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SUPRAMOLECULAR STRUCTURES MODELING PHOTOSYNTHETIC REACTION CENTER FUNCTION

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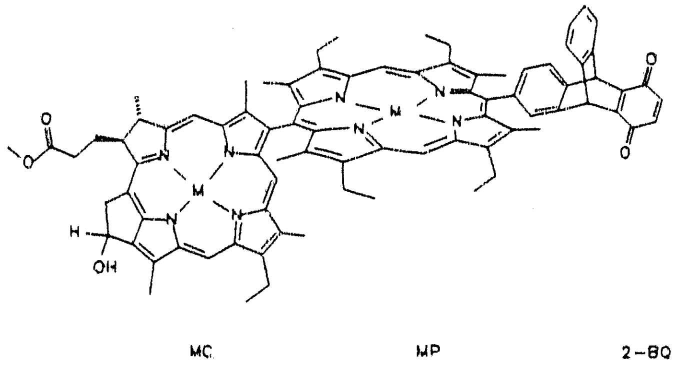
1. INTRODUCTION

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. This contrasts sharply with photosynthetic reaction centers, which maintain medium-independent electron transfer rates with relatively small free energies of charge separation. Using 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]:

$$k_{cr} = (2\pi/\hbar)\, V^2 \cdot \mathrm{FCWD} \qquad (1)$$

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, 2*J*, 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. We have recently reported the observation of such spectra for the first time using a molecular triad in the solid state.[6] This work has been extended by the preparation of **1** and **2** (M = Zn), the first molecules based on a chlorophyll electron donor to exhibit spin-polarized EPR spectra analogous to those observed in photosynthetic reaction centers from both green plants and purple bacteria in the solid state in a low temperature glass. The EPR spectra of the radical ion pairs produced within **1** and **2** can be used to examine how V changes with molecular structure, and how the surrounding medium influences the FCWD term in equation 1.



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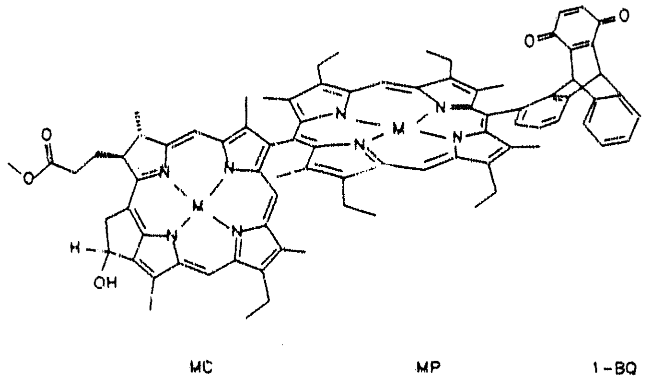

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2. EXPERIMENTAL

Compounds **1** and **2** were synthesized by methods that will be described in future publications. Redox potentials for each donor-acceptor molecule were determined by methods described previously.[7] 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.[8] 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 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

The π system of the chlorophyll electron donor, ZC, in compounds **1** and **2** is rigidly positioned 90° to that of the adjacent porphyrin, ZP. The methyl groups surrounding the attachment positions in both macrocycles serve to fix the geometry by providing steric constraints. This serves to electronically decouple the π systems of these two macrocycles. In addition, the ring E keto group is reduced to a hydroxy in ZC. This produces two changes that combine to greatly increase the free energy available for charge separation in this molecule. First, the lowest excited singlet state of ZC increases to 2.00 eV from the usual 1.86 eV in the keto containing molecule. Second, reduction of the ketone to a hydroxy makes the macrocycle 0.24 V easier to oxidize. Thus, the total free energy available for photoinduced charge separation increases by 0.38 eV by simple reduction of the ring E keto group.

The triptycene benzoquinone moiety is also spatially fixed relative to the porphyrin. In **1** this results in about a 60° angle between the O-O axis of the benzoquinone and the porphyrin macrocyclic plane, while in **2** the O-O axis is parallel to the plane of the porphyrin. The benzoquinone reduces at -0.47 V vs SCE in butyronitrile.[7] Thus, the total free energy available for the charge separation ^{1*}ZC-ZP-BQ -> ZC^{+}-ZP-BQ^{-} is 1.13 eV in polar solvents. In a low temperature glass such as 2-methyltetrahydrofuran (MTHF), this value should decrease to about 0.3 eV.[1] Thus, both **1** and **2** should readily undergo charge separation in the low temperature glass, Figure **1**.

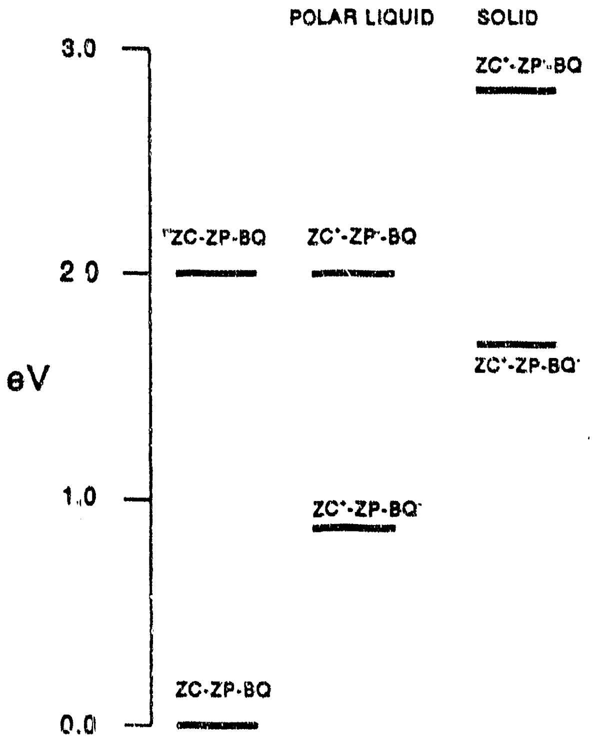

Figure **1**. Energy levels for ZC-ZP-BQ.

Femtosecond transient absorption and emission measurements with no applied magnetic field show that **1** and **2** undergo a single step photoinduced electron transfer reaction, $^{1*}\mathrm{ZC\text{-}ZP\text{-}BQ}$ -> $\mathrm{ZC^{+}\text{-}ZP\text{-}BQ^{\cdot}}$, in τ = 10 and 3 ps, respectively at 77 K. The faster rate of reaction for **2** relative to **1** suggests that V for the charge separation reaction in **2** is somewhat larger than that in **1**. There is no evidence for participation of a distinct chemical intermediate of the porphyrin. Thus, the porphyrin functions to promote a superexchange interaction between $\mathrm{ZC^{+}}$ and $\mathrm{BQ^{\cdot}}$.[9] This behavior is consistent with the fact that the energy level of $\mathrm{ZC^{+}\text{-}ZP^{-}\text{-}BQ}$ in the glassy solid is significantly higher than that of $^{1*}\mathrm{ZC\text{-}ZP\text{-}BQ}$, Figure **1**. The recombination reaction, $\mathrm{ZC^{+}\text{-}ZP\text{-}BQ^{\cdot}}$ -> ZC-ZP-BQ, for both **1** and **2** occurs with about a 1 ms time constant at 77 K.

The time-resolved EPR spectrum of $\mathrm{ZC^{+}\text{-}ZP\text{-}BQ^{\cdot}}$ in **1** is given in Figure **2**, while that of the corresponding isomer **2** is shown in Figure **3**. The spectrum is displayed in the first derivative mode. It is readily seen that irradiation of **1** and **2** produces an intense EPR signal which consists of an emissive, **E**, low field line and an absorptive, **A**, high field line. At 30 K the $\mathrm{ZC^{+}}$ and $\mathrm{BQ^{\cdot}}$ free radicals display gaussian lines: $\mathrm{ZC^{+}}$, g_{iso} = 2.0028, FWHM = 10 G; $\mathrm{BQ^{\cdot}}$, g_{iso} = 2.0047, FWHM = 5 G. Replacement of either ZC or BQ in **1** or **2** by a p-tolyl group results in no observed EPR signals. The solid curves in Figures **1** and **2** show the simulation of the spin-polarized spectrum. Using the known structures of **1** and **2** the gross features of the spectra can be simulated reasonably well. Thus, as expected, the anisotropic spin-spin interactions within the radical pair are a sensitive probe of structure.

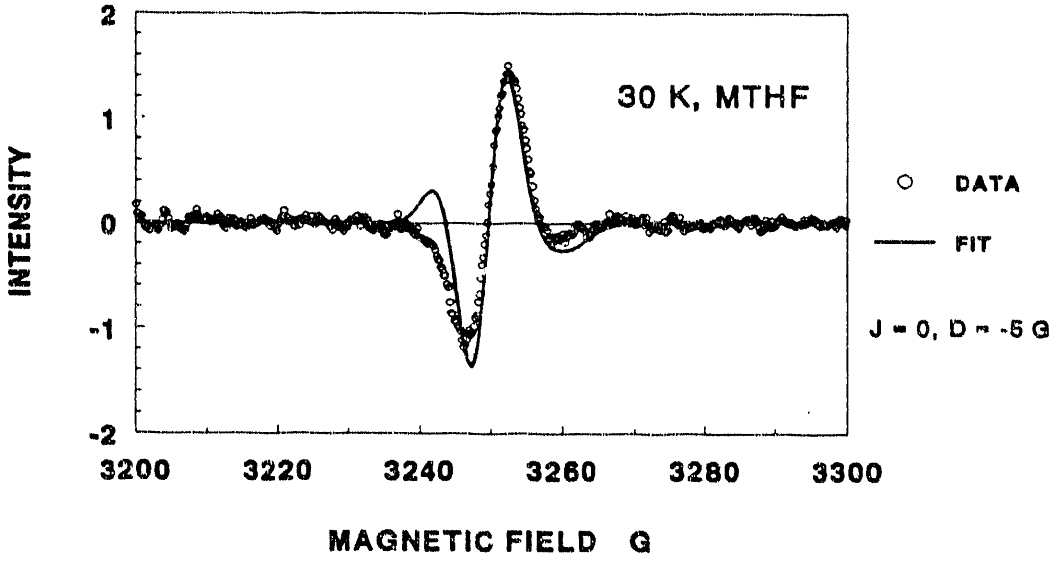

Figure 2. Spin-polarized EPR spectrum of $\mathrm{ZC^{+}\text{-}ZP\text{-}BQ^{\cdot}}$ from **1**.

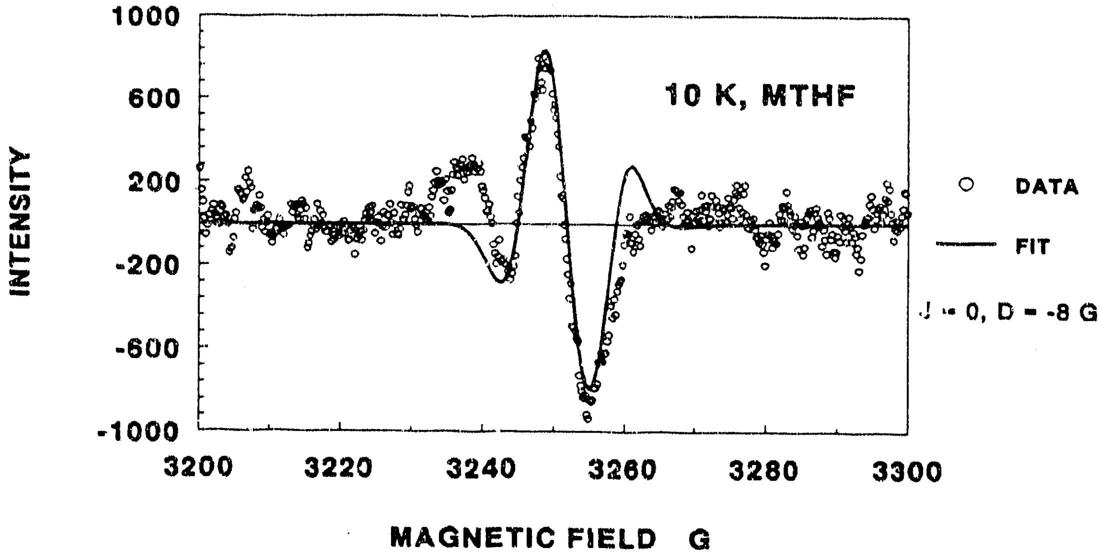

Figure 3. Spin-polarized EPR spectrum of ZC^{+}-ZP-BQ^{-} from 2.

4. DISCUSSION

Spin polarization in ZC^{+}-ZP-BQ^{-} results from the fact that the 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-BQ^{-} produces polarized spectra. If ZC^{+}-ZP-BQ^{-} is a correlated radical pair, a pair of partially overlapping anti-phase doublets is expected.[10-12] The polarization pattern observed, **E A E**, is similar to that observed for P700^{+} - A$_1^{-}$ in Photosystem I of green plants,[13] and P865^{+}-Q^{-} in bacterial reaction centers.[14] Recently, Stehlik et al. [15] and Norris et al. [16] 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-BQ^{-} the g tensor of BQ^{-} is quite anisotropic because about 80% of the spin density in BQ^{-} is centered on the oxygen atoms. The g tensor for ZC^{+} is much less anisotropic. The simulations shown in Figures 2 and 3 use the Stehlik model. The key parameters that were included in the simulation are J = 0 G G, D = -5 G for 1 and J = 0, D = -8 G for 2, and the orientation of ZC relative to BQ in both 1 and 2. The dipolar coupling, D, for ZC^{+}-ZP-BQ^{-} was calculated using the classical expression for the magnetic dipole-dipole interaction,[17] the ZC^{+} - BQ^{-} distance and orientation, and the spin distributions of ZC^{+} and BQ^{-}. It is important to note that the distances and orientations between the BQ^{-} π system relative to that of ZC^{+} used in the simulations were determined independently from the known structures of 1 and 2. The simulations fit the observed spectra reasonably well except for the wings of the spectra. The discrepancy between experiment and simulation in these regions of the spectra could be due to neglect of kinetic modeling in the Stehlik treatment, or to the fact that an isotropic *g* value was used for ZC^+, since the *g*-tensor for ZC^+ is unknown. Nevertheless, the rotation of the quinone relative to the primary electron donor ZC is shown to cause a predictable change in the overall shape of the EPR spectrum. 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.

5. Conclusions

Our observation of spin-polarized EPR spectra in **1** and **2** 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 weak radical pair interactions found only in natural photosynthesis. With this knowledge we will be able to design efficient biomimetic supermolecules that can be used to probe the influence of the surrounding medium on the charge separation process.

6. ACKNOWLEDGEMENT

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