Ultrafast photoinduced electron transfer reactions in supramolecular arrays: From charge separation and storage to molecular switches

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ABSTRACT

Photochemical electron transfer reactions on a picosecond time scale have been studied in two covalently-linked donor-acceptor systems. The first molecule is a chlorophyll-porphyrin-quinone triad that closely mimics photosynthetic charge separation by undergoing picosecond electron transfer in low temperature glasses to yield a radical ion pair that lives for 2 ms and exhibits spin-polarization. The second molecule is an electron donor-acceptor-donor molecule, consisting of two porphyrin donors rigidly attached to opposite ends of the two-electron acceptor N,N'-diphenyl-3,4,9,10-perylenebis(dicarboximide). This molecule acts as a light intensity dependent molecular switch on a picosecond time scale.

1. INTRODUCTION

### 1.1 Donor–acceptor systems for charge separation and storage

Current work in our laboratory has focused on the influence of solvent motion on the rates and energetics of photochemical charge separation in glassy solids.[1] The efficiencies of many non-adiabatic electron transfer reactions involving photochemical electron donors with relatively low excited state energies, such as porphyrins and chlorophylls, are poor in the solid state. Recent work has shown that placing a porphyrin-acceptor system in a glassy solid at low temperature significantly raises the energy of its ion-pair state. This destabilization can be as much as 0.8 eV relative to the ion pair state energy in a polar liquid. Armed with this information we have set out to design photochemical systems that produce long-lived radical ion pairs in glassy solids with high quantum efficiency. These systems maintain their efficiency when placed in other glassy matrices, such as polymers.

An important consequence of this effort is the design of molecules that minimize the electronic interaction between the oxidized donor and reduced acceptor. This minimization can be attained by careful design of the spacer groups linking the donor and acceptor and by using more than a single electron transfer step to increase the distance between the separated charges as is done in natural photosynthesis.[2] Semi-classical electron transfer theory predicts that the rate constant for charge recombination, k_{cr}, depends both on the electronic coupling matrix element, V, between the radicals within the ion-pair and the Franck-Condon weighted density of states, FCWD.[3] The FCWD term depends on the free energy of the recombination reaction, as originally given by Marcus [4]:

$$k_{cr} = (2\pi/h)\, V^2 \cdot FCWD \tag{1}$$

For an optimized free energy of reaction, equation 1 predicts that a radical ion pair that lives for milliseconds should possess $V < 0.001$ cm^{-1}. Under these conditions the electron-electron exchange interaction between the radicals, $2J$, which is on the same order of magnitude as V, is sufficiently weak that differences in local magnetic fields surrounding each radical result in singlet-triplet mixing of the radical pair spin

sublevels.[5] This mixing produces a non-Boltzmann population of the spin sublevels of the radical pair and may result in the appearance of spin-polarized EPR spectra. Achieving high quantum yield charge separation in low temperature solids is a prerequisite for observing the structure dependent, anisotropic spin-spin interactions, such as the dipolar interaction, D, in radical pairs. Such spectra have been reported recently for the first time for a molecular triad in the solid state.[6] This work has been extended by the preparation of **1**, the first molecule based on a chlorophyll electron donor to show spin-polarization in the solid state in a low temperature glass.

ZC   ZP   NQ

1

1.2 Donor–acceptor systems for molecular switching

Molecular electronic switches, wires, micro-sensors for chemical analysis, and opto-electronic components for use in optical computing are currently under active investigation.[7-13] The principal advantages of using molecules in these applications are high component density, increased response speeds, and high energy efficiency. The design and production of energy-efficient, state-of-the-art electronic devices depends increasingly on the ability to produce ever-higher densities of circuit elements within integrated circuits.[13] Since energy and electron transfer processes within molecules can take place on a picosecond time scale, it should be possible to produce efficient devices that respond very rapidly. Molecules that employ reversible electron transfer reactions for optical switching should possess both speed and photostability advantages over molecular switches based on photochemical changes in molecular structure.

We have designed an electron donor-acceptor-donor molecule, **2**, consisting of two porphyrins, HP, rigidly attached to N,N'-diphenyl-3,4,9,10-perylene-bis(dicarboximide), PBDCI, that exhibits light intensity dependent optical switching using two ultrafast electron transfer reactions. PBDCI is an excellent, photostable [14] electron acceptor that has been employed in dyes, electro-photography, and liquid crystal displays. Compound **3** possesses a single donor, and serves as a reference.

2. EXPERIMENTAL

Compounds **1-3** were synthesized by methods that will be described in future publications. Redox potentials for each donor-acceptor molecule were determined by methods described previously.[15] The laser system used in these experiments consists of a CW mode-locked frequency-doubled Nd-YAG laser that pumps a dual-jet, dispersion compensated dye laser to obtain 160 fs pulses at 585 nm. These pulses are amplified to 15 µJ/pulse at a 1 kHz repetition rate by a three stage dye amplifier

pumped by a frequency-doubled Nd-YAG regenerative amplifier. Transient spectra are obtained using a white light continuum probe pulse with an experimental arrangement described previously.[16] Solutions with an absorbance of about 0.3 at 585 nm (1 cm pathlength cells) were used. Kinetic parameters were obtained by iterative reconvolution of the data with least squares fitting using the Levenberg-Marquardt

2

3
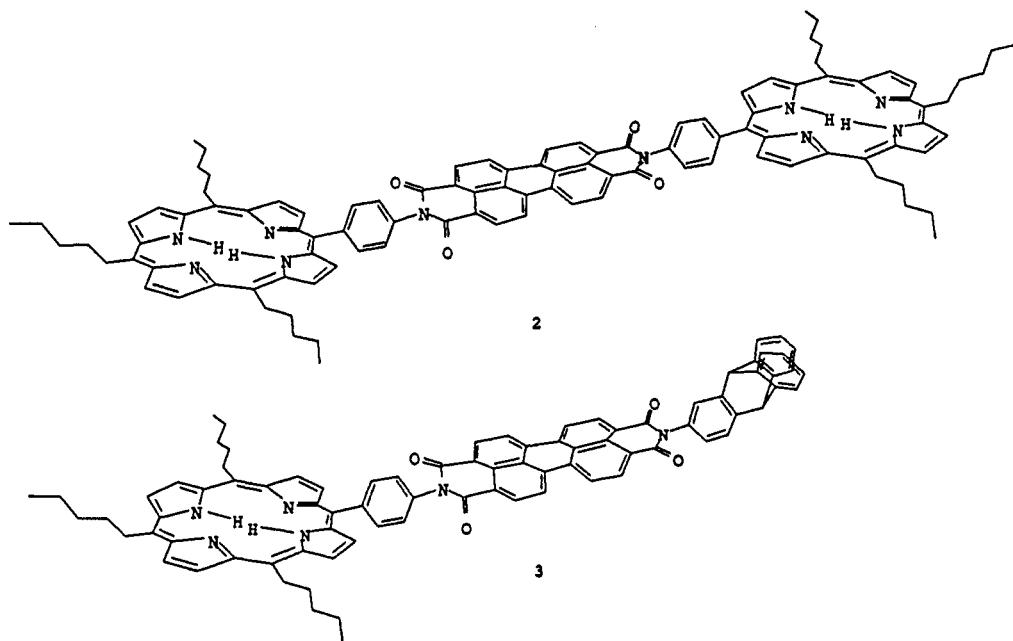
algorithm. EPR spectra were obtained on a Varian E-9 system equipped with an Air Products liquid helium low temperature dewar and controller. Sample concentrations were 5×10^{-4} M in MTHF. Samples were prepared in sealed tubes following 3 freeze-pump-thaw cycles. The samples were irradiated with light > 540 nm from a filtered xenon-arc lamp modulated at 500 Hz. The time-resolved EPR signals were detected with a lock-in amplifier. The microwave frequencies were determined with an HP frequency counter. *g*-Factors were determined by calibration with weak samples of DPPH.

3. RESULTS

3.1 Spin-polarized radical ion pairs

Femtosecond transient absorption and emission measurements with no applied magnetic field show that **1** undergoes a single step photoinduced electron transfer reaction,[1] *ZC-ZP-NQ -> ZC$^+$-ZP-NQ$^-$, in τ = 10 ps at 77 K. There is no evidence for participation of a distinct chemical intermediate of the porphyrin. Thus, the porphyrin functions to promote a superexchange interaction between ZC$^+$ and NQ$^-$.[17] The recombination reaction, ZC$^+$-ZP-NQ$^-$ -> ZC-ZP-NQ, occurs with τ = 2 ms at 77 K.

The time-resolved EPR spectrum of ZC$^+$-ZP-NQ$^-$ is given in Figure 1. The spectrum is displayed in the first derivative mode. It is readily seen that irradiation of **1** produces an intense EPR signal which consists of a strong, emissive, **E**, low field line and a weaker, absorptive, **A**, high field line. At 60 K the ZC$^+$ and NQ$^-$ free radicals display gaussian lines: ZC$^+$, g_{iso} = 2.0028, FWHM = 10 G; NQ$^-$, g_{iso} = 2.0047, FWHM = 5 G. Removing the Zn atom from ZC in **1** makes the initial electron transfer reaction endergonic in the solid state. Thus, in the absence of subsequent electron transfer excitation of **1** results in formation of the pheophytin lowest excited triplet state, which shows a strong EPR signal with zero field splitting parameters $|D|$ = 0.0397 cm^{-1} and $|E|$ = 0.0021 cm^{-1}. Replacement of either ZC or NQ in **1** by a p-tolyl group results
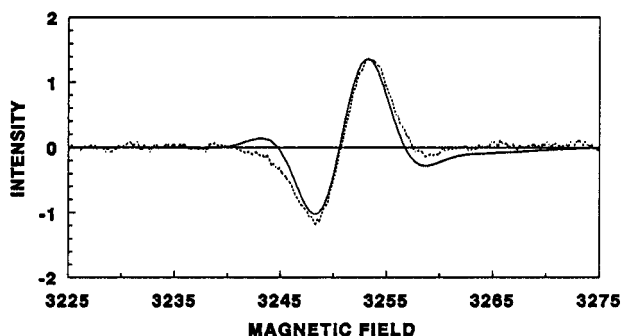
Figure 1.
Spin-polarized EPR spectrum
of ZC$^+$-ZP-NQ$^-$ at 60 K. Data
(----) and simulation (——)
using the parameters given
in the text.

in no observed EPR signals at 60 K. The solid curve in Figure 1 shows the simulation of the spin-polarized spectrum. Using the known structure of 1 the spectrum can be simulated reasonably well. Thus, as expected, the anisotropic spin-spin interactions within the radical pair are a sensitive probe of structure.

3.2   Ultrafast optical switching

The PBDCI electron acceptor in molecules 2 and 3 easily undergoes one- and two-electron reductions at $E_{1/2}^-$ = -0.50 V and $E_{1/2}^{-2}$ = -0.73 V *vs* SCE in pyridine, while $E_{1/2}^+$ for one-electron oxidation of the porphyrin is 0.92 V. The PBDCI$^-$ and PBDCI^{-2} ions possess very characteristic intense ($\epsilon \approx 10^5$ M^{-1} cm^{-1}) optical absorptions at 713 nm and 546 nm, respectively.[18] Thus, photoinduced electron transfers from the lowest excited singlet states of the porphyrins to PBDCI can be detected readily using transient optical absorption spectroscopy. Pyridine solutions (5 x 10^{-5}M) of 2 and 3 were excited with 160 fs laser pulses at 585 nm with a 1 kHz repetition rate. The optical absorbance of the samples at 585 nm were 0.3 and were limited by solubility of these compounds in pyridine. Time-resolved transient absorption spectra of 2 and 3 following excitation were monitored with a fs white light continuum. The overall instrumental response was 200 fs, the diameter of the excitation beam in the sample was 200 μ, and the pathlengths of the collinear excitation and probe beams through the stirred sample were 1 cm. Single photon excitation of both 2 and 3 result in formation of HP$^+$ - PBDCI$^-$, as characterized by the intense absorption of PBDCI$^-$ at 713 nm. The rate constant for HP$^+$ - PBDCI$^-$ formation at low light intensities in both 2 and 3 is 1.1 ± 0.2 x 10^{11} s^{-1}.

The lifetime of HP$^+$ - PBDCI$^-$ in both 2 and 3 was measured as a function of laser excitation intensity up to the 15 μJ/pulse (1.4 x 10^{17} photons-cm^{-2}, 20 photons/molecule) available to us, Figure 2. The lifetime of the HP$^+$ - PBDCI$^-$ ion-pair in 3 is independent of excitation intensity, while the lifetime of the same ion-pair in 2 decreases as the laser intensity increases, reaching a value that saturates at about half the lifetime of the ion-pair in 3. In addition, at high light intensities the rate constant for formation of HP$^+$ - PBDCI$^-$ within 2 increases to 2.0 ± 0.2 x 10^{11} s^{-1}, while that for 3 remains constant.

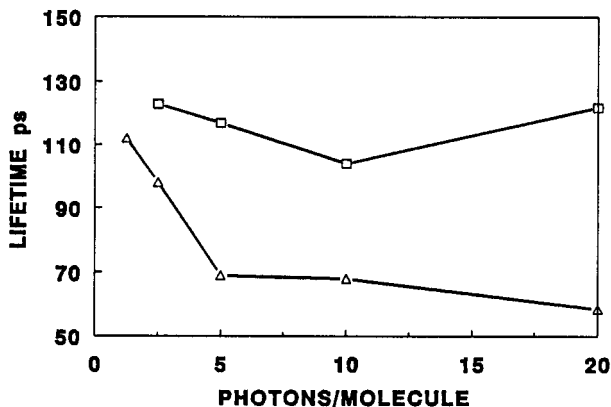Figure 2. Plot of HP$^+$ - PBDCI$^-$ lifetime within 2 (Δ) and 3 (■) *vs* excitation intensity.
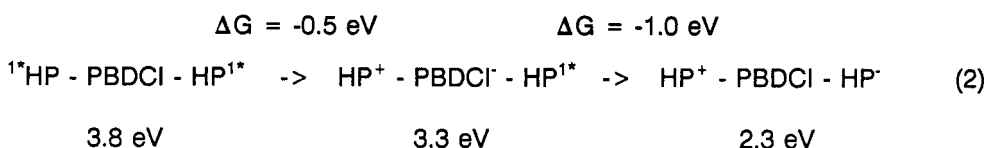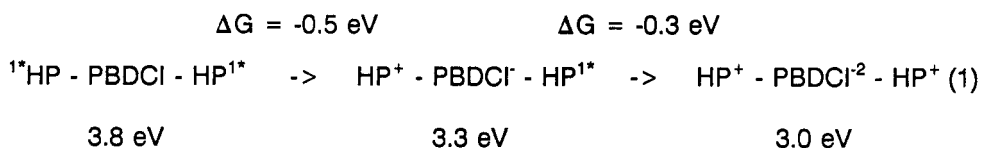
4. DISCUSSION

4.1 Radical pair phenomena

Spin polarization in ZC^+-ZP-NQ^- results from the fact that this radical pair retains a memory of the photoexcited singlet state from which it was born, i.e. the spins within the radical pair remain correlated. In this case S-T_0 mixing within ZC^+-ZP-NQ^- produces polarized spectra. If ZC^+-ZP-NQ^- is a correlated radical pair, a pair of partially overlapping anti-phase doublets is expected.[19-21] The polarization pattern observed, **E A E**, is similar to that observed for $P700^+$ - A_1^- in Photosystem I of green plants,[22] and $P865^+$-Q^- in bacterial reaction centers.[23] Recently, Stehlik et al. [24] and Norris et al. [25] have developed theoretical models that can be used to simulate these spectra. These models focus on the influence of J, D, and g-anisotropy on the EPR spectra of radical pairs. In addition, the Norris model considers the kinetics of radical pair formation. The dipolar coupling, D, between the two radicals is strictly analogous to a classical dipole-dipole interaction, and thus, depends on the distance and orientation of the radicals relative to one another. Moreover, these theories explicitly include the anisotropies of the g tensors of each radical.

In ZC^+-ZP-NQ^- the g tensor of NQ^- is quite anisotropic because about 80% of the spin density in NQ^- is centered on the oxygen atoms. The g tensor for ZC^+ is much less anisotropic. The key parameters that were included in the simulation are $J = 0$ G G, $D = -4$ G, and the orientation of ZC relative to NQ. The dipolar coupling, $D = -2$ G, for ZC^+-ZP-NQ^- was calculated using the classical expression for the magnetic dipole-dipole interaction,[26] the ZC^+ - NQ^- distance and orientation, and the spin distributions of ZC^+ and NQ^-. It is important to note that the distance and orientation between the NQ^- π system relative to that of ZC^+ used in the simulation was determined independently from the structure of **1**. The simulations fit the observed spectra reasonably well. This agreement gives us confidence that such theoretical descriptions of the anisotropic spin-spin interactions can be used to determine the structure of radical pairs for which independent detailed structural information is lacking. Further comparisons of the EPR signals from our supramolecular arrays with those from the donor-acceptor arrays within photosynthetic reaction center proteins for which no x-ray structures are known will yield information concerning the distances and orientations of the donors and acceptors within these proteins.

4.2 Molecular switching phenomena in compound 2

Since we are monitoring the population of $PBDCl^-$ in **2** and **3** at 713 nm, it is clear that another process that is competitive with HP^+ - $PBDCl^-$ ion-pair recombination is depleting the $PBDCl^-$ population in **2** at high light intensities. At these intensities the 160 fs duration of the excitation flash insures that both porphyrins within **2** are excited simultaneously. Energetic considerations suggest two likely mechanisms for the increase in the $PTDCl^-$ depletion rate within **2**:[27]

$$\Delta G = -0.5 \text{ eV} \qquad\qquad \Delta G = -0.3 \text{ eV}$$

$$^{1*}HP - PBDCl - HP^{1*} \quad \rightarrow \quad HP^+ - PBDCl^- - HP^{1*} \quad \rightarrow \quad HP^+ - PBDCl^{-2} - HP^+ \quad (1)$$

$$3.8 \text{ eV} \qquad\qquad 3.3 \text{ eV} \qquad\qquad 3.0 \text{ eV}$$

$$\Delta G = -0.5 \text{ eV} \qquad\qquad \Delta G = -1.0 \text{ eV}$$

$$^{1*}HP - PBDCl - HP^{1*} \quad \rightarrow \quad HP^+ - PBDCl^- - HP^{1*} \quad \rightarrow \quad HP^+ - PBDCl - HP^- \qquad (2)$$

$$3.8 \text{ eV} \qquad\qquad 3.3 \text{ eV} \qquad\qquad 2.3 \text{ eV}$$

Two photon excitation of **2** yields HP^{1*} - PBDCl - HP^{1*} which has the 3.8 eV total energy of two HP lowest excited singlet states available to perform further reactions.
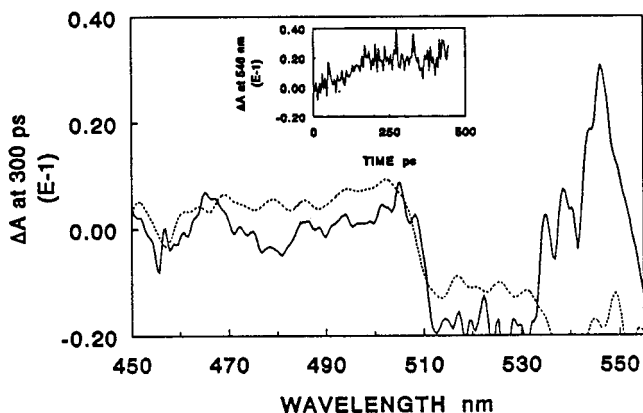
Figure **3**.
Transient absorption spectra of **2** (——) and **3** (---) at 300 ps, 20 photons/molecule. Inset: Appearance kinetics of $PBDCI^{-2}$ in **2** at 546 nm.

Rapid electron transfer follows in both mechanisms to yield HP^+ - $PBDCI^-$ - HP^{1*} with a free energy of formation of -0.5 eV. The $2.0 \pm 0.2 \times 10^{11}$ s^{-1} rate constant for this process is consistent with rate vs free energy relationships for porphyrin-acceptor molecules that we have observed previously.[15] The fact that the rate constant for the initial electron transfer at high light intensity in **2** is twice that for electron transfer following single photon excitation is a consequence of statistics. Singlet-singlet annihilation in **2** is not favored because photoinduced charge separation is kinetically faster. The free energy for the formation of HP^+ - $PBDCI^{-2}$ - HP^+ from HP^+ -$PBDCI^-$ - HP^{1*} is -0.3 eV, while that for the formation of HP^+ - $PBDCI$ - HP^- is -1.0 eV. The contribution of mechanism 1 to the overall photochemistry of **2** can be determined by observing whether the spectroscopically distinct species $PBDCI^{-2}$ is formed.

Figure **3** shows that a 546 nm absorption, which is characteristic of $PBDCI^{-2}$, does indeed appear at high light intensities in **2**, but not in **3**. This suggests that mechanism 1 is responsible for the increased rate constant for the decay of $PBDCI^-$ at high light intensities. The inset to Figure **3** shows that the 546 nm band appears with a $5.6 \pm 0.5 \times 10^9$ s^{-1} rate constant. The somewhat slower rate for the formation of HP^+ - $PBDCI^{-2}$ - HP^+ relative to that for the formation of HP^+ - $PBDCI^-$ -HP^{1*} is once again consistent with rate vs free energy relationships measured earlier.[15] The excitation intensity independent HP^+ - $PBDCI^-$ ion-pair recombination rate constant obtained from **3** is $8.3 \pm 0.2 \times 10^9$ s^{-1}. Thus, the rate of disappearance of HP^+ - $PBDCI^-$ from two parallel processes at high light intensities in **2** should be the sum of the rate constants for HP^+ - $PBDCI^-$ ion-pair recombination and HP^+ - $PBDCI^{-2}$ - HP^+ formation: $1.5 \pm 0.6 \times 10^{10}$ s^{-1}. The measured rate constant for the disappearance of HP^+ - $PBDCI^-$ at high light intensities in **2** is $1.6 \pm 0.2 \times 10^{10}$ s^{-1}, within experimental error of the predicted value based on mechanism 1. Mechanism 2 may be disfavored by electronic coupling considerations, even though the free energy of reaction for the production of HP^+ - $PBDCI$ - HP^- is favorable. The ion-pairs within the charge separated species HP^+ - $PBDCI^{-2}$ - HP^+ recombine on approximately a 5 ns time scale. The long lifetime of these ion-pairs is consistent with the so-called inverted region behavior of electron transfer reactions involving high energy ion-pairs.[15]

5. CONCLUSIONS

Our observation of spin-polarized EPR spectra in **1** depends on achieving a delicate balance of structure dependent electronic interactions between the donors and acceptors within the supramolecular array. This strongly suggests that we now know how to precisely mimic the interactions found only in natural photosynthesis. With this knowledge we will be able to design efficient biomimetic supermolecules for the efficient conversion of photon energy into chemical energy in the solid state.

The photophysical behavior of **2** constitutes a light intensity dependent optical switch. As the light intensity is increased, **2** switches from being a strong transient absorber at 713 nm to one in which the transient absorption occurs at 546 nm. Such

molecules could be used to modulate two light beams at different colors on a picosecond time scale. Moreover, **2** should be able to switch using two different excitation wavelengths. Since the PBDCI molecule absorbs strongly at 526 nm (ϵ = 10^5 M^{-1} cm^{-1}) and possesses a 2.3 eV lowest excited singlet state,[14] excitation of PBDCI will initiate the first electron transfer to produce HP^+ - $PBDCI^-$ - HP. The second electron transfer may be initiated by application of a second photon, e.g. at 585 nm, that is absorbed principally by the remaining ground state porphyrin. Thus, this molecule should also be able to perform logic operations.

Acknowledgement

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27. Free energies for mechanisms 1 and 2 are calculated from the redox potentials of HP and PBDCI along with the 1.92 eV lowest excited singlet state energy of HP as described in ref. 15.