Final Report

Fundamental Studies of Charge Migration and Delocalization Relevant to Solar Energy Conversion

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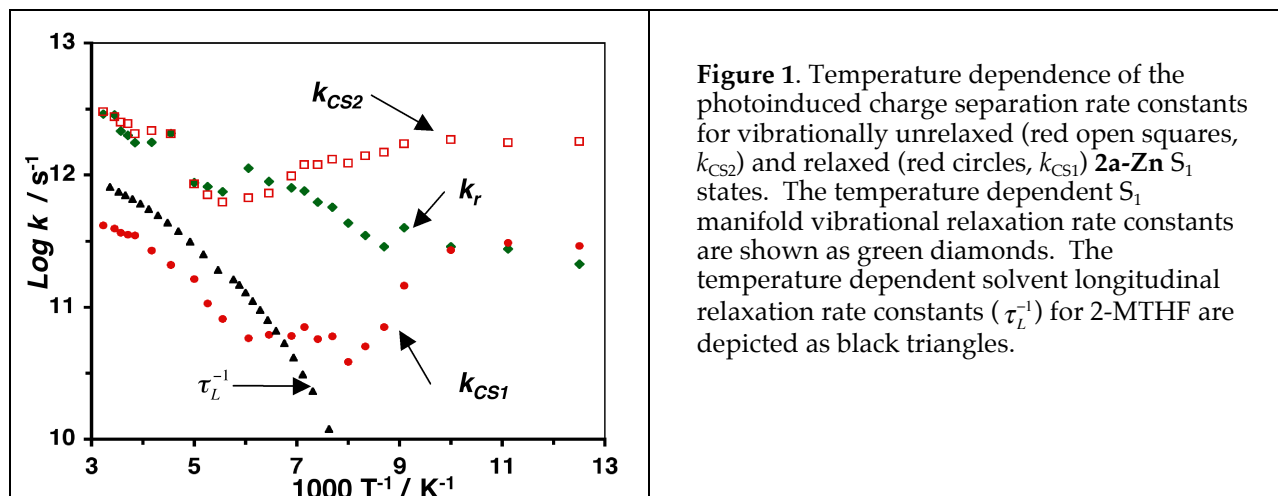Ph: 919-660-1670
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Fundamental Studies of Charge Migration and Delocalization Relevant to Solar Energy Conversion (DE-FGO2-02ER15299)

Final Report: This program aimed to understand the molecular-level principles by which complex chemical systems carry out photochemical charge separation, transport, and storage, and how these insights could impact the design of practical solar energy conversion and storage devices. Towards these goals, this program focused on: (1) carrying out fundamental mechanistic and transient dynamical studies of proton-coupled electron-transfer (PCET) reactions; (2) characterizing and interrogating via electron paramagnetic resonance (EPR) spectroscopic methods novel conjugated materials that feature large charge delocalization lengths; and (3) exploring excitation delocalization and migration, as well as polaron transport properties of meso-scale assemblies that are capable of segregating light-harvesting antennae, nanoscale wire-like conduction elements, and distinct oxidizing and reducing environments.

Key scientific results achieved through the aegis of DE-FGO2-02ER15299 include:

A Temperature-Dependent Mechanistic Transition for Photoinduced Electron Transfer Modulated by Excited-State Vibrational Relaxation Dynamics. The electron transfer (ET) dynamics of an unusually rigid π-stacked (porphinato)zinc(II)-spacer-quinone (PZn-Q) system, [5-[8′-(4′′-[8′′′-(2′′′′,5′′′′-benzoquinonyl)-1′′′-naphthyl]-1′′-phenyl)-1′-naphthyl]-10,20-diphenylporphinato]zinc(II) (**2a-Zn**), in which sub van der Waals interplanar distances separate juxtaposed porphyryl, aromatic bridge, and quinonyl components of this assembly, have been measured by ultrafast pump-probe transient absorption spectroscopy over a 80-320 K temperature range in 2-methyl tetrahydrofuran (2-MTHF) solvent. Analyses of the photoinduced charge separation (CS) rate data are presented within the context of several different theoretical frameworks. Experiments show that at higher temperatures, the initially prepared **2a-Zn** vibronically excited S_1 state relaxes on an ultrafast timescale, and ET is observed exclusively from the equilibrated lowest energy S_1 state (CS1). As the temperature decreases, production of the photoinduced charge-separated state directly from the vibrationally unrelaxed S_1 state (CS2) becomes competitive with the vibrational relaxation timescale. At the lowest experimentally

interrogated temperature (~80 K), CS2 defines the dominant ET pathway. ET from the vibrationally unrelaxed S_1 state is temperature independent and manifests a subpicosecond time constant; in contrast, the CS1 rate constant is temperature dependent, exhibiting time constants ranging from $4{\times}10^{10}$ s^{-1} to $4{\times}10^{11}$ s^{-1}, and is correlated strongly with the temperature-dependent solvent dielectric relaxation timescale over a significant temperature domain. This work not only documents a rare, if not unique example of a system where temperature dependent photoinduced charge separation (CS) dynamics from vibrationally relaxed and unrelaxed S_1 states can be differentiated, but demonstrates a temperature-dependent mechanistic transition of photoinduced CS from the nonadiabatic to the solvent-controlled adiabatic regime, followed by a second temperature-dependent mechanistic evolution where CS becomes decoupled from solvent dynamics and is determined by the extent to which the vibrationally unrelaxed S_1 state is populated.

Figure 1. Temperature dependence of the photoinduced charge separation rate constants for vibrationally unrelaxed (red open squares, k_{CS2}) and relaxed (red circles, k_{CS1}) **2a-Zn** S_1 states. The temperature dependent S_1 manifold vibrational relaxation rate constants are shown as green diamonds. The temperature dependent solvent longitudinal relaxation rate constants (τ_L^{-1}) for 2-MTHF are depicted as black triangles.

Orientational Dependence of Cofacial Porphyrin-Quinone Electronic Interactions within the Strong Coupling Regime. The relative magnitudes of the electronic coupling matrix element (H_{DA}) in two electronically excited face-to-face (porphinato)zinc(II)-quinone (PZn-Q) assemblies (^{1}1β-ZnA* and ^{1}1β-ZnB*) that feature a sub-van der Waals donor-acceptor (D-A) interplanar separation, and differ only with respect to the quinonyl orientation relative to the porphyrin plane, were evaluated. Experiment indicates that the extent to which ([P-Q]*, ψ_e) and CT ([P$^+$-Q$^-$], ψ_{CT}) configurations are mixed in ^{1}1β-ZnA* greatly exceeds that for the ^{1}1β-ZnB* structure. A simple orbital overlap analysis

suggests that the weaker coupling in ^{1}1β-ZnB* relative to ^{1}1β-ZnA* arises from orientation-driven overlap cancellations, and differences in the extent to which the Q O atoms contribute to D-A mixing. Of the handful of studies that probe the dependence of D-A orientation upon ET, few, if any, have probed its impact in the limit of strong D-A electronic interaction. This study demonstrates the sensitivity of CT transition moments to D-A orientation at contact, and underscores the strong dependence of D-A coupling upon the nature of π-stacking. Ongoing work focuses on modeling and probing the factors that determine the magnitude of D-A electronic coupling in ^{1}1β-ZnA* and ^{1}1β-ZnB* initially prepared excited states.
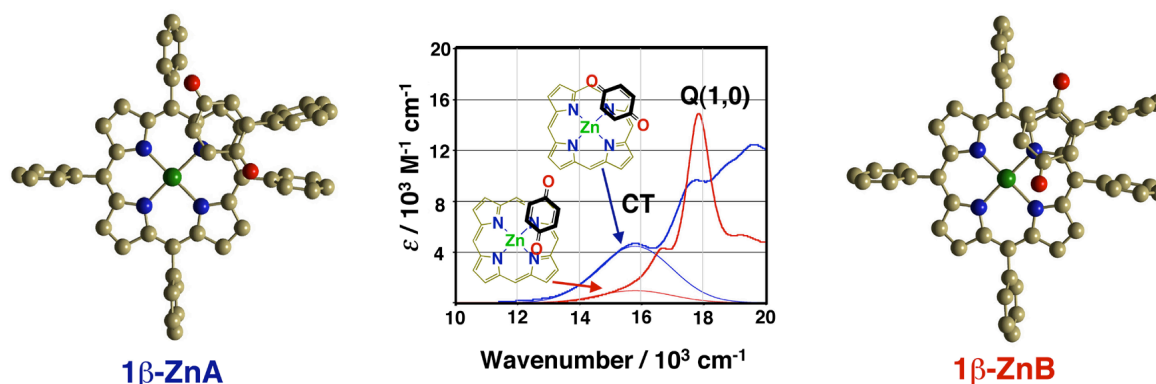
Figure 2. (a) Linear visible spectra of ^{1}β-ZnA (blue) and ^{1}β-ZnB (red); thin lines depict Gaussian deconvolutions of the CT bands.

Probing Dark Conductivities in Amorphous Solids of Sterically Unencumbered, Low Molecular Weight Ethyne-Bridged (Porphinato)zinc(II) Oligomers. Dark conductivity (DC) measurements for a family of *meso*-to-*meso* ethyne-bridged (porphinato)zinc(II) (**PZn$_n$**) oligomers that feature a wide range of peripheral ancillary substituents. These substituents confer substantial solubility to these **PZn$_n$** species, and include 2,6- and 3,5-dialkoxyphenyl groups, as well as sterically unencumbered alkylether moieties. Two- and four-probe DC data obtained for thin film and pressed pellet solid-state samples of undoped **PZn$_n$** oligomers are self-consistent, and underscore that the measured DCs for these low molecular weight oligomers span an impressively wide range ($2 \times 10^{-12} - 4 \times 10^{-5}$ S/cm). These studies illustrate that **PZn$_n$** species bearing 2,6- and 3,5-dialkoxyphenyl solubilizing groups behave as insulators over the **PZn$_1$**–**PZn$_5$** length scale, while those that feature alkylether substituents show dramatic augmentation of DC with increasing oligomer length. Comparison of **PZn$_n$** DC values to key benchmark materials provides a number of important conclusions: (i) The dark conductivity of *undoped*, low molecular

weight PZn_n oligomers rival that of porous Si; (ii) Sterically unencumbered PZn_n oligomers enable augmented inter-chain electronic coupling in the solid state and provide electronically functional thin films via direct spin casting; (iii) Ancillary group modification in PZn_5 oligomers can modulate the measured DC by more than four orders of magnitude; and (iv) Solid-state samples of an undoped PZn_5 oligomer that bears ancillary alkylether solubilizing groups possesses the largest DC yet measured for an amorphous organic materials. The established light-harvesting characteristics of PZn_n compounds coupled with these DC properties highlight the potential utility of these species in photochemical charge separation, transport, and storage.
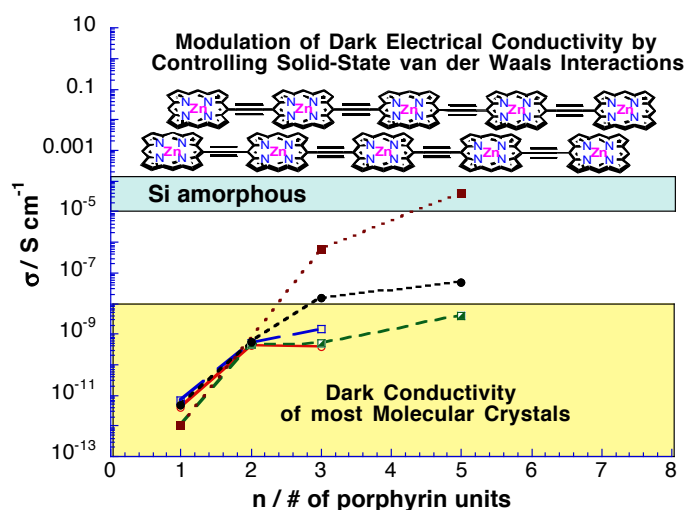
Figure 3. 2-Probe dark conductivity (DC) data for PZn_n thin films that highlight how this bulk-phase property depends on nature of macrocycle ancillary substituents and oligomer length. The established DC range of amorphous Si is highlighted. Benchmark DC values for representative undoped semiconducting polymers (not shown in Figure) include: polyacetylene (DC ~10^{-5} S/cm), polythiophene (DC <10^{-5} S/cm), polyaniline (DC ~10^{-10} S/cm). PZn_n DC values and standard deviations were determined from a minimum of 3 independent measurements.

Conjugated Chromophore Arrays with Unusually Large Polaron Delocalization Lengths. Variable temperature X-band EPR spectroscopic data for the cation radical states of *meso-to-meso* ethyne-bridged (porphinato)zinc(II) oligomers (PZn_n species) $[PZn_2\text{-}PZn_7]^+$, which span an ~18-75 Å length scale, evince peak-to-peak EPR line widths ($\Delta B_{p\text{-}p}$) that diminish with conjugation length. Analysis of these EPR data show that PZn_n^+ structures possess the largest hole polaron delocalization lengths yet measured; experiments carried out over a 4 - 298 K temperature domain show remarkably that the charge delocalization length remains invariant with temperature. These cation radical EPR data are well described by a stochastic, near barrierless, one dimensional charge

hopping model developed by Norris for N equivalent sites on a polymer chain where the theoretical EPR line width is given by: $\Delta B_{p\text{-}p}(\text{N-mer}) = (1/N^{1/2})\Delta B_{p\text{-}p}(\text{monomer})$; $\mathbf{PZn_n}^+$ oligomers are the first such systems to verify a Norris-type hole delocalization mechanism over a substantial (~75 Å) length scale (Figure 4). This study demonstrates that polymeric building blocks having low magnitude inner sphere reorganization energies enable the development of electronic materials having long polaron delocalization length.
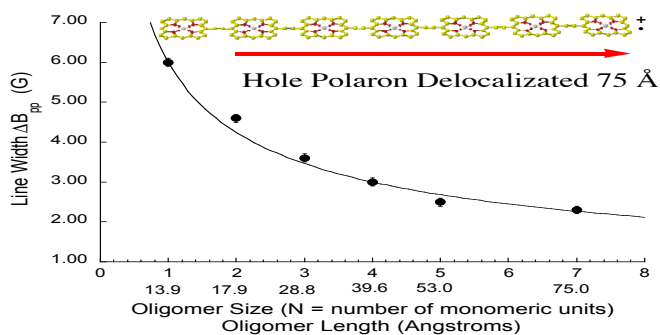
Figure 4. Plot of EPR peak-to-peak line width of the radical cationic (hole-polaron) states of $\mathbf{PZn_1}$-$\mathbf{PZn_7}$ at 298 K. The abscissa is gives oligomer size represented by number of monomeric PZn units N and oligomer length in Å. The solid line is a fit to $6.0/(N^{1/2})$ (G).

Revealing the Degree of Charge Transfer in Ground and Charge-Separated States via Ultrafast Visible Pump / Mid IR Probe Spectroscopy. We have demonstrated a new fs visible pump/mid-IR probe spectroscopic approach to assess directly the ground and excited state degrees of charge transfer (CT) in donor-spacer-acceptor (D-Sp-A) structures. Two classes of (porphinato)zinc(II) (PZn)-based D-Sp-A compounds with either quinonyl (Q) or N-(N'-octyl)pyromellitic diimide (PI) electron acceptors were interrogated. These data show that the acceptor mode frequency shift, $\Delta\nu_A$, determined by this method provides a more accurate measure of the degree of CT in ground and charge-separated states relative to other techniques which rely on the ground-state frequency shift alone; this added accuracy, coupled with the ability of this method to interrogate the electronic interaction matrix element between ground and CS states, enable determination of new experimental benchmarks to test the power of complimentary computational methods, and provides a means to probe the degree of CT in transitions that either overlap strongly with other bands or possess low oscillator strength.

Publications Acknowledging DE-FGO2-02ER15299:

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3) A Temperature-Dependent Mechanistic Transition for Photoinduced Electron Transfer Modulated by Excited-State Vibrational Relaxation Dynamics, Y. K. Kang, T. V. Duncan, and M. J. Therien, *J. Phys. Chem. B.* **2007**, *111*, 6829-6838

4)   Synthesis of Water-Soluble Poly-(*p*-phenyleneethynylene) in Neat Water Under Aerobic Conditions via Suzuki-Miyaura Polycondensatin using a Diborylethyne Synthon, Y. K. Kang, P. Deria, P. J. Carroll, and M. J. Therien, *Org. Lett.* **2008**, *10*, 1341-1344.

5)   Ultrafast Excited State Dynamics of Nanoscale Near Infrared Emissive Polymersomes, T. V. Duncan, P. P. Ghoroghchian, I. V. Rubstov, D. A. Hammer, and M. J. Therien, *J. Am. Chem. Soc.* **2008**, *130*, 9773-9784.