPR (>3T). HF-EPR (Figs. a and b) provides the spectral resolution necessary to record an ENDOR spectrum at a specific orientation of a radical with respect to the magnetic field. Figs. c and d show the HF-ENDOR spectra of Q_A^- , chemically generated vs. photogenerated as a partner in the transient $P^+Q_A^-$ SCRCP.

In these samples of “normal” protonated RCs, Q_A is deuterated. Therefore, ENDOR of Q_A^- monitors “matrix” protons that are not covalently bound to Q_A . The spectrum of transient Q_A^- reveals a derivative-like, complicated lineshape, which differs considerably from the ENDOR spectrum of chemically reduced Q_A . These observations can be explained within the SCRCP model by taking into account hyperfine interactions (HFI) of a particular nucleus with both radicals in the SCRCP. The position of the ENDOR lines is determined by HFI with the electron on Q_A^- , while the derivative line shapes, widths, and intensities contain information on HFI with P^+ . Thus, SCRCP ENDOR has the potential for mapping the overlap of electronic wave

functions of the donor and acceptor in the protein environment. This new information will lead to a better understanding of the electron transfer pathways in the photosynthetic RC proteins and, importantly, of how the protein environment controls electron transfer reactions.



We are developing a detailed model of the SCRPE ENDOR phenomenon. The model will be tested with systems that provide simplified ENDOR spectra such as linked donor-acceptor (D-A) systems having isotopically substituted nuclei on the bridge that connects D and A. This new “tool” for monitoring electron transfer pathways will be used to study PSI and may help in understanding possible dual pathways in this system.

Probing protein conformational changes correlated to electron transfer. In PB RCs, the electron transfer step between Q_A and Q_B , the secondary quinone, is temperature activated, coupled to proton movement, and believed to be rate limited by protein motion. Previously, we demonstrated that this step is slowed by metal ion binding to a protein surface site. Recent studies suggest that metal binding causes an electrostatic perturbation of the coupled uptake and/or rearrangement of protons. Putative conformational and electrostatic changes accompanying $Q_A^-Q_B \rightarrow Q_A Q_B^-$ electron transfer are addressed with advanced EPR techniques.

A method, based on monitoring matrix ENDOR lines, was developed to study electron transfer induced local changes of protein structure. We have confirmed, with HF-EPR, that three distinct conformational substates of the RC can be trapped at low temperatures. Importantly, the HF-matrix ENDOR spectra of Q_B^- for these kinetically distinct states indicate that, within 10 Å of Q_B , there are no conformational changes of the protein structure associated with electron transfer.

Using advanced EPR techniques, including hyperfine correlation spectroscopy (HYSCORE), we have determined that the coordination environment of Cu^{2+} is structurally distinct from that of other surface bound metal ions. We propose that these local structural differences correspond to the observed metal ion specific differences in allosteric modulation of electron transfer.

Based on these developments we will monitor local protein structure around different cofactors (P^+ , $Q_{A/B}^-$, H, where H is bacteriopheophytin) in differently trapped protein conformations (for example in the presence and absence of different metal ions bound to the surface and iron sites) in order to determine conformational substates, which are responsible for effective electron and proton transfer reactions.

Publications

ANALYTICAL TREATMENT OF EPR SPECTRA OF WEAKLY COUPLED SPIN CORRELATED RADICAL PAIRS IN DISORDERED SOLIDS: APPLICATIONS TO THE CHARGE SEPARATED STATE IN TiO₂ NANOPARTICLES

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METAL ION MODULATED ELECTRON TRANSFER IN PHOTOSYNTHETIC PROTEINS

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U. Heinen, O. Poluektov, E. Stavitski, T. Berthold, E. Ohmes, S. L. Schlesselman, J. R. Golecki, J. Moro, H. Levanon, M. C. Thurnauer, and G. Kothe
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PULSED EPR/ENDOR CHARACTERIZATION OF THE Cu^{2+} SURFACE SITE IN PHOTOSYNTHETIC BACTERIAL REACTION CENTERS

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HIGH-FIELD EPR STUDIES OF ELECTRON TRANSFER INTERMEDIATES IN PHOTOSYSTEM I

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MAGNETIC RESONANCE AND ELECTRON TRANSFER STUDIES OF CAROTENOIDS

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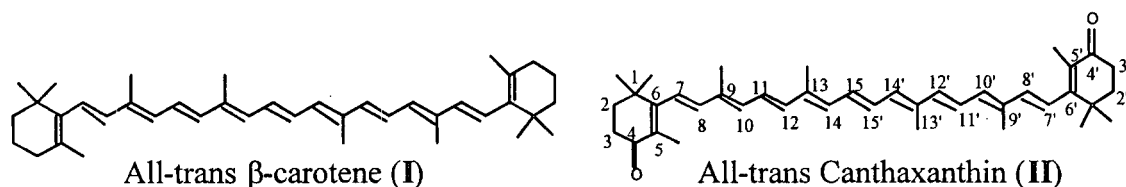
Carotenoids, intrinsic components of reaction centers and pigment-protein complexes in photosynthetic membranes, play a photoprotective role in plants and bacteria. Their robust nature in living materials requires extensive characterization of their electron transfer and radical trapping ability, structure in and on various hosts and photochemical behavior. Such information is needed before optimum use of them can be made in artificial photosynthetic systems.

Variable High Field EPR Studies of Electron Transfer between Metal Ions and Carotenoids. With the assistance of Dr. Brunel's group at the National High Magnetic Field Laboratory at Florida State University, electron transfer (ET) and isomerization of carotenoids (Car) imbedded in MCM-41, Ti-MCM-41, Cu-MCM-41 and Fe-MCM-41 upon irradiation and in the absence of light were studied. The ET efficiency in MCM-41 was highest for the carotenoid with the lowest oxidation potential. Although the presence of transition metal ions in the framework of MCM-41 increased the ET efficiency of all carotenoids, the extent of enhancement did not depend on oxidation potential, but rather on whether complexes are formed between carotenoids and metal ions. Complex formation with transition metal ions results in a large blue shift of the maximum absorption wavelength. O₂ present in Ti-MCM-41 also plays an important role in the ET reactions. Complex formation between Car and Cu²⁺ favors light-driven electron transfer from Car to Cu²⁺ and also permits the thermal back electron transfer from Cu⁺ to Car^{*+}. The distance between Cu²⁺ and the central double bond of Car is about 2.7 Å as determined from ESEEM measurements of predeutero β-carotene.

Isomerization of Carotenoids in the Presence of MCM-41 and Metal-Substituted MCM-41 Molecular Sieves. High selective isomerization efficiency of Car imbedded in MCM-41 or in transition metal ion-substituted MCM-41 can be obtained by photo or chemical oxidation. The isomerization occurs primarily via Car^{*+}. The environment of the MCM-41 pores causes a selectivity of isomerization for all *trans*-β-carotene (I) whose location is close to the internal pore surface in these solid hosts. This is in contrast to the isomerization in solution by photoexcitation, iodine or acid-catalysis, and electrolysis, and this also differs from the isomerization on silica-alumina. Canthaxanthin (II) does not penetrate the pores of MCM-41, and gives rise to an isomerization distribution similar to that found in solution. The presence of transition metal ions also affects the isomerization. This study contributes to our understanding of the isomerization behavior of carotenoids in the rigid environments of photosystem II, and points to potential applications in catalysis. Further work should ascertain how

different pore sizes and different functional groups on the surface of the pores affect the selectivity.

Reaction of Carotenoids and Ferric Chloride: Products, Equilibria, and Isomerization. In the oxidation of carotenoids, ethyl all-trans-8'-apo- β -caroten-8'-oate and **I**, with ferric chloride, several equilibria occur between Fe^{3+} , Fe^{2+} , Cl^- , the neutral carotenoid, and its radical cation and dication. The radical cation and dication were found to abstract an electron from Fe^{2+} . Isomerization of carotenoids occurs during the oxidation. In the presence of air, the stable 5,8-peroxide is formed in high yield during the oxidation, as shown by $^1\text{H-NMR}$, LC-MS, and optical studies. A mechanism for the formation of this compound is proposed.



Deprotonation of Carotenoid Radical Cation: Didehydrodimer Formation. Deprotonation of the carotenoid radical cation ($\text{Car}^{\bullet+}$) in CH_2Cl_2 was studied by electrochemistry, optical, MALDI-TOF, and EPR spectroscopy. Water enhances deprotonation of the carotenoid radical cation. The formation of a didehydrodimer ($\# \text{Car}$) $_2$ ($\# \text{Car}$: Car with one less proton) was confirmed by the above measurements. The structure of the dimer is proposed on the basis of semiempirical calculations, optical, and EPR studies.

Inclusion Complexes of Carotenoids with Cyclodextrins. Direct evidence of carotenoid/cyclodextrin inclusion complex formation was obtained for the water-soluble sodium salt of β -caroten-8'-oic acid (**III**) by using ^1H NMR and UV-Vis absorption spectroscopy. It was shown that this carotenoid forms a stable 1:1 inclusion complex with β -cyclodextrin (stability constant $K_{11} = 1500 \text{ M}^{-1}$). By using the EPR spin trapping technique, the scavenging ability of **III** toward OOH radicals was compared in DMSO and aqueous CD solutions. A considerable decrease in PBN/OOH spin adduct yield was detected in the presence of uncomplexed **III** because of a competing reaction of **III** with the OOH radical. No such decrease occurred in the presence of the **III**/CD complex. However, a small increase in spin adduct yield (pro-oxidant effect) is observed and is most likely due to the reaction of the carotenoid with Fe^{3+} to regenerate Fe^{2+} , which in turn regenerates the OOH radical. Our data show that CD protects the carotenoid from reactive oxygen species. On the other hand, complexation with CD results in considerable decrease in antioxidant ability of the carotenoid. Complexes of β -ionone with CD were also studied.

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RESOLVING CONFORMATIONAL ENVELOPES OF DESIGNED PHOTOSYNTHETIC ARCHITECTURES

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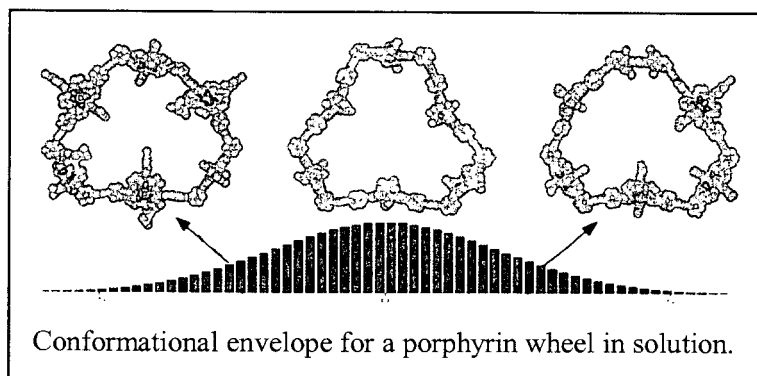
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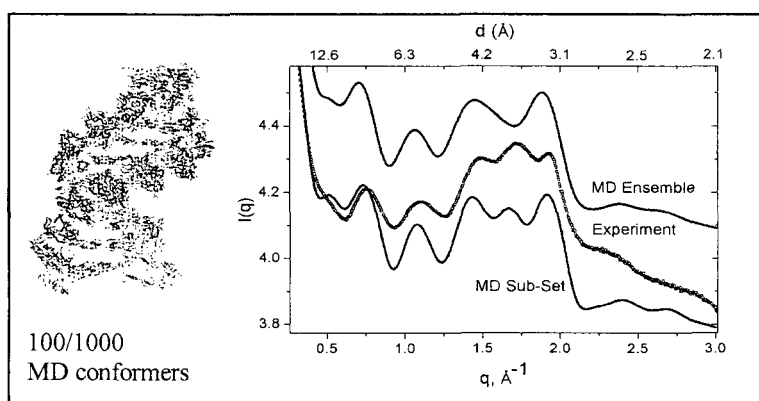
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The photosynthesis research program at Argonne National Laboratory is directed at resolving fundamental mechanisms for photosynthetic function in natural and artificial photosynthesis. Central questions under investigation include investigating roles of donor/acceptor structure, local environmental tuning, and atomic reorganization in the control of energy-conserving light-induced electron transfer. One of the major challenges for resolving fundamental mechanisms in natural and artificial photosynthesis lies in obtaining structural information correlated to time-dependent photochemical function. This talk will present results on our development of synchrotron high-angle scattering techniques for the resolution of structure and dynamics of molecular systems in liquids and other photochemically relevant non-crystalline media. Results will be presented on the analyses of designed, artificial photosynthetic architectures and opportunities will be discussed for extending these methods for time-resolved applications in both natural and artificial photosynthesis.

Macrocyclic multiporphyrin architectures based on covalent connectivity. Precisely designed, modular supramolecular architectures are being developed by the Lindsey group to accomplish a variety of photosynthetic functions. We have characterized structures of a hexameric, diphenylethyne-linked porphyrin macrocyclic array and the corresponding host-guest complex formed by inclusion of a tripyridyl guest molecule in solution using high-angle X-ray scattering. Scattering measurements made to 6 Å resolution coupled with pair distance function (PDF) analyses demonstrated that (1) the porphyrin architectures are not rigid but are distributed across a conformational ensemble with a mean diameter that is 1.4 Å shorter than the diameter of a symmetric, energy-minimized model structure, (2) the conformational envelope has limits of 3 Å positional dispersion and full rotational freedom for all six porphyrin groups, and (3) insertion of the tripyridyl guest molecule expands the diameter of the host conformer by 0.6 Å and decreases the configurational dispersion by two. These results validate the molecular design, provide a new measure of conformational ensembles in solution that can not be obtained by other techniques, and establish a structural basis for understanding the photophysical and guest-hosting functions of the hexameric porphyrin architectures in liquids.



DNA molecular-wire, π -stacked architectures. Duplex DNA sequences are widely explored as model architectures for long-range electron transfer through aromatic face-to-face, π -stacked spacers. The Lewis group is investigating fundamental sequence and distance dependent electron transfer processes in DNA. Measurements of DNA conformation in liquids are critical for interpreting mechanisms for electron transfer. Scattering patterns measured for a series of DNA sequences to 2 Å resolution were found to resolve both nearest-neighbor and longer range base-pair distance correlations. Sequence and temperature dependent measurements combined with molecular modeling studies show that scattering peak positions are strongly correlated to DNA conformation while configurational dynamics are reflected in peak broadening and angle-dependent attenuation of scattering patterns. High angle scattering measurements are found to resolve discrepancies between crystallographic and NMR structures, and provide a new approach for quantitatively checking molecular dynamics (MD) simulations. Currently available MD simulations yield ensembles of DNA conformers with averaged calculated scattering patterns that fall far from agreement with experimental data. However, experimental scattering is found to be in good agreement with scattering calculated from conformational sub-sets of the MD ensembles. These results suggest the opportunity of using scattering measurements for optimizing molecular force-fields for the solution state.



Functional supramolecular assemblies based on coordination chemistry. Metal/ligand directed-assembly techniques are widely utilized for obtaining discrete, high-symmetry supramolecular entities. The Hupp group is devising novel architectures for photochemical energy conversion based on rhenium coordination chemistry. Key features of these designs include multiporphyrin host macrocyclics capable of chiral guest discrimination, induced-fit transition states, and tunable nanoscale chemical environments that mimic molecular recognition and site-specific tuning of cofactors in natural photosynthesis. These architectures comprised of high-Z atoms held in fixed, nanoscale geometries are found to be almost ideal molecular samples for X-ray scattering. In favorable cases, well-defined X-ray scattering patterns are measured beyond 1 Å spatial resolution. These measurements permit accurate calibration of the scattering technique and resolution of details of solvent-solute interactions that are critical for understanding light-induced charge-transfer reactions.

Outlook. High-angle scattering patterns are found to contain unique information on structures and configurational dispersions for macromolecules in solutions that can be combined with pulsed EPR and X-ray spectroscopies to obtain both global and local structural information. Synchrotron scattering techniques can be extended to 100 ps time-resolution for measurement of structural dynamics correlated to photochemistry in natural and artificial photosynthesis.

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Session III

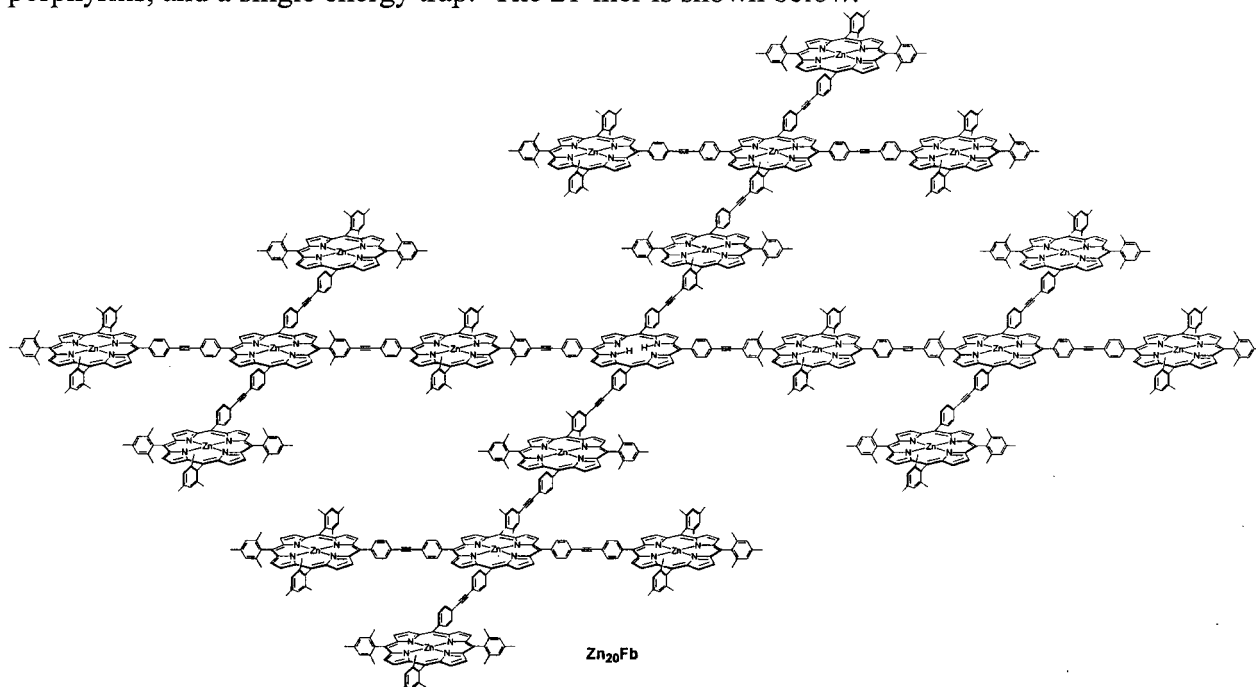
***Biomimetic Light-Harvesting
and Organic Semiconductors***

TOWARDS THE RATIONAL DESIGN OF SYNTHETIC LIGHT-HARVESTING ARRAYS

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My long-term goal is to be able to create, in a rational manner and with modest effort, arrays comprised of large numbers of porphyrinic pigments that collect solar radiation and funnel energy to one site in the array with quantum efficiency >95%. This is a challenging problem for several reasons: (1) we don't know enough about electronic interactions to design arrays from first principles, (2) the requisite number of pigments and architectural organization are beyond the limits of current synthetic methods, and (3) physical chemical studies to elucidate mechanisms of energy flow are quite challenging.

Our approach over the past decade has been to synthesize covalently linked multiporphyrin arrays and study their light-harvesting properties. We have found that the dominant mechanism for energy transfer in such systems entails a linker-mediated through-bond process. To explore how energy flows in large architectures, we prepared a series of multiporphyrin arrays to probe the contribution of energy transfer between second-neighbor ("nonadjacent") porphyrins and to determine the rate of energy transfer between identical porphyrins at adjacent sites. The arrays, organized in linear or branched architectures, contain up to 21 constituents, domains of 2-5 zinc porphyrins, and a single energy trap. The 21-mer is shown below.



The study has involved iterative cycles of molecular design, synthesis, determination of rates via transient absorption spectroscopy, and kinetic analysis. A rate constant of $(30 \pm 10 \text{ ps})^{-1}$ was deduced for bidirectional energy transfer between adjacent zinc porphyrins joined by a

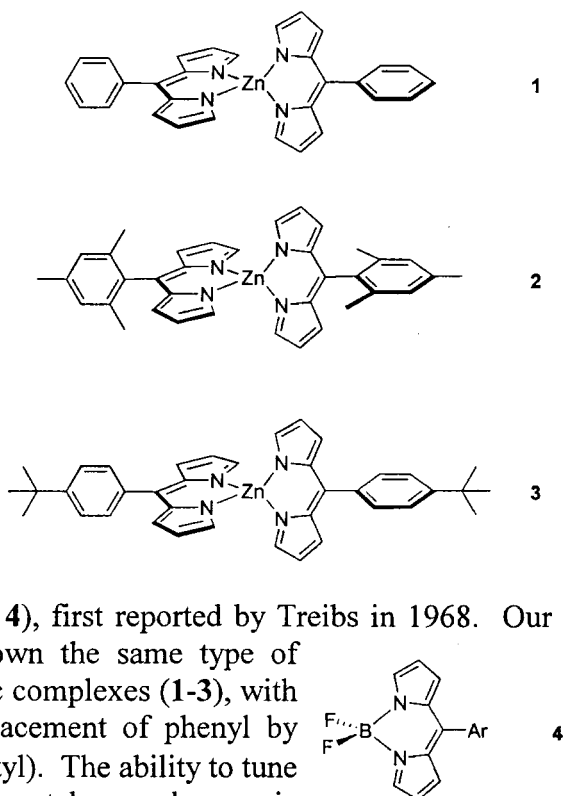
diphenylethyne linker. The value is $(50 \pm 10 \text{ ps})^{-1}$ when porphyrin-linker internal rotation is hindered by *o,o'*-methyl groups on one aryl ring of the linker. Rates of nonadjacent energy transfer are typically only 5-to-10-fold less than rates of adjacent transfer. Thus, the nonadjacent pathway has a significant impact on the overall rate of energy flow to the trap, even in architectures as small as triads.

These findings provide information that is essential for the rational design of multichromophore arrays whose function is to transfer excitation energy efficiently over large distances to a trap site. The arrays of current interest contain a variety of pigments (perylene, porphyrin, chlorin, phthalocyanine, etc.) to adequately cover the solar spectrum.

A complementary approach to covalent synthesis is provided by self-assembly. We are examining the use of self-assembly of porphyrinic pigments (in crystals) to prepare light-harvesting arrays. An additional example is provided by self-assembling accessory pigments such as bis(dipyrrinato)metal(II) complexes. Bis(dipyrrinato)-metal complexes, first discovered by Fischer in 1924, have generally been regarded as non-fluorescent. We found that replacement

of the 5,5'-substituted phenyl rings of the bis(dipyrrinato)zinc complex **1** with mesityl groups in **2** transforms the molecule from a very weak emitter that deactivates rapidly after photoexcitation ($\Phi_f = 0.006$; $\tau \sim 90 \text{ ps}$) to a brightly fluorescent chromophore with a long-lived singlet excited state ($\Phi_f = 0.36$; $\tau \sim 3 \text{ ns}$). In contrast, the 5,5'-(*p-tert*-butylphenyl)-substituted complex **3** has properties virtually identical to **1**. These results demonstrate that steric constraints on aryl-ring internal rotation dramatically alter the excited-state properties of 5,5'-aryl-substituted bis(dipyrrinato)metal complexes. These insights establish the foundation for tuning the photophysical properties of these chromophores for use in diverse photochemical applications.

The bis(dipyrrinato)metal complexes are cousins of the dipyrrinatoboron-difluoride dyes (e.g., **4**), first reported by Treibs in 1968. Our studies of the fluorescent properties of **4** have shown the same type of structural effect as observed in the bis(dipyrrinato)zinc complexes (**1-3**), with a dramatic increase in fluorescence yield upon replacement of phenyl by mesityl: $\Phi_f \sim 0.05$ (Ar = phenyl); $\Phi_f \sim 1.0$ (Ar = mesityl). The ability to tune the excited-state characteristics of the dipyrrinato-metal complexes via relatively minor structural alterations should open the door to a number of applications. The dipyrrinatoboron-difluoride dyes are well suited as accessory pigments and markers in biological systems. The bis(dipyrrinato)zinc complexes are well suited for applications where the combination of self-assembly and intense absorption/fluorescence in the visible region are desirable attributes.



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ENERGY AND ELECTRON TRANSFER IN NONCONJUGATED DENDRIMERS

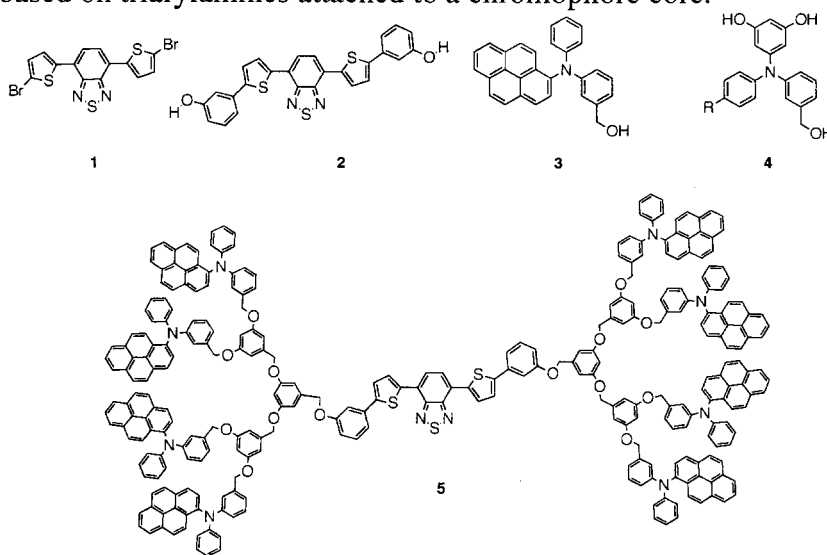
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This project seeks to develop an understanding on the effect of dendritic architecture on the vectorial transfer of energy and electrons. The unique structure of dendrimers provides an entropic advantage for these processes. The core, periphery, and the branching points are the three locations in dendrimers, where variety of functionalities could be incorporated. In order to minimize the electronic influence between the functionalities in these locations and thus be able to undertake a structure-property relationship study, we have chosen a nonconjugated dendrimers backbone. Here, we outline a few examples of the studies carried out under this program.

We synthesized two types of molecules: (i) dendrimers with an energy acceptor core functionalized with dendrons containing triarylamine units that function both as energy donor and electron transfer agent. (ii) dendrimers in which each repeat unit of the dendrons is based on triarylamines attached to a chromophore core.



The chromophore core of choice in our dendrimers synthesis is based on a benzthiadiazole ring flanked by two thiophene units. The triarylamine units at the periphery of the dendrimers are based on diarylaminopyrene and the repeat units within the dendrimers were based on substituted triarylamines. Precursor to the chromophore core, 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (1), was synthesized in two steps from bromothiophene and benzthiadiazole. The synthesis of the chromophore core 2 was achieved using a two-step, one-pot procedure that involves a Stille coupling and deprotection of silyl protecting groups using aqueous potassium fluoride. Diarylaminopyrene based unit 3 and other triarylamine based repeat units 4 were synthesized using a palladium-catalyzed C-N bond forming method as the key step. Dendrimers are then assembled with these building blocks using the methodologies described in the literature. Structures of dendrimers are illustrated using a G-2 dendrimer 5 as an example.

In the first dendrimers design, we are interested in achieving energy transfer from the periphery of the dendrimers to the core, followed by a charge transfer from the core to the periphery. This type of sequential photoinduced events has not been achieved in dendrimers and these macromolecules do provide an interesting scaffold for this. The overlap between the emission spectra of the donor and the absorption spectra of the acceptor (shown in Figure 1a) demonstrates that energy transfer is feasible in this molecular design. We estimated the $\Delta E_{0,0}$ using the combination of absorption spectra, emission spectra, and cyclic voltammetry. These estimates suggest that the diarylaminopyrene unit is capable of reducing the excited state of the benzthiadiazole core. These estimates also suggest that the excited state of the diarylaminopyrene donor can be directly oxidized by the chromophore core prior to the energy transfer. In order to investigate the possibilities, we carried out time-resolved studies.

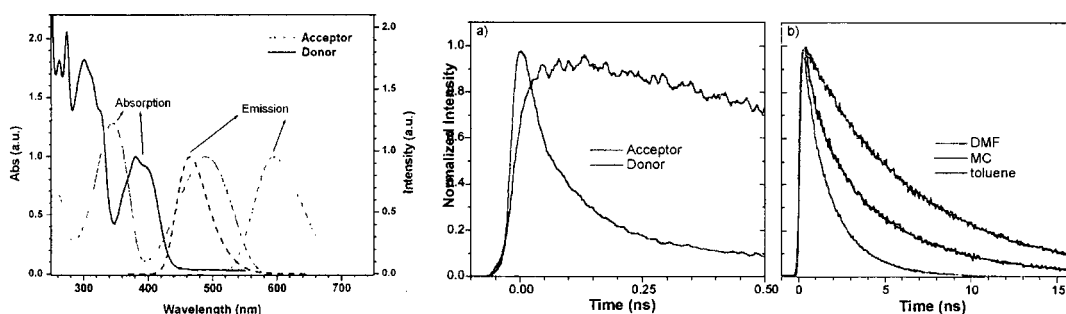


Figure 1. (a) Linear absorption spectra of donor and acceptor. Dashed lines are the emission spectra; solid lines are the absorption spectra. (b) Fluorescence decay of donor and fluorescence raise of acceptor in compound **3**; (c) Solvent dependence of fluorescence decay of the acceptor core. Note different time scales between the two graphs.

In Figure 1b, we show the fluorescence decay of the donor region of **5** centered at 480 nm. The lifetime is shorter by almost 2 orders of magnitude in the dendrimer than in the unattached donor **3**, 65 ps versus 7 ns. At 600 nm, we see a growing in of the acceptor emission on the same timescale, indicative of energy transfer to the core. From this data, which is consistent with fluorescence excitation spectra as well, we find that energy transfer from donor to acceptor occurs within 200 ps after photoexcitation in all dendrimers and solvents studied. In addition to this fast component, all dendrimers studied also had a small (<10%) component that decays on the order of 6 ns. This decay is slightly faster than that of the free donor in solution (7 ns), and has been observed in other benzyl-ether energy transfer dendrimers. After the energy transfer takes place, the next question is whether charge transfer can occur between the triaryl amines on the periphery and the excited state of the core, which should result in quenching of the acceptor fluorescence. Figure 1c shows the acceptor fluorescence decay in different solvents. The charge transfer quenching should be very sensitive to solvent polarity, and indeed this is what is seen in Figure 1c, where the nanosecond decay rate increases dramatically as we go from toluene, where the fluorescence decay is the same as that of the free benzthiadiazole, to the more polar DMF, where it is a factor of 3 faster. As the decay rate increases, the fluorescence decays become more nonexponential, especially for the larger dendrimers. Both energy transfer and charge transfer processes exhibited interesting generation dependence. Then trends could be rationalized using a back-folded conformation model that affords through-space interactions. Investigations are underway to dissect the possibilities.

As mentioned above, one of main objectives of this project is to study the effect of dendritic architecture on the energy and charge transfer efficiencies. For this purpose, we synthesized the corresponding linear analogs for the dendrimers. One of the caveats of this approach is that when a dendrimer is compared with a linear analog, these two types of molecules will differ either in distance between the photoactive units or the number of units in the periphery. In order to circumvent this issue, we have now synthesized dendrimers that contain only two diarylaminopyrene units in the periphery (one in each dendron). Photophysical comparison of these dendrimers with the corresponding linear analogs will be presented.

We have also synthesized dendrimers in which each repeat unit within the dendrimers contains a triarylamine unit. We hypothesized that the proximity and continuous presence of the charge transport units relative to the chromophore core will provide a useful pathway for photoinduced charge separation. Syntheses of these dendrimers and preliminary photophysical studies on these dendrimers will also be presented.

In summary, we report the first evidence for sequential energy transfer and charge transfer processes in dendrimers. We have also synthesized dendrimers that could be compared with their corresponding linear analogs to truly investigate the potential of dendrimers as light harvesting materials. Dendrimers in which each repeat unit contains a triarylamine-based charge transport unit have been synthesized. Investigation of the above-mentioned dendrimers and linear analogs using pump-probe experiments, synthesis and study of dendrimers that contain both an oxidizing dendron and a reducing dendron attached to a chromophore core, and comparison of these dendrimers with the corresponding linear analogs will be part of the future studies. In addition, we have also obtained preliminary results that suggest that *meta*-conjugated compounds could result in improved charge separation efficiency. Therefore, study of dendrimers based on phenylacetylene linkages (*meta*-conjugated) will also be undertaken.

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- 4) Thomas, K.R.J.; Thompson, A.; Bardeen, C.; Thayumanavan, S. "Sequential Energy and Electron Transfer in Nonconjugated Dendrimers" *J. Am. Chem. Soc.* submitted.
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SYNTHESIS, CHARACTERIZATION, AND CATALYTIC APPLICATIONS OF ORGANIC-INORGANIC SHELL-CORE COMPOSITES

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Nanoparticle-cored dendrimers obtained by the reduction of hydrogen tetrachloroaurate in the presence of sulfide terminated dendrimer wedges constitute a new family of functionalized metal clusters important to chemical catalysis. In addition, they can be used as micelle mimics, as drug delivery agents, and as chemical sensors, as well as in roles involving purely synthetic mimics for artificial photosynthesis. As highly ordered treelike functional polymers, these monodisperse macromolecules contain three regions of architectural importance: 1) an initiator core; 2) interior layers called ‘generations’ of variable polarity and electronic coupling; and 3) an external layer of terminal groups attached to the outermost branching unit.

We have examined a series of composites with sized gold nanoparticles at the core, capped by self-assembled disulfide-containing dendron wedges. Analysis by transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), ultraviolet (UV) and infra-red (IR) spectroscopies revealed composites with densities of branching units variant by more than an order of magnitude, depending upon generation number. These materials enclosed large void spaces near the metal core cluster, thus exposing size-specified host cavities for various guest reactants. As a result, a large fraction of the metal surface is accessible via penetration through porous openings that expose unpassivated metal sites. Such composites thus can show good catalytic activity.

These shell-core nanocomposites can also be used as monodisperse, unimolecular micelles in which the associated groups remain covalently bound, or as nanoreactors with high catalytic turnover number derived from the inherent resistance to metal aggregation and precipitation derived from the shell protection. Upon hydrolysis of ester-terminated aggregates in the covalent micelles, the solubility properties of these materials can be varied and the influence of the non-homogeneous medium can be exploited to alter chemical kinetics. Examples will be presented to illustrate the utility of the former class of compound as a heterogeneously dispersed medium (as indicated by optical spectra) and the latter class as reagents of choice for carbon-carbon bond formation in catalytic Heck or Suzuki aryl halide couplings.

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TOWARD A UNIFIED TREATMENT OF ELECTRONIC PROCESSES IN ORGANIC SEMICONDUCTORS

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A heuristic approach to describing excitonic processes, doping and transport in organic semiconductors is developed and applied primarily to understanding photovoltaic applications. A simple equation is proposed that semiquantitatively defines “excitonic” semiconductors, XSCs, a classification that includes most organic semiconductors and some inorganic materials.

$$\gamma = \frac{r_c}{r_b} \approx \left(\frac{q^2}{4\pi n^2 \epsilon_0 k_B r_0 m_e} \right) \left(\frac{m_{eff}}{\epsilon^2 T} \right)$$

$\gamma > 1$: Excitonic semiconductor, XSC

$\gamma < 1$: Conventional semiconductor, CSC

The γ function approximately distinguishes between XSCs and CSCs based on their electrostatic properties and on the spatial extent of the charge carrier wavefunctions (Bohr radii). This distinction is more fundamental than that between organic and inorganic semiconductors.

The same electrostatic and spatial factors that cause exciton formation upon light absorption in XSCs, as opposed to the formation of free electron-hole pairs, also control the doping process and carrier transport. Quantitative doping studies in liquid crystal perylene diimides establish that most added charge carriers are not free but rather are electrostatically bound to their conjugate dopant counterions because $\gamma > 1$. We show that these results can be generalized to many XSCs that are not purposely doped. A superlinear increase in conductivity with doping density is thus expected to be, and apparently is, a universal attribute of XSCs. The interactions between the crystal structure, its dielectric properties and the doping efficiency are probed via two substitutional dopant molecules in two different crystalline host lattices (Figure 1).

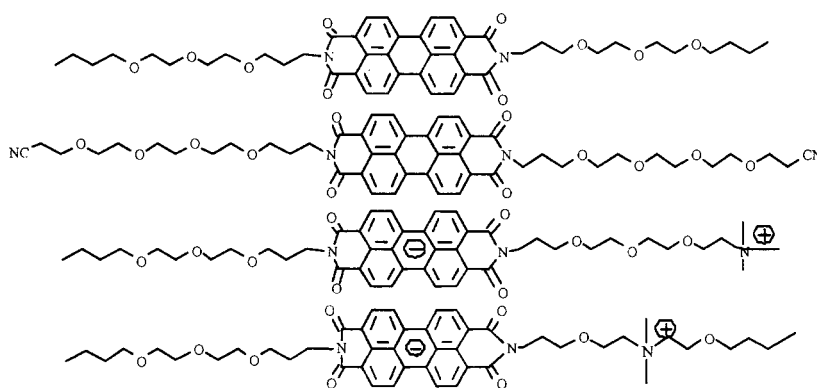


Figure 1. Liquid crystal perylene diimides. The top two are semiconductor hosts: PPEEB and its cyano-analog, PPE₄CN, respectively. The bottom two are n-type dopants: the “end dopant” and the “middle dopant”, respectively.

Remarkably small differences are observed between the two different dopants in PPEEB. This we explain by consideration of the large tilt angle of the “smectic C-like” crystal structure of the PPEEB. Even more remarkable were the huge differences in equilibrium free carrier density between undoped PPEEB and PPE₄CN. Simply adding cyano groups to the ends of the side chains caused the free carrier density to increase by seven orders of magnitude (Figure 2). Strangely, the conductivity in the initially formed red phase was enhanced in air relative to N₂, suggesting p-type conductivity, while the conductivity reverted to n-type in the thermodynamically stable black phase. This behavior was not caused by the relatively small increase in dielectric constant between PPEEB and PPE₄CN, but by the large increase in dipole density: two distinctly different properties in solid state systems.

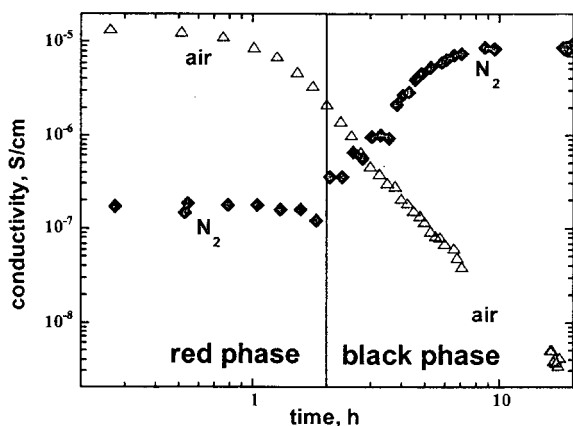


Figure 2. The change in conductivity of *undoped* PPE₄CN as it undergoes the red-to-black phase transition in air and in an N₂ glove box. In undoped PPEEB, $\sigma \approx 10^{-12}$ S/cm.

An analogy is drawn between purposely doped XSCs and adventitiously doped XSCs such as π -conjugated polymers: in both cases the number of free carriers is a small, and field-dependent, fraction of the total carrier density. The Poole-Frenkel mechanism accounts naturally for the expected interactions between carriers bound in a Coulomb well and an applied electric field. Together with a field-dependent mobility, this mechanism is expected to semiquantitatively describe the conductivity in doped XSCs.

In sum, a quantitative study of n-type doping in highly crystalline organic semiconductor films establishes the predominant influence of electrostatic forces in these low-dielectric materials. Based on these findings, a self-consistent model of doped (purposely or not) organic semiconductors is proposed in which: 1) the free carrier density, n_f , is a small fraction of the total charge density; 2) a superlinear increase in n_f with doping density is expected; 3) n_f increases with applied electric field; and 4) the carrier mobility is field-dependent regardless of crystallinity.

Future studies will attempt to separate the effects of the carrier concentration from the carrier mobility; investigate a newly-conceived doping method that facilitates the formation of organic p-n junctions; quantify exciton diffusion lengths, and measure the rates of exciton quenching and electron-hole recombination at solid state organic heterointerfaces as a function of thermodynamic driving force.

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Session V

*Nanohybrid Assemblies for Solar
Photoconversion*

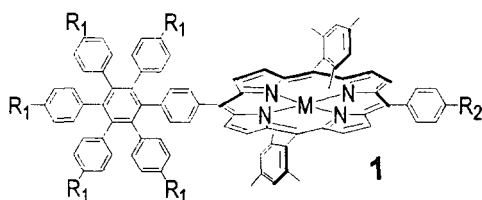
MIMICKING BACTERIAL PHOTOSYNTHETIC FUNCTION

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The goal of our research has been, in general terms, the mimicry of various steps of the solar energy conversion process that occurs in bacterial photosynthesis. In previous work in our laboratories, we have developed principles that allow us to design and synthesize synthetic analogs of photosynthetic reaction centers consisting of porphyrins or related chromophores covalently linked to electron donor and acceptor moieties. Such "artificial reaction centers" can use light to separate charge with quantum yields approaching unity. The resulting charge-separated states can store a significant amount of the photon energy for long enough that it may be used through reactions with other donors and acceptors in solution or in membranes, or through interactions with conductive surfaces. We have now expanded this research to include mimicry of two other photosynthetic functions exhibited by bacteria: light-harvesting by antenna-reaction center complexes and hydrogen production via "photofermentation."

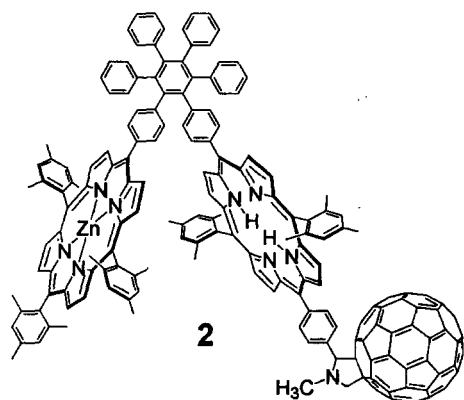
Light-harvesting antenna-reaction center complexes. A variety of different structural motifs are found in natural antenna systems. In several of the bacteria, antennas include rings of chlorophyll and carotenoid molecules. Light absorbed by these pigments generates excited states that can move around the ring by energy transfer processes, and ultimately move out of the ring to another antenna or to the reaction center. With such structures in mind, we are attempting to construct model antenna systems based on structure 1 shown below. The groups R_1 are porphyrin derivatives or other chromophores that can absorb light and transfer it to the porphyrin indicated in the structure.



If that porphyrin bears an electron-accepting moiety at R_2 , the excitation energy from the antenna chromophores may be converted into electrochemical potential energy via photoinduced electron transfer. This system was chosen for investigation because the hexa-arylbenzene

core may be built up via Diels-Alder condensation of a substituted diarylacetylene and a substituted cyclopentadienone. These two materials may in turn be prepared from simpler precursors using well-known reaction sequences. In the past, we have used this strategy to prepare a variety of sterically hindered and highly substituted hexa-arylbenzenes for stereochemical study. The advantage of this approach is that the R_1 groups may be mixed or matched as desired to achieve, for example, isoenergetic excitation energy "hopping" among the chromophores, or vectorial energy transfer to a trap that can initiate electron transfer. In addition, systems could be devised in which the hole resulting from photoinduced electron transfer from the first excited singlet state of the porphyrin shown could either remain on that porphyrin, or migrate into the "antenna," with resulting consequences for charge-separation lifetime and subsequent antenna function.

To begin to investigate this approach, we have synthesized model triad 2, which features two porphyrins, a free base (P_{2H}) and a zinc (P_{2Zn}) porphyrin, linked to the hexaphenylbenzene



core. The free base porphyrin, with its lower-lying excited singlet state, acts as an excitation energy trap. In addition, it bears a fullerene (C₆₀) as an electron acceptor. Spectroscopic studies in 2-methyltetrahydrofuran show that excitation of the zinc porphyrin antenna moiety to form $^1P_{Zn}-P_{2H}-C_{60}$ is followed by singlet-singlet energy transfer to the free base porphyrin ($\tau = 59$ ps), yielding $P_{Zn}-^1P_{2H}-C_{60}$. The free base porphyrin first excited singlet state decays by photoinduced electron transfer to the fullerene ($\tau = 25$ ps), producing a $P_{Zn}-P_{2H}^{\bullet+}-C_{60}^{\bullet-}$ charge-separated state. Charge shift ($\tau = 167$ ps) yields $P_{Zn}^{\bullet+}-P_{2H}-C_{60}^{\bullet-}$. This final charge-separated state is formed with quantum yields >90% following excitation of any of the

three chromophores. Charge recombination in 2-methyltetrahydrofuran ($\tau = 50$ ns) occurs by an apparently endergonic process to give triplet states of the chromophores, rather than the ground state. In benzonitrile, charge recombination yields the ground state ($\tau = 220$ ns). The high efficiencies of the various energy and electron transfer processes suggest that this molecular architecture will be useful for the design of more complex antenna-reaction center complexes. We are currently attempting to prepare several such systems.

Biomimetic hydrogen production. The purple photosynthetic bacteria we have been using as a source of inspiration for our biomimicry do not generate enough photochemical redox potential to split water. Under certain conditions, however, they can use sunlight as an energy source for hydrogen production. During this process, sometimes called "photofermentation," electrons are obtained from oxidation of fixed carbon compounds to carbon dioxide. Photosynthetic energy in the form of ATP is used to boost the potential of these electrons to the point that they can reduce hydrogen ions to hydrogen gas via a nitrogenase enzyme. Thus, photofermentation is a biological analog of the steam reforming process (based on methane and water) that is responsible for nearly all commercial production of hydrogen.

In an attempt to functionally mimic the biological process, we have constructed a photoelectrochemical cell that oxidizes carbohydrates or alcohols, uses light to boost the reduction potential of the resulting electrons, and reduces hydrogen ions to gaseous hydrogen. The photoanode consists of a nanoparticulate TiO₂ electrode coated with a porphyrin sensitizer (S). Key to the operation of the cell is the coupling of the anode photoreactions to the oxidation of biological fuels such as glucose or alcohols by an NADH/NAD⁺ redox carrier. Electron donation to the oxidized sensitizer S⁺ by NADH is facile, ultimately generating NAD⁺, which is not reduced by charge recombination reactions at the photoanode. Dehydrogenase enzymes oxidize the biological fuel, and in the process reduce the NAD⁺ coenzyme back to NADH. These reactions are coupled to the cathode through an ion-permeable membrane. The cathode comprises a composite of nanoparticulate platinum on carbon immersed in a buffer solution at the same pH as the anode compartment. In preliminary experiments, it was found that excitation of the photoanode with light of wavelengths absorbed only by the porphyrin sensitizer results in evolution of gaseous hydrogen from the cathode. The mechanistic details and efficiency of this cell are being investigated.

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A PHOTOACTIVE LIPID MEMBRANE COUPLED TO A PLANAR SEMICONDUCTOR THROUGH A CONDUCTING POLYMER

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We have initiated a collaborative research program to develop a polymeric, lipid membrane-based, supramolecular assembly that uses photon energy to drive a biomimetic energy transduction process, specifically vectorial proton pumping. The creation of a light-driven proton pump interfaced to an electrically active support is a necessary first step toward efficient coupling of these types of photosynthetic processes to useful molecular devices, e.g. biosensors and energy conversion devices.

The overall design of the assembly is illustrated in Figure 1. The planar supported lipid bilayer (PSLB) is self-organized using synthetic lipids, then chemically cross-linked to provide chemical and physical stability. Artificial photosynthetic reaction centers, being developed in the laboratories of Tom Moore, Ana Moore, and Devens Gust of Arizona State University, are incorporated into the stabilized bilayer to provide for light-activated proton pumping. The PSLB is interfaced to a planar semiconductor, e.g. an indium tin oxide (ITO) layer, via a thin, conductive polymer film (e.g. polyaniline), which provides a water-swollen “cushion” for accumulation of translocated protons and transduction of the light-driven pmf into a change in

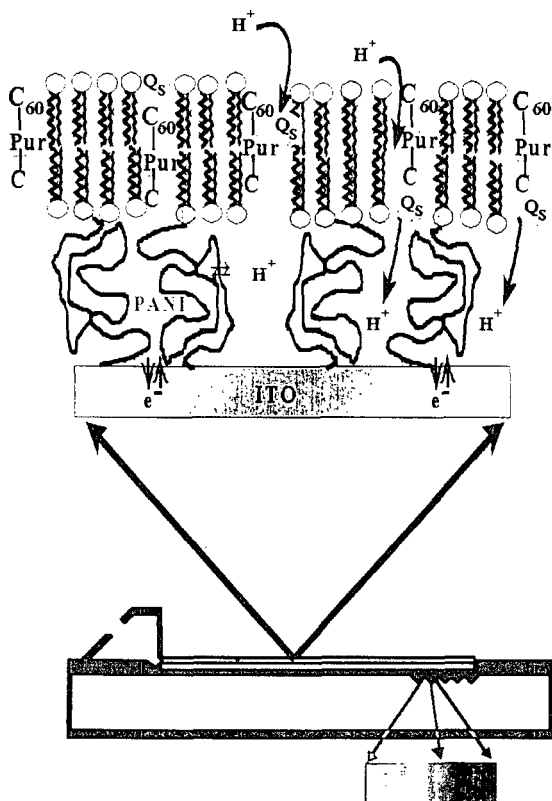


Fig. 1. Proposed energy transduction system composed of a planar ITO electrode is modified with a ca. 3-10 nm thick hydrophilic, conductive polymer cushion (e.g. polyaniline), which in turn supports a planar lipid bilayer (5 nm thick) that has been stabilized by cross-linking polymerization, and incorporates an artificial photosynthetic reaction center (C-Pur-C₆₀; Moore, Gust, and Moore). Upon light absorption, the C-Pur-C₆₀ undergoes charge separation and electron transfer to produce C⁺-Pur-C₆₀⁻, which reduces the diffusive quinone (Q_s) at the outer interface and oxidizes it at the inner interface. Thus Q_s shuttles protons from the outer medium across the membrane to the water-swollen space occupied by the polymer cushion. The ITO film (ca. 25-100 nm thick) is the upper layer of a spectroelectrochemical planar waveguide. Broadband, polarized planar waveguide ATR spectroscopy, performed under potential control or during potentiometric characterization of the biomimetic process, is used to initiate nanometer-scale proton pumping, quantitatively determine its efficiency, and characterize key structural and functional properties of the multilayer architecture.

interfacial potential. Alternately, a thin, porous sol-gel coating functionalized with conductive polymer 'nanowires' is used to couple the PSLB to the underlying ITO. The ITO layer functions as the working electrode in a spectroelectrochemical planar waveguide device, which allows simultaneous electrochemical and optical characterization. Recent progress toward creation of the individual components of this device is summarized below.

Conductive polymer films deposited on planar ITO electrodes.

The surface chemistry and surface roughness of ITO are incompatible with formation of a continuous lipid bilayer coating. Hydrophilic polymers can be used to overcome the chemical incompatibility as well as generate a smoother surface. We have used electrostatically driven self-assembly to deposit thin (ca. 3 nm) films composed of poly(aniline) (PANI) and poly(acrylic acid) (PAA); the potentiometric and optical response of these films to pH is Nernstian over a range of 3-9. Terminating the film with PAA allows subsequent deposition of a continuous, fluid PSLB by vesicle fusion. In a second approach to the incompatibility problem, we coat the ITO with a thin, porous layer of a silica-based sol-gel glass. The sol-gel surface chemistry and morphology supports deposition of a continuous PSLB, but the sol-gel layer is non-conductive. Thus, prior to PSLB formation, the sol-gel/ITO is soaked in a solution of a monomer (e.g., aniline), which diffuses into the pores. Electropolymerization creates conductive nanowires that extend from the ITO surface throughout the sol-gel layer. For both approaches, the next step is to introduce proton pumping chemistries into the PSLB and characterize their performance.

Planar supported (poly)lipid bilayers.

Although fluid PSLBs have been used widely in biomimetic devices, they lack the high stability desired for technological implementation because the non-covalent forces between the constituent lipids are relatively weak. Thus, for example, the lamellar structure cannot be maintained when the PSLB is removed from water. Polymerization of the lipid monomers is a logical solution to this problem. We recently demonstrated creation of highly PSLBs on SiO₂ substrates via self-assembly of bis-SorbPC (Fig. 2) followed by *in situ* radical-initiated polymerization. The cross-linked bilayer structure is preserved upon repeated drying/ rehydration, sonication in surfactants, and immersion in organic solvents. The biocompatibility of these films is excellent, e.g., the degree of protein adsorption on poly(PSLBs) was found to be equivalent to that on a fluid (unpolymerized) PC lipid bilayer.

However, it is not clear if poly(lipid) membranes are sufficiently impermeable to ions to allow their use in devices in which a transmembrane gradient must be formed and maintained. To assess the ion permeability, we have developed a liposome-based assay based on entrapment of a calcium-chelating fluor. Initial results indicate that membranes formed from lipids containing polymerizable groups in the acyl chains are highly permeable to ions. Consequently, we have synthesized and begun to evaluate lipids in which the polymerizable group is linked to the headgroup of the molecule (Fig. 2).

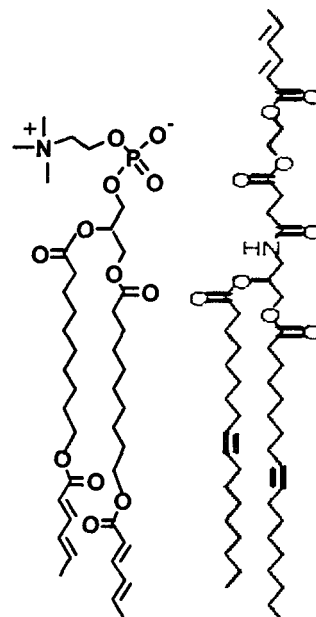


Fig. 2. Left: bis-SorbPC. Right: Dioleoyl lipid bearing an ethyleneoxy headgroup

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2. Chenhao Ge, Sergio B. Mendes, Neal R. Armstrong, and S. Scott Saavedra, **2004**, submitted. "Voltammetric and Waveguide Spectroelectrochemical Characterization of Ultrathin Poly(Aniline)/Poly(Acrylic Acid) Films Self-Assembled on Indium-Tin Oxide."
3. Chenhao Ge, Fathima Marikkar, Brooke Beam, Todd McBee, Neal R. Armstrong, and S. Scott Saavedra, in preparation. "Potentiometric and Spectroelectrochemical Sensing Properties of Ultrathin, Self-Assembled Poly(Aniline)/Poly(Acrylic Acid) Multilayer Films on Indium-Tin Oxide Planar Waveguide Electrodes."
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FUNDAMENTAL STUDIES OF LIGHT-INDUCED CHARGE TRANSFER, ENERGY TRANSFER, AND ENERGY CONVERSION WITH SUPRAMOLECULAR SYSTEMS

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Summary of Project. This project seeks to exploit supramolecular chemistry: a) to interrogate and understand fundamental aspects of light-induced charge transfer and energy transfer, and b) to construct solar energy conversion systems that make use of unique assembly motifs to address key conversion efficiency issues.

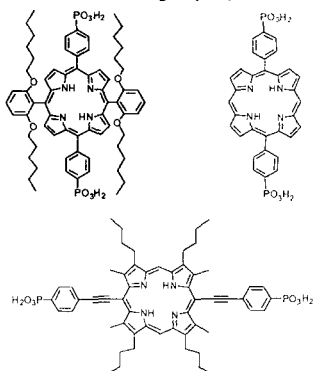
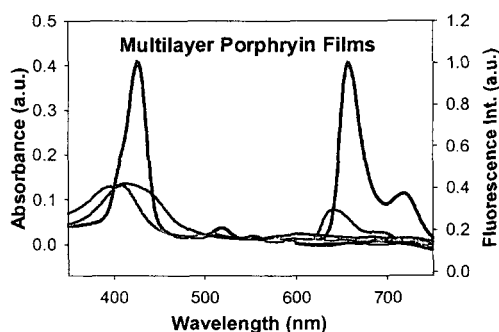
Multilayer sensitization. The use of flat or low-area photoelectrodes, sensitized with multiple dye layers, should eliminate the ubiquitous metal-oxide trap states that are responsible, in part, for suboptimal photovoltages in conventional dye-sensitized photoelectrochemical solar cells. Flat-electrode cell designs may also solve photovoltage loss problems attributable to the iodide/triiodide shuttle system of standard dye-sensitized cells by permitting the system to be replaced by more energetically favorable redox couples.

Highly chromophoric, phosphonate-functionalized, porphyrinic molecular squares have been assembled in layer-by-layer fashion (sequential exposure to Zr^{4+} and dye) on flat TiO_2 surfaces and used as multilayer sensitizers. Oriented squares confer well-defined ionic porosity to light-collecting molecular films – a necessary ingredient for local charge compensation and efficient sensitization.

Reverse solar cells. Photocurrent measurements with porous square films on ITO in water as solvent have yielded a surprising result: Rather than injecting electrons into the metal-oxide platforms, the illuminated dye layers consume electrons, drive the redox shuttle in the reverse direction, and produce photocurrents of opposite sign to conventional cells. The basis for the effect is extremely efficient oxidative quenching by triiodide, based on preformed I_3^- /porphyrin complexes. Holes are then transported by dye-to-dye hopping to the underlying electrode. Because transport occurs in the dye ground state, the difficult problem of transport-limiting kinetic competition between excited-state relaxation and exciton hopping is circumvented, and the cells operate well even with dozens of layers of sensitizing dye.

Photovoltages in the reverse-current cell are intrinsically limited to a few hundred mV. A second-generation cell featuring appropriately passivated ITO, however, could generate much higher photovoltages. Importantly, extensions to nonaqueous environments reveal that, in conventional cells, the reverse pathway can act as a previously unrecognized parasitic drain on forward photocurrent output.

Alternative assemblies and black chromophores. For several reasons, replacement of Re-containing squares with individual porphyrins is desirable. Multilayer assemblies of single-porphyrin units tend to be ineffective in sensitization applications, however, because lifetime-attenuating aggregation readily occurs in film environments. Notably, the molecular square motif discussed above sterically inhibits aggregation.

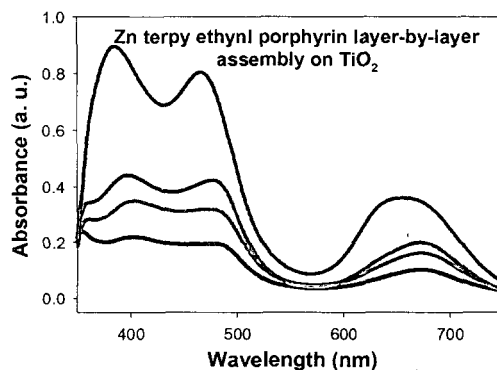


Phenyl ether functionalization also eliminates aggregation in films, while additionally engendering the ionic porosity that likewise is a hallmark of the square design.

Porphyrins are strong absorbers in the blue part of the spectrum, but less effective elsewhere. Therein has shown, however, that black porphyrinic chromophores can be created via extended conjugation and polarization with terpyridine-coordinated metal ions. With synthetic advice from the Therien group, we have found that closely related porphyrinic chromophores can be prepared, and layered stepwise on TiO_2 . One example that covers about 60-70% of the visible spectrum is shown below.

Molecular photovoltaics. Very preliminary work in a new direction is focused on using supramolecular assembly approaches and

nanoscale porosity to build highly oriented interleaved chromophoric (porphyrin or porphyrin-square) and electron-transport (perylene diimide) structures that function as excitonic photovoltaics. The design appears to solve a key problem in molecular photovoltaics: the efficient transport of locally created excitons to an electron-transport/hole-transport interface. Here every locally generated exciton is in direct contact with an oriented molecular column of electron-accepting material, thereby eliminating fully the exciton propagation requirement. Preliminary work shows that substantial photocurrents can be generated, current can be predictably increased with extended multilayer structures, and cell photovoltages can be manipulated in predictable ways via external field alteration (electrode work function alteration).



Optical electron transfer investigations of isolated model systems. Supramolecular coordination chemistry has been used to construct symmetrical organic mixed-valence systems in which D and A sites are cofacially oriented by peripheral metal ions and ligands defining any of several molecular rectangles. Based in part on intervalence Stark spectroscopy, we find that coupling behavior can vary from weakly class II to strongly class III delocalized. The differences reflect detailed geometric configurational differences that can either facilitate or negate direct D/A orbital overlap.

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INTEGRATING SINGLE WALL CARBON NANOTUBES INTO DONOR-ACCEPTOR NANOHYBRIDS

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Nanoscale carbon materials (*i.e.*, fullerenes and nanotubes) are attractive platforms for applications in photovoltaics. These nanoscale materials have extended, delocalized π -electron systems, which, in combination with photoexcited electron donors, may make them useful for managing charge transfer within novel, ultra-high efficient photoelectrochemical cells for water splitting and reduction of CO₂ to fuels. The application of the proposed donor-acceptor conjugates is relevant to the mission of the DOE's solar photochemistry program and is of interest to scientists working in the fields of photo- / radiation-chemistry, electron donor-acceptor interactions, supramolecular chemistry and photovoltaics.

As far as fullerenes and especially C₆₀ are concerned, a recent breakthrough in our work includes a 24% efficient charge-separation within a molecular tetrad. The lifetime of the spatially-separated (~49 Å) radical pair, which is the product of a sequence of energy and electron transfer reactions, reaches well beyond milliseconds (0.38 s). Such an extended charge separation had not previously been accomplished in an artificial photosynthetic reaction center.

Single wall carbon nanotubes (SWNT), on the other hand, may also serve as the electron acceptor component in donor-acceptor ensembles, just as fullerenes have been the electron acceptors in much recent research. Notably, the expected electrical conductivity behavior associated with the tubular structure and good chemical stability opens new promising scenarios for their use as "molecular wires" with high surface areas in the design of electro- and photoactive ensembles. However, there are several obstacles in the way of integrating SWNT into functional donor-acceptor constructs and their use in practical applications. Controlled modification of their surface with multifunctional groups – chromophores, electron donors, biomolecules, etc. – is required to fully realize their potential in nanotechnology.

The objective of ongoing efforts in our laboratories is the systematic investigation of novel SWNT ensembles. The organic functionalization of carbon nanotubes has produced a class of completely new materials with anticipated great impact on sustainable energies as well as on nanoscience and nanotechnology as a whole. While the shape and size of functionalized SWNTs are largely retained, effects are expected to arise from the randomly occurring interruption of the conjugated π -system.

I will discuss recent advances in the design, synthesis, purification, characterization, and examination of the potential for applications of new multifunctional SWNT materials as two- or three-dimensional architectures for high mechanical strength and electron donor-acceptor

chemistry. For example, we reported recently on the photoinduced electron transfer within a novel single wall carbon nanotube – ferrocene nanohybrid (SWNT-Fc), which yields a long-lived charge-separated (SWNT)⁻-(Fc)⁺ state. The presence of SWNT⁻, detected by laser flash photolysis, has been confirmed by time-resolved pulse radiolysis and steady-state bulk electrolysis.

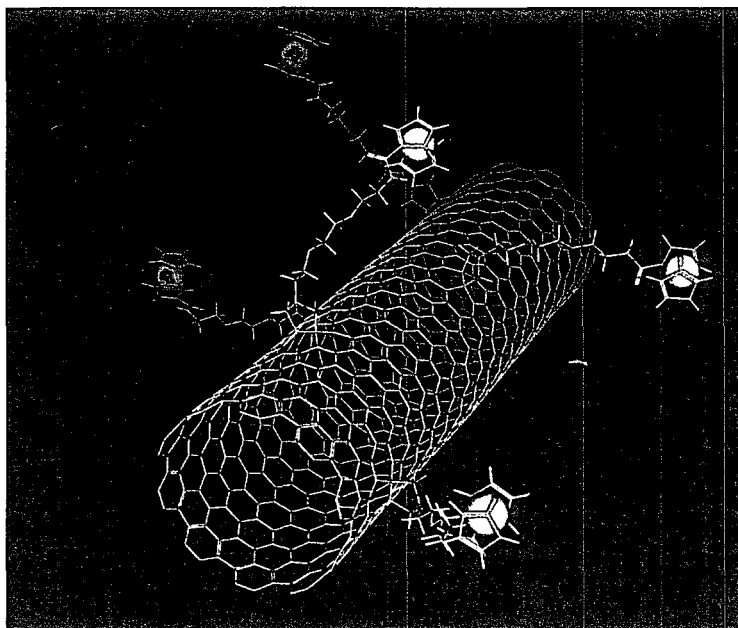


Figure 1: Partial structure of single wall carbon nanotube – ferrocene nanohybrid (SWNT-Fc)

In complementary work we tested the coulomb complex formation of water-soluble SWNT grafted with poly(sodium 4-styrenesulfonate) (SWNT-PSS) and a 5,10,15,20-tetrakis-(2',6'-bis-(N-methylene-(4''-tert-butylpyridinium))-4'-tert-butylphenyl)porphyrin octabromide salt (H_2P^{8+}) *en route* to versatile donor-acceptor ensembles. Photoexcitation of the porphyrin chromophore in SWNT-PSSⁿ⁻ / H_2P^{8+} is followed by a rapid and efficient intra-ensemble charge separation to generate a charge-separated state that lives for tens of microseconds.

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PHOTOCHEMICAL PROPERTIES OF NANOSCALE ASSEMBLIES OF LINKED SEMICONDUCTOR QUANTUM DOTS AND SINGLE WALL CARBON NANOTUBES

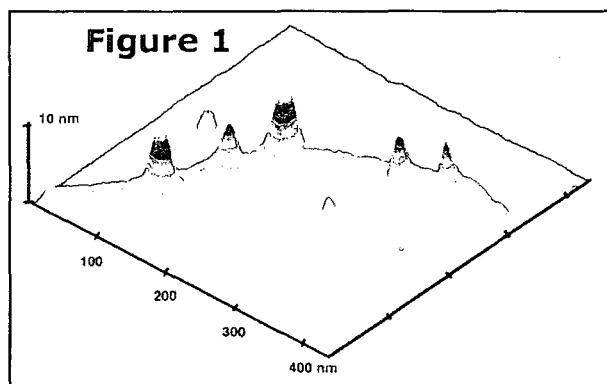
C. Engrakul, M. Jones, R.J. Ellingson, Y.-H. Kim, J.M. Nedeljković, W. Metzger, S.P. Ahrenkiel, M.C. Hanna, K.M. Jones, T. Gennett[†], A.C. Dillon, K.E.H. Gilbert, P.A. Parilla, S.B. Zhang, A.J. Nozik, O.I. Mičić, G. Rumbles, and M.J. Heben

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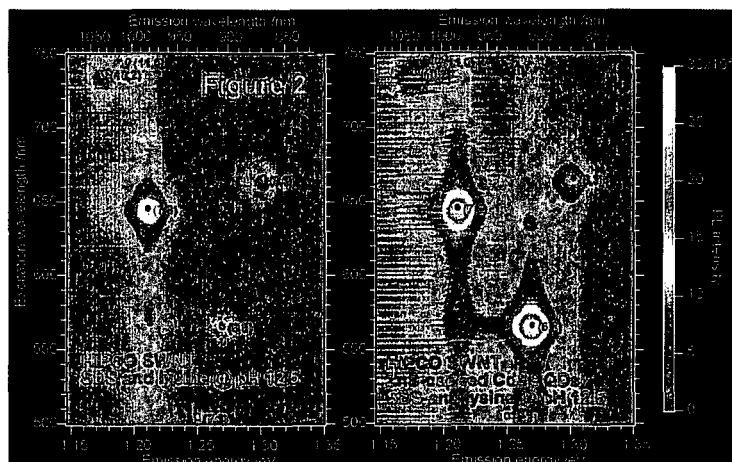
The project is directed at (1) coupling semiconductor quantum dots (QDs) and carbon single-wall nanotube wires (SWNTs) to form QD-SWNT assemblies, (2) elucidating the optical and electronic properties of these assemblies, and (3) tailoring the energetics and construction of the assemblies such that the relaxation of photoexcited states can be harnessed to do useful photochemical work. A long-term goal is the construction of hybrid nanoscale systems in which sunlight can be efficiently harvested and converted to generate electricity or fuels, such as hydrogen. The effort includes the synthesis, purification, and characterization of QD and SWNT materials, chemical and physical methodologies targeted at bringing SWNTs and QDs into intimate electronic contact, as well as steady-state and time-resolved optical absorption and emission spectroscopies designed to probe the nature and degree of coupling.

Several strategies are employed to form QD-SWNT assemblies. In the simplest approach, size-selected InP and CdSe QDs (as well as CdSe quantum rods) are adsorbed onto purified SWNTs by gentle refluxing in organic solvents. Transmission electron microscopy shows linear arrays of QDs formed along the axes of the nanotube bundles. The QDs remain affixed and ordered after repeated washings in solvent, indicating strong binding interactions. The energetics of binding and linear ordering were modeled using atomistic pair-wise summation of the Lennard-Jones 12-6 potentials for the QD-SWNT and QD-QD interactions. The model describes a preference for larger QDs to align edge-to-edge in the troughs between neighboring SWNTs, consistent with observations.



The energy and charge transfer properties of the solid materials prepared by the above-described method are not readily probed by spectroscopic means. Soluble QD-SWNT assemblies can be formed by combining aqueous solutions of SWNTs prepared by sonication in sodium dodecylsulfate (SDS)¹ with water-soluble ZnS-encased CdSe QDs capped with the amino acid, lysine.² Figure 1 shows an atomic force microscopy image of a necklace of lysine-capped (CdSe)ZnS QDs linked by a SWNT strand. The solutions of SDS-solubilized SWNTs and lysine-capped (CdSe)ZnS were both highly luminescent, and the individual solutions as well as

the mixtures were examined by photoluminescence excitation spectroscopy (PLE) over a range of pH values. Comparison of the PLE data with excitation of E_{22} SWNT van Hove singularities and detection of emission from E_{11} transitions shows striking changes in the relative PL intensity of the (7,5), (6,5) and (8,3) SWNT peaks upon addition of the QDs (Figure 2)³. The origin of this enhancement in PL is not clearly understood at the present time, and will be discussed in the presentation. Also of note is the observation of excitons in the SWNT spectra.⁴



The reported PL quantum yield (QY) for SWNT is $\sim 10^{-3}$ based on the assumption that all SWNT species in the sample are isolated and therefore luminescent.¹ However, transient absorption (TA) spectroscopy studies of the solubilized SWNTs indicate significant coupling between a substantial portion of the SWNT in the sample,⁵ suggesting that the actual QY might be significantly higher. To understand the potential for managing charge and energy transfer within these nanoscale systems, it will be essential to determine the PL quenching mechanisms and how the energy levels of QDs and SWNTs align and communicate. To the latter end, we have performed first-principals calculations which show that various band alignments can be obtained depending on the SWNT/semiconductor combination.⁶ For example, a (17,0) semiconducting SWNT forms a type-I band alignment with GaAs, and a type-II alignment with InAs.

To gain more intimate contact between QDs and SWNTs, we have begun investigating methods to directly synthesize semiconductor nanostructures on the surfaces of SWNTs. Approaches include deposition of InP and InAs by organometallic chemical vapor deposition, and solution-based methods such as the deposition of monodisperse indium droplets followed by reaction with H_3As or H_3P to yield InAs or InP, respectively. We also intend to fully determine the optical cross-section and QY of individual SWNT types, and to apply and develop methods for obtaining type- and chirality-pure SWNT samples. We will extend our PLE capabilities into the infrared region to fully characterize the lower energy transitions in SWNTs, and perform detailed TA, time-resolved PL, and PLE studies of coupled QD-SWNT assemblies.

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4. See poster by M. Jones, et al., in this Program.
5. See poster by R.J. Ellingson, et al., in this Program.
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“Ultrafast Photoresponse of Coupled Single-Walled Carbon Nanotubes”, R.J. Ellingson, C. Entrakul, M. Samec, A.J. Nozik, and M.J. Heben. This publication was submitted to Physical Review B in November of 2003, and is currently being edited in response to referee review.

“Spectroscopic Analysis of Excitons in Solubilized Single-Wall Carbon Nanotubes”, M. Jones, C. Entrakul, W. Metzger, A.J. Nozik, M.J. Heben, and G. Rumbles. Manuscript in preparation.

“Extended Linear Arrays of Semiconductor Nanocrystals on Single Wall Carbon Nanotubes”, C. Entrakul, Y.-H. Kim, J.M. Nedeljković, S.P. Ahrenkeil, K.E.H. Gilbert, J.L. Alleman, S.B. Zhang, A.J. Nozik, O.I. Mičić, and M.J. Heben. Manuscript in preparation.

UNDERSTANDING NANOSCALE QUANTUM DOT CHEMISTRY: INTERACTIONS WITH PROTEINS

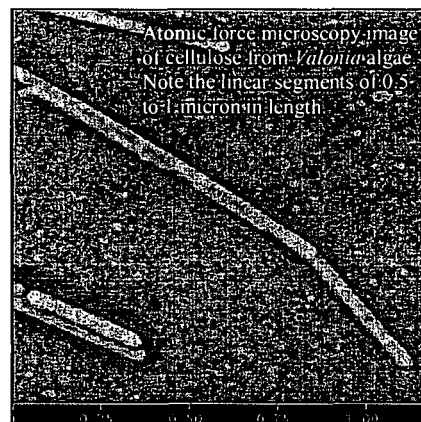
M.E. Himmel, S.-Y. Ding, G. Rumbles, J. Feng, M. Jones, O.I. Mičić, and A. Nozik
Center for Basic Sciences and National Bioenergy Center
National Renewable Energy Laboratory, Golden, CO 80401

Project Scope

The majority of published research conducted on semiconductor nanoparticles has dealt with either individual nanoparticles or with quantum dot (QD) arrays assembled from individual nanoparticles. We propose to first validate the concept of using natural and/or recombinant (genetic engineered) biomacromolecules to build QD-protein conjugates into arrays with highly controlled patterns. Precision assembly of these arrays is non-trivial and requires considerable control over the random order nature of existing composites based on polymer entrapment or surface adsorption through general chemical interaction. The question remains, how must these nanoscale bodies be arranged for usable photoconversion properties to be controlled and eventually exploited? Here, we report the first novel assembly of quantum dots using a directed approach that capitalizes on the self-assembling properties of naturally occurring bacterial proteins, known collectively as the cellulosome. The scaffoldin component of the cellulolytic bacterium *Clostridium thermocellum* is a non-hydrolytic protein, which organizes the hydrolytic enzymes in a large complex, called the cellulosome. We were successful in assembling photoluminescent CdSe(ZnS) QDs on bacterial cellulose filaments in linear arrays using the highly specific cellulose binding domain, cohesin, and dockerin proteins from the cellulosome.

Recent Results

Using molecular genetics, we have cloned certain protein domain elements of the cellulosome to form a non-natural (designed functional) fusion protein that embodies the cohesin domain (19 kDa; 45x25x25 Å), a cellulose-binding domain (CBD type 3, 17 kDa; 42x26x26 Å), a dockerin domain (8 kDa; 25x25x35 Å), and a streptavidin binding tag (Strep-TagII). The recombinant fusion protein was purified using the StrepII tag and affinity chromatography. SDS-polyacrylamide gel electrophoresis analysis confirms a monomer molecular weight consistent with the expected 50 kDa fusion protein. Using the highly specific cohesion/dockerin interaction site, this recombinant fusion protein self-assembles in solution to form a linear structural complex, which also binds to cellulose through the CBD. Once the protein polymer was allowed to initiate self-assembly, it was incubated with bacterial cellulose microfibrils or crystals. These forms of cellulose are produced from the fermentations of the bacterium, *Acetobacter xylinum* and the algae, *Valonia*. The bacterial protein, streptavidin (50 kDa; 54x25x25 Å) was then incubated with the (cohesin-CBD-dockerin-Strep-TagII)_n cellulose complex. Streptavidin is a tetrameric protein that binds very tightly to the small molecule, biotin, as well as the strep-Tag II. Finally, this protein



chimera was incubated with CdSe(ZnS) quantum dots that had been rendered water soluble by treatment with a multi-functional polymer ligated to biotin (Quantum Dot Corporation, Hayward, CA). These QDs are about 100 Å in diameter and highly luminescent. Direct observation using high-resolution light microscopy (500 to 560 nm excitation) demonstrated specific binding of the QD-protein complexes to the surface of cellulose 1 α and 1 β crystals. We noted the absence of random points of light emission, illustrating the fidelity of the interaction between the cellulosome cellulose binding domain and the cellulose surface. We also noticed the dramatic effect observable in real time, the blinking of QDs more remotely located on a cellulose strand. QDs found in closer proximity do not blink, but emit steadily when viewed by eye.

Future Work

We feel that bacterial cellulose is an especially effective choice for templating protein linked QDS. We will next look at the electrooptic properties of these new QD-protein composites and QD decorated cellulose filaments. We also note that thermal carbonization to our new QD decorated cellulose filaments may be expected to create carbon fibers embedded with QDs, resulting in novel QD arrays with more measurable photoelectronic properties. Ultimately, the separation distance of the QDs on the cellulose track is dictated by the interaction of the cellulose-binding domain with the exposed surface cellodextrin and the bioconjugate bulk surrounding the QD. We will approach the problem in two parts: first focusing on the chemistry necessary for creating photoluminescent and water soluble, monodisperse QDs of the smallest particle size possible and second on ensuring that the QD bioconjugates can be tethered to the cellulose track as closely as possible. The role that these closely coupled QDs play in transporting and trapping excitons as well as dissociating them into charge carriers will be investigated using a variety of spectroscopies, including time-resolved and steady-state photoluminescence, and femtosecond transient absorption.

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Session VII

***Semiconductor Nanoparticle-Based
Energy Conversion***

COMPUTATIONAL STUDIES OF BIOMOLECULE INTERACTIONS WITH TITANIUM OXIDE NANOPARTICLES

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Bio-inorganic materials for energy conversion involve charge transfer between a biomolecule to a nanoparticle. The goal of our computational studies is to find electronic properties of the interfaces in TiO₂/linker/DNA triads and to help understand experimental observations. Computational studies involve modeling of nanoparticle surface structure and its electronic structure; modeling chemical binding and charge separation between organic linkers and the nanoparticle; and modeling of junctions between linker and biomolecule such as DNA.

A thermodynamic model describing the relative stability of different shapes of nanoparticles as a function of their size was developed for arbitrary crystalline solids and applied to titanium oxide. The model makes use of surface energies and surface stresses calculated by density functional theory, which were determined for TiO₂ using periodic models. It was shown that the stable shape of clean anatase nanoparticles does not depend on their size. However, anatase nanoparticles undergo a phase transition to rutile phase at an average size of about 9.2 nm, in agreement with experimental evidence, and the point of the transition does depend on the shape of the particle. It has also been shown that a commonly used description of TiO₂ nanoparticles as spheres is not valid,

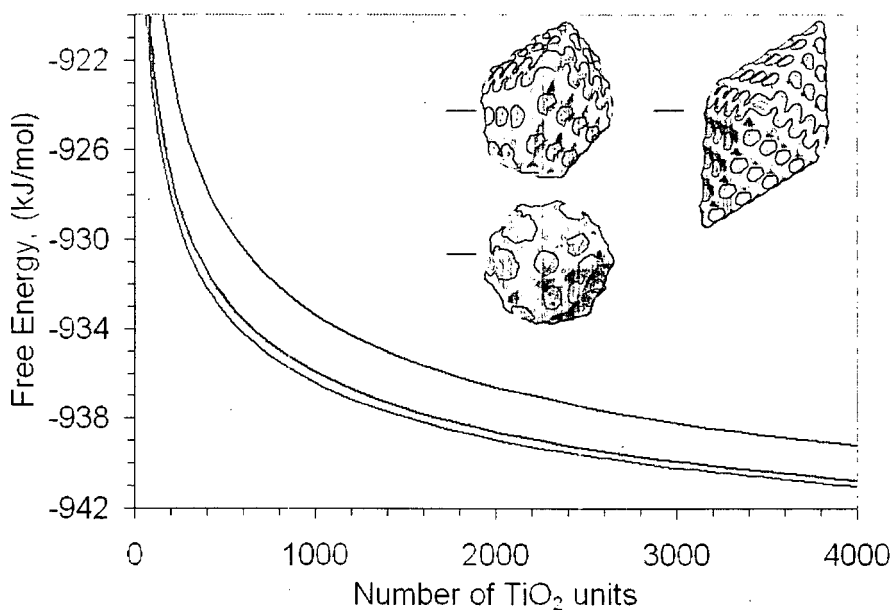


Figure 1. Calculated free energy as a function of nanoparticle size for anatase tetragonal bipyramid, tetragonal bipyramidal frustum and sphere. Surface energies and stresses for the model were calculated using DFT with Perdew-Wang exchange-correlation functional and Projected Augmented Wave potentials as implemented the VASP computer code. The size range of the particles shown is from about 1.5 to about 6.2 nm.

as it does not represent the minimum energy morphology, nor does it reproduce the correct size-regime of the phase transition. Furthermore, the surface chemistry of the nanoparticles was shown to strongly affect the relative stability of anatase nanoparticle shapes. As an example, hydrogen coverage of the surface was considered and it was shown that the size at which the phase transition occurs changes dramatically with respect to bare nanoparticles. These studies will help experimental efforts to synthesize TiO_2 with selectivity in phase, size and shape and to characterize resulting properties.

Our studies on catechol-modified anatase nanoparticles have been used to explain a large red shift of about 1.6 eV in the optical spectra. We have also studied modification of the titanium oxide nanoparticles by dopamine using *ab initio* molecular orbital theory and density functional theory. Our results confirm a suggested explanation for the large optical shift, which was observed in the case of dopamine as well as catechol. This involves under-coordinated sites having $\text{Ti}=\text{O}$ double bonds, which are reactive towards these ligands and result in bidentate dissociative bonding.

The photoexcitation of DNA/dopamine/nanoparticle triads leads to a hole transport through the linker to DNA. Carboxyl thymine, which is used in experiments to covalently bind DNA to surfaces, was used to study linker charge transfer properties by calculating oxidation potentials of dopamine linked to carboxyl thymine. Density functional calculations have been undertaken to study electronic properties of isolated and base-paired carboxy-T without/with amino group in gas phase and in solution. It was found that electron donating properties of thymine are increased by consecutive addition of carboxyl and secondary amide functional groups. In aqueous solution, these modifications lead to thymine ionization potential becoming close to that of adenine in the base pair.

Future work will concentrate on the goal of achieving realistic description of structure and electronic properties of DNA/linker/ TiO_2 triads. Studies of nanoparticle shape stability will be expanded to modeling of anatase in aqueous environments, including basic/acidic conditions. This will help to find optimal synthetic routes for nanoparticles with different surface chemistries. The shapes obtained from these aqueous models will provide a realistic distribution of surface sites that will be used in further studies of the electronic and optical properties of DNA/linker/ TiO_2 triads. Time-dependent density functional calculations will be employed to provide a better theoretical description of optical properties of these systems.

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STUDIES OF SPECTRAL SENSITIZATION OF ANATASE (101) SINGLE CRYSTAL ELECTRODES USING CARBOXYLATED CYANINE DYES

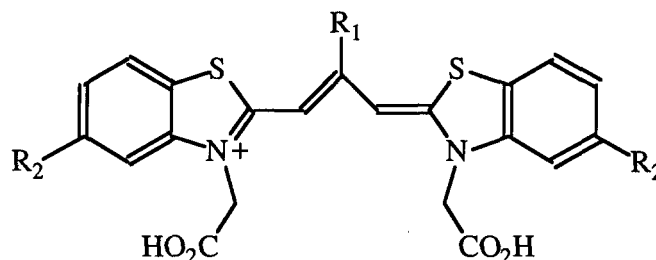
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The nanocrystals used in dye-sensitized solar cells are usually the anatase form of TiO₂. Although efficient and stable solar cells can be made from the dye sensitized nanocrystalline materials, there has been little fundamental information reported on the mode of dye binding or the organization of the dyes bound to the metal oxide surface. We report on the use of well-characterized terraced anatase single crystal surfaces as models for the nanocrystalline surface in order to elucidate aspects of the dye/semiconductor interface. A structurally similar series of thiacyanine dyes is used in combination with photocurrent spectroscopy, AFM and Monte Carlo simulations to help reveal details of the dye binding to the oxide surface. The presence of the ethyl group (R₁) on the bridge prevents aggregation of one set of dyes (G7, G11, G13) beyond dimers whereas extended aggregates are possible from the other dyes (G15, G12, G17).

Name	R ₁	R ₂
G15	H	H
G7	C ₂ H ₅	H
G12	H	CH ₃
G11	C ₂ H ₅	CH ₃
G17	H	OCH ₃
G13	C ₂ H ₅	OCH ₃



High incident photon current efficiency (IPCE) and absorbed photon current efficiency (APCE) values are obtained for these dyes bound to the anatase (101) surface. This is made possible through an ultraviolet (UV) light treatment of the anatase (101) surfaces immediately prior to dye adsorption, which improves both the reproducibility of dye coverage and the incident photon-to-current efficiencies (IPCE) for sensitization. The UV treatment does not pit or roughen the anatase surface (Figure 1) and results in IPCEs of up to 1% for sensitization of these single crystal substrates.

A well-defined surface structure allows the adsorption isotherms and adsorption and desorption kinetics of these dyes to be studied. The photocurrent spectra showed features associated with surface-bound dye monomers, dimers and aggregates that could be followed as a function of the dye surface coverage. Figure 2a shows photocurrent spectra as a function of dye coverage for dye G15. Peaks in the photocurrent spectrum can be identified with the monomer and H aggregate forms of the dye. Deconvolution of the photocurrent peaks, as a function of dye concentration that the freshly phototreated surface was exposed to, reveals the contributions of the monomer and aggregate forms of the dye to the surface coverage (Figure 2b).

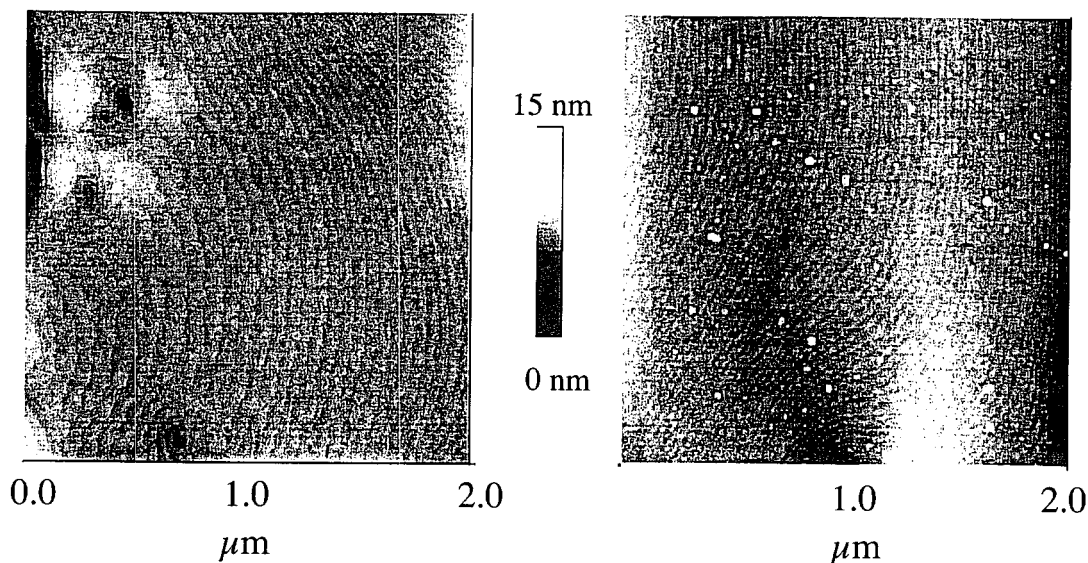


Figure 1. AFM images of anatase (101) surface after the polishing and annealing procedure (left) and after repeated UV treatments totaling almost two hours (right).

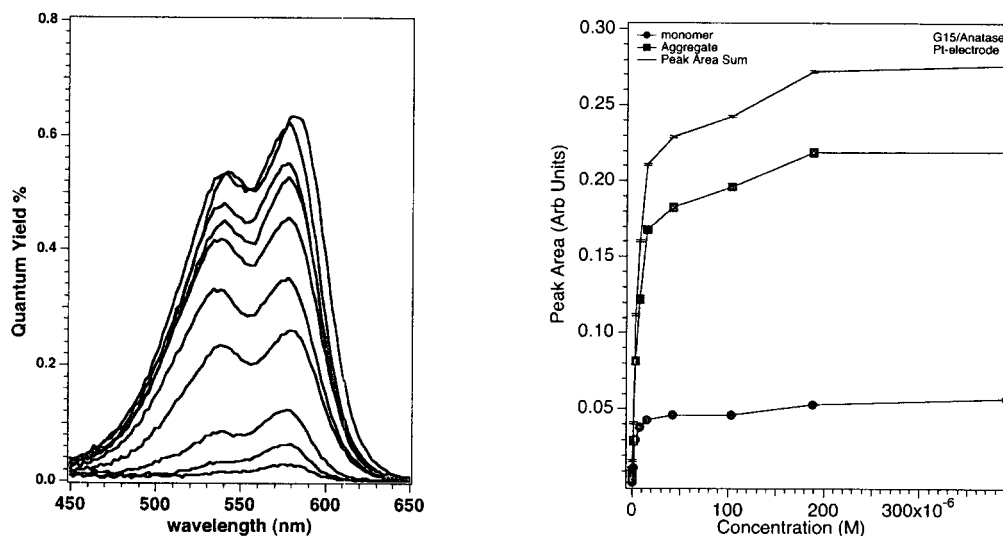


Figure 2 a) -Plot of the dye-sensitization of the anatase (101) surface by G15. b) - Isotherm generated from peak fitting the areas of the monomer and aggregate peaks of the G15 sensitization spectra shown in a).

The desorption kinetics of several of these dyes into pure acetonitrile solutions and solutions with added water (a competitive adsorber) were also studied. Strongly bound and more weakly bound populations of dye molecules were seen in all cases. Adsorption thermodynamics and surface dynamics of molecules adsorbed to a square lattice by two site attachments were simulated with Monte Carlo techniques. Diffusional “walking” of the molecules can result in the reorganization of molecules into ordered structures. Models for the surface structures of the adsorbed dye layers that are consistent with the simulations and photocurrent and desorption measurements are proposed and will be presented. Comparisons with data from nanocrystalline TiO_2 layers and other TiO_2 polytypes will also be made.

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UNIQUE APPROACHES TO SOLAR PHOTON CONVERSION BASED ON SEMICONDUCTOR NANOSTRUCTURES AND NOVEL MOLECULAR CHROMOPHORES; DYNAMICS OF ELECTRON RELAXATION, INTERFACIAL CHARGE TRANSFER, AND CARRIER MULTIPLICATION

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We are conducting basic studies of the optical, electronic, and photoredox properties of semiconductor quantum dots (QDs) and quantum rods (QRs), and arrays of QDs and QRs; the detailed relaxation and charge transfer dynamics of photogenerated electrons and holes in these nanostructures are also under study. These dynamics include: (1) the rate and efficiency of impact ionization (photogenerated carrier multiplication) of hot electrons in QDs and QRs, (2) the rate of electron transfer from QDs and QRs adsorbed on nanocrystalline oxide surfaces into the oxide conduction band and also from QDs and QRs into conducting polymers, (3) electron relaxation/cooling from excited states of the QDs and QRs to their ground state, (4) electron transport through QD and QR arrays, and (5) radiative and non-radiative electron-hole recombination. These studies will provide the scientific underpinning for potential applications of these unique nanostructures for ultrahighly efficient and low cost photoconversion systems that convert solar radiation to chemical fuels and electricity. This is because QDs and QRs have the potential to utilize the energy of solar photons much more efficiently ($QY > 1$) through photocurrent multiplication by impact ionization of hot electrons, and by photovoltage enhancement through hot electron transfer and conversion. In order to realize this potential, it is necessary to understand and control the competing dynamics of hot electron cooling, impact ionization, electron transfer, Auger recombination, and non-radiative and radiative recombination. In QDs, electron cooling is expected to be much slower because of a phonon bottleneck, and impact ionization is expected to occur at much lower photon energy thresholds compared to bulk semiconductors because of the absence of the requirement to conserve momentum.

Investigation of impact ionization in QDs and QRs is based on two approaches: (1) a new optical method using fs transient absorption vis and IR spectroscopy, and (2) by measuring the photocurrent-wavelength characteristic of QD-sensitized nanocrystalline TiO_2 electrodes. Low-bandgap QDs and QRs ($E_g < 0.5$ eV), such as InAs, PbSe, and PbS, have been synthesized and studied in order to greatly increase the fraction of absorbed solar irradiance, especially after quantization increase the bandgap of the QD and QR. The optical method pumps the QDs with supra-bandgap photons and probes the subsequent exciton density and decay dynamics to determine the efficiency of impact ionization (see poster by R.J. Ellingson et al.). This new technique has the great advantage of being a contactless method and hence ideal for measuring impact ionization in colloidal QDs. Efficient impact ionization has now been observed with PbSe QDs, and similar experiments are underway for InAs QDs. The current-potential method measures the photocurrent as a function of excitation wavelength, and a sudden rise of the

photocurrent at a given wavelength indicates the threshold photon energy for impact ionization. Preliminary results with InAs QD-sensitized TiO₂ indicate that efficient impact ionization is occurring at a threshold photon energy of about twice the QD HOMO-LUMO transition energy (450-600 nm, depending upon the InAs QD size), which is the theoretically predicted value for the threshold. These initial results provide encouragement that photocurrent multiplication through impact ionization of hot electrons could be an important process in QDs and may lead to much more efficient photoconversion devices.

Quantum rods (QRs) of Groups III-V, II-VI, and IV-VI have been successfully prepared (O.I. Mičić), and the femtosecond dynamics of hot electron relaxation as a function of quantum rod diameter with constant rod length has been established for the first time. For CdSe QRs, samples with a length of ~ 30 nm but with different diameters (2.5 and 8.0 nm) were investigated. We found that the intra-band energy relaxation is about 8 times faster in the thin rods compared to the thick ones. This result is similar to those for II-VI and III-V QDs and can be explained by an enhanced Auger cooling mechanism in nanocrystals.

The dynamics of photoinduced electron transfer from two types of quantum dots to nanocrystalline TiO₂ have been determined by transient absorption spectroscopy. The first system consisted of CdS QDs that were produced in-situ on the TiO₂ nanoparticles by successive ionic layer adsorption and reaction, and results in very strong and intimate contact of the CdS QDs with the TiO₂ substrate. The results showed that the electrons were transferred to the TiO₂ nanoparticles from the discrete CdS conduction band states with two characteristic time constants: 10 ps and 50 ps. The second system consisted of pyridine-capped InP QDs prepared by colloidal chemistry and then adsorbed onto the nanocrystalline films. The electron transfer in this system was found to occur from surface states on the InP QDs, but the time constant could not be established.

Another very interesting and important approach to carrier multiplication is via singlet exciton fission and quantum cutting in molecular systems. Future work will investigate novel molecular chromophores that undergo singlet fission or quantum cutting. As with impact ionization, singlet fission and quantum cutting will be monitored via both transient absorption spectroscopy and the photocurrent-potential characteristics of chromophore-sensitized nanocrystalline TiO₂ cells.

A new THz spectrometer has been developed (see poster by M. Beard et al.) and will be used to study the transport properties of charge carriers in QD and QR arrays. Understanding the differences in behavior between QDs and QRs, and the comparison to bulk transport will be emphasized. The dependence of carrier transport on QD and QR size, shape, inter-nanoparticle distance, nanocrystal packing order and disorder, nanocrystal orientation, surface chemistry, and electronic structure will be investigated. Visible pump-THz probe spectroscopy will also be investigated as a new tool to determine impact ionization in QD-sensitized TiO₂ electrodes.

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THEORETICAL STUDIES OF ELECTRON TRANSFER AND OPTICAL SPECTROSCOPY IN COMPLEX MOLECULES

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Overview:

During the past several years, we have continued to develop and test quantum chemical methods for modeling optical excitations and electron transfer in solution and in the solid state. Our computational protocols involve calculation of diabatic coupling matrix elements [6], determination of redox potentials in solution (including transition metal containing systems) [4], and both ab initio and empirical pseudopotential approaches to the calculation of excited state properties. Embedding methods have been developed for modeling ionic solids such as metal oxides, using quantum chemical clusters surrounded by classical ions. We have also pursued a wide range of applications, including transition metal complexes, STM imaging of molecules on surfaces [5], and studies of solid state systems including Si nanoparticles and TiO₂ surfaces. The ability to treat large systems using quantum chemical techniques is a central theme of many of these studies, and we have made considerable progress along these lines over the past several years. However, a lot more work needs to be done before these techniques reach the point where they can be routinely used to answer practical questions that will be of importance in the analysis and design of solar photochemistry devices.

Recent Results:

Silicon Nanoparticles: In collaboration with Prof. Louis Brus, we have initiated a program to use DFT based ab initio quantum chemical methods to understand the properties of silicon nanoparticles. Silicon is the dominant material that is used in microelectronics and photovoltaic devices; as such devices operate on increasingly small length scales, empirical models begin to break down, and the application of ab initio quantum chemical techniques, which can provide reliable answers over a wide range of chemical and structural variation, becomes highly relevant to this problem. Following is a summary of the progress that we have made to date.

Our original efforts [2] were focused on particles containing 35 and 66 Si atoms, respectively. We carried out full geometry optimizations and computed a range of electronic properties, including band gaps, optical spectra, ionization potentials and electron affinity, etc. The focus of the study was on the effects of terminating the nanoparticle with hydrogen versus oxide termination. Experiments suggest a dramatic red shift in luminescence when H-terminated nanocrystals are oxidized. The calculations are in agreement with these results: H terminated particles exhibit dipole allowed transitions in the UV, while oxide terminated particles exhibit dipole-forbidden transitions in the visible/near infrared. The computational results allow a detailed analysis of wavefunctions, structures, and energetics to be produced which explain the above results at an atomic level of detail.

More recently [1], we have extended our initial studies to larger nanoparticles (Si 87), additional terminating groups (F), and individual atom dopants (Al, P), which have been studied in the interior and on the surface of the cluster. In addition to more extensive characterization of the properties discussed in [2] (and treatment of additional systems), properties such as

reorganization of the structure upon charge transfer, effects of defects, and trapping sites were investigated. Radical nanocrystals experimentally show a 0.9eV luminescence at low temperature; we see a similar phenomenon in the calculations and are able to provide a microscopic explanation. The structures and electrical properties of Al and P dopants show a number of interesting features. For example, if P is located in the nanoparticle core, and a hydrogen is removed from the surface, an electron spontaneously transfers from the P to the radical site to form a lone pair at the missing H atom. This may explain experimental results in which the surface dangling bond ESR signal in oxide passivated Si decreases as P doping increases – the lone pair would be ESR silent, thus suppressing the signal in the absence of P doping.

TiO₂: We have carried out calculations of the work function of anatase, using our embedded cluster methodology, and they agree reasonably well with experiments. These results are currently being written up for publications.

III/V Semiconductor Particles: We have used pseudopotential methods to study optimal transitions in ZnS and CdSe [3]. Calculations of the oscillator strength show interesting behavior as a function of particle size, and are in reasonable qualitative agreement with available experimental data.

Future Plans:

At present we are focused on continuing our work on modeling Si and TiO₂ nanoparticles. For TiO₂, we intend to investigate the binding of dye molecules to the surface, and transfer and trapping of electrons from dye molecule (as a result of light excitation) to a trapping site in the TiO₂. The ultimate goal is to build models of the Gratzel cell and understand its function as a solar energy device. For Si, we will continue to extend our calculations to larger systems, and construct more realistic models that can be compared with experiment. One direction we intend to pursue is modeling of doped Si nanowires, which the Lieber group has investigated experimentally.

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SPECTROSCOPY AND DYNAMICS OF GaSe AND InSe NANOPARTICLES AND NANOPARTICLE AGGREGATES

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GaSe and InSe form two-dimensional nanoparticles, exactly four atoms thick and having diameters from 2.5 to 9 nm. The electron and hole intraband spectroscopy of these nanoparticles are studied using femtosecond transient absorption polarization methods. Transient absorption spectra and absorption anisotropy spectra are shown in figure 1. These results may be interpreted

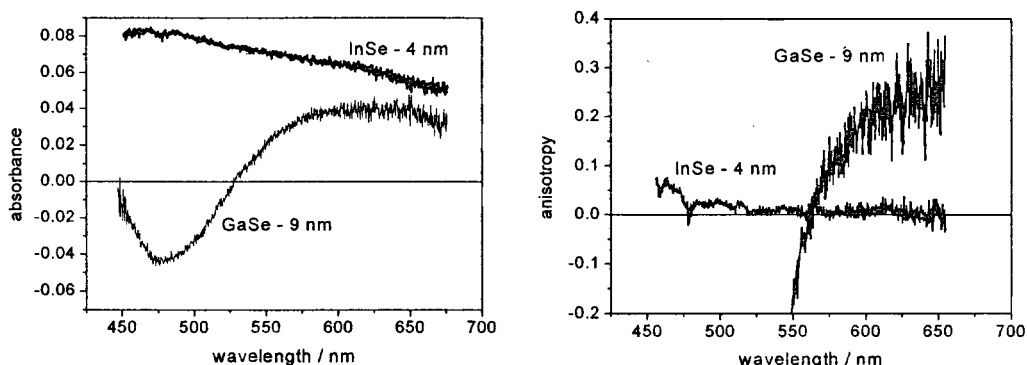


Figure 1. Transient absorption spectra (left panel) and transient absorption anisotropies (right panel) of 9 nm GaSe and 4 nm InSe nanoparticles. Both types of particles have absorption onsets at about 400 nm.

in terms of a simple effective mass model. Due to the approximately cylindrical symmetry of these particles, the electron and hole states are described by particle-in-a-cylinder wavefunctions and the optical transitions may be calculated from these wavefunctions. The results indicate that the GaSe transient absorption spectrum is dominated by hole intraband transitions. In contrast, the InSe nanoparticle spectra are due to x,y- and z-polarized electron intraband transitions.

The spectroscopic and dynamical characteristics of GaSe nanoparticle aggregates have also been studied. The absorption spectra of GaSe nanoparticles changes dramatically as the concentration is increased. This process is reversible and is interpreted in terms of the particles forming strongly interacting aggregates in high concentration, room temperature solutions. Concentration-dependent absorption spectra are shown in figure 2. These spectra may be quantitatively understood in terms of a model in which the disk-like nanoparticles are stacked to form one-dimensional aggregates. The model is based on the spectroscopy of the two lowest nanoparticle monomer excited states and dipolar coupling between nanoparticle monomers. Time-resolved emission and emission anisotropy results indicate that delocalized excitons migrate through the aggregate rapidly compared to exciton decay. These results also show that the mobility of the exciton within the aggregate depends on the size dispersion of the nanoparticles. The largest particles act as exciton traps in polydisperse samples resulting in

reduced exciton mobilities, compared to monodisperse samples. These nanoparticle aggregate spectra and dynamics are reminiscent of those in J-aggregates of organic dyes.

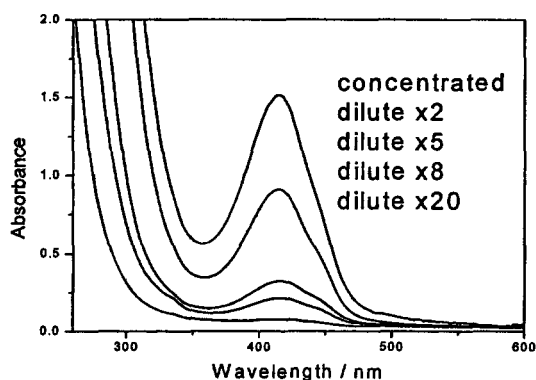


Figure 2. Concentration dependent absorption spectra of monodisperse (\pm <8%) 9 nm GaSe nanoparticles. The concentrations range from no dilution (the concentrated solution in the TOP/TOPO reaction mixture) to diluted by a factor of 20 in TOP/TOPO. The resolved peak at 415 nm is almost completely lost in the most dilute sample.

The above results along with known energetics suggest that it should be possible to form InSe-GaSe nanoparticle heterojunctions and that these junctions should exhibit rapid, efficient and long-lived photo-induced charge separation. Preliminary results confirm this expectation.

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V. Chikan and D. F. Kelley, "Carrier Relaxation Dynamics in GaSe Nanoparticles", *Nano Letters*, **2**, 1015 (2002).

D. F. Kelley "Nanoparticles of Layered Semiconductors" in *Molecular and Supramolecular Photochemistry*, Vol. 10, *Semiconductor Photochemistry and Photophysics*, K. S. Schanze and V. Ramamurthy, eds., Marcel Dekker, New York, 173, (2003).

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PHOTOCATALYSIS AND PHOTOELECTROCHEMISTRY USING INORGANIC COLLOIDS AND NANOCRYSTALS

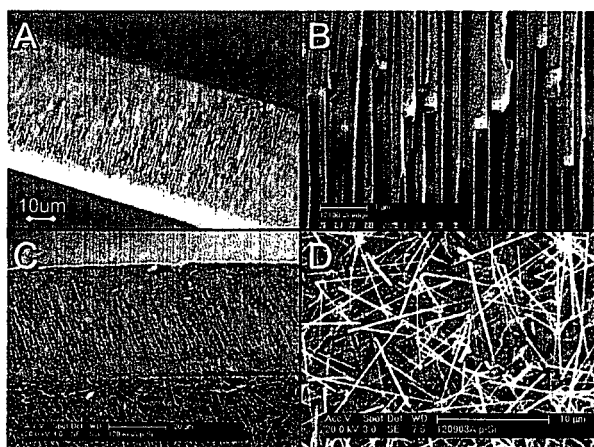
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Our DOE-supported work has focused on the use of nanoscale inorganic compounds (metal oxide colloids, layered metal oxide semiconductors, and template-grown semiconductor nanowires) in photocatalysis and photoelectrochemistry. This work is being directed towards the synthesis and characterization of particle-based systems for catalyzing thermodynamically uphill photochemical reactions, such as the photolysis of water.

Our recent work in particle-based photocatalysis has sought to address the problem that wide bandgap oxides, such as KTaO_3 , are the only known materials that can catalyze the photolysis of water with high quantum yield (>10%). Two strategies we have pursued to develop visible light photocatalysts are to make organized assemblies of dye-sensitized metal oxide semiconductors, and to substitute nitrogen for oxygen in oxide semiconductors, thereby shifting their bandgaps into the visible region. We have continued to study colloidal iridium oxide as a water oxidation catalyst for use with dye-sensitized metal oxides. $\text{IrO}_x \cdot n\text{H}_2\text{O}$ colloids contain Ir in a mixed III/IV oxidation state. Time-resolved spectroscopic studies of the reaction of $[\text{Ru}(\text{bpy})_3]^{3+}$ with these colloids show an initial fast electron transfer, corresponding to oxidation of Ir(III) to Ir(IV). Subsequent oxidation, probably to Ir(V), occurs more slowly, on a timescale of 0.1-0.2 s. The oxygen evolution reaction occurs on a timescale of seconds with a kinetic isotope effect $k_{\text{H}}/k_{\text{D}} = 1.0 \pm 0.3$. The slow rate of oxygen evolution and the weak kinetic isotope effect are reminiscent of previous observations by Hurst and Brudvig in the $[(\text{bpy})_2\text{Ru}(\text{OH}_2)]_2\text{O}^{4+}$ and $[\text{H}_2\text{O}(\text{tpy})\text{Mn}(\text{O})_2\text{Mn}(\text{tpy})\text{OH}_2]^{3+}$ homogeneous catalytic systems, respectively. This suggests a similar mechanism, in which oxygen evolved from a metal hydroperoxy (M-O-OH) intermediate. We have also synthesized and studied the layer perovskite oxynitrides $\text{Rb}_{1.8}\text{Ca}_2\text{Nb}_3\text{O}_{9.2}\text{N}_{0.8} \cdot 0.6\text{H}_2\text{O}$, and $\text{Rb}_{1.7}\text{LaNb}_2\text{O}_{6.3}\text{N}_{0.7} \cdot 0.6\text{H}_2\text{O}$, which are visible-light absorbing structural analogues of the known UV photocatalyst $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$. Three-dimensional perovskite oxynitrides, such as LaTiO_2N , are known to evolve H_2 and O_2 from aqueous solutions containing sacrificial donors (MeOH) and acceptors (Ag^+), respectively. A lamellar oxynitride would in principle allow us to incorporate colloidal catalysts by intercalation as we have done with $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$ and related materials. Unfortunately, the layered oxynitrides are too unstable in aqueous solutions to be useful photocatalysts.

We are also synthesizing semiconductor nanocrystals using anodic aluminum oxide (AAO) membranes as templates. The goal of this work is to make arrays of single crystal semiconductor wires for photoelectrochemistry, and series p-n junction nanowires for overall water splitting using visible light. As an initial goal, we are making liquid junction photoelectrochemical cells from arrays of vapor-grown Si and CdSe nanocrystals. Short

(~250nm) Au segments are first grown within the pores of the AAO membrane via electrodeposition, and are subsequently used as a catalyst for the decomposition of SiH₄ gas in the VLS process, or as a catalyst for laser-assisted growth of CdSe. The confines of the pores dictate a linear geometry for the resulting nanocrystals. Sufficiently long growth causes the wires to breach the surface of the membrane, yielding fields of overgrown semiconductor nanowires. In order to utilize protruding Si nanocrystals as photoelectrodes in a liquid junction cell we have electrodeposited Co behind the Au catalyst. Optimization of plating conditions has resulted in the controlled growth of relatively uniform 45-55 μm Co wires within the 60 μm thick membranes. This allows the subsequent electrodeposition of ~250nm Au caps atop the Co wires, positioning the catalyst within 10-15 μm of the membrane surface, which has proven to be the optimum depth for successful VLS growth.



A) Cross section of an AAO membrane after electrodeposition (of Co and Au), showing the typical length and uniformity of the wires. B) SEM image of a similarly prepared membrane resolving individual Co wires and their Au caps. C) SEM showing a cross section of the membrane in panel A after VLS growth of p-type Si nanowires. D) Membrane from A and C viewed by SEM from above, showing overgrown Si wires still bearing Au caps.

We have examined the light and dark I-V curves of the Si nanowire electrodes in non-aqueous Ru(bpy)₃ solutions. Initial photoelectrochemical experiments have yielded only ohmic responses. Several possible causes for the lack of photocurrent and/or photovoltage have been identified and are currently under investigation. Initially we focused primarily on the possibility that defects in the electrode membrane could allow solution to access the Co metal behind the Si wires. We have since determined that this is not the case, as no anodic stripping of Co is observed, even at relatively high potentials. Intentional degradation of either the wires or the membrane itself demonstrates that any exposed Co can be readily oxidized. We have also addressed concerns with the doping levels of the Si wires. Early samples were prepared with a p-type (boron) doping level of 10¹⁹ cm⁻³, which would result in a depletion width of only a few nm. The dopant concentration has since been reduced to 10¹⁷ cm⁻³. A third possible source of leakage current is the Au cap that remains after VLS nanowire growth. Initial attempts to remove the Au show that cyanide or triiodide etching conditions (as optimized with pure Au samples) are inadequate. We have also attempted to insulate exposed Au via the self-assembly of octadecanethiol, and by electropolymerization of insulating polymers (poly(*o*-phenylenediamine)). However, neither coating appears to withstand the cathodic potentials of the photoelectrochemical experiments.

Recent DOE Chemical Sciences-Sponsored Publications

M. Suzuki, C. C. Waraksa, T. E. Mallouk, H. Nakayama, and K. Hanabusa, "Enhanced Photocatalytic Reduction of Methylviologen by Self-Assembling Ruthenium(II) Poly(pyridyl) Complexes with L-Lysine Containing Side Chains," *J. Phys. Chem. B*, 106, 4227-4231 (2002).

N. D. Morris and T. E. Mallouk, "A High-Throughput Optical Screening Method for the Optimization of Colloidal Water Oxidation Catalysts," *J. Am. Chem. Soc.*, 124, 11114-11121 (2002).

M. Suzuki and T. E. Mallouk, "Photosensitized Production of Doubly Reduced Methylviologen Followed by Highly Efficient Methylviologen Radical Formation using Self-Assembling Ruthenium(II) Complexes," *J. Chem. Soc., Chem. Comm.*, 1534-5 (2002).

J. Peña, J. K. N. Mbindyo, A. J. Carado, T. E. Mallouk, C. D. Keating, B. Razavi, and T. S. Mayer, "Template Growth of Photoconductive Metal-CdSe-Metal Nanowires," *J. Phys. Chem. B* 106(30), 7458-7462 (2002).

J. H. Haeni, A.M. Ellis, D. G. Schlom, S. A. Chambers, J. Schottenfeld, T. E. Mallouk, J. Robertson, W. Tian, and X. Q. Pan, "Band Structure of Sr_2TiO_4 / SrTiO_3 Heterojunctions," submitted to *Appl. Phys. Lett.*

J. A. Schottenfeld, G. Chen, P. C. Ekerdt, and T. E. Mallouk, "Synthesis and Characterization of Layered Perovskite Oxynitride Photocatalysts from Dion-Jacobson Oxide Precursors," submitted to *Chem. Mater.*

B. A. Lewis, J. Wang, K. Jambunathan, H. Prakasam, T. S. Mayer, and T. E. Mallouk, "Laser Assisted Vapor/Liquid/Solid Growth of Photoconductive CdSe Nanocrystals in Porous Alumina Templates," submitted to *Chem. Mater.*

N. D. Morris, M. Suzuki, and T. E. Mallouk, "Kinetics of Electron Transfer and Oxygen Evolution in the Reaction of $[\text{Ru}(\text{bpy})_3]^{3+}$ with Colloidal Iridium Oxide," submitted to *J. Phys. Chem.*

Session VIII

***Characterization and Reactions
of Excited States***

TIME-RESOLVED X-RAY DIFFRACTION AND THE STRUCTURES OF EXCITED STATES OF MOLECULAR COMPLEXES

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While X-ray crystallography has since its inception been used for the determination of ground-state structure of molecules and solids, this limitation is now being removed by application of pump-probe techniques in which a pulsed laser pump source is synchronized with the probing X-ray pulses.^{1,2,3} They allow determination of excited state structure at atomic resolution, though with accuracy limited by the necessarily incomplete conversion of the molecules to their excited state.

In our first experiments at the X3 beamline at Brookhaven National Laboratory⁴ the Pt-Pt bond shortening on photoexcitation of the binuclear platinum complex $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ (Fig. 1) was determined.⁵ However, the flux requirements of the

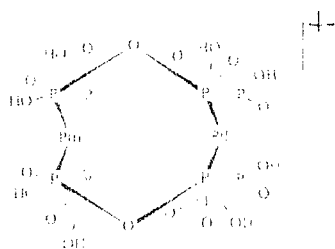


Figure 1.

experiment are such that further progress required their continuation at the third generation Advanced Photon Source at Argonne National Laboratory. In particular the limited survival time of the crystals in a beam in which the number of photons per pulse must be comparable to the number of molecules in the crystal requires a maximal X-ray flux. The Argonne time-resolved station constructed at the Chem/Mat CARS beamline includes a dual-laser facility delivering 355 and 532 nm wavelength light at pulse rates up to $\sim 25\text{kHz}$ and energies of up to $600 \mu\text{J/pulse}$. In current experiments the

sample crystal is probed for μs immediately following each of the 50ns laser pulses. Data are collected by the standard procedure of rotating the crystals over a narrow range, typically 0.3° for 1-2 sec, during which the crystal is exposed to the pulsed laser beam. To maximize the sensitivity of the experiment the 'light-on' frame is followed after detector read-out by a 'light-off' frame collected over the identical rotation range. For the $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ ion (below referred to as Ptpop) a shortening of the d^8-d^8 Pt-Pt distance by 0.28\AA , from 2.91 to 2.63\AA was obtained, a value in agreement with some, but not all, DFT calculations on the isolated molecule, the results of which are dependent on the choice of functional. The shortening is a result of the promotion of an electron from an orbital which is antibonding in the Pt-Pt region to a weakly bonding $p\sigma$ orbital. The result has been reproduced at the SPRING-8 synchrotron source in Japan.⁶ In a recent APS study we have found a much larger contraction of 0.8\AA in the d^8-d^8 dinuclear Rhodium complex $[\text{Rh}_2(1,8\text{-diisocyanop-}p\text{-menthane})_4]^{2+}$ in which the Rh-Rh potential is exceedingly shallow, facilitating the large contraction.

The excited triplet state of the $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ ion is extremely reactive, with a large spin density centered on the Pt nuclei. In cocrystals of $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ with dimethylviologen (MV^{2+}) the $50 \mu\text{s}$ lifetime (17K) of the anion is reduced to $12\text{-}15 \mu\text{s}$ for the $\text{K}_2\text{MV}(\text{Ptpop})$ salt (**1**, Fig. 2), while the phosphorescence is completely quenched for the $(\text{MV})_2(\text{Ptpop})$ salt (**2**).⁷ Our time-resolved crystallography experiments of (**1**) show that the Pt-Pt bonds in the two crystallographically independent anions shorten by $0.23(4)$ and $0.28(5)\text{\AA}$, in excellent agreement with the earlier results. The quenching is attributed

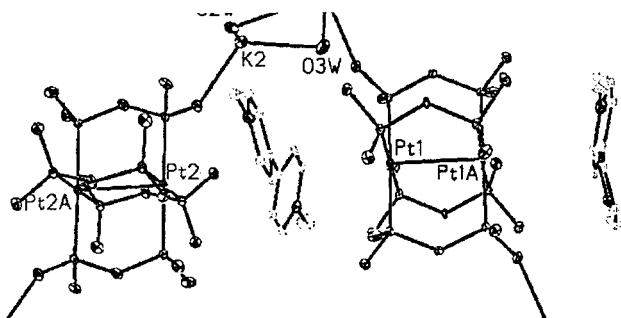


Figure 2.

distortion upon excitation of $[\text{Cu}(\text{I})(\text{dmp})(\text{dppe})]^+$ (dmp =2,9-dimethylphenanthroline), dppe =1,2-bis(diphenylphosphino)ethane) (Fig. 3) in its PF_6^- salt, which crystallizes with two molecules in the asymmetric unit.⁸ The conformational changes that occur on excitation are illustrated for one of the molecules in Fig. 4. They involve a decrease in the rocking and wagging distortions, as predicted by the theoretical calculation on the dmpe (=1,2-bis(dimethylphosphino)ethane) complex, but a flattening of only 2.2° , as

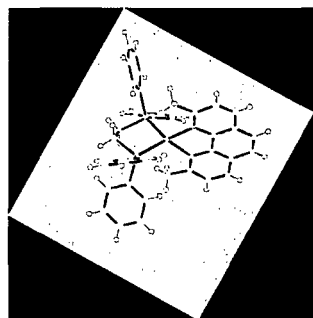


Figure 3.

illustrated in the figure, which is much less than the 8° predicted by the calculation. The second molecule is already somewhat flattened in the ground state and shows no further changes in this distortion. The results illustrate the effect of the confining medium on photochemical behavior in the solid state. **Future work:** Further improvements in the TR Diffraction capability will include a) experiments at shorter time-scales by use of the pulsed structure of the synchrotron source b) use of a multilayer rather than a Si monochromator to yield a 'pink' rather than a highly monochromatic beam with an increased X-ray flux, to reduce the length of laser exposure of the samples, and c) installation of a detector with multi-readout ports to reduce detector readout-time. We plan to study the distortion in $\text{Cu}(\text{dmp})_2$ salts (17K lifetime 400ns-3 μ s depending on the counterion), not accessible with our current time-limitation and extend the work to other complexes of importance for solar energy capture.

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to electron transfer to the methylviologen, and accompanied by the appearance of a new absorption band at $\sim 640\text{nm}$, manifesting itself as a green coloration of the crystals which persists for days, and an enhanced ESR signal.

In a more complex experiment involving not only the change in heavy atom structure we have analyzed the

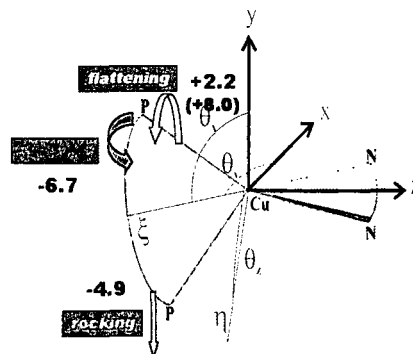


Figure 4.

DOE Supported Publications (2003-2004)

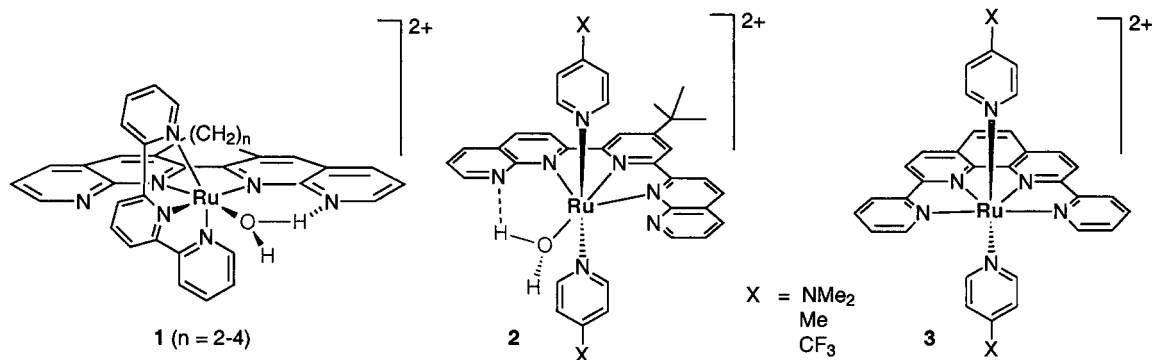
- 1 “What can time-resolved diffraction tell us about transient species?: excited-state structure determination at atomic resolution”, P. Coppens, *Chem. Commun.* (Focus article) **2003**, 1317-1320.
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DESIGNING LIGANDS TO PROMOTE PHOTOOXIDATION OF A Ru(II) AQUA COMPLEX AS A FIRST STEP IN WATER DECOMPOSITION

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The lowest energy excited state for Ru(II) polypyridyl complexes is a metal-to-ligand charge transfer (MLCT) state where photoexcitation promotes an electron from a metal *d*-orbital to a π^* -orbital on the most electronegative ligand. In the excited state, this ligand is effectively reduced and therefore its proton affinity should be enhanced. We would like to use this more basic, photoreduced ligand to assist deprotonation of a metal bound water molecule and thus hopefully promote effective photooxidation of the system. In designing ligands to meet these criteria we have initially selected the 2,2'-bi-[1,8]-naphthyridine (binap) system which is a much better electron acceptor than 2,2'-bipyridine and also contains an uncomplexed, appropriately situated basic site.

A series of 3,3'-bridged binaps was synthesized by the Friedlander condensation of 2-aminonicotinaldehyde with cyclic 1,2-diketones. Complexation these binaps with [Ru(tpy)Cl₃] (tpy = 2,2':6',2''-terpyridine) followed by hydrolysis leads to the aqua-complexes **1** which have been thoroughly characterized by NMR, IR, electronic spectroscopy, and single crystal X-ray diffraction. Using analogous Friedländer methodology, the [1,8]naphthyridine moiety can also be incorporated into the terpyridine component leading to complexes such as **2**. Neither **1** nor **2** exhibits the photobleaching that would be expected to accompany oxidation to a Ru(III) species.



More careful consideration of the valence bond structure of the proton transferred species which would be required for photooxidation led us to consider systems in which the basic site would be one bond further removed from the coordination site. To this end we prepared 2,9-di-(2'-pyridyl)-1,10-phenanthroline by the Stille coupling of 2,9-dichloro-1,10-phenanthroline and 2-tri-*n*-butylstannyl pyridine. We expected that this ligand would lead to tridentate coordination with Ru(II), allowing for the introduction of water in the equatorial plane as in complex **2**. Instead the unusual tetradentate complex **3** was obtained. The properties of complexes **2** and **3** are sensitive to the nature of the 4-

pyridyl substituent X (Figure 1) and, surprisingly, **3** does exhibit photobleaching which may be inhibited by the addition of ascorbic acid or 2-propanol.

An additional refinement in ligand structure was made by the synthesis of 3,3'-dimethylene-2,2'-bi[1,10]phenanthroline which does bind Ru(II) in a tridentate fashion, leading to the proposed formation of complex **4**.

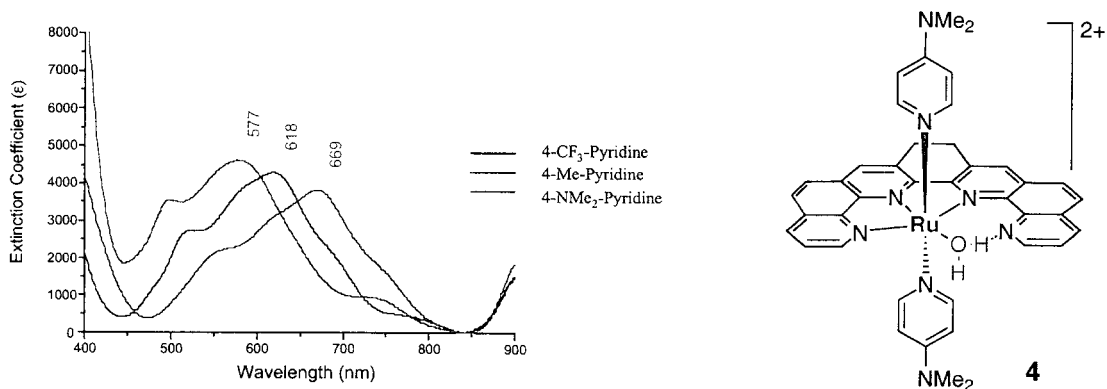


Figure 1. Electronic absorption spectra of complexes **2**

Future studies will more carefully investigate the properties of complexes such as **2 - 4** particularly with regard to the potential photooxidation of a metal-aqua to a metal-oxo. We have also begun to design and prepare bridging ligands to orient two M=O moieties in proximity to one another so that pathways to the formation of a M-O-O-M species can be explored.

DOE Supported Publications 2003-2004

"The Preparation and Study of Di-(2-quinolyl)- and Di(2-[1,8]naphthyridyl) Derivatives of Pyrimidine and Pyrazine as Bridging Ligands for Ru(II)," Darren Brown, Seema Muranjan, and Randolph P. Thummel, *Eur. J. Inorg. Chem.* **2003**, 3547-3553.

"Ru(II) Complexes of Di-[1,10]-phenanthrolyl Diazines," Darren Brown, Ruifa Zong and Randolph P. Thummel, *Eur. J. Inorg. Chem.* (in press).

"Enhanced Luminescence in a Pt(II) Complex Involving a Six-Membered Chelate Ring," Yi-Zhen Hu, Michael H. Wilson, Ruifa Zong, Celine Bonnefous, David R. McMillin, and Randolph P. Thummel, *Inorg. Chem.* (submitted for publication).

"The Design and Study of Bi[1,8]-naphthyridine Ligands as Potential Photooxidation Mediators in Ru(II) Polypyridyl Aqua Complexes," Ruifa Zong, Frederic Naud, Carrie Segal, John Burke, Feiyue Wu, and Randolph Thummel, *Inorg. Chem.* (submitted for publication).

"2,9-Di-(2'-pyridyl)-1,10-phenanthroline: a Tetradentate Ligand for Ru(II)," Ruifa Zong and Randolph P. Thummel (in preparation).

PHOTOINDUCED CHEMICAL REACTIONS OF METAL COMPLEXES: M-M BOND FORMATION/CREAVAGE AND SMALL MOLECULE ACTIVATION

Etsuko Fujita

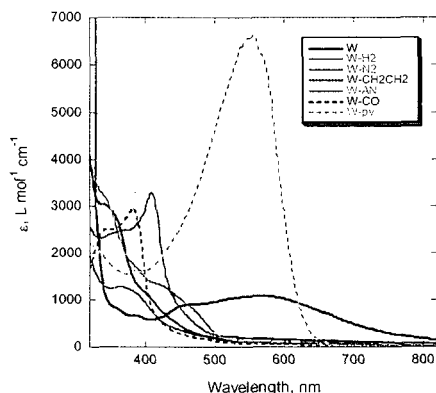
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Our work addresses the factors controlling the rates bond formation between photoproducted metal-based intermediates (such as reduced/oxidized catalysts with a vacant coordination site) and small molecules in the early stages of photoconversion processes. Photogeneration of H₂ and the photoreduction of CO₂ have been our major focus in recent years. We are broadening our studies to include the photochemical activation of small molecules such as H₂, CH₂CH₂, CH₄, CO, and N₂ because of their relevance to our future energy needs, energy conservation, and environmental concerns.

Why is Re-Re Bond Formation/Cleavage in [Re(bpy)(CO)₃]₂ Different from that in [Re(CO)₅]₂? The Re(dmb)(CO)₃S (dmb = 4,4'-dimethyl-2,2'-bipyridine and S = solvent) radical reacts with CO₂ to form a dinuclear species with a bridged CO₂ molecule, (CO)₃(dmb)Re-CO(O)-Re(dmb)(CO)₃, as an intermediate in the CO₂ reduction system. When CO₂ is not present, Re(dmb)(CO)₃(THF) and Re(bpy)(CO)₃(THF) (bpy = 2,2'-bipyridine) dimerize with rate constants $k_d = 20 \pm 3$ and $11 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$, respectively, in THF. The dimerization processes are strikingly slow compared to those of typical metal radicals including Re(CO)₅ ($k_d = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). In order to understand such slow reactions, we have performed B3LYP hybrid DFT and fully *ab initio* RHF/MP2 calculations on several conformations of [Re(bpy)(CO)₃]₂ (*cis*, *trans*, skewed *cis*, skewed *trans*), [Re(CO)₅]₂ (staggered) and on their constituent monomer radicals and anions. The experimental infrared spectrum and photochemical properties of the [Re(CO)₃(bpy)]₂ dimer are best described by the calculated properties of the skewed *cis* conformer in which the first antibonding Re-Re unoccupied orbital is LUMO+29. The Re(bpy)(CO)₃(THF) ligand radical, an 18-electron species, is more stable than Re(bpy[•])(CO)₃ or Re[•](bpy)(CO)₃, suggesting that the extremely slow dimerization rate may arise from the solvent blocking the binding site (*i.e.*, the equilibrium concentration of five-coordinate monomer is very small). Our experiments suggest that the dimerization process proceeds *via* a pre-equilibrium with the Re centered radical with an equilibrium constant of 10⁻⁵ - 10⁻⁴ favoring the ligand-centered radical. Theoretical and experimental results clearly indicate that the reactivity of metal complexes depends on the electron population on the metal. (with J. T. Muckerman)

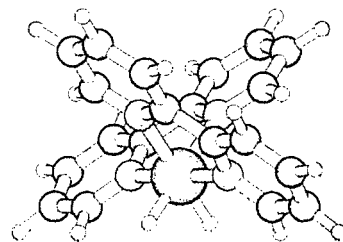
Characterization of Transient Species and Products in Photochemical Reactions of Re(dmb)(CO)₃Et with and without CO₂. Transient FTIR spectra of *fac*-Re(dmb)(CO)₃(Et) (Et = C₂H₅⁻) after laser excitation (355 nm) were investigated in THF under Ar and CO₂ atmospheres. The CO stretching bands of Re(dmb[•])(CO)₃(THF) grow (2008 and 1897 cm⁻¹) and those of Re(dmb)(CO)₃(Et) bleach (1987 and 1875 cm⁻¹) at times < 1 μsec, consistent with clean cleavage of the Re-Et bond. Under a CO₂ atmosphere the long-lived radical (τ > 100 μs) converts slowly to the formate complex, Re(dmb)(CO)₃(OC(O)H) (2020, 1916, 1873, and 1630 cm⁻¹). When the solvent is slightly wet, the bicarbonato complex, Re(dmb)(CO)₃(OC(O)OH), is also observed after photolysis under CO₂. Under Ar, [Re(dmb)(CO)₃]₂ and Re(dmb)(CO)₃H were observed. (with K. Shinozaki and B. S. Brunshwig)

Thermodynamics, Kinetics and Isotope Effects on M-L Bond Formation/Cleavage ($L = H_2, D_2, CH_2CH_2, CO, N_2, etc$) Studied by Photochemical Methods. Bond formation between a transition-metal complex and a substrate is an important step in many catalytic reactions. In order to clarify the nature of the interaction of $H_2, H^+, CH_2CH_2, CO, N_2$ and other small

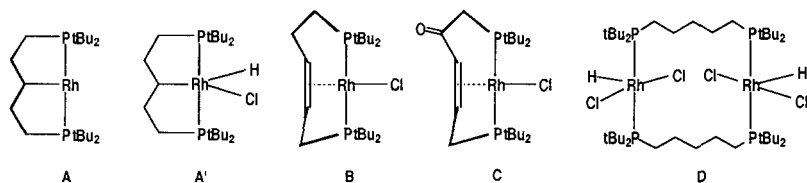


molecules with low-valent metal centers, we investigated the thermodynamics, kinetics and isotope effects as a function of temperature and pressure. When a toluene solution containing $W(CO)_3(PCy_3)_2L$ ($Cy = \text{cyclohexyl}$), $L = H_2, D_2, CH_2CH_2, N_2,$ or CH_3CN and a known amount of L was irradiated with a 355 nm laser pulse, $W-L$ bond dissociation took place to form $W(CO)_3(PCy_3)_2$. Subsequently clean regeneration of $W(CO)_3(PCy_3)_2L$ was observed for the first time. The rate constants of $W-L$ bond formation are $1.8 \times 10^6, 1.5 \times 10^6, 3.3 \times 10^4, 2.7 \times 10^5,$ and $3.6 \times 10^6 M^{-1} s^{-1}$ for $W-H_2, W-D_2, W-CH_2CH_2, W-N_2,$ and $W-CH_3CN$, respectively. The binding equilibrium constants ($K_L = k_f/k_r$) are 1900, 2200, 58, 2700, and $>7000 M^{-1}$ for $W-H_2, W-D_2, W-CH_2CH_2, W-N_2,$ and $W-CH_3CN$, respectively. The small activation volumes ($-3, -7, -3,$ and $3 mL^3 mol^{-1}$ for $W-H_2, W-CH_2CH_2, W-N_2,$ and $W-CH_3CN$, respectively) for ligand substitution reactions suggest that $W-L$ bond reformation involves the replacement of an agostic $W---H-C$ interaction of the cyclohexyl group of the PCy_3 ligand. We are extending this study with use of transient step-scan FTIR. (with R. van Eldik and D. Grills)

Experimental and Theoretical Studies on the Thermodynamics and Kinetics of H_2 and D_2 Binding to $Rh(bpy)_2^+$. Since $Rh(bpy)_2^+$ and $Rh(H)_2(bpy)_2^+$ are in equilibrium, the system is ideal to determine both the activation and equilibrium parameters experimentally. B3LYP hybrid DFT and fully *ab initio* RHF/MP2 calculations including solvent effects on $Rh(bpy)_2^+$ and $Rh(H)_2(bpy)_2^+$ were carried out to compare the experimental data and to gain more detailed insight into the transition state. (with N. Sutin, C. Creutz, B. S. Brunschwig, J. Muckerman, and R. van Eldik)



CO_2, H_2, H^+ , and N_2 Activation by Rhodium Complexes with *T-shaped* Ligands. The two-electron-reduced species **A** of the rhodium(III) complex **A'** ($R = t\text{-Bu}$) is known to react with L ($L = CO_2, H_2, H^+, CH_2CH_2,$ and $N_2,$ etc) to form $Rh-L$. While we were preparing the complex **A'**, we isolated three new complexes (**B**, **C**, and **D**) and their crystal structures were determined. We have begun to study the kinetics and thermodynamics of



$Rh-L$ bond formation with **A**, mechanisms of the subsequent chemical conversion processes, and reactivity of the further reduced $Rh(0)$ complexes using transient UV-vis, FTIR, LEAF, and stopped-flow techniques. (with Y. Hayashi and D. Szalda)

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7. Synthesis, Structure and Reactivity of a Hydroxymethyl-Cobalt Complex in Water: Mechanisms for Formaldehyde and H₂ Formation", C. Creutz, M. H. Chou, E. Fujita, and D. J. Szalda, *Coord. Chem. Rev.*, submitted.
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BIMETALLIC REDOX SITES FOR PHOTOCHEMICAL CO₂ SPLITTING IN MESOPOROUS SILICATES

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The main goal of our work is to utilize transition metal molecular sieves for the synthesis of fuels and chemicals from abundant resources like CO₂ and H₂O under visible light. Our effort in the past 2 years has focused on the preparation and spectroscopic characterization of mesoporous silicates featuring bimetallic redox sites that afford visible light activation of CO₂-reducing centers by metal-to-metal charge-transfer (MMCT) excitation. FT-IR and mass spectrometric studies are conducted for exploring MMCT-induced CO₂ activation. In parallel work, we have elucidated the single UV photon-induced reaction of CO₂ with H₂O in a Ti framework substituted silicate sieve. Time-resolved step-scan FT-IR studies are pursued to elucidate the behavior of small transient radical intermediates in these nanoporous solids.

Photoactivation of Ti Centers in Mesoporous Silicates by MMCT Excitation: Ligand-to-metal charge-transfer excitation of isolated framework Ti centers of silicate molecular sieves is known to initiate reduction of CO₂ by H₂O under UV radiation. In order to accomplish the photosynthetic transformation by visible light, we are exploring the possibility of engaging a second metal center as electron donor, linked to the Ti by an oxo bridge. The great flexibility in the selection of metal and oxidation state offered by this approach opens up access to solar light-absorbing chromophores with a wide range of redox properties. We have developed methods for the assembly of covalently anchored, all-inorganic oxo-bridged (MMCT) systems on mesoporous silicate surfaces, with each metal in a pre-selected oxidation state. Assembly of Ti-O-Cu(I) and Ti-O-Sn(II) groups was accomplished by using precursor complexes with highly labile CH₃CN ligands that were readily replaced by anchored TiOH and surface SiOH groups upon exposure to the silicate sieve. The Ti(IV)/Cu(I) → Ti(III)/Cu(II) MMCT absorption is manifested by deep-yellow coloration of the material, with an absorption tail extending from the UV to 600 nm. The assignment to an MMCT transition was confirmed by the observed decrease of the absorption under growth of the Cu(II)(d-d) band at 800 nm upon exposure of the TiCu(I)-MCM-41 material to an O₂ atmosphere. Direct proof for an oxo bridge between Ti and Cu, and of covalent anchoring of the inorganic moiety on the silica surface was obtained by FT-IR spectroscopy. The Cu(I)-O-Si and Cu(I)-O-Ti linkages give rise to bands at 930 and 640 cm⁻¹ (Si-O and Cu(I)-O stretch, respectively). Upon oxidation of the Cu by exposure to an O₂ atmosphere, the latter decreases and is replaced by a Cu(II)-O mode. The Cu-O bond modes allow monitoring of the oxidation state and structural integrity of the anchored unit.

Using a similar approach, we have assembled Ti-O-Sn(II) moieties on the pore surface. An optical absorption in the 300–500 nm region is attributed to the

Ti(IV)/Sn(II) \rightarrow Ti(III)/Sn(III) MMCT chromophore. A Ti-O-Sn(II) bridge is manifested by an infrared band at 610 cm^{-1} . Shift of the vibrational frequency and decrease of the optical absorption upon oxidation of Sn(II) to Sn(IV) confirmed the assignment of the MMCT group. This was further corroborated by the detection of Ti(III) by EPR spectroscopy when irradiating TiSn(II)-MCM-41 at cryogenic temperature. We conclude that excitation of the Ti-O-Sn(II) site leads to activation of Ti under visible light.

Photochemical Splitting of CO₂ by MMCT Excitation in ZrCu(I) Silicate Sieve:

Using the method developed for the synthesis of Ti-O-Cu(I) redox sites, we have prepared the corresponding Zr-O-Cu(I) moieties on the MCM-41 pore surface exhibiting a Zr(IV)-O-Cu(I) \rightarrow Zr(III)-O-Cu(II) MMCT absorption extending into the visible region. Irradiation of the chromophore of ZrCu(I)-MCM-41 loaded with 1 atm of $^{13}\text{CO}_2$ gas at RT resulted in growth of ^{13}CO (2100 cm^{-1}) and H_2O (1600 cm^{-1}). When using C^{18}O_2 , the products were C^{18}O and H_2^{18}O indicating that oxygen of carbon dioxide ends up in a water molecule. This indicates splitting of CO_2 upon MMCT excitation, resulting in the formation of CO molecules adsorbed at Cu(I) sites in the pore system, and transient surface OH radicals that are reduced by Cu(I) to H_2O . Analogous experiments with TiCu(I)-MCM-41 gave 10 times lower yields, consistent with the lower reducing power of transient Ti(III) compared to Zr(III). This is to our knowledge the first observation of CO_2 reduction by a binuclear MMCT moiety in a solid oxide material.

Photochemical Splitting of CO₂ by H₂O in TiMCM-41 Sieve: In an attempt to determine the single photon reaction steps of CO_2 activation at framework Ti centers when using water as electron donor, we have monitored the photochemistry of $\text{CO}_2 + \text{H}_2\text{O}$ gas mixtures (and isotopic modifications) loaded into TiMCM-41 sieve. Irradiation of a pressed wafer of the sieve loaded with 12 Torr D_2O and 1 atm of $^{13}\text{CO}_2$ gas with 266 nm light resulted in evolution of CO gas. The growth was proportional to the water concentration, confirming that water acts as stoichiometric electron source. Mass spectrometric monitoring of the gas phase of the miniature IR cell following photolysis showed build-up of O_2 . A laser power study revealed a linear dependence of the CO absorbance growth. We conclude that LMCT excitation of the framework TiO site results in the conversion of CO_2 and H_2O to CO and O_2 by a single photon. The proposed mechanism is splitting of CO_2 to CO and surface OH radical. The radicals combine or dismutate by reaction with other surface OH radicals produced by H_2O oxidation and CO_2 splitting to form H_2O_2 , or O_2 and H_2O . An important implication of the mechanism is that photoreduction of CO_2 by H_2O leads exclusively to the formation of oxidizing radicals (surface OH radicals), not a mixture of reducing and oxidizing intermediates. This is the first insight into primary redox steps of CO_2 photoactivation by H_2O at the gas-inorganic solid interface. Insights gained by the results are guiding us in the design of nanoporous MMCT materials for conducting the reaction at visible photon energies.

Future work will focus on the exploration of an MMCT-based Z-scheme that combines CO_2 splitting with H_2O oxidation at bimetallic redox sites by visible light.

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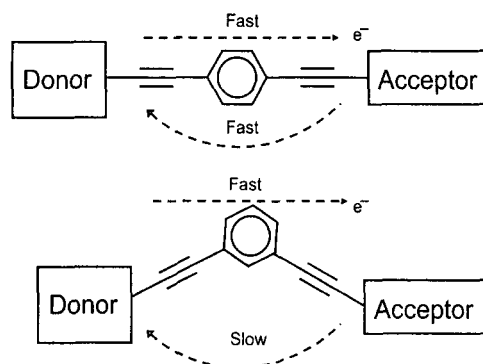
Posters

RAPID CHARGE SEPARATION AND SUPPRESSION OF CHARGE RECOMBINATION IN DONOR-BRIDGE-ACCEPTOR COMPLEXES BY CONTROLLING THE STRUCTURE OF THE PHENYLACETYLENE BRIDGE

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Our earlier work, both theoretical and experimental, on phenylacetylene dendrimers demonstrated how the through-bond coupling depends sensitively on the electronic state and nuclear configuration of the molecule. In particular, although meta-substitution appears to prevent electronic communication between substituents in the ground state, in the excited state this coupling can increase by an order of magnitude. The origin of this switching-on of the electronic coupling lies in the subtle changes in bond-order that occur in the relaxed excited state geometry. Besides allowing us to understand the fundamental photophysics of the meta-branched phenylacetylene dendrimers, this variable meta-coupling may have practical implications for the design of photochemical charge separation supermolecules. For example, one can envision the scenario outlined in the figure, where both the meta- and para-conjugated chains act as molecular wires in their excited states, but after charge separation the meta-conjugated chain acts as an insulator in its ground state, while the para-conjugated chain still retains its high conductivity. By designing the structure and bonding of the bridge, we may be able to create one-way, meta-conjugated wires which enhance charge separation and suppress charge recombination.



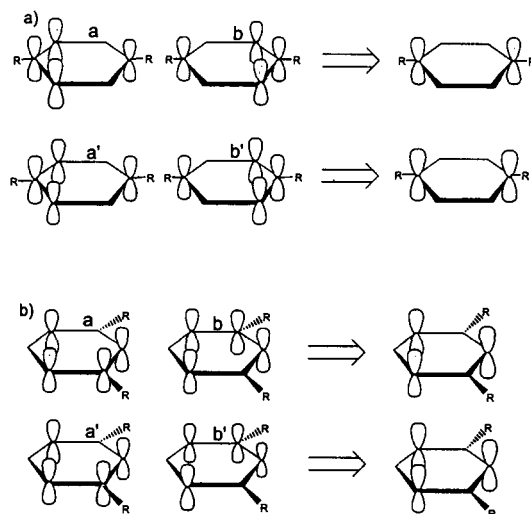
In order to test this idea, we have synthesized donor-bridge-acceptor compounds where the bridge is a phenylacetylene chain of varying length and connectivity. We report on time-resolved absorption and emission experiments designed to measure both the charge separation and recombination rates. Preliminary experiments on the simplest molecules in this series suggest that our hypothesis is correct: charge separation occurs within 200 fs after photoexcitation in all compounds, showing that meta linkages do not prevent efficient excited state charge transfer. However, the rate of charge recombination to the neutral ground state is at least a factor of 10 slower in the meta-bridged compounds. These results suggest that it should be possible to build asymmetric charge separation molecules by designing a bridge which has different electronic properties in its ground and excited states.

Other aspects of our work, including theoretical modeling of energy transfer in molecular networks and the development of a new femtosecond three-pulse pump-dump-probe experiment to probe anomalous (time-varying) energy and rotational diffusion, will also be presented.

ENERGY TRANSFER IN PHEYLACETYLENE DENDRIMERS – THE EFFECT OF META-SUBSTITUION AND NEW METHODS FOR SIMULATION OF EXCITATION ENERGY TRANSFER IN LARGE MOLECULES

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Dendrimeric structures based on phenylacetylene units arranged in a self-similar Cayley-tree geometry have been considered as promising candidates for artificial light-harvesting molecules. These dendrimers are unusual in that the monomer units are not separated by sp^3 hybridized centers, but instead the entire structure is at least formally conjugated. However, this conjugation goes through meta-substitution of the phenyl units. Based on the observed absorption spectra, this meta-substitution has been thought to lead to effectively decoupled monomer units, i.e. these molecules have been considered to be in the weak-coupling regime. We have carried out spectroscopic experiments on well-characterized dendrimeric units which show that while the absorption spectra indeed support the weak-coupling description, the emission spectra are more consistent with a strong-coupling description.¹ Theoretical studies using multireference electronic structure methods and including dynamical electron correlation effects agree with our experimental findings and furthermore provide a detailed explanation of the phenomenon.² In particular, we decompose the electronic coupling to show that these molecules appear weakly coupled in absorption because of a cancellation of terms which is very sensitive to molecular geometry. Excited state relaxation unmasks the strongly coupled nature of the excited states in these molecules. This can be viewed as a “through-bond” type of coupling, where the meta-substitution pattern leads to *enhanced* conjugation in the excited state. We show that this can be understood in both meta- and para-substituted cases with simple cartoon diagrams of the relevant transition densities, as demonstrated in the figure.



Direct simulation of ultrafast energy transfer in these molecules requires new approaches for generating the required potential energy surfaces and their couplings. We have developed a semiempirical multireference configuration interaction approach, and investigated the feasibility of optimizing parameters in this model to reproduce *ab initio* results for benzene.³ We show that parameterization using very limited *ab initio* information can lead to ground and excited state potential energy surfaces which are globally valid. We investigate the feasibility of a “divide-and-conquer” approach, optimizing parameters for subunits and then combining them to obtain an improved description of a molecule.⁴

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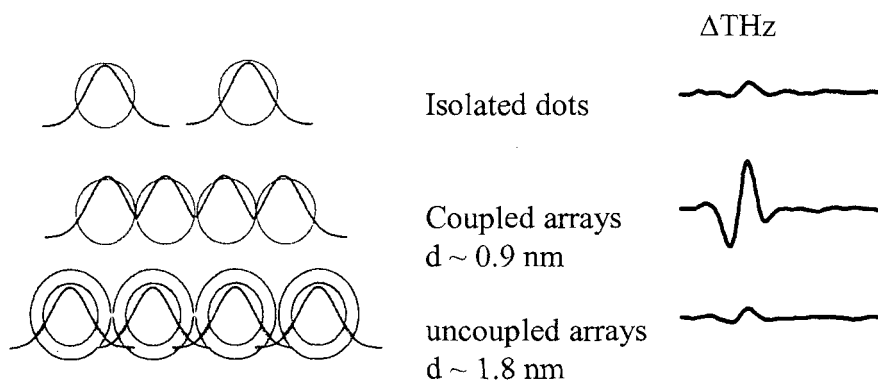
TIME-RESOLVED TERAHERTZ PHOTOCONDUCTIVITY

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Terahertz time-domain spectroscopy (THz-TDS) is a relatively new spectroscopic tool used to investigate electro-optic and photoconversion materials. Its salient features include the ability to measure the frequency-dependent complex conductivity, $\tilde{\sigma}(\omega)$, in a non-contact fashion. Characterization in the THz frequency regime is critical to elucidate the microscopic details of charge-transport since typical carrier scattering rates in semiconductors are in excess of 0.1 ps^{-1} . In contrast to dc conductivity measurements THz spectroscopy measures transport phenomena on a localized length scale given by $L = \sqrt{D/\omega}$, where D is the electron (hole) diffusion length. Thus, THz spectroscopy is ideally suited to study transport phenomena in materials whose charge carriers are localized, for example, nanostructured and organic semiconducting materials. Additionally, the inherent pulsed nature of THz-TDS enables optical pump – THz probe experiments. The resulting spectrometer is the only technique capable of characterizing the photoinduced carrier transport with sub-ps to nanosecond temporal resolution. Such a spectrometer has recently been constructed at NREL.

Recent TRTP measurements show unambiguously the onset of photoconductivity in InP nanoparticle arrays as the interdot coupling is tuned. Further examples of photoconductivity in PbSe arrays will be presented. Photoconductivity in dye-sensitized TiO_2 , GaAs, colloidal CdSe nanoparticles, and arrays of InP quantum dots (conducted at Yale University) will be shown as examples of time-resolved THz spectroscopy.



CHARGE SEPARATION DISTANCE FOR FLEXIBLE DONOR-BRIDGE-ACCEPTOR SYSTEMS AFTER ELECTRON TRANSFER QUENCHING

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The initial charge separation distance after electron transfer quenching of excited electron acceptor (or donor) molecules by electron donors (or acceptors) and its evolution during the recombination process are critical to understanding the mechanism of the decays of photoinduced geminate ion pairs and free ion formation. In our recent work,^{1,2} we have shown that there exists a significant barrier between two kinetically distinguishable radical ion pairs (*i.e.* contact ion pairs and solvent-separated ion pairs). This offers us an opportunity to use transient photocurrent techniques that we developed to probe the charge separation distance of flexible donor-bridge-acceptor systems after photoinduced intramolecular electron transfer. Figure 1 demonstrates the “dipole signal” of D-(CH₂)₄-A (DBA4), where D and A are 4-N,N-dimethylaniline and 9-anthroyl, in a weakly polar solvent, 1,4-dioxane and a moderately polar solvent, 1,2-dichloroethane with 800 V applied after absorption of 10 μJ at 355 nm. We find the dipole moments increase strongly with solvent polarity. Analysis of dipole signals in these and other solvents indicates that the average charge separation distances for DBA4 in toluene, 1,4-dioxane, ethyl acetate, THF, dichloromethane, 1,2-dichloroethane, 2-methylpentanone-3,3-pentanone and benzonitrile are 1.9, 2.2, 3.6, 3.9, 4.0, 4.8, 4.2 and 5.5 Å, respectively. These results prove that electron transfer quenching indeed can happen at large separations in polar solvents. They also reveal that there is a barrier for ion pairs formed at large separations hindering collapse to a contact separation of around 3.5 Å.

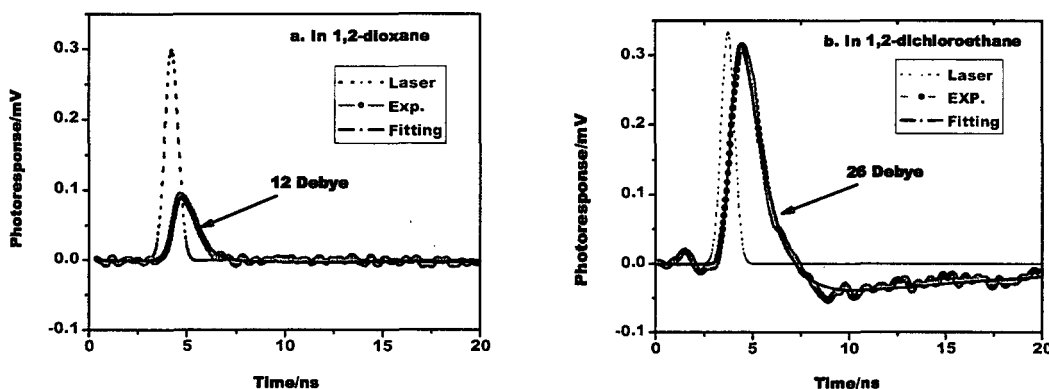


Figure 1. Photoreponses of DBA4 in 1,4-dioxane and in 1,2-dichloroethane after absorption of 10 μJ at 355nm with 800 V applied. 50 Ω scope input.

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CONSTRUCTION AND CHARACTERIZATION OF GENETICALLY MODIFIED SYNECHOCYSTIS PCC 6803 PHOTOSYSTEM II CORE COMPLEXES CONTAINING CAROTENOIDS WITH FEWER CONJUGATED π -BONDS THAN β -CAROTENE

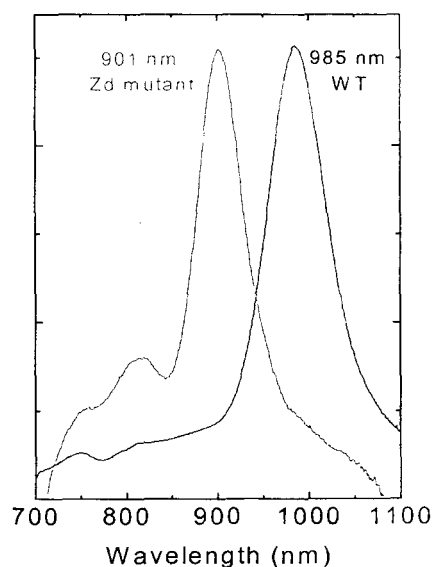
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Photosystem II (PS II) is a membrane-bound protein complex that is responsible for catalyzing the oxidation of H₂O to O₂ in oxygenic photosynthesis. If the primary electron-transfer reactions responsible for this reaction are blocked, then alternate electron-transfer reactions occur resulting in the oxidation of cytochrome b-559, β -carotene and/or chlorophyll (chl). It has been postulated that β -carotene enables these long-distance electron-transfer reactions from the periphery to the center of PS II by acting as a molecular wire. We manipulated the carotenoid biosynthetic pathway of *Synechocystis* PCC 6803 to produce carotenoids with fewer π -conjugated bonds by replacing the ζ -carotene desaturase (Zd) gene with the phytoene desaturase (Pd) gene of *Rhodobacter capsulatus*. This strain successfully assembles PS II and HPLC pigment analysis revealed that the PS II core complex of this strain contains the same number of chlorophylls and carotenoids as the wild type. However, instead of β -carotene (11 double bonds), it contains β -zeacarotene (9 double bonds) as the major carotenoid. Near-infrared optical spectroscopy of the modified reaction centers indicates β -zeacarotene and chl molecules are photooxidized at low temperature. The carotenoid radical cation absorption peak is at 901 nm, an 84 nm blue shift relative to the β -carotene radical cation peak, which correlates to a decrease in π -bond conjugation by two bonds. β -zeacarotene has a higher reduction potential than β -carotene and this results in the formation of more chlorophyll radical cations relative to carotenoid radical cations in the modified PS II reaction centers. PS II reaction centers containing modified carotenoids reveal new insights into the secondary electron transfer pathways and provide a new system for systematic studies of electron- vs. energy-transfer properties of carotenoids with varied extents of π -conjugation.



SURFACE OXIDATION AND EXCITED STATE DYNAMICS IN SEMICONDUCTOR SINGLE WALL CARBON NANOTUBES

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Single walled carbon nanotubes (SWNTs) are one-dimensional aromatic structures with remarkable electronic properties which are qualitatively predicted by simple Huckel theory. The one-dimensional density of electronic states (DOS) of SWNTs is characterized by sharp van Hove singularities; the resulting π - π^* optical transitions between filled and empty singularities are strongly allowed. When isolated from metallic tubes, semiconducting nanotubes exhibit band gap photoluminescence in the near-IR. Our samples consist of isolated SWNTs in micellar suspension.

Using optical Kerr gating, we measured the SWNT fluorescence lifetime to be ~ 10 psec. This fast relaxation arises from non-radiative trapping processes at defects, the existence of which explains the relatively low observed fluorescence efficiency in isolated SWNTs. From the measured decay rate and a determination of fluorescence quantum efficiency, we deduce a radiative lifetime of 110 ns. When multiple electron-hole pairs are present in a nanotube, the fluorescence lifetime is further shortened by rapid electron-hole pair annihilation. We identify this process as an Auger recombination with an Auger rate of ~ 1 ps⁻¹ for just 2 electron-hole pairs in a SWNT. In the context of applications for SWNTs, these results suggest that high luminescence quantum yields are potentially achievable only by improved synthetic methods that minimize defects; in this ideal case, the luminescence yields will still be limited by Auger processes.

SWNT surface oxidation in air is inferred from many experiments as a source of defects, but the chemical nature of the oxide species is not understood. Structure calculations predict that the ground state $^3\Sigma$ oxygen interacts weakly with SWNTs, but the excited state $^1\Delta$ oxygen is expected to bind to the nanotube sidewalls. We study nanotube oxidation and the associated absorption bleaching and luminescence quenching at low pH. We time-resolve oxygen desorption and find first order kinetics with an estimated activation energy of about 1.2 eV. Controlled re-oxidation using 1,4-naphthalene-1,4-endoperoxide as a $^1\Delta$ oxygen source at micromolar concentration shows that only a few (<10) surface oxides per 400 nm long carbon nanotube quench the luminescence. Electronic structure calculations suggest that the surface oxide made by $^1\Delta$ attack is a 1,4-endoperoxide oriented along the SWNT axis. In contrast with the luminescence quenching, we theoretically estimate that roughly 250 holes per 400 nm tube are necessary to bleach the corresponding band gap transition in absorption. The picture that emerges is that a SWNT one-photon excited state is indeed remarkably sensitive to the entire length of the emitting SWNT.

BUILDING BLOCKS AND BRIDGES FOR CHARGE SEPARATION: QUANTUM CHEMICAL CHARACTERIZATION

Ian Carmichael

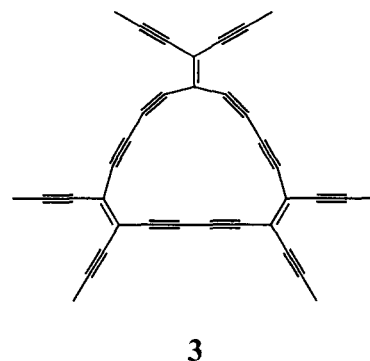
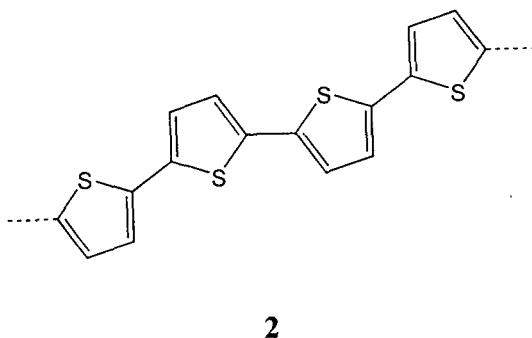
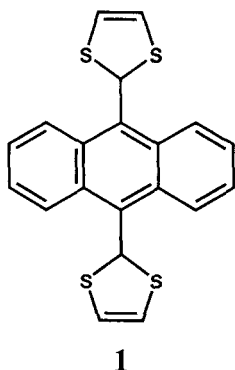
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Quantum-chemical calculations are conducted that are designed to provide a molecular-level understanding of key components in charge separation reactions within supramolecular assemblies and to elucidate their interactions in the resulting chemistry. Both *ab initio* molecular orbital (LCAO) and Density Functional Theory (DFT) approaches are employed.

Donor and acceptor structures are accurately evaluated and the forces that govern the intramolecular structural relaxations accompanying the redox process are determined. Computational techniques are devised and assembled to give a reliable description of key fingerprint properties for the resulting oxidized and reduced transients. Characteristic energy level structures in various unsaturated bridges are predicted and the influence of substituents, added to ensure solubility, is probed. The possible involvement of redox chemistry within the bridge is addressed from theory.

Donors investigated include extended tetrathiafulvalenes (**1**), (*sub*)phthalocyanines, and metalloporphyrins, while the acceptors are mainly carbon-core species, such as functionalized Fullerenes and (*pseudo*)annulenes (**3**). These species are typically too large to allow the convenient application of the more accurate LCAO-based techniques. While such calculations are, when coupled with access to suitable computational platforms, within the scope of DFT methods, a number of deficiencies in popular functionals act to reduce expectations of accuracy. Care must first be taken to evaluate functional performance for the reliable calculation of a desired property against the results of high-level LCAO-based methods in smaller model systems.

Typical bridges investigated include (*poly*)thiophenes (**2**), phenylenes, vinylenes and combinations thereof. Similar caveats to those outlined above hinder routine calculation of optical, electro-optical, and magneto-optical properties of the bridges, again due to failings in widely available functionals, but progress can once more be made by calibration against results from both high-level *ab initio* methods and accurate experimental data, where available, for component monomers and dimers.



PHOTOEXCITED STATE STRUCTURES OF METAL COMPLEXES AS BUILDING BLOCKS FOR NANOSCALE SUPERMOLECULES PROBED BY PULSED X-RAYS

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Metal complexes have been used as building blocks of nanoscale supermolecules. These metal complexes not only serve as linkers to integrate molecular constituents into nanoscale supermolecules with the bottom-up approach, but also function as light-harvesting chromophores, electron donors/acceptors, as well as conduits for transporting charges. These functions are intimately related to structures of their excited states, the vehicles for converting light energy. We will present our recent work on the determination of two photoexcited metal complex structures using the laser pulse pump, X-ray pulse probe XAFS with 100-ps time resolution. A tungsten complex, $WP_4ClC_{61}H_{53}$, ligated by four phosphorous ligands and containing a triple bond with a carbon atom, is a likely electron donor at its excited state. Within the time resolution provided by synchrotron X-ray pulses, i.e. 30-100 ps, we observed $W\equiv C$ bond elongation due to the metal to ligand charge transfer, reducing the bond order. The excited state structural information is combined with dynamic information from ultrafast optical spectroscopy for the donor, the acceptor, and the donor/acceptor complex formed by the tungsten complex coupled to a zinc tetraphenylporphyrin (ZnTPP). The other excited state structure being investigated is the zinc bis-dipyrrin complex, which has been shown to have a conformationally controlled excited lifetime and luminescent properties. One of the excited state structures of a Zn-complex with a 2-ns lifetime has been determined, which undergoes structural rearrangement after light excitation. The local structural changes determine the branching ratio for this molecule to convert light energy to luminescence and to heat. Such structural information is valuable in rational design of the nanostructured materials with targeted functions.

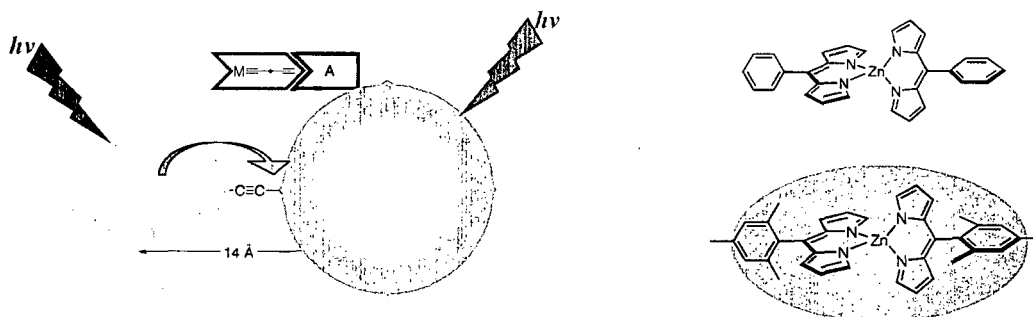


Fig. 1 Examples of energy and electron transfer building blocks whose excited state local structures have been examined by X-ray pulses with 30-100 ps time resolution.

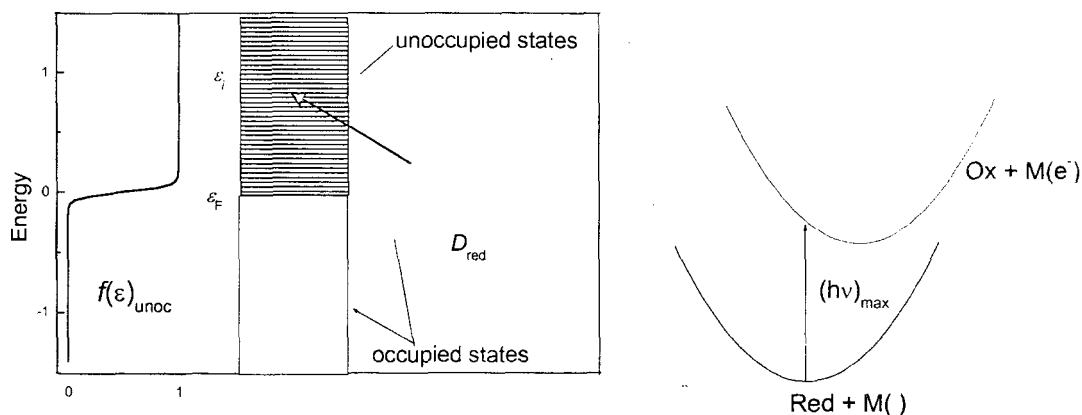
CHARGE TRANSFER ABSORPTION BETWEEN A MOLECULE AND A BULK METAL?

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Charge transfer spectroscopy provides a wealth of information pertinent to molecular interactions and to electron transfer reactions. For metal complexes charge transfer between metal center and ligand provides information on metal-ligand electronic coupling mechanisms, an area that has been most broadly explored for mixed-valence systems for which, following the Hush framework, the band maxima and integrated intensities of binuclear transition-metal complexes, ion pairs and organic redox couples have been compared with activation barriers and rates for thermal electron-transfer reactions. Such a spectroscopic approach would seem to offer a powerful probe of solute or adsorbate-surface interactions at bulk surfaces and for nanoparticle systems where the relative surface areas are very large. Indeed charge transfer from adsorbed ferrocyanide ion to TiO_2 nanoparticles has been reported.

Charge-transfer absorption between solute metal ions and metallic electrodes was predicted by Hush in 1968, although there have been no experimental reports of this phenomenon. Both electron transfer to the metal ("reductant-to-metal charge transfer", RMCT) and from the metal to oxidized solute ("metal-to-oxidant charge transfer", MOCT) processes are predicted. RMCT is illustrated below.



This contribution considers the shapes and intensities expected for such absorption bands in the bulk (bulk metal or very large nanoparticle) limit and how these change in the small metal nanoparticle limit.

TOWARDS PROTEIN - METAL OXIDE HYBRID NANOPARTICLES: TiO₂ IN CONJUNCTION WITH THE AVIDIN-BIOTIN SYSTEM

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Rational design of hybrid biomolecule – nanoscale semiconductor conjugates enables coupling of functionality of biomolecules with the capability of semiconductors for solar energy capture. The particular challenge is to combine the intrinsic functionality of proteins (which are binding, catalytical, optical, mechanical, or switching capabilities) with photoinduced charge separation in semiconductors. Protein-TiO₂ hybrid architectures link initial charge separation in nanoparticles with the charge-transfer induced chemistry that can be exploited in employment and/or alteration of protein functionality. Avidin-biotin complexation was chosen as a model system for host-guest assembly of protein-TiO₂ hybrid architecture because of the high association constant (10^{15} M^{-1}) of noncovalent binding between protein (avidin, ~ 60 kDa) and molecule (biotin). In the construction of TiO₂ nanoparticles functionalized with biotin we used dopamine as a conduit of photogenerated charges. The conjugation was performed by condensation reaction of amino groups on dopamine and N-hydroxy-succinimide on biotin derivative. In the first step the succinimidyl group on the end of the valeric acid chain of biotin is replaced with dopamine through its terminal amino group. In the second step TiO₂ nanoparticles were added into a solution. Dopamine end-labelled biotin binds to the surface of TiO₂ nanoparticles through the bidentate complex of dopamine OH groups with undercoordinated Ti atoms. The formation of hybrid TiO₂/biotin-avidin composites was demonstrated using 4-hydroxy-azobenzene-2-carboxylic acid (HABA) assay for detection of avidin.

The photoinduced charge transfer between TiO₂ nanoparticles and biotin was investigated using low temperature EPR. It was found that photogenerated holes localize on biotin molecules (resulting in formation of sulfur and/or carbon centered radicals) revealing extended charge separation. When avidin binds to the biotin molecule on the surface of nanoparticles, a new radical that is a result of the oxidation of amino acid group(s) of avidin is observed. We have studied the effect of spacer distance between TiO₂ and avidin on overall charge transfer. The extension of the valeric acid side chain in biotin from 13.5 to 22.4 Å results in the decrease in the yield of avidin oxidation. Selective conjugation of biotin to axially anisotropic nano-objects was obtained by linking biotin to corner sites of ~ 400 nm elongated rods. As a consequence, supramolecular architecture, Figure 1 (end-to-end wire, or tripod nanocomposite configuration), was obtained upon addition of avidin. The avidin is capable of binding up to four biotin molecules. The photoexcitation of nanorods results in charge separation from corner sites as identified by EPR spectroscopy. In that respect, corner defects in nanorods behave as corner defects in nanoparticles, and could be exploited in complex electron transport including vectorial transport (end-to-end wire architecture) necessary for creating an efficient photoconversion system.

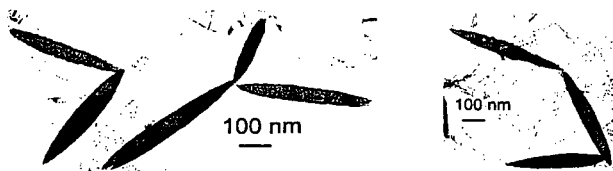


Figure 1. TEM images of organized hybrid TiO₂/biotin-avidin nanorods.

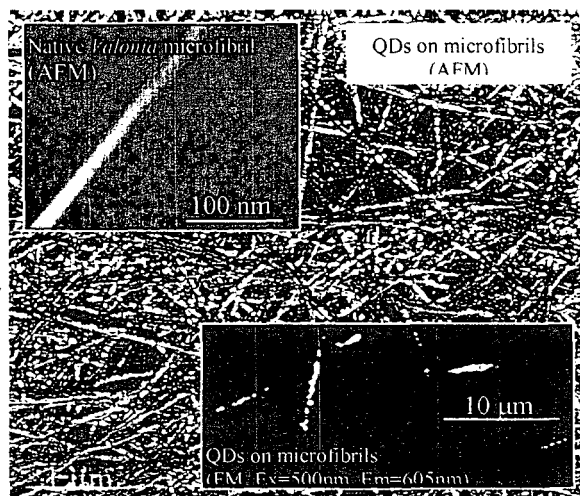
QUANTUM DOTS ARRAYED ON MICROFIBRILS USING PROTEIN SCAFFOLDS

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The precision assembly of quantum dot (QD) arrays is nontrivial and requires considerable control over the random order nature of existing composites based on polymer entrapment or surface adsorption. We have recently reported the assembly of QD-protein arrays using recombinant biomacromolecules scaffolds (Ding et al., NanoLetters, 2003). In this presentation, we describe the novel assembly of QDs using a directed approach that capitalizes on the self-assembling properties of naturally occurring bacterial proteins, known as the cellulosome. Based on x-ray crystallographic data and computer modeling approaches, a series of functional cellulosomal components were selectively cloned, modified with functional peptide tags, expressed from *E. coli*, and purified. These proteins were the cellulose-binding domain (CBD, 17 kDa; 42x26x26 Å), the cohesin domain (19 kDa; 45x25x25 Å), and the dockerin domain (8 kDa; 25x25x35 Å). The dockerin and cohesin protein containing complexes were allowed to self-assemble (the natural function of these domains), and the CBD module assured selective (and directional) binding of the assembly to the surface of the cellulose microfibril. Native cellulose microfibrils (~20 to 40 nm x microns in length) from the *Valonia* algae are utilized as the substrates to mimic the natural organization of cellulosome. The (CdSe)ZnS TOP/TOPO QDs used were modified with two types of capping exchange: Tris titrated QD-MPA and Qdot® Biotin Conjugates (Quantum Dot Corporation, Hayward, CA). The ionic interaction between the 6x-histidine tag(s) from the recombinant protein and the ZnS shell of QDs was assumed for the QD-MPA/protein conjugates, whereas the biotin/avidin interaction was assumed for the system Qdot® Biotin/protein. PL spectroscopy was employed to characterize these QD/protein/microfibril nanostructures and revealed PL properties similar to the original (TOP/TOPO capped QDs in toluene). The patterns of these QD-protein arrays were visualized using fluorescence microscopy (FM), atomic force microscopy (AFM), SEM, and TEM. A high-speed CCD camera was also used to record the “blinking” behavior of these QDs bound to the microfibril. We propose to continue to explore the biochemical and electrooptical properties of the QD/protein/microfibril complexes, working now to reduce the QD separation distance. The role these closely coupled QDs will play in transporting and trapping excitons, as well as dissociating them into charge carriers, will be investigated using time-resolved and steady-state photoluminescence spectroscopy. We also note that thermal carbonization to our new QD decorated cellulose filaments may be expected to create carbon fibers embedded with QDs, resulting in novel QD arrays with more measurable photoelectronic properties.

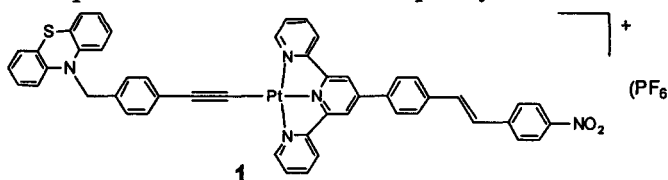


**NEW DYADS AND TRIADS FOR PHOTOINDUCED CHARGE SEPARATION
CONTAINING THE PLATINUM(TERPYRIDYL)(ARYLACETYLIDE)
CHROMOPHORE AND AN UNUSUAL VAPOCHROMIC SYSTEM**

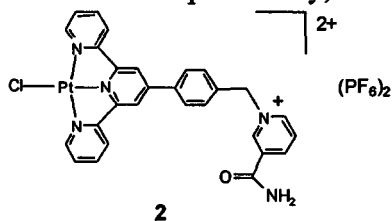
Thaddeus J. Wadas, Soma Chakraborty, Quan-Ming Wang and Richard Eisenberg

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A key step in the conversion of light to stored chemical energy in a molecularly-based system for artificial photosynthesis is photoinduced charge separation. In the present project, efforts have focussed on the synthesis and study of dyads and triads to accomplish this objective. Until recently, the charge transfer chromophore in these systems has been a Pt(diimine) bis(arylacetylide) complex to which the donor is attached via the acetylide ligand and the acceptor is linked to the diimine ligand to facilitate charge separation following excitation to the $^3\text{MLCT}$ state. During the past year, studies have extended to the Pt(terpyridyl) aryacetylide chromophore which is cationic and thus soluble in more polar media. A number of chromophore-acceptor (C-A) and donor-chromophore (D-C) complexes have been prepared and examined with regard to electron transfer quenching and charge separation. Phenothiazines have been employed as the donors in these systems and the acceptors have included pyridinium and nitrophenyl moieties. While the C-A dyads exhibit some chromophore emission indicative of partial quenching, highly efficient quenching is found for the D-C dyads consistent with facile reductive quenching. Several new D-C-A triads such as **1** have also been synthesized. Electrochemical studies show that the donor and acceptor are oxidized and reduced respectively more easily than the chromophore itself. Initial transient absorption studies on **1** reveal the charge separated (CS) state with signals for phenothiazine $^{\bullet+}$ and nitro-phenyl $^{\bullet-}$. The lifetime of the CS state in **1** is 300 ns in DMF/CH₃CN at room temperature with excitation at 405 nm, as compared with a 70 ns lifetime for a related triad having a Pt(diimine)(arylacetylide)₂ chromophore with the same donor and acceptor. The increased lifetime of the CS state in the terpyridyl-containing triad may result from greater donor-acceptor separation, as well as other factors.



In the course of characterizing a nicotinamide-containing C-A dyad, a vapochromic effect was found. Specifically, **2** was found to exhibit a red luminescence that changed rapidly in the presence of MeOH vapors to orange. The effect was completely reversible and found for MeOH, MeCN and pyridine only. The structure of **2** has been determined in both red and orange forms using the *same* crystals. The studies reveal that the crystalline state possesses significant flexibility to allow expansion and contraction of the lattice leading to changes in Pt...Pt distances and Pt...Pt...Pt angles that affect the nature of the HOMO in these systems and consequently the emitting state in this system.

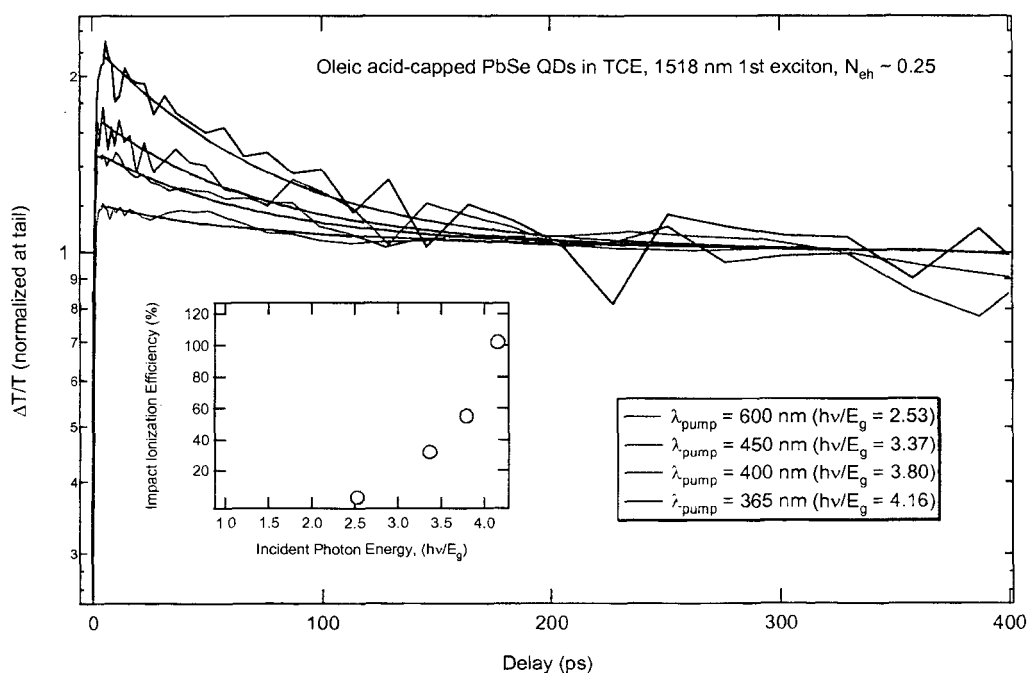


IMPACT IONIZATION IN COLLOIDAL SEMICONDUCTOR QUANTUM DOTS

Randy J. Ellingson, Matt Beard, Pingrong Yu, Suzanne Ferrere, and Arthur J. Nozik
Center for Basic Sciences, National Renewable Energy Laboratory, Golden, Colorado

We demonstrate efficient impact ionization (II) in colloidal semiconductor quantum dots (QDs), a development which represents an important potential route to improved solar energy conversion efficiencies in semiconductor absorbers. Impact ionization, which is the inverse of Auger recombination, is a well-known effect in bulk semiconductors and occurs when hot charge carriers with sufficient kinetic energy scatter a valence band electron to the conduction band to produce an additional electron-hole pair. We discuss results of our transient absorption studies of PbSe and InAs colloidal QDs, and present evidence for II occurring for QDs photoexcited with just one absorbed photon per dot. PbSe QDs show a threshold of approximately three times the first exciton absorption.

To observe II in colloidal QDs, we probe the dynamics of the photoinduced absorption change at the first exciton energy. Photoexciting at a photon energy below the threshold for II and measuring the dependence of the relaxation dynamics as a function of the per-dot excitation level allows determination of the biexciton lifetime (Auger recombination yielding one exciton from two) in the absence of impact ionization. We subsequently probe the dynamics at the first exciton energy, for excitation at one photon per QD, as a function of excitation photon energy. Impact ionization is quantified through analysis of the dynamics determined by Auger recombination, with the same characteristic time constant as found for direct two exciton generation. These experiments confirm a recent report of II in PbSe QDs (R. D. Schaller and V. I. Klimov, Phys. Rev. Lett., in press). We also present results of photocurrent quantum yield studies for InAs QD-sensitized nanocrystalline TiO₂ electrodes. Implications for solar energy conversion are also discussed.



VIBRONIC FEATURES OF THE 77 K NEAR-INFRARED EMISSION SPECTRA OF TRANSITION METAL DONOR-ACCEPTOR COMPLEXES

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We have been using a calibrated InGaAs-array-based emission system for the determination of the long wavelength, charge transfer emission spectra of several series of transition metal donor-acceptor complexes, and to complement studies with SPEX Tau-2 and Fluorolog spectrometers. These studies have been aimed at: (1) the determination of heretofore unknown, long wavelength CT emission spectra of selected complexes (e.g., Xie, *et al.*, *Inorg. Chem.*, **2003**, *42*, 5040); (2) systematically examining the attenuation of reorganizational energies with decreases of the excited state-ground state energy gap; (3) evaluating the contributions of the highest frequency vibrational modes such as the N-H and C-H stretch; and (4), ultimately, characterizing some of the reaction channels that lead to efficient excited state electron-transfer.

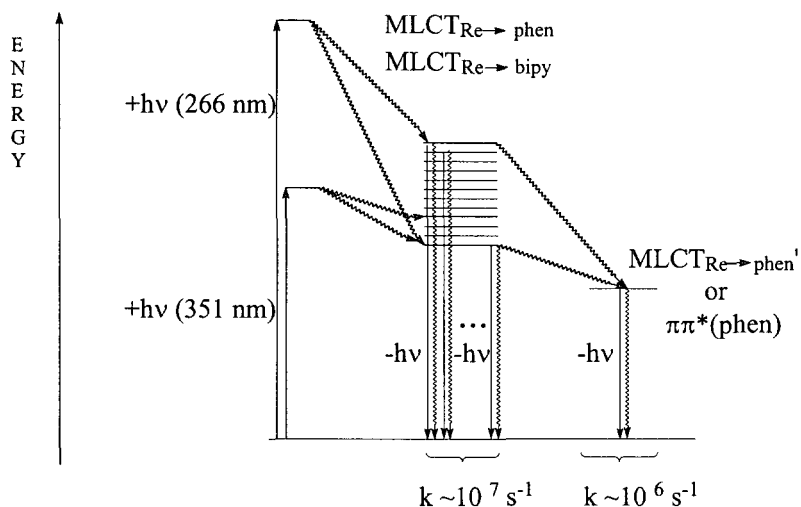
Very recent work has shown that the $[\text{Ru}(\text{NH}_3)_4(\text{dpp})]^{2+}$ and $[\{\text{Ru}(\text{NH}_3)_4\}_2(\text{dpp})]^{4+}$ complexes (dpp = 2,3-bis(2-pyridyl)pyrazine) emit at 971 and 1031 nm, respectively, in DMSO/water at 77 K. It appears that the overall distortion of the dpp ligand is reduced and the distribution of distortion modes is changed by the bridging of two metals in the Ru/dpp MLCT excited state of the dimer relative to the monometallic complex. Some of this difference is a consequence of the greater configurational mixing that results from the smaller excited state-ground state energy gap in the dimer. We have systematically examined this effect of the variations in configurational mixing in some series of am(m)ine-polypyridine complexes of Ru(II). These observations indicate that the reorganizational energies are attenuated very markedly as the energy gap decreases, in reasonable accord with the perturbation theory-based expectations and previous observations (Seneviratne, *et al.*, *Inorg. Chem.*, **2002**, *41*, 1502). Various aspects of our analysis of the vibronic contributions are in good agreement with "emission" spectra constructed from the resonance-Raman vibrational frequencies reported for excitations of $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$ and of $[\text{Ru}(\text{bpy})_3]^{2+}$.

The electron-transfer emission of $[\text{Cr}(\text{Am})_{(6-n)}(\text{CNRu}(\text{NH}_3)_5)_n]^{(3+n)+}$ complexes is very sensitive (in intensities or lifetimes) to am(m)ine perdeuteration and the resulting isotope effects are very large ($k_{\text{NH}}/k_{\text{ND}} \cong 15\text{-}30$; Endicott, *et al.*, *Coord. Chem. Rev.*, **2000**, *208*, 61)). An N-H mediated nuclear tunneling mechanism for excited state back electron-transfer implies an N-H stretching vibronic contribution to the emission. By means of the very careful comparison of the emission spectra of proteo and deutero complexes we have found the corresponding, weak vibronic components (typically at about 1100 nm). The apparent reorganizational energy for the N-H stretch appears to be about 30 wavenumbers and it is reasonably consistent with the tunneling mechanism.

**PHOTOCHEMICAL AND REDOX PROPERTIES OF POLY-(4-VINYLPYRIDINE)₆₀₀
POLYMERS DECORATED WITH MIXED $-\text{Re}^{\text{I}}(\text{CO})_3\text{L}^+$
(L= 1,10-PHENANTHROLINE AND 2,2'-BIPIRIDINE) CHROMOPHORES**

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The photochemical and photophysical properties of polymers containing ~ 200 and ~ 300 mixed groups $-\text{Re}^{\text{I}}(\text{CO})_3\text{L}^+$, L=1,10-phenanthroline and 2,2'-bipyridine, derivatized on poly-(4-vinylpyridine)₆₀₀ were investigated in homogeneous solution. A biphasic decay of the polymers' luminescence is the same observed for the decay of the transient absorption spectrum. The rate constant of the faster phase depends on the monitoring wavelength and has been associated with luminescent MLCT excited states of chromophores in specific environments. The lowest energy $\pi\pi^*$ and/or MLCT of the $-\text{Re}^{\text{I}}(\text{CO})_3(1,10\text{-phenanthroline})^+$ were associated with the slow phase of the luminescence decay, a process with a monitoring wavelength independent rate constant. Emission and excitation spectra are consistent with a conversion of excited $-\text{Re}^{\text{I}}(\text{CO})_3(2,2'\text{-bipyridine})^+$ groups to excited $-\text{Re}^{\text{I}}(\text{CO})_3(1,10\text{-phenanthroline})^+$ groups, scheme. Also the excited state electron transfer reactions with TEA or TEOA and the ground state reduction of the polymers with radiolytically-generated e^-_{solv} or $\cdot\text{CH}_2\text{OH}$ radicals mainly produces $-\text{Re}^{\text{I}}(\text{CO})_3(1,10\text{-phenanthroline})^{\bullet-}$ in spite of the similarity of the couples 1,10-phenanthroline/1,10-phenanthroline $^{\bullet-}$ and 2,2'-bipyridine/2,2'-bipyridine $^{\bullet-}$ reduction potentials, i.e., -1.11V and -1.05V vs NHE. Applications of the polymers decorated with Re(I) and/or macrocyclic complexes in schemes for the reduction of CO_2 to CO and H^+ to H_2 will be shown.



MORPHOLOGICAL AND PHOTOELECTROCHEMICAL CHARACTERIZATION OF CORE-SHELL NANOPARTICLE FILMS FOR DYE-SENSITIZED SOLAR CELLS

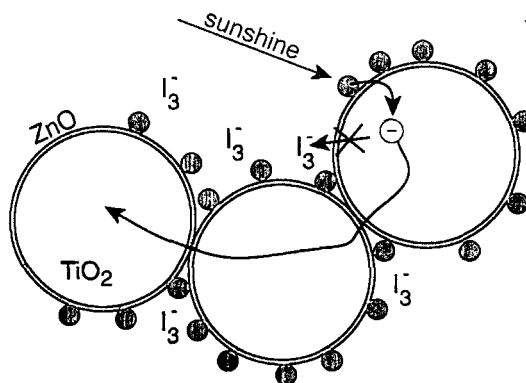
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The morphological properties of core-shell nanoparticle films involving a ZnO-like shell on SnO₂ and TiO₂ cores were characterized by XRD, SEM, X-ray absorption near-edge spectroscopy (XANES), and extended X-ray absorption fine structure spectroscopy (EXAFS). Detailed information was obtained about the uniformity, composition, and crystallinity of the shell surrounding the cores and the effect of shell morphologies on the film morphology, adsorbed dye concentration, light scattering, electron transport, recombination, and overall cell efficiency.



XANES and EXAFS studies reveal thin ZnO-like shells around the nanoparticles at low Zn levels. In the case of SnO₂ cores, ZnO nanocrystals are formed at high Zn/Sn ratios (ca. 0.5). SEM studies show that Zn-modification of SnO₂ nanoparticles changes the film morphology from a compact mesoporous structure to a less dense macroporous structure. In contrast, Zn-modification of TiO₂ nanoparticles is found to have no apparent influence on film morphology. For SnO₂ cores, adding ZnO improves the solar cell efficiency by increasing light scattering and dye uptake and decreasing recombination. In contrast, adding a ZnO shell to the TiO₂ core decreases the cell efficiency, largely owing to a loss of photocurrent resulting from slow electron transport associated with the buildup of the ZnO surface layer.

TRAPPED TRIPLETS STATES IN A CONJUGATED POLYMER

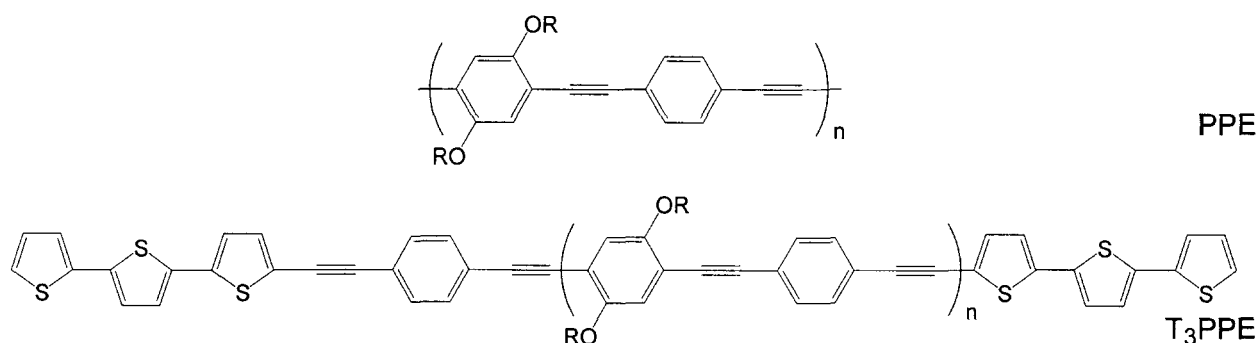
Alison M. Funston,[†] Eric E. Silverman,[‡] John R. Miller[†] and Kirk S. Schanze[‡]

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Long, conjugated molecules may serve as conduits for transport of charge or electronic excitation. Polyphenyleneethynylene (PPE) has been shown to rapidly transport holes to terthiophene (T_3) end-cap groups. PPE triplet excited states are produced in very low yields by direct photoexcitation, but they are easily produced by photosensitization or by pulse radiolysis.



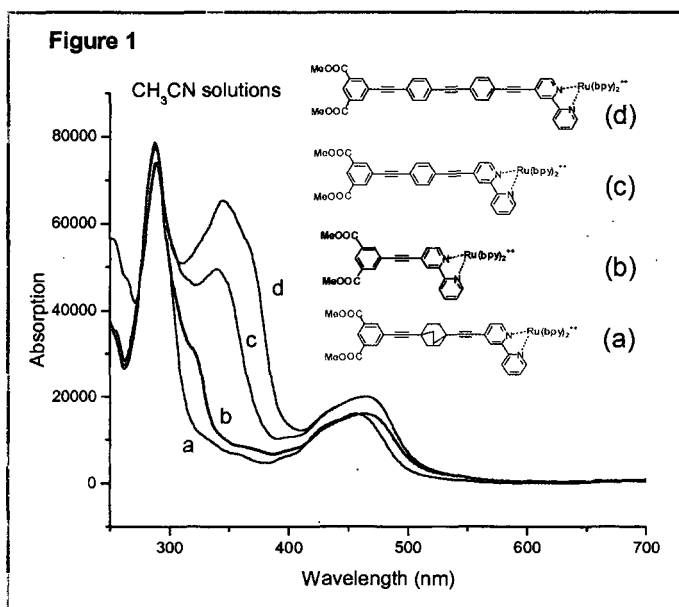
Triplet states of PPE (PPE^{3*}) formed by pulse radiolysis in toluene have a strong absorption band at 780, nm, while the triplet of terthiophene end capped polymer (T_3PPE^{3*})^{3*} has two bands identified as due to triplets located in the chain, T_3PPE^{3*} (780 nm), and at the T_3 end caps, $T_3^{3*}PPE$ (700 nm). Both PPE^{3*} and $(T_3PPE)^{3*}$ have lifetimes $> 280 \mu s$, limited by reactions with radicals. The 780 nm and 700 nm bands of $(T_3PPE)^{3*}$ undergo concentration dependent spectral changes indicating bimolecular triplet transfer from T_3PPE^{3*} to T_3PPE^{3*} ($k = 6.8 \times 10^9 M^{-1} s^{-1}$).

PPE^{3*} and T_3PPE^{3*} both transfer triplet energy to terthiophene (T_3) added to the solution with rate constants near $5 \times 10^9 M^{-1} s^{-1}$. T_3^{3*} , on the other hand, transfers triplet energy *to* T_3PPE to create the end cap-centered triplet, $T_3^{3*}PPE$. The results indicate that the triplet energies are in the order $PPE^{3*} \sim T_3PPE^{3*} > T_3^{3*} > T_3^{3*}PPE$. Thus, while T_3PPE^{3*} readily transfers its excitation energy in intermolecular reactions, the more energetic intramolecular triplet energy transfer to create $T_3^{3*}PPE$ is not observed and is shown to be slower than $3 \times 10^3 s^{-1}$. Triplets are apparently trapped in the PPE chain and move very slowly along the chain. Triplet transport in PPE is slower by a factor of at least 3×10^4 than the hole transport reported earlier for the same molecules. Possible reasons for the very slow migration include conformation changes that trap the triplet. Some evidence for conformational relaxation is seen in small spectral shifts.

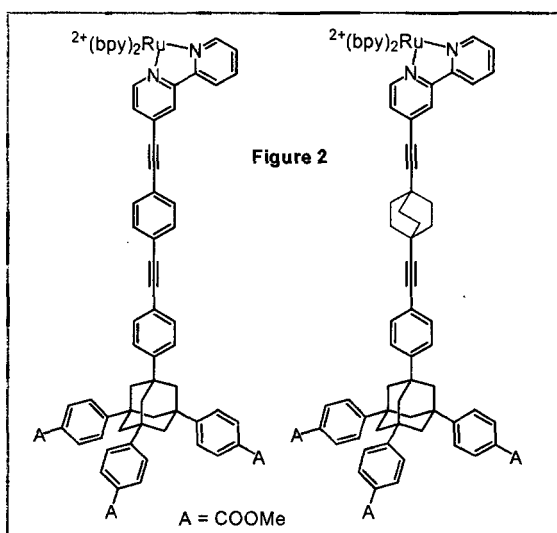
EFFECT OF BRIDGE LENGTH AND SATURATION IN RIGID SENSITIZERS FOR TiO₂ SEMICONDUCTOR NANOPARTICLES

Elena Galoppini, Qian Wei, Dong Wang, Piotr Piotrowiak, and Mykhaylo Myahkostupov
Rutgers University, Chemistry Department, 73 Warren Street, Newark, New Jersey

We have developed rigid sensitizers made of tripodal and rigid-rod linkers substituted with Ru^{II}-polypyridyl complexes and bound to TiO₂ nanoparticles thin films to study electron transfer processes at sensitizer-nanoparticles interfaces. Here we describe the



most recent studies, involving two series of newly synthesized "tripods" and "rods" with bridges that vary in length (number of Ph-E units) and structure (conjugated vs. non-conjugated) shown in Figures 1 and 2. The effect of the length and saturation of the bridge on the photophysical properties of the tripodal and rigid-rod sensitizers will be described. The molecules have been studied in solution as well as TiO₂-bound. As expected, the length of the conjugated bridge influences key photophysical properties. For example as the number of (Ph-E)_n



units increased in the rods and tripods series so did the intensity of the π - π^* transition near 350 nm. This band is not observed in Ru(bpy)₃²⁺ or in the tripods and rods with a saturated Bco unit in the bridge. This effect is shown, for the rods, in Figure 1. Preliminary ultrafast (femtosecond) laser measurements of charge injection for tripods and rods bound to TiO₂ surfaces suggest that the bridge length influences the electron injection rates, as slower rates were observed in the longest rods. The study aimed to determine and quantify the effect of the bridge length and saturation on the injection rates in tripods and rods is in

progress and the results will be reported and discussed at the meeting.

INVESTIGATION OF SMALL MOLECULE ACTIVATION BY TIME-RESOLVED INFRARED SPECTROSCOPY

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A promising strategy for the activation and conversion of small, stable molecules, such as H_2 , H_2O and N_2 , into useful chemicals and/or fuels involves the use of photoactivated transition metal catalysts that possess vacant coordination sites. Adducts of small molecules with unsaturated transition metal complexes are *key intermediates* in these photocatalytic mechanisms. Therefore, it is vital that we fully understand the properties of the photoactivated catalyst, the nature of these metal-adduct interactions and the kinetic and thermodynamic parameters associated with their formation and subsequent reactions.

The family of complexes, $M(CO)_3(PR_3)_2$ ($M = Cr, Mo, W$; $R = iPr, Cy$), are stable unsaturated 5-coordinate precursors that are ideally suited to such studies. The sixth coordination site is occupied by an agostic C-H bond from one of the phosphine ligands, which is easily displaced by molecules such as H_2 , D_2 , N_2 and C_2H_4 to form $M(CO)_3(PR_3)_2L$.

We have previously investigated the kinetics and thermodynamics of the photoinduced W-L bond cleavage of $W(CO)_3(PCy_3)_2L$ ($L = H_2, D_2, N_2, C_2H_4$ etc.) and the subsequent back reaction to the parent molecule, using laser flash photolysis. In the present work, these studies have been extended by the use of step-scan FTIR (s^2 -FTIR) spectroscopy. s^2 -FTIR is a powerful form of time-resolved infrared (TRIR) spectroscopy, a combination of flash photolysis and fast infrared detection, which allows FTIR spectra of transient species to be recorded on timescales down to *ca.* 10 ns. The ν_{CO} vibrations of metal carbonyl complexes are extremely sensitive to electronic and molecular structure and provide an excellent spectroscopic handle for distinguishing different intermediates, such as dihydrogen/dihydride complexes and for probing their kinetic development. The results of the s^2 -FTIR investigation are compared with our previous flash photolysis studies. The kinetic data obtained are found to be in excellent agreement and we demonstrate how s^2 -FTIR provides a powerful complementary spectroscopic technique for the elucidation of photocatalytic mechanisms.

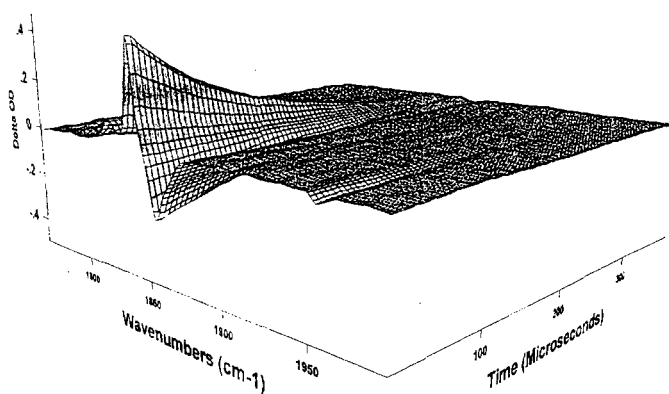


Figure: s^2 -FTIR spectra obtained after 355 nm excitation of $W(CO)_3(PCy_3)_2(N_2)$ in hexane saturated with 2 atm N_2 .

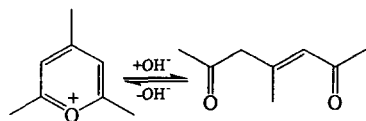
VESICLE-BASED SYSTEMS FOR WATER PHOTOLYSIS AND PHOTOREGULATED TRANSMEMBRANE REDOX

Linyong Zhu and James K. Hurst

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The aqueous-organic interface and compartmentation afforded by closed bilayer membranes offers a unique opportunity for controlling coupled chemical reactions within mesoscopic assemblies. Our research in this area has been directed along two lines: (1) developing efficient systems for H₂ photoproduction and (2) developing light-modulated electron transport systems.

Concerning topic (1), we have previously demonstrated that neutral pyrylium radicals, formed either by oxidative quenching of photosensitizers or directly by reductive quenching by solvent, can function as electroneutral transmembrane electron/OH⁻ antiporters in bilayer membranes [Khairutdinov & Hurst, *J. Am. Chem. Soc.* **123**, 7352-9 (2001)]. The unique ability of these compounds to cycle rapidly across the membrane in two different oxidation states is a consequence of the capacity of the oxidized ions to undergo ring-opening pseudobase formation to neutral 1,5-diketones:

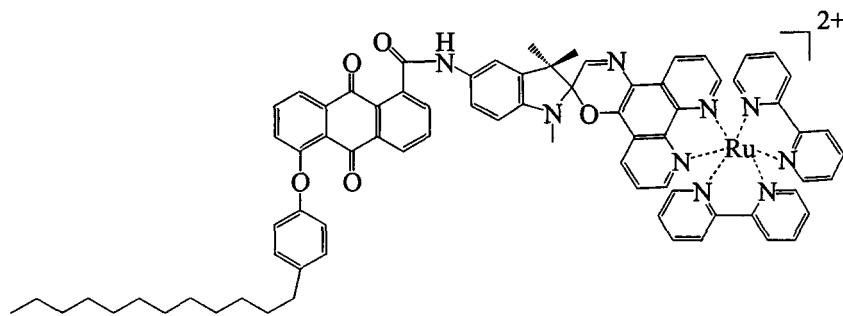


The cyclic electron transport properties of these compounds were originally demonstrated using sacrificial electron donors and acceptors in the opposite aqueous phases; in more recent (unpublished) work, we have found

that replacing the internal acceptor with occluded colloidal platinum leads to formation of H₂ and that the reaction can be driven for thousands of photocycles without any evidence of degradation. Current research efforts, which will be reported, include exploring membranes with varying compositions and derivatized pyrylium ions to optimize system performance. To this end, we have synthesized pyrylium ions containing 4-dialkylaminophenyl substituents: these ions have optical bands favorable for photoexcitation with solar photons and exhibit very low fluorescence quantum yields, yet retain one-electron reduction potentials sufficient to drive Pt-catalyzed water reduction.

Our research in the second area has focused upon synthesizing amphiphilic functional triads consisting of ruthenium photosensitizers linked to electron acceptors via photoisomerizable spirooxazines, which are expected to act as electron gates.

One target compound (shown here) has now been synthesized; preliminary studies indicate that the spiro carbon undergoes reversible spiro ↔ mero interconversions both in solution and when the triad is incorporated into membrane bilayers.



Photoexcitation also leads to reduction of an occluded electron acceptor; mechanistic details are now being investigated.

NEW THEORETICAL DEVELOPMENTS FOR NANOSCALE ENERGY AND CHARGE TRANSFER PROCESSES: MULTICHROMOPHORIC EXCITATION ENERGY TRANSFER AND NON-CONDON ELECTRON TRANSFER

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For the construction of reliable nanoscale photoelectronic devices, satisfactory microscopic understanding of how electronic excitation energies and charge carriers are generated, transported, and trapped in given nanostructured systems is essential. With the accumulation of ongoing experimental results on this subject, it is becoming evident that many of these processes involve new issues requiring more advanced theoretical studies. Among these, we have focused on two important issues, the effects of quantum coherence on the transfer of delocalized excitation energies[1] and the non-Condon effects in electron transfer[2], which have crucial implications in understanding natural photosynthesis, in designing artificial photosynthetic devices, and in employing organic molecules for electronic devices.

[1] The theory of Förster resonance energy transfer (FRET) (or excitation energy transfer) has been generalized for multichromophoric and nonequilibrium situations. This theory clarifies that the far field linear spectroscopic information is insufficient for the determination of the transfer rate and that the distance dependence of the rate can vary with the disorder and temperature. Our theory elucidates approximations involved in previous theories developed by Sumi [J. Phys. Chem. B **103**, 252 (1999)] and by Scholes and Fleming [J. Phys. Chem. B **104**, 1854 (2000)]. Application of our theory to energy transfer from the B800 unit to the B850 unit in the LH2 (light harvesting complex 2) of purple bacteria demonstrates that multichromophoric quantum coherence is responsible for the large enhancement of the rate (about a factor of 5) and for very dispersive dynamics, in agreement with experimental observations.

[2] The spin-boson model has been generalized for torsional non-Condon (NC) effects, by introducing a torsional oscillator modulating the electronic coupling by a trigonometric function. In the nonadiabatic limit, nonequilibrium rate expressions have been derived for both photoinduced and relaxed initial conditions, and a new Fermi golden rule (FGR) expression has been derived in the stationary limit. The classical limit of the FGR expression becomes a sum of three Marcus-type expressions. Model calculations demonstrate that the interference between the Condon and the NC mechanisms can result in dramatic changes in the reaction rate, and that the NC effect can cause the activation energy to decrease with increasing temperature.

Related Publications

1. “Multichromophoric Förster resonance energy transfer”, S. Jang, M. D. Newton, and R. J. Silbey, Phys. Rev. Lett., in press (2004)
2. “Theory of torsional non-Condon electron transfer: a generalized spin-boson model and its nonadiabatic limit solution”, S. Jang and M. D. Newton, in preparation.

SPECTROSCOPIC ANALYSIS OF EXCITONS IN SOLUBILIZED SINGLE-WALL CARBON NANOTUBES

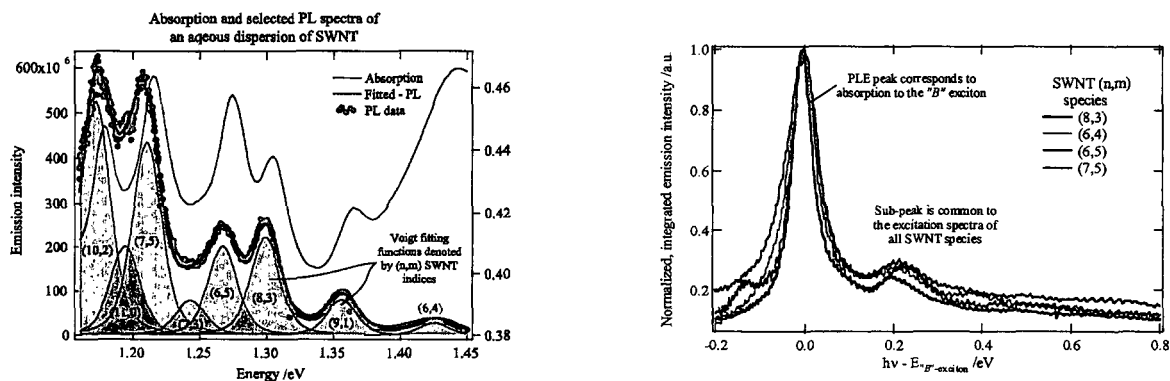
M. Jones, C. Engtrakul, W. Metzger, R.J. Ellingson, A.J. Nozik, M.J. Heben and G. Rumbles
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401

We have successfully recorded and analyzed steady state and time-resolved PL spectra of single-wall carbon nanotubes (SWNTs) in aqueous solution. Within the spectral region available to us, we have identified 9 SWNT species, with the most prominent emission originating from the (7,5), (8,3) and (6,5) tubes. Spectral analysis of these features reveals a number of interesting phenomena, including: (i) PL and PLE peaks that appear near-Lorentzian in functional form; (ii) the appearance of a higher-energy sub-band in the PLE spectra; (iii) a small Stokes shift and (iv) a dominant PL lifetime of 130 ps.

The Lorentzian lineshape functions signify weak coupling of the exciton with the surrounding bath (surfactant and solvent), and suggests a prominent intra-nanotube dephasing mechanism. This interpretation is in agreement with the small, observed Stokes shift. The measured PLE spectra are associated with what is normally referred to as the E_{22} van Hove singularity, but due to electron-hole correlation effects should, more correctly, be attributed to the B exciton¹. A smaller, sub-peak (see figure below) is shifted by ~ 200 meV with respect to the B exciton. This may be due to a vibrational overtone coupled to the exciton or an excitonic excited state.

The 130 ps, fluorescence lifetime of the three, prominent, emitting tubes is far longer than would be expected for a system that has a reported photoluminescence quantum yield (PLQY) of $\sim 10^{-3}$. These data yield a natural, radiative lifetime of 130 ns, suggesting a radiative transition that is not fully allowed. Determination of PLQY for a single nanotube type is, however, a difficult measurement to make, since it requires an accurate measurement of the absorption cross-section. The PLQY is probably higher than reported, due to absorption by bundled nanotubes that do not contribute to the PL signal. If so, the calculated natural radiative lifetime will decrease and become more indicative of an allowed transition.

By extending our spectroscopic capabilities further into the near-IR and by refining our synthetic procedures, we will greatly improve our understanding of how the photophysics of SWNTs depend on nanotube diameter and chirality. These studies will then form a foundation for our long-term objective: to study the interactions between SWNTs and colloidal quantum dots.



¹ C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, et al., *Appl. Phys. A* **78**, 1129 (2004).

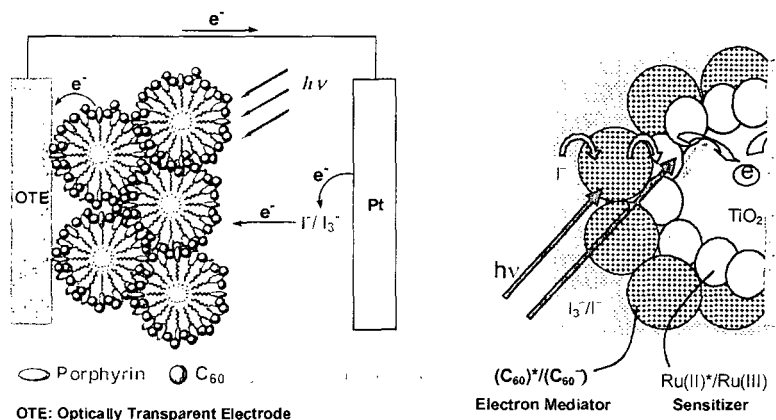
MOLECULAR CLUSTERS AS LIGHT HARVESTING ANTENNAS AND ELECTRON SHUTTLES

Prashant V. Kamat, Taku Hasobe[#] and Mehul Haria

Radiation Laboratory and Department of Chemical & Biomolecular Engineering
University of Notre Dame, Notre Dame, Indiana 46556-0579

Donor acceptor based molecular clusters in photochemical solar cells provide new ways to improve the efficiency of charge separation and charge transport in photosensitizer-based electrode systems. A quaternary self-organization of porphyrin (donor) and fullerene (acceptor) units has been investigated by clustering with gold nanoparticles ($(H_2PC_{15^-}Au+C_{60})_m$) and assembling them as three-dimensional arrays onto nanostructured SnO_2 films. The composite clusters with broad absorption in the UV and IR exhibit an incident photon-to-photocurrent efficiency (IPCE) as high as 54% and broad photocurrent spectral response (up to 900 nm). The net power conversion efficiency of the OTE/ $SnO_2/(H_2P-C_{15^-}Au+C_{60})_m$ electrode is 1.5%, and is ~50 times higher than that of the individual cluster systems. The cooperative effect between H_2P and C_{60} clusters is evident from the efficient electron transfer between singlet excited porphyrin and C_{60} in the composite system and enhanced photocurrent generation.

In the second example, we demonstrate ways to minimize the excited state interaction with



Scheme 1. Left: Photochemical solar cell based on quaternary self-organization of porphyrin (donor) and fullerene (acceptor) units. Right: Using an electron mediator to shuttle electrons for sensitizer regeneration

the redox couple in a $Ru(bpy)_2(dcbpy)^{2+}$ (Ru(II) complex) based solar cell. The approach uses C_{60} clusters as electron shuttles that effectively regenerate the sensitizer but at the same time minimize direct interaction between the excited sensitizer and redox couple (Scheme 1 Right).

The C_{60} modified electrodes (viz., OTE/ $SnO_2/Ru(II)/(C_{60})_n$ and OTE/ $TiO_2/Ru(II)/(C_{60})_n$) delivered photocurrent with a greater efficiency than the SnO_2 and TiO_2 films modified with only Ru(II) dye (viz., OTE/ $SnO_2/Ru(II)$ and OTE/ $TiO_2/Ru(II)$). The luminescence quenching of $Ru(II)^*$ by I_3^- which occurs with a rate constant of $1.9 \times 10^{10} M^{-1} s^{-1}$, is suppressed following the deposition of a layer of C_{60} clusters. The present approach of using C_{60}/C_{60}^- as an electron shuttle could pave the way towards the design of efficient photoelectrochemical cells.

[#] In collaboration with Prof. S. Fukuzumi, Osaka University, Japan and Prof. H. Imahori, Kyoto University, Japan.

FIRST-PRINCIPLES THEORY OF CARBON NANOTUBE-SEMICONDUCTOR JUNCTIONS: BINDING ENERGY, BAND OFFSET, AND CHARGE TRANSFER

Yong-Hyun Kim, M. J. Heben, and S. B. Zhang
National Renewable Energy Laboratory, Golden, Colorado 80401

The integration of carbon nanotubes with semiconductor quantum dots is a new direction in nanochemistry with high potential in novel solar photoconversion applications. Here, we report first-principles calculations on the structural and electronic properties of single-wall carbon nanotubes on the surfaces of semiconductors: Si, III-V and II-VI compounds (e.g., InAs, GaAs, and CdSe); the results include the binding mechanism and energy, band alignment, and interfacial charge transfer as a function of the surface orientation. Few semiconductors have good lattice compatibility with nanotubes. The “best” matched ones are zigzag nanotubes with InAs and CdSe with a strain $< 0.7\%$. In these cases, surface binding energy can be maximized in the non-polar (110) and (In, Cd)-terminated (111) directions, i.e., 0.1 eV/\AA . For the (As, Se)-terminated (111) direction, however, the binding is minimal, $< 0.05 \text{ eV/\AA}$. An approximate but otherwise universal band alignment scheme is also established between various semiconductor (110) surfaces and carbon nanotubes so that one can predict band offsets without having to resort to sophisticated calculations. For example, using available semiconductor band alignments (see Figure below), a $(17,0)$ nanotube should form a type-I alignment with GaAs, but a type-II alignment with InAs — a prediction confirmed by direct calculations. Moreover, the local dipole field of the polar (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces are large enough to affect the band alignments, causing rigid shifts of the nanotube electronic states with respect those of the semiconductors. An interfacial charge transfer will take place, whose direction is determined solely by the direction of the dipole field.

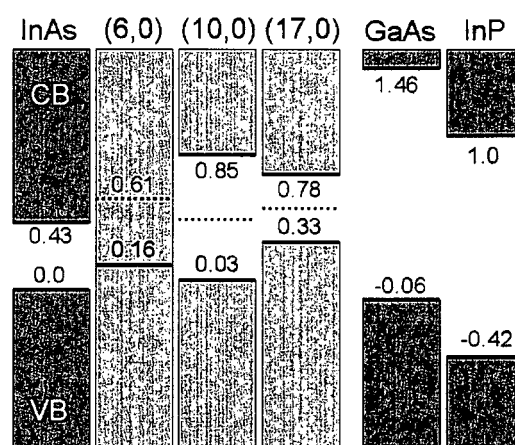


Figure Calculated band alignments of zigzag nanotubes with respect to InAs, GaAs, and InP. Red dotted lines correspond to the graphene Fermi level, which tends to align [Kim, Heben, and Zhang, *Phys. Rev. Lett.* (accepted for publication)].

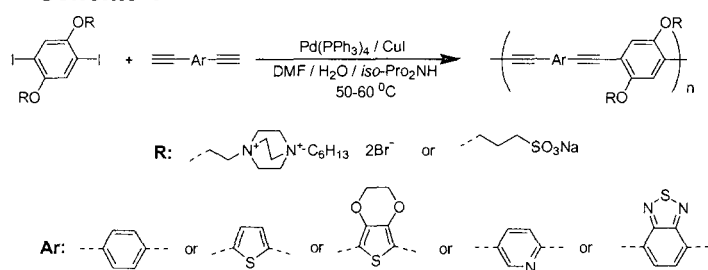
CONJUGATED POLYELECTROLYTES: SYNTHESIS, PHOTOPHYSICAL CHARACTERIZATION AND SELF-ASSEMBLY

Mauricio R. Pinto, David Witker, Chunyan Tan, Lindsay M. Hardison, Mikolai Fajer, Jeremiah Mwaura, Valeria D. Kleiman, John R. Reynolds and Kirk S. Schanze

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Conjugated polyelectrolytes (CPEs) are soluble in water and other polar solvents and, due to their amphiphilic properties, have the potential to be self-assembled from water. CPEs also exhibit interesting optical properties such as strong visible light absorption, efficient fluorescence and, in certain cases, long-lived triplet states. Due in part to the delocalized nature of the singlet exciton in CPEs, oppositely charged fluorescence quencher ions are able to efficiently quench the fluorescence from CPEs at low concentrations. This effect, which is termed “amplified quenching” involves the formation of an ion-pair complex between the quencher and the CPE chain, and our studies imply that the process is facilitated by the formation of CPE aggregates.

Scheme 1

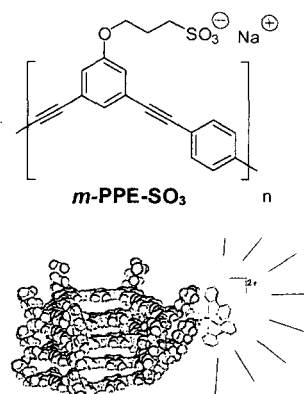


In order to investigate the effect of polymer structure, charge type and excited state energy on the amplified quenching effect, we have prepared a series of ten new CPEs. As shown in Scheme 1, these polymers are synthesized by Sonogashira coupling of a diethynyl substituted arene and a 1,4-*bis*-(alkoxy)-2,5-diiodobenzene. The

charge type of the resulting CPE is controlled by using either alkylammonium (cationic) or sulfonate (anionic) functional groups on the 1,4-*bis*-(alkoxy)-2,5-diiodobenzene unit, whereas the band gap of the resulting polymer is tuned by varying the diethynyl arene moiety. In preliminary work, we have characterized the photophysical properties of this series of CPEs in several solvents. In general, the results indicate that the polymers exist as non-aggregated chains in polar, non-aqueous solvents (e.g. DMSO, DMF and CH_3OH) and that they aggregate in water.

We have demonstrated that the *meta*-linked CPE *m*-PPE- SO_3 (Scheme 2) undergoes a random coil to helical conformational transition when the solvent is changed from CH_3OH (a good solvent) to water (a poor solvent). Helical self-assembly is driven by hydrophobic interactions and favorable π -stacking interactions. Investigation of the fluorescence quenching of *m*-PPE- SO_3 indicates that quenching is more efficient for the helical conformation and for quenchers that are able to intercalate between π -stacked arylene units. Investigations also show that the metallo-intercalator $\text{Ru}(\text{dppz})(\text{bpy})_2^{2+}$ binds strongly to the helical CPE. The bound form of the complex is highly luminescent (e.g. Scheme 2), and excitations produced on the polymer efficiently sensitize emission from the intercalated complex.

Scheme 2



CONJUGATED POLYELECTROLYTES AND ASSEMBLIES: PHOTOPHYSICS AND PHOTOVOLTAIC INTERACTIONS

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Valeria D. Kleiman, John R. Reynolds and Kirk S. Schanze

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This project seeks to capitalize on the unique combination of optical, electronic and materials properties of conjugated polyelectrolytes (CPE). In solution, the π -conjugated structures lead to amplified quenching of photoluminescence, an amplification which depends critically on the dynamics and efficiency of energy transfer. CPEs are also promising materials for organic photovoltaics (solar cells and photodetectors) as the ionic side groups allow the fabrication of nanostructured multilayer assemblies. In this work, ultrafast studies of energy transfer and quenching in π -conjugated polyelectrolytes along with the self assembly and characterization of polymer based photovoltaics has been undertaken.

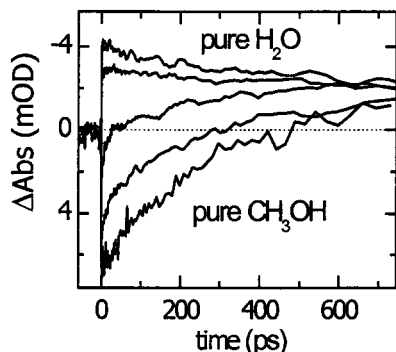
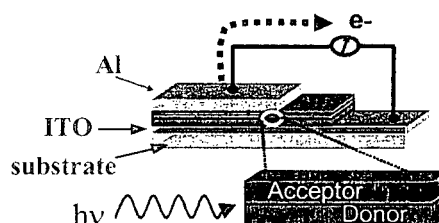


Figure 1. Transient absorption for *m*-PPESO₃. In pure CH₃OH, the data shows photoinduced absorption from the free coil. As the H₂O composition is increased, the stimulated emission from the aggregate dominates the signal.

Energy transfer dynamics in sulfonate-substituted CPEs in solution were investigated by time-resolved fluorescence and transient absorption spectroscopies. Intrachain energy transfer was studied by quenching the polymer's fluorescence with a cationic dye. Modeling of the experimental energy transfer dynamics reveals that trap sites interrupt the migration of singlet excitons limiting the quenching efficiency. Time-resolved transient absorption anisotropy indicates that trap sites are created by interchain aggregation. To understand this and its implications in energy transfer, we studied the dynamics of intrachain energy transfer in a *meta*-linked polymer which self-assembles into a helical aggregate. For this polymer (*m*-PPE-SO₃) it was found that the extent of energy transfer strongly depends on the aggregation state of the polymer, which can be controlled by changing the solvent.

Thin layer-by-layer (LBL) films composed of CPEs were assembled via electrostatic adsorption of cationic and anionic polyelectrolytes. The thickness of the resulting films is controlled by varying the number of bilayers deposited (*ca.* 10 Å per bilayer) to yield films with smooth surfaces. Application of these CPE multilayer films to energy conversion is under investigation. Donor and acceptor CPEs were assembled in a solid state photovoltaic configuration as illustrated in Scheme 1. Illumination produces photocurrent and the magnitude of the current is a function of the nature of the materials and the structure of the nano-assembled layers.

Energy transfer dynamics in sulfonate-substituted CPEs in solution were investigated by time-resolved fluorescence and transient absorption spectroscopies. Intrachain energy transfer was studied by quenching the polymer's fluorescence with a cationic dye. Modeling of the experimental energy transfer dynamics reveals that trap sites interrupt the migration of singlet excitons limiting the quenching efficiency. Time-resolved transient absorption anisotropy indicates that trap sites are created by interchain aggregation. To understand this and its implications in energy transfer, we studied the dynamics of intrachain energy transfer in a *meta*-linked polymer which self-assembles into a helical aggregate. For this polymer (*m*-PPE-SO₃) it was found that the extent of



Scheme 1. Schematic diagram of an organic photovoltaic cell featuring a thin-film donor:acceptor material as the active medium.

LIGHT-DRIVEN CHARGE TRANSFER IN FACE-TO-FACE DONOR SPACER-ACCEPTOR SUPRAMOLECULAR SYSTEMS

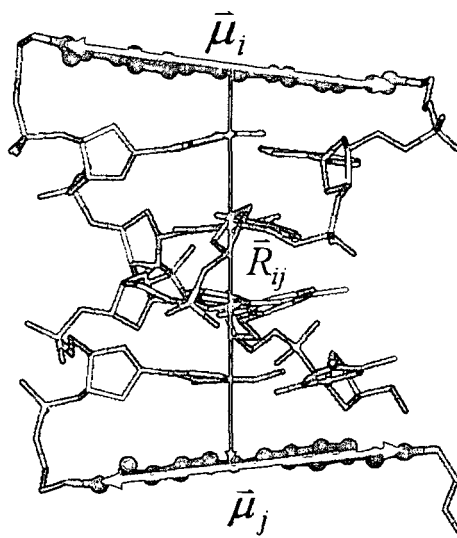
Frederick D. Lewis

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The objective of this project is to investigate photoinduced electron transfer in supramolecular systems which possess an electron donor and acceptor separated by aromatic spacers having a face-to-face or π -stacked geometric relationship. Synthetic duplex DNA hairpin structures provide the platform for our investigations.

During the current year we have made significant progress in our study of DNA hairpin structure. A high resolution crystal structure for a stilbenediether-linked hairpin has been reported.¹ The conformations of the two stilbenes in the unit cell differ in linker conformation, one having a π -stacked geometry and the other an edge-to-face geometry with respect to the adjacent base pair. Edge-to-face π - π interactions had not been previously reported for DNA. Rapid and reversible formation of mini-G-quadruplex structures has been observed for conjugates possessing stilbenediether linkers connecting two short poly(G) sequences.² Quadruplex formation is proposed to result from dimerization of meta-stable mini-hairpins.

We have also introduced a variation on the hairpin motif, the end-capped hairpin. These structures possess a second linker at the 'open end' of the hairpin (see Figure).³ They display exceptional thermodynamic stability, a single A:T base pair being sufficient to enforce a folded, π -stacked structure at room temperature in aqueous solution. By increasing the number of base pairs in the hairpin stem, the distance between stilbenes (R_{ij}) is increased by 3.4 Å and the dihedral angle between their transition dipoles ($\mu_{i,j}$) is increased by 35°. Thus the length of the DNA duplex determines both the distance and dihedral angle between the two stilbenes. The use of donor and acceptor stilbenes at opposite ends of an end-capped hairpin permits investigation of the distance dependence of both electron transfer and exciton coupled CD.⁴ Exciton coupling is strongly dependent upon the dihedral angle, however electron transfer is not.



(1) Egli, M.; Tereshko, V.; Mushudov, R.; Sanishvili, R.; Liu, X.; Lewis, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 10842-10849.

(2) Lewis, F. D.; Wu, Y.; Zhang, Y. *Chem. Commun.* **2004**, 636-637.

(3) Lewis, F. D.; Liu, X.; Wu, Y.; Zuo, X. *J. Am. Chem. Soc.* **2003**, *125*, 12729-12731.

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CHEMICAL CONTROL OVER THE ELECTRICAL PROPERTIES OF THE III-V SEMICONDUCTOR SURFACES AND OVER CHARGE TRANSPORT IN MESOPOROUS PHOTOELECTRODES

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Despite its extensive use in device applications, a limited number of methods are currently available to control the chemical behavior of GaAs surfaces. Novel GaAs passivation schemes that do not employ expensive epitaxial techniques are potentially very useful in preparing photoelectrodes and other electrical and electrochemical energy conversion systems from GaAs, which has a nearly ideal band gap for solar energy conversion purposes. Our work has explored the reaction of trichlorophosphine (PCl_3) and triethyl phosphine with single crystal GaAs(111)A and (111)B. X-ray photoelectron spectra of treated surfaces show that while Ga oxidizes at essentially the same rate as on an untreated surface, the As signal on the phosphine treated (111)A surfaces becomes remarkably resistant to oxidation in air. The inherent thermodynamic instability of the $\text{As}_2\text{O}_3/\text{GaAs}$ interface is known to lead to the formation of As^0 , which has been implicated as a trap state for carrier recombination. Photoluminescence intensity measurements indicate that an initial increase in PL signal indicating that such surfaces are initially chemically passivated against As_2O_3 growth and have good electronic properties. Long term stability measurements are in progress on such systems in both air and vacuum ambients.

In a separate portion of the work, the driving force dependence of rate constants of electron transfer reactions at the ZnO-liquid interface has been investigated. A series of non-adsorbing, one-electron outer-sphere redox couples have been synthesized, with reduction potentials spanning over 550 mV. In addition, the driving force has been extended by an additional 165 mV by adjusting the pH. Self-exchange rate constants were derived from NMR line broadening experiments under the same experimental conditions which allowed us to confirm that our series of redox couples have constant reorganization energies with a magnitude of approximately 0.65 eV. Differential capacitance vs. potential and current density vs. potential measurements have been used to investigate the interfacial energetic and kinetic behavior of ZnO contacts. We have shown that these ZnO contacts display ideal energetic and kinetic features. The rates of electron transfer were found to be first order in both surface-electron and acceptor concentration. This allows for the precise determination of rate constants as a function of driving force. Results have shown excellent agreement with electron transfer theory. We have shown the first indication of the inverted region for heterogeneous electron transfer reactions at semiconductor electrodes to outer sphere non adsorbed redox species, and have confirmed the value of $10^{-16} \text{ cm}^4 \text{ s}^{-1}$ as the maximum rate constant in this semiconductor/liquid electrolyte system as well. The implications of these results for efficient photoconversion devices from III-V materials will be presented in the poster.

ULTRAFAST ELECTRON INJECTION FROM ADSORBATES TO NANOCRYSTALLINE SEMICONDUCTOR THIN FILMS: SEMICONDUCTOR DEPENDENCE

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The objective of our DOE funded research is to understand electron transfer dynamics between semiconductor nanoparticles and molecular adsorbates. This knowledge is essential to many semiconductor nanoparticle based devices and processes, including photocatalytic waste degradation and dye sensitized solar cells.

Using femtosecond infrared spectroscopy, we are carrying out a systematic study of the dependence of electron injection rate on the property of adsorbate, spacer, anchoring group, semiconductor and the interfacial environment. We previously showed that electron injection from Ru N3 to TiO₂ and ZnO are dramatically different despite their similar conduction band edge position. The injection kinetics in TiO₂ is dominated by < 100 fs (>60%) component and those in ZnO is dominated by a ~100ps component (>90%). This result suggests that the conduction band composition plays a significant role in determining the injection rate. We hypothesized that the faster rate to TiO₂ can be attributed to its d-conduction band nature, which has much higher density of states than the sp band in ZnO. To further test this notion, we have investigated two other semiconductors and with more different adsorbates. In this poster, we compare injection dynamics in TiO₂, Nb₂O₅, SnO₂ and ZnO from Ru(dcbpy)₂(NCS)₂ (Ru N3) and a series of organic dyes. These results appear to support the notion of faster injection to a d-conduction band.

Comparison of injection dynamics from RuN3 to TiO₂, Nb₂O₅, SnO₂ and ZnO: Injection in all films can be characterized by a two-state injection model with a < 100 fs component and slower components on the ps and longer time scale. The fast component is attributed to injection from the unrelaxed ¹MLCT state and the slow component to the relaxed ³MLCT state near the edge. The amplitudes of the <100 fs component are small (< 10%) in ZnO and SnO₂ films and much larger in TiO₂ (~60%) and Nb₂O₅ (~40%) films. These amplitudes depend on the ratio of rate of injection from the unrelaxed state and relaxation to the ³MLCT state. Assuming the rate of the latter process, these amplitudes reflect the relative injection rate into these semiconductors, following this order TiO₂>Nb₂O₅>>ZnO~SnO₂.

Comparison of injection dynamics from organic dyes to TiO₂, SnO₂ and ZnO: The existence of two injection path ways in RuN3 (i.e. ¹MLCT and ³MLCT) complicates its injection kinetics. The slow injection component corresponds to injection to states near the band edge and their rate depends on sample condition and not the intrinsic property of the conduction band. To overcome that problem, we compare injection rates to these semiconductors from a series of styrene dyes whose excited state potential are much higher than the band edge and whose triplet plays negligible role in the injection. For the three semiconductors (TiO₂, SnO₂ and ZnO) examined so far, the injection kinetics appear to be simpler. They are no longer biphasic, although still non-single exponential. Similar trend of semiconductor dependence is observed.

CHARGE-TRANSFER TO LIGAND-FIELD STATE RELAXATION DYNAMICS IN Fe(II)-BASED CHROMOPHORES

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Over the past decade, the so-called Grätzel Cell¹ has revolutionized approaches for developing cheap, efficient solar energy conversion schemes. Significant effort has been expended to enhance the performance characteristics of devices based on the sensitization of nanoparticle anatase TiO₂ that is the centerpiece of the Grätzel technology. Much of this work has focused on the use of inorganic charge-transfer chromophores such as Ru^{II} polypyridyls. These compounds have the advantage of possessing redox-active excited states that are accessible through visible and/or near-infrared excitation. However, with injection efficiencies already near 100%, there is little room for further improvement in such devices with regard to this particular aspect of the cell's dynamics. Such compounds also fail to take advantage of the unique opportunities afforded by "hot" injection – electron transfer from non-thermalized excited states – identified as an operative mechanism in Grätzel cells by several groups, including our own.²

For these reasons among others, we are beginning to focus our attention on the development of Fe^{II}-based chromophores for applications in solar energy conversion. Ferrere and Gregg³ have previously demonstrated the viability of a Fe^{II}-based device, albeit with significantly lower efficiency than that found for Ru^{II}-based analogs. Previous work from our group has shown that the charge-transfer lifetime for a prototypical Fe^{II} polypyridyl species is exceedingly short (Figure 1),⁴ the rapid charge-transfer to ligand-field-state conversion likely competes effectively with charge injection, thereby lowering the yield of conduction band electrons in the TiO₂ material and limiting the utility of Fe^{II}-based sensitizers.

This presentation will illustrate some of the approaches we are taking to both understand charge-transfer state deactivation as well as lengthen charge-transfer state lifetimes of Fe^{II} chromophores in order to make such compounds viable options for dye sensitization applications. The syntheses, electronic structures, and static and time-resolved spectroscopies of several systems along these lines will be described.

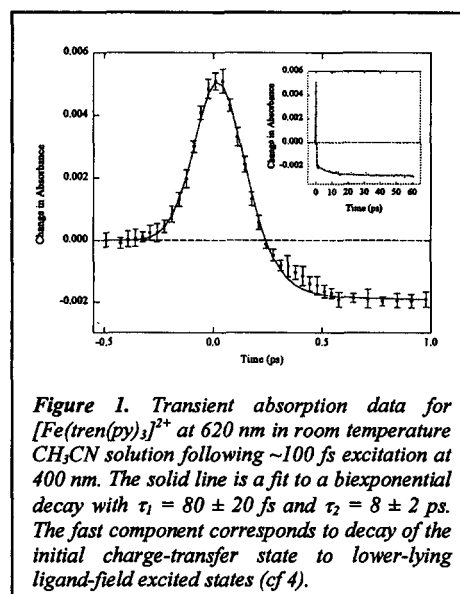


Figure 1. Transient absorption data for $[\text{Fe}(\text{tren}(\text{py})_3)]^{2+}$ at 620 nm in room temperature CH_3CN solution following ~ 100 fs excitation at 400 nm. The solid line is a fit to a biexponential decay with $\tau_1 = 80 \pm 20$ fs and $\tau_2 = 8 \pm 2$ ps. The fast component corresponds to decay of the initial charge-transfer state to lower-lying ligand-field excited states (cf 4).

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COLLECTING TiO₂ ELECTRONS CREATED BY 'HOT' MOLECULAR EXCITED STATES WITH COORDINATED DIIMINE LIGANDS

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Our DOE-supported research has focused on the mechanisms for interfacial electron transfer at nanocrystalline TiO₂ interfaces. Our experimental approach has been to characterize novel molecular and supramolecular sensitizers, based on (dπ)⁶ coordination compounds of our own design, with steady state and time resolved spectroscopic and electrochemical techniques. Fundamentally, we seek to provide molecular level descriptions that detail how to direct, store, and react photogenerated interfacial redox equivalents for applications in solar energy conversion. This poster will report our most recent findings on the trapping of TiO₂ electrons created by interfacial electron transfer from vibrationally 'hot' molecular excited states.

We recently communicated the photophysical and interfacial electron transfer properties of nanocrystalline (anatase), mesoporous TiO₂ thin films sensitized to visible light with [Ru(bpy)₂(deebq)](PF₆)₂ or [Os(bpy)₂(deebq)](PF₆)₂, where bpy is 2,2'-bipyridine and deebq is 4,4'-diethylester-2,2'-biquinoline.¹ The absorption spectra display two visible bands reasonably assigned to M → bpy (~ 440 nm) and M → deebq (~560 nm) and the Os compound shows an additional band in the near IR region that has been assigned to a direct singlet-to-triplet transition (~ 860 nm). Both compounds bind strongly to the nanocrystalline TiO₂ films, abbreviated Ru/TiO₂ and Os/TiO₂, with typical surface coverages of 7 (± 2) × 10⁻⁸ mol/cm².

Neither the thermally equilibrated emissive excited state or the reduced forms of these sensitizers efficiently inject electrons into TiO₂ because the conduction band edge position, E_{cb}, is energetically inaccessible, i.e. E⁰(M^{III/II*}) > E⁰(M^{2+/-}) > E_{cb}. However, the Franck-Condon (and upper) excited states are energetically capable of interfacial electron transfer. Upon thermalization, these injected electrons may reduce neighboring sensitizers or form an excited state of the injecting sensitizer. The former is found to occur with quantum yields that decrease with excitation energy, for example for Os/TiO₂ φ(417 nm) = 0.14 ± 0.03, φ(532.5 nm) = 0.08 ± 0.03, and φ(683 nm) = 0.05 ± 0.01. The quantum yields were independent of the excitation irradiance (from 1-20 mJ/pulse) and were zero in fluid solution, on insulating ZrO₂ films, or when the corresponding 4,4'-diethylester-bipyridine (deeb) compounds were used under otherwise identical conditions.

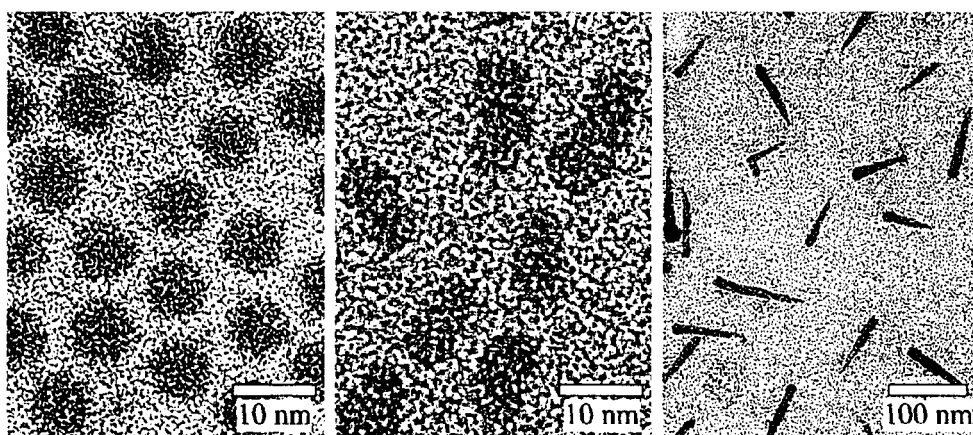
We have extended these studies to a larger family of heteroleptic Ru and Os compounds. These compounds have allowed us to quantify 'remote' injection and trapping by ligands that were not directly anchored to the semiconductor surface. In addition, we have co-anchored non-chromophoric electron acceptors with these sensitizers to investigate how the semiconductor mediates lateral electron transfer processes. In some cases, it has been possible to control the trapping yield with Lewis basic cations that adsorb to TiO₂ and alter the semiconductor density of states. Finally, we have identified kinetic models that quantify the rate constants for lateral charge transfer. With some assumptions, these rate constants report on intermolecular distances on the nanocrystalline semiconductor surface.

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GROWTH OF CATALYST-FREE InP, InAs, AND InSb QUANTUM RODS VIA REACTION OF INDIUM DROPLETS WITH GROUP-V HYDRIDES

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We continue to develop non-aqueous colloidal chemical synthesis of III-V semiconductor quantum rods. One-dimensional, rod-shaped nanocrystals have potential advantages over spheres in improved photoconversion properties, electronic transport, linearly polarized emission, and lasing action. Catalysts in the form of zinc-blende cubic-lattice liquid-metallic droplets have been widely used to initiate growth of wirelike nanocrystallites. The presence of residual catalyst spherules at the rod tip in the final product interferes with optical and electronic properties of the nanorods. Therefore, we developed an approach to grow III-V semiconductor nanorods that are catalyst free. InP, InAs, and InSb quantum rods were synthesized via the reactions of monodispersed colloidal indium droplets with $P(\text{SiMe}_3)_3$, $\text{As}(\text{SiMe}_3)_3$, and $\text{Sb}(\text{NMe}_2)_3$, respectively. To the best of our knowledge, there is no prior literature describing the formation of freestanding zinc-blende III-V semiconductor nanorods or nanowires with no residual metallic catalyst remaining in the final product.



In⁰ particles

Short length InP rods

Long length InP rods

The first step in our procedure is the synthesis of colloidal monodispersed zero-valent indium particles that we prepared by thermal decomposition of organoindium compounds in organic solvent in the presence of a colloidal stabilizer. Diluted solution and a low temperature of about 140-260 °C are required for the formation of freestanding quantum rods.

A photoactive InP-TiO₂ composite was also prepared by the same procedure. With this composite material synthesized with in-situ InP nanocrystals on the TiO₂ surface, we want to achieve better electric contact between InP and TiO₂ and better electron and hole separation inside an InP-TiO₂ particle in order to use this material as a photoactive electrode in solar cells. The physical characteristics and optical signatures of these InP quantum rods will continue to be explored.

ELECTRONIC CHARGE TRANSFER THROUGH OLIGOMERIC ORGANIC SPACERS: PROBING THE NATURE OF TUNNELLING

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Elucidation of mechanisms of long range electronic transfer (*et*) via tunnelling, hopping, or other dynamical processes, remains a strong thrust of research in the context of achieving improved schemes for solar energy conversion. We consider a number of probes of tunnelling, taking due account of the energetics and electronic structure of various *et* systems comprised of donor (D)/acceptor (A) pairs (or analogous 'contacts' with electrodes) linked by oligomeric organic spacers, with particular focus on the use of theory to interrelate independent probes (e.g. rate constant (*k*) and conductance (*g*)) of *et* through a given spacer type. Experimental results for self-assembled conductive junctions involving metal electrodes provide crucial tests of theoretical models.

A key factor controlling tunnelling probability is the modulation of D/A electronic coupling due to fluctuations in nuclear coordinates. Torsional modes are particularly important in this connection, especially in cases of oligomers such as OPE (oligo phenyleneethynylene), the subject of intensive experimental and theoretical study, where large-amplitude fluctuations are possible due to low intrinsic barriers for phenylene torsions. For some sets of OPE species, expected exponential decay of rate with overall D/A separation is observed (from experiment and calculation). However, for other, nominally homologous, OPE sequences, the decay is not even monotonic, thus implying complex torsional effects associated with intermolecular contacts involving the OPE spacers (with J. Smalley *et al* (BNL)). An extension of the spin-boson model including torsional non-Condon effects has been developed with S. Jang (BNL).

Fluctuations in the overall *et* reaction coordinate can also affect tunnelling by modulating the virtual injection gap serving as the barrier in superexchange tunnelling, an increasingly pronounced effect as intrinsic energy gaps become smaller and approach the energy scale of nuclear reorganization (as, for example, in the case of hole transport in DNA). Examples of these effects are illustrated, with emphasis on the central role played by multiple, nonorthogonal reaction coordinates.

To address the possibility of significant intermolecular interaction between nearby conductive spacers, large scale DFT band structure calculations have been carried out for self-assembled monolayers (SAMs) of phenylthiolate supported on copper and gold substrates (with V. Perebeinos (IBM)). Analysis of band dispersion (transverse *k* components) reveals the importance of metal substrate-mediated as well as direct adsorbate-adsorbate interactions in establishing the overall dispersion, with implications regarding the extent to which transport in self-assembled systems may be viewed as a simple superposition of 'single molecule' events.

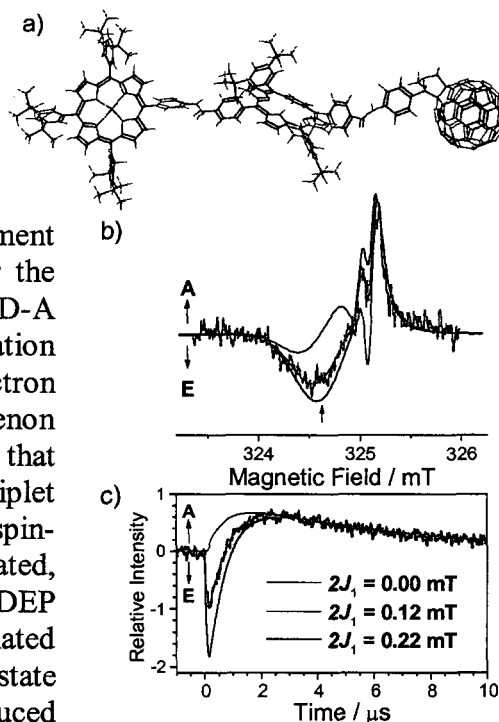
Predicted relationships between *k* and *g* for transport through alkane and OPE spacers have been compared with recent experimental results, using an adaptation of the model of Nitzan based on strong chemisorption of terminal thiolates to metal surfaces. Theory and experiment are generally within an order of magnitude agreement, thus providing support for the underlying unified tunnelling model.

PRIMARY CHARGE RECOMBINATION CHARACTERIZED USING THE EXCHANGE INTERACTION ACCOMPANING PHOTOINDUCED ELECTRON-TRANSFER IN A FULLERENE-PORPHYRIN LINKED TRIAD

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Extensive studies have been performed to produce photoinduced, long-distance charge-separated (CS) states of covalently linked donor-acceptor (D-A) molecular systems that mimic natural photosynthesis. In these sequential electron-transfer (ET) systems, eliminating charge-recombination (CR) from the primary CS state is a key to the overall energy efficiency of the photoconversion process. To attain effective artificial D-A photomolecular devices, characterization of backward ET is useful. In this study the electronic coupling matrix element (V_{CR}) for the primary CR process is characterized for the photoinduced primary CS state $ZnP-H_2P^{+•}-C_{60}^{-•}$ of the D-A triad molecule of Figure 1a. The method of characterization depends on a recent development of time-resolved electron paramagnetic resonance (TREPR) involving the phenomenon of chemically induced electron polarization (CIDEP) that depends in part on the connection between the singlet-triplet splitting $2J$ of a radical ion pair (RIP) and V_{CR} . The spin-polarized RIP EPR signal is explained by singlet initiated, sequential electron transfer polarization in which the CIDEP developed in $ZnP-H_2P^{+•}-C_{60}^{-•}$ is captured in the correlated radical pair polarization (CRPP) of the secondary CS state ($ZnP^{+•}-H_2P-C_{60}^{-•}$). Since the CIDEP effect is produced through the $S-T_0$ mixing characterized by $2J_1$ of the initial RIP, both the sign and the magnitude of $2J_1$ can be extracted from the electron spin polarization (ESP) observed in the secondary RIP. Figure 1b shows the TREPR spectrum (black line) observed 0.3 μ s after the 532 nm laser irradiation of the triad in benzonitrile at room temperature. The simulated time-evolution of the EPR spectrum as based on a stochastic-Liouville equation approach is compared to experimental data in Figures 1b and 1c. This work demonstrates the use of TREPR spectroscopy for the characterization of multi-array sequential ET systems.



ENDOR OF SPIN-CORRELATED RADICAL PAIRS IN PHOTOSYNTHESIS: A TOOL FOR MAPPING ELECTRON TRANSFER PATHWAYS

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Many of the important functions of biological systems are connected to electron transfer (ET) reactions. These ET reactions occur in supramolecular assemblies such as proteins. ET reactions in photosynthetic reaction center (RC) proteins are the first steps in the solar energy conversion process. These reactions occur between cofactors held within integral membrane RC proteins and involve the photoexcitation of the primary donor followed by rapid, sequential electron transfer to a series of acceptors resulting in the charge separated state, P^+Q^- , where the primary donor P is a chlorophyll dimer and the secondary electron acceptor Q is a quinone molecule. The most important aspects of the efficient ET in photosynthetic RCs are redox properties, geometry, and wave function overlap between donor and acceptor cofactors. Additionally, conformational dynamics, as well as interaction with the protein surroundings, are important factors of the ET process. The latter factor determines ET pathways. In photosynthetic RCs the ET occurs through the bonds of the protein scaffold and depends upon the overlap of wave functions of the cofactors and protein surroundings. Identification of the possible ET pathways is crucial for better fundamental understanding of protein structure-function relationships.

Electron nuclear double resonance (ENDOR) spectroscopy is a method of choice for probing electron wave function delocalization. ENDOR provides information on the interactions of the unpaired electron with magnetic nuclei in the protein. This interaction parameter is directly related to the density of the electron wave function on a particular nucleus. Thus, it is feasible to reconstruct wave function delocalization of the donor and acceptor and locate a probable ET pathway through the nuclei having maximum overlap of the donor and acceptor wave functions.

We report on a new effect, which was discovered when the high-frequency ENDOR spectra of the spin-correlated radical pairs were recorded right after the electron transfer event. The ENDOR lines narrow, are more resolved, alternate in intensity with respect to the nuclear Larmor frequency, and appear in the derivative form. We demonstrated that this is due to the spin-correlated radical pair (SCRCP) nature of the observed spins. We developed a deconvolution procedure to amplify the contribution from SCRCP ENDOR. The SCRCP ENDOR contains data on protein nuclei interaction with both unpaired electrons of the donor and acceptor at the same time, thus allowing for mapping spin density delocalization in the protein environment between the electron donor and acceptor in the SCRCP. This new information will provide a unique opportunity to probe the electron-transfer pathways in natural and artificial photosynthetic assemblies, as well as on the ET induced conformational dynamics.

Using time-resolved features of high-frequency EPR spectroscopy, we observed relaxation of the spin density after the charge separation process. This relaxation occurs on the hundreds of microseconds time scale at 50 K. We connected this relaxation to the protein surroundings reorganization needed to accommodate the donor-acceptor charge-transfer state.

FREE RADICAL-MEDIATED HETEROGENEOUS PHOTOCATALYTIC REDUCTION OF METAL IONS IN UV-IRRADIATED TITANIUM DIOXIDE SUSPENSIONS

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Heterogeneous photocatalysis using UV-irradiated titanium dioxide (TiO₂) suspensions or films in aqueous media, is now a mature field. The photocatalytic reduction of metal ions in such media has both fundamental and practical interest. While metal ions with rather positive standard reduction potentials [i.e., positive of 0 V versus the standard hydrogen electrode reference (SHE)] such as Cu²⁺, Cr⁶⁺, Au³⁺, Ag⁺ etc, have been widely investigated, only few studies exist on metal ions that are much more difficult to be reduced, for example: Cd²⁺, Zn²⁺, Mn²⁺, Tl⁺. In this paper, we consider the photocatalytic reduction of these four species using organic free radicals that are photogenerated at the TiO₂/water interface. Formate was used as the reducing agent (i.e., free radical source) in this study.

Trends in the reactivity of the four metal ions above were compared with corresponding rate constants reported in the literature for the homogeneous reactions of these metal ions with CO₂^{•-} in aqueous media. Using Tl⁺ as a model metal ion, a simple kinetics scheme was developed for the indirect reduction route, leading to a rate expression:

$$R_5 = k'k'' [D^-] [M^+]$$

with k' and k'' being composite rate constants, D^- is the formate ion and M^+ is the Tl⁺ ion. The initial photocatalytic reduction rate, R_5 , was plotted against the initial concentration of formate with Tl⁺ concentration held constant. Similar plots were also constructed from experiments varying the Tl⁺ ion concentration at fixed formate ion levels. Such plots are shown in Figure 1. An important test of the efficacy of our model is that the values obtained for the slopes ($k'k''$) from the sets of experiments are the same within experimental error. This aspect along with other trends relating to the indirect photocatalytic reduction route will be presented in the poster.

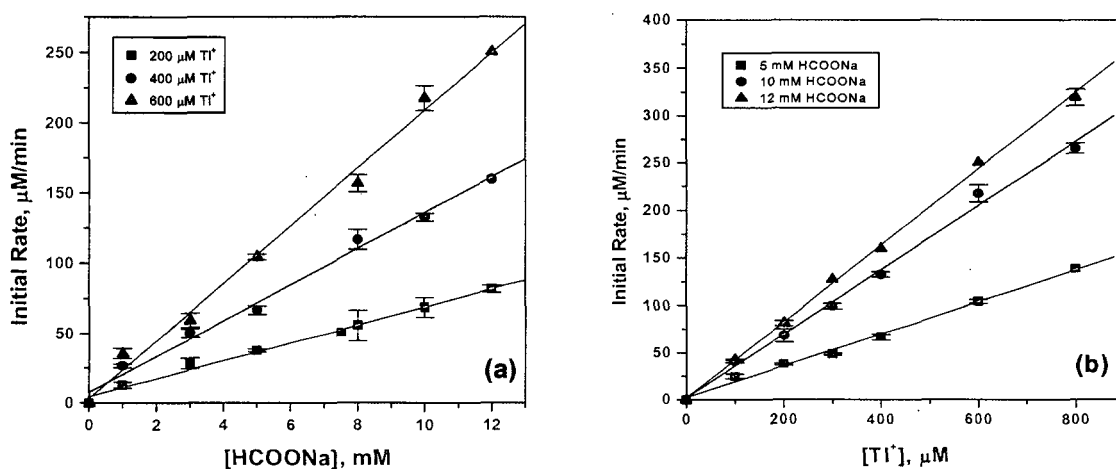


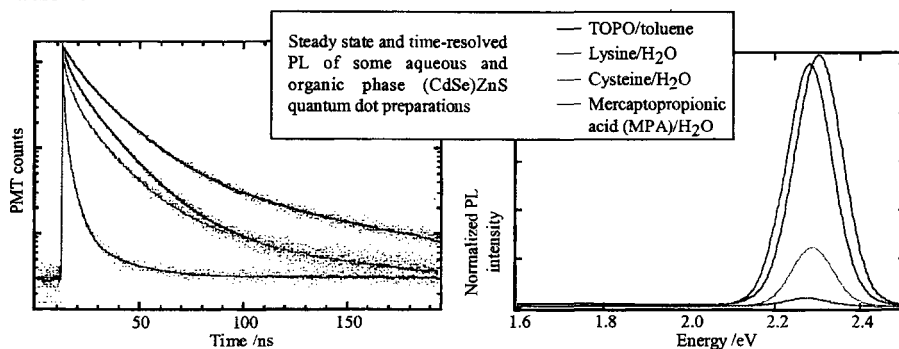
Figure 1. (a) Test of the model prediction (represented by the rate expression above) for three initial concentrations of Tl(I). (b) As in (a) but for the set of experiments where Tl(I) concentration was varied while holding the formate concentration constant at the three values shown. The lines are least-squares fits and the error bars are shown for cases where replicate experiments were performed.

INTERACTIONS OF COLLOIDAL QUANTUM DOTS WITH AMINO ACIDS, POLYPEPTIDES AND PROTEINS

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We have developed procedures to replace conventional tri-octylphosphine oxide (TOPO), group used in the synthesis of colloidal (CdSe)ZnS core-shell quantum dots (QDs), with natural and modified amino acids. Amino acids not only confer water solubility on the QDs but also offer insights into the most suitable groups for binding proteins and polypeptides to the quantum dot surface. We have specifically investigated the three most nucleophilic, amino acids: cysteine, lysine, and histidine; containing thiol, primary amine and imidazole groups, respectively. Using photoluminescence (PL) spectroscopy, we have studied the efficiency with which these species bind to the quantum dot surface, the stability of the water-soluble product and the ability for the group to negate the effect of surface states. Lysine has proved to bind most strongly and passivate the surface to such an extent that the QD PL quantum efficiency, and stability in solution closely resembles that of the original TOPO-capped species; however, lysine conjugates are only stable at $\text{pH} > 11$. This value is too high for studying interactions with most proteins, which denature at high pH, but they have been used to study the interactions with single-wall carbon nanotubes (SWNTs), which are soluble and stable at high pH. Cysteine is very effective at displacing TOPO and can produce metastable solutions at neutral pH values. However, over a few hours (pH dependent) thiol oxidation occurs forming cysteine, with a disulphide bond, which, as it is a poor ligand, causes QD precipitation. Oxidation can be inhibited with dithiothreitol and other well-known biochemical reagents. Histidine binds slowly to the dots but, when formed, produces compounds with good reasonable stability and PL efficiency at neutral pH. Interestingly, calculations show that this group has the strongest surface binding energy (in the absence of solvent) of all three amino acids.

Exploiting the ability of these amino acids to act as suitable capping groups, we have designed strategies to direct the interaction of QDs with proteins in a number of ways. The amino acid ligand can be biotinylated and incubated with avidin-containing proteins to form an irreversibly bound, QD-protein bioconjugate. Alternatively, genetic modification of the N- and C- termini of self-assembling proteins with suitably nucleophilic peptide chains can facilitate a more selective binding of proteins directly to the QD surface. Both approaches afford better control of the construction of QD arrays or chains, either on substrates (see abstract S-Y. Ding) or as free entities in solution.



EVIDENCE FOR HIGHLY DISPERSIVE PRIMARY CHARGE SEPARATION KINETICS AND GROSS HETEROGENEITY IN THE ISOLATED PS II REACTION CENTER OF GREEN PLANTS

K. Riley, R. Jankowiak, G. J. Small and V. Zazubovich

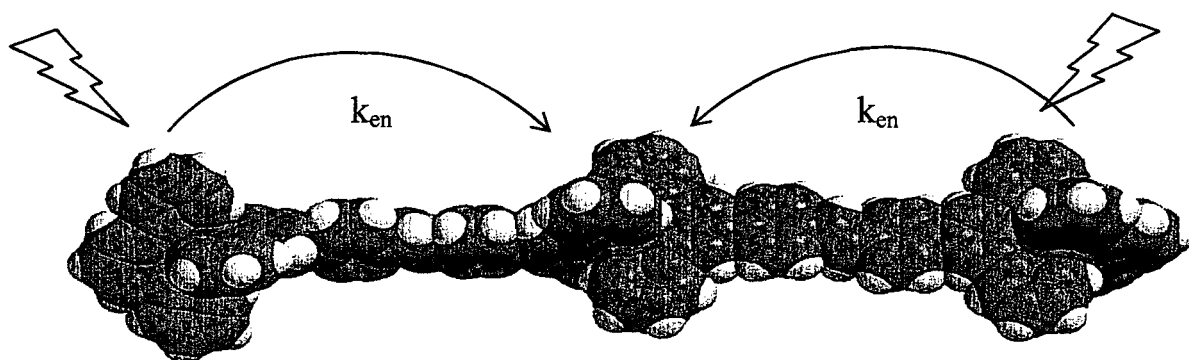
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Despite the availability of an X-ray structure and many frequency and time domain spectroscopic studies, important issues related to structural heterogeneity, $Q_y(S_1)$ excitonic structure, primary charge separation (CS) and excitation energy transfer dynamics of the isolated reaction center (RC) of photosystem II (PS II) remain unsolved. The main issues to be addressed in this presentation are (1) whether or not the primary CS kinetics are highly dispersive (due to structural heterogeneity), as proposed by Prokhorenko and Holzwarth (*J. Phys. Chem. B* **2000**, 104, 11563) based on photon echo data (1.3 K), and (2) the nature of the relatively weak lowest-energy Q_y absorption band at ~ 684 nm that appears as a shoulder on the intense primary electron donor band (P680) at liquid helium temperatures. Results of low temperature persistent non-photochemical hole burning (NPHB) and triplet bottleneck hole burning (TBHB) spectroscopic experiments (including effects of pressure and external electric (Stark) fields) are presented for the RC from higher plants. It is found that both NPHB and TBHB are possible within the P680 and 684 nm bands. Both types of hole spectra exhibit a weak dependence on burn wavelength (λ_B) between 680 and 686 nm. Furthermore, the permanent dipole moment change ($f \Delta\mu$, with f the local field correction), as determined by Stark-NPHB spectroscopy, is identical (0.9 ± 0.1 D) for the two bands, as are the linear electron-phonon coupling parameters determined by NPHB (Huang-Rhys factors $S_{17} = 0.7$ and $S_{80} = 0.2$ for 17 cm^{-1} and 80 cm^{-1} phonons). These similarities, together with fluorescence line narrowed spectra lead us to favor the gross heterogeneity model in which the 684 nm band is the primary electron donor band (P684) of a subset of RCs that may be more intact than P680-type RCs. Several other interpretations for the 684 nm pigment(s) are discussed, but considered to be less likely than the P680-P684 model. Based on the linear pressure shift rates for the P680 and P684 nm bands determined from NPHB and TBHB spectra, it is concluded that population of either P680* (* $\equiv Q_y$ state) or P684* results in both TBHB (due to charge recombination of the primary radical ion pair) and NPHB. Importantly, acceptable theoretical simulations of the observed line-narrowed TBHB spectra were not possible using a single primary CS time. (The spectra consist of the zero-phonon hole (ZPH) and phonon sideband hole structure.) However, satisfactory fits (including λ_B and burn intensity dependences) were achieved using a distribution of CS times. The TBHB is due to P680- and P684-type RCs with the faster CS kinetics since the persistent non-photochemical holes were saturated prior to measuring the TBHB spectra. (The most efficient NPHB RCs have the slower CS kinetics as well as higher fluorescence quantum yields.) For the TBHB spectra the same distribution (Weibull) was used for the P680- and P684-type RCs. The distribution describes quite well the distribution of Prokhorenko and Holzwarth for CS times shorter than 25 ps. It was found that the values of parameters (e.g. electron-phonon coupling, site distribution function) used to simulate the NPHB spectra also provided reasonable fits to the TBHB spectra. Finally, the data indicate that electron exchange does not contribute significantly to the inter-pigment interactions.

MIXED Ru(II) / Fe(II) COMPLEXES OF TERPYRIDYL PHENYLENEVINYLENE LIGANDS WITH LONG EXCITED STATE LIFETIMES

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Terpyridyl complexes of Group VIII metals have been employed with increasing regularity in recent years as sensitizers for light induced electron transfer reactions. From a synthetic viewpoint they are interesting because modification of the central pyridine can allow straightforward preparation of bridging ligands that can be used in the preparation of oligometallic light harvesting chromophores.¹ However, terpyridyl complexes of Fe(II) and Ru(II) generally have relatively low energy ligand field states that result in nonradiative relaxation of the photoactive MLCT state on the ps time scale. While this is not a problem for charge injection into semiconductors, it does limit possibilities for making efficient light harvesting arrays since the efficiency of self-exchange energy transfer processes will be decreased by competitive nonradiative relaxation reactions. Recently we have found that this problem can be avoided by using bridging ligands that have low energy excited states localized on the bridging ligand. This poster serves to illustrate (a) the excited state lifetime of bimetallic Ru(II) complexes having bis-terpyridyl phenylene vinylene bridging ligands is a strong function of the degree of unsaturation in the bridge and (b) efficient energy migration to the lowest energy chromophores occurs in mixed metal trimetallic complexes consisting of two terminal Ru(II) terpyridyl chromophores and a central Fe(II) or Os(II) terpyridyl complex. A representative complex is shown below.



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(1) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelli, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993-19.

VIBRATIONAL DYNAMICS IN PHOTOINDUCED ELECTRON TRANSFER

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One objective of the prior funding period was to study how vibrational states (geometry distortions) are involved in photoinduced electron transfer rates. A second objective was to begin studies of reorganization energy in electron transfer, where the environment around the molecules is constrained similar to polymeric or other solid state media.

We have performed DFT calculations for the $V(CO)_6$ radical, the $Co(Cp)_2$ radical, and the $Co(Cp)_2|V(CO)_6$ radical pair. Primary interest was in the $V(CO)_6$ radical in both the isolated species and in the radical pair. Several stable structures were found for the Jahn-Teller active 17 electron $V(CO)_6$ radical for both the isolated radical and in the radical pair. We confirmed prior studies that identified a D_{3d} structure as most stable, a D_{4h} structure at higher energies and a transition state of D_{2h} structure. We also found a new stable structure of C_{2h} geometry that is close ($\sim 130\text{ cm}^{-1}$) to the lowest energy D_{3d} structure. We calculated the relative energies of the isolated radical structures and the radical pair structures as a function of the metal-metal distance. In addition, we estimated interconversion barriers between these structures and found similar results for both the isolated radical and the radical pair. This similarity suggests that the radical pair is rapidly interconverting at room temperature in the same manner as the isolated radical. This has implications in the interpretations of ultrafast electron transfer dynamics. Specifically, a rise was observed for the radical carbonyl stretch vibration in the radical pair when the ion pair charge transfer absorption created excess vibrational energy in the radical pair. The rise time is not likely to be due to rapid geometric interconversion, but is probably due to anharmonic coupling between highly excited low frequency modes and the high frequency carbonyl stretches leading to a broadened carbonyl absorption band immediately after excitation. The observed rise time in absorption is conjectured to correlate with cooling of the low frequency vibrations to the solvent over 200 fs.

Electron transfer rates were measured for methyl viologen-hexacyanoferrate and methyl viologen-hydroquinone complexes in solution and in trehalose-water glass matrices. Rates measured in the glass were a factor of 2.5-3 smaller than those observed in aqueous solution, whereas linear absorption spectra were shifted by less than 300 cm^{-1} with only minor differences in line shape. Our data is consistent with a water solvation layer around the ion pair that is interacting via hydrogen bonds with a water-trehalose glass matrix. The electron transfer rate data is sensitive to changes in the reorientational motions of the water solvation layers, and our data can be modeled by adding a 10% component of $>15\text{ ps}$ diffusive bath relaxation to a water solvation model. These data suggest a microscopic picture where the immediate environment around the ion pair is of limited extent, perhaps only 2-3 solvent layers. The general significance of this work is to develop a more complete understanding of internal and external reorganization in electron transfer, since many practical applications of electron transfer, such as in novel photovoltaic systems, might involve electron transfer active molecules having local interactions in a polymeric or other solid state matrix.

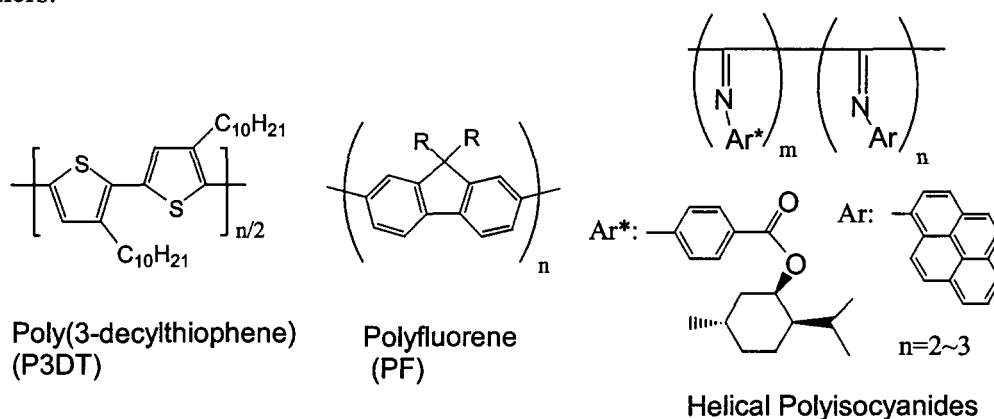
CHARGE DELOCALIZATION IN CONDUCTING POLYMERS

Norihiko Takeda, Sadayuki Asaoka, and John R. Miller

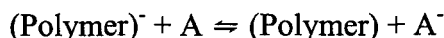
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Negative (electrons) or positive (holes) charges can be attached to conducting polymers in organic solvents by chemical or pulse-radiolysis techniques. Examples of conducting polymers studied are shown below. Electron attachment (reduction) of P3DT and PF in THF resulted in bleaching of neutral absorption band (450nm and 380nm, respectively) and growth of two radical anion absorption bands in visible and near-IR region. By comparing absorption coefficients for neutral and anion bands, delocalization lengths of anions were estimated to be about 10 units for P3DT and 5 units for PF. The different values for two polymers are consistent with the longer unit length of PF compared to P3DT. Chemical reduction experiments also showed that multiple charges can be injected into a single polymer chain without changing spectral shapes, suggesting radical ions can exist as separate polarons up to a certain point in these long molecules.

Charge delocalization lengths depend on structural deformation of the polymer backbone. Semiempirical (AM1) and DFT calculations were performed to get insights into structural relaxation upon charge attachment. Comparisons with oligomers with different lengths will be investigated to support the estimated delocalization lengths for polymers.



The equilibrium between conducting polymers and electron acceptors with known electrochemical potentials were studied by pulse-radiolysis to establish accurate reduction potentials of these polymers. The results are compared with electrochemical studies of same molecules in THF electrolytes.



The fundamental information obtained about charges injected into conducting polymers in this study will be useful for future studies of these materials as molecular wires in solar energy conversion devices. Polyfluorenes end-capped with charge acceptors are under investigation to get further information about charges attached to conducting polymers.

INTERROGATING PHOTOINDUCED ELECTRON TRANSFER REACTIONS USING VISIBLE PUMP / IR PROBE SPECTROSCOPY

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We have demonstrated the utility of time-resolved visible pump / mid-infra-red (IR) probe spectroscopy to interrogate directly, and provide unique information regarding, conformationally dependent photoinduced ET dynamics and the subsequent structural evolution of the resulting charge-separated (CS) state. Exemplary polarized visible pump / IR probe experiments involving *N*-[5-(10,20-diphenylporphinato)zinc(II)-*N'*-(octyl)pyromellitic diimide (**PZn-PI**) and [5-[4'-(*N*-(*N'*-octyl)pyromellitic diimide)phenyl]ethynyl]-10,20-diphenylporphinato]zinc(II) (**PZn()PI**) show that it is possible to assess the mean **PZn**-to-**PI** interplanar torsional angle of electronically excited structural conformers that undergo ET within the sub-ps time domain for both of these donor-spacer-acceptor (**D-Sp-A**) systems. Further transient spectroscopic experiments carried out on **PZn()PI** determine how this angle evolves with time. Because vibrational transition moments are often known and typically localized, this work underscores that polarized visible pump / IR probe spectroscopy defines a valuable tool to interrogate structure in both electronically-excited and CS states; this fact, coupled with the ultrafast time resolution and high sensitivity offered by this technique, make it ideally suited to probe a range of mechanistic issues relevant to charge transfer reactions. Work in progress shows that this technique can for example, provide a direct measure of the extent to which charge migrates in a photoinduced electron transfer event.

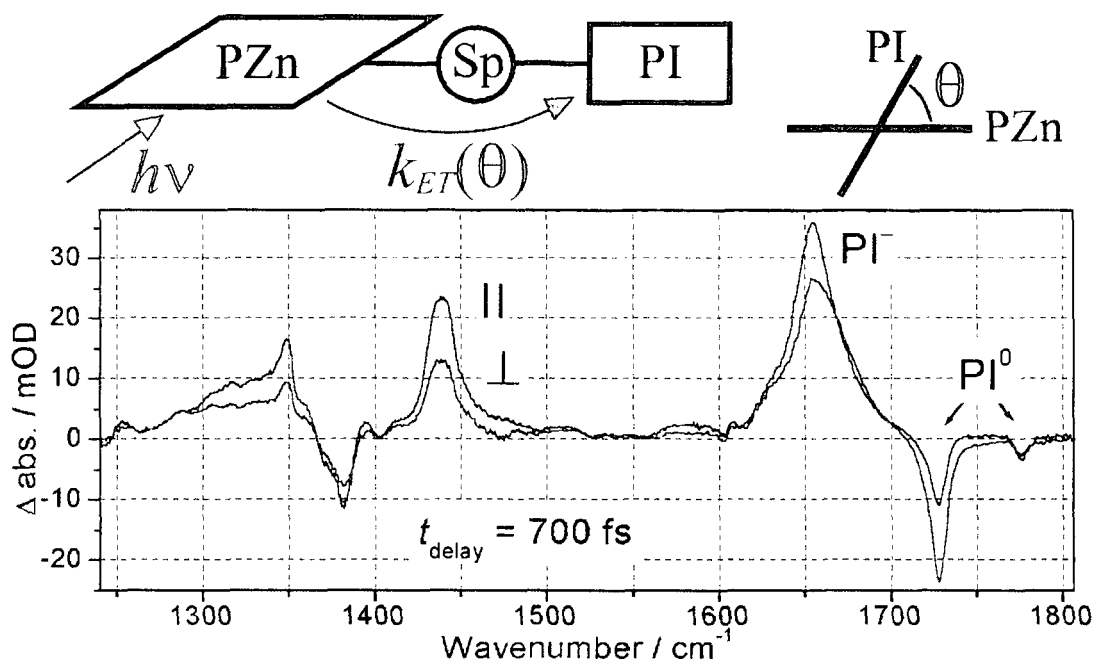


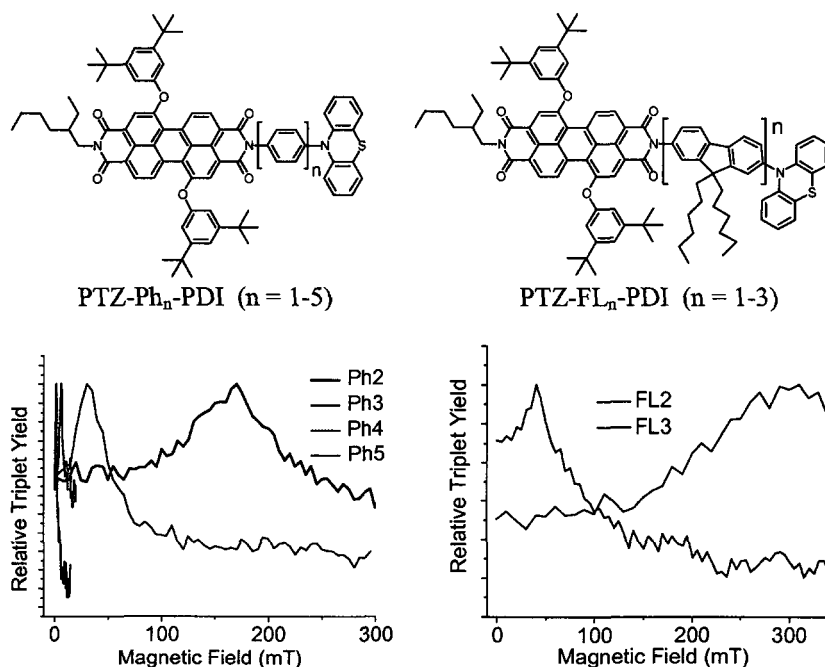
Figure 1. Polarized transient IR spectra of **PZn()PI** with deconvoluted A- and B-polarized absorptive components highlighted.

MAKING A MOLECULAR WIRE: PHOTOINDUCED CHARGE AND SPIN TRANSPORT THROUGH CONJUGATED OLIGOMERS

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A molecular wire is best understood as a molecular bridge that can move charge rapidly and efficiently over many chemical bond lengths. A major challenge lies in finding molecules that exhibit efficient long distance charge transport mechanisms for applications in solar energy conversion. Charge transport through molecules occurs primarily by means of two mechanisms, coherent superexchange and incoherent charge hopping. Rates of charge transport through molecules in which superexchange dominates decrease approximately exponentially with distance, which precludes using these molecules as effective molecular wires. In contrast, charge transport rates through molecules in which incoherent charge hopping prevails should display nearly distance independent, wire-like behavior. To achieve this goal one must 1) isolate the contributions of each mechanism to charge transport, 2) find the link between these contributions and the energy levels of the system, and 3) choose redox components (donors, bridges, and acceptors) that drive the system toward incoherent behavior at long distances. Here we compare results on two D-B-A systems that address these issues directly, where D = phenothiazine (PTZ), B = *p*-oligophenylene (Ph_{*n*}, *n*=1-5) or *p*-oligofluorene (FL_{*n*}, *n*=1-3), and A = perylene-3,4,9,10-bis(dicarboximide) (PDI), by measuring the interaction between two unpaired spins within the system's charge separated state via magnetic field effects on the yield of radical pair and triplet recombination product.



CAROTENOID RADICALS AND THEIR POTENTIAL INVOLVEMENT IN THE REGULATION OF PHOTOSYNTHETIC LIGHT HARVESTING

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Regulation of light excitation energy in the photosynthetic apparatus is vital for plants. A specific process, namely nonphotochemical quenching (NPQ), is essential for fast adaptation to changes in incident light intensity because it maintains a balance between light harvesting and photoprotection. Although NPQ, which is characterized by chlorophyll fluorescence quenching, has been known and studied for years, the exact underlying photophysical mechanism is unknown. In order to gain deeper insight on the mechanism of NPQ, we performed an ultrafast spectroscopic study on intact thylakoid membranes in two states, one in which maximum, steady state NPQ existed in the photosynthetic apparatus (quenched) and the other in which no NPQ existed (unquenched).

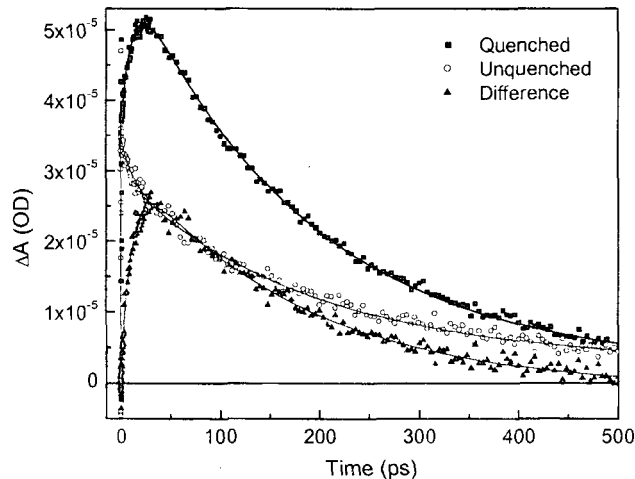


Figure. Kinetic traces of thylakoid membranes from spinach excited at 664 nm and detected at 1000 nm under quenched (full squares) and unquenched (open circles) conditions. Full triangles represent the difference of quenched and unquenched traces.

After excitation of thylakoid membranes from spinach at 664 nm, corresponding to the blue edge of the chlorophyll Q_y absorption band, the kinetic traces probed in the near-IR region (900 – 1080 nm), where the absorption of the carotenoid radical is expected, were markedly different for quenched and unquenched conditions (see Figure). The difference of the two kinetic traces (quenched – unquenched) is well fit by two exponential functions with time constants of ~ 10 ps and ~ 180 ps for the rise and decay components, respectively. Additional studies on *Arabidopsis thaliana* plant mutants confirm that the different kinetics observed in spinach during quenched and unquenched conditions depend on all of the known requirements for NPQ, namely the presence of the carotenoid zeaxanthin, the PsbS protein and the transthylakoid pH gradient (ΔpH).

The implications of the observed dynamics will be discussed in terms of the information they provide about the quencher and the quenching mechanism.

RESOLVING THE CONFORMATIONAL ENVELOPE FOR DNA IN SOLUTION WITH WIDE ANGLE X-RAY SCATTERING

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In recent years, synthetic DNA is widely used as a building block for molecular electronics, and as a linker for light-activated donor/acceptor assemblies, owing to its good conductivity and rigid structure. Information on the structure and conformational dynamics of DNA in solution is critical for fully understanding its chemical functions. We have begun a program that examines synthetic DNA structure and structural dynamics in solution, and DNA-guest interactions, using synchrotron wide angle X-ray scattering (WAXS). Scattering patterns measured to 2 angstrom resolution were found to resolve both nearest-neighbor and longer range base pair distance correlations. Measurements and molecular modeling studies on a series of sequences and temperature show that scattering peak positions are strongly sensitive to DNA conformation while configurational dynamics are reflected in peak broadening and attenuation. Significant differences were observed between poly(A)-poly(T) and poly(AT) sequences (Fig 1), and between poly(CG) in low salt and in high salt solution, respectively. X-ray scattering measurements were also done for a few DNA sequences in order to compare solution state conformation with differing structural models obtained from crystallography and NMR methods (Fig 2). In conclusion, wide-angle scattering provides a direct, high-throughput structural approach for quantitative identification of DNA structure and configurational dispersion in functionally relevant solution conditions.

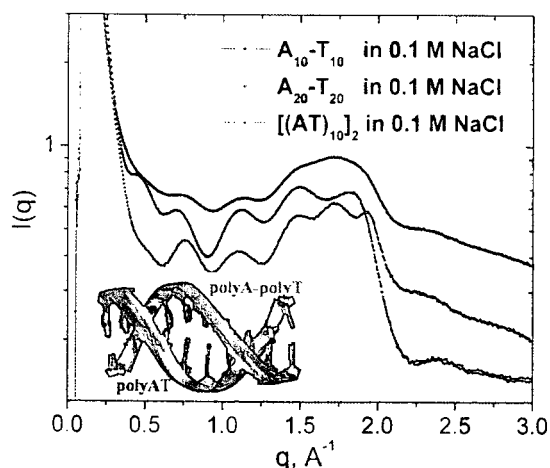


Figure 1. WAXS for poly(A)-poly(T) and poly(AT)

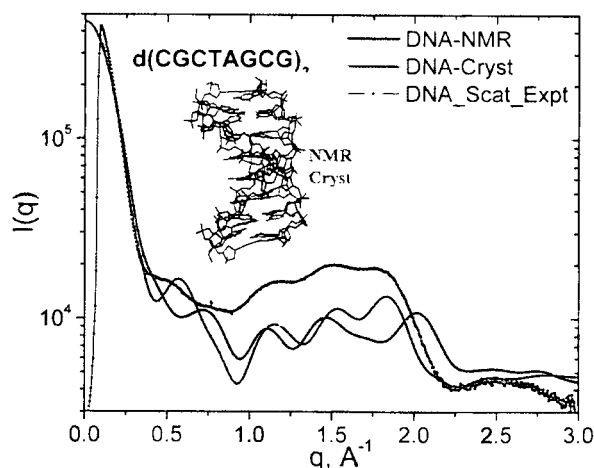


Figure 2. Comparison with crystallographic and NMR structural models.

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