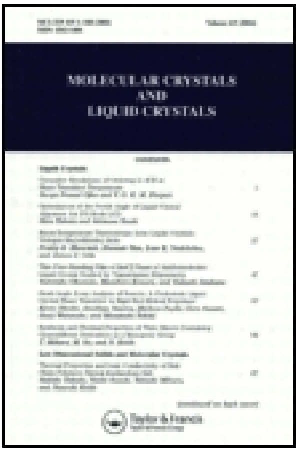

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Spin-Polarized Radical Ion Pair Formation Resulting from Two-step Electron Transfer from the Lowest Excited Singlet State of a Fixed-Distance Photosynthetic Model System at 5 K

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SPIN-POLARIZED RADICAL ION PAIR FORMATION RESULTING FROM TWO-STEP ELECTRON TRANSFER FROM THE LOWEST EXCITED SINGLET STATE OF A FIXED-DISTANCE PHOTOSYNTHETIC MODEL SYSTEM AT 5 K.

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ABSTRACT A photosynthetic reaction center model consisting of a zinc porphyrin primary electron donor, ZP, positioned between a naphthoquinone electron acceptor, NQ, and an N,N,N,N-tetraalkyl-p-phenylenediamine secondary electron donor, TAPD, was synthesized. The resulting rigid structure places the TAPD donor at a fixed 23 Å center-to-center distance from the NQ acceptor. Excitation of ZP with 540 nm light in butyronitrile glass at 5 K results in two-step sequential electron transfer: TAPD-^{1*}ZP-NQ -> TAPD-ZP$^+$-NQ$^-$ -> TAPD$^+$-ZP-NQ$^-$. The final TAPD$^+$-ZP-NQ$^-$ radical pair lives for 4 ms and exhibits a spin-polarized EPR spectrum characteristic of a spin-correlated radical pair. The EPR spectrum of this long-lived, spin-polarized radical ion pair closely mimics the bacteriochlorophyll cation - quinone anion radical pair produced in photosynthetic reaction centers.

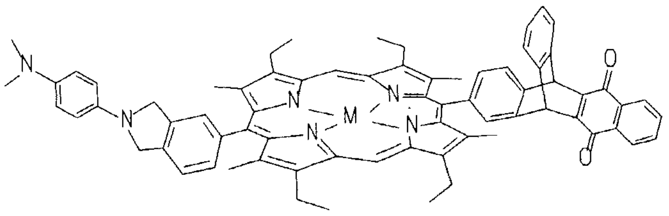
Keywords: Photosynthetic model system, zinc porphyrin donor, N,N,N,N-tetraalkyl p-phenylene diamine donor, naphthoquinone acceptor,electron transfer

INTRODUCTION

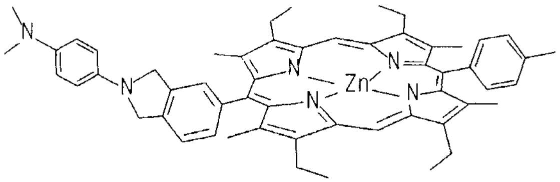
Photoinduced, multi-step charge separation in bacterial photosynthetic reaction centers proceeds from the lowest excited singlet state of the dimeric bacteriochlorophyll electron donor in two steps to yield a weakly interacting dimer cation - quinone anion radical pair, P$^+$-Q$^-$, separated by 28 Å.[1] The chromophores within the reaction center are positioned at precise distances and orientations to insure that the electronic coupling between P$^+$ and Q$^-$ is sufficiently weak to allow P$^+$-Q$^-$ to live for about 100 ms.[2] At long distances the electron-electron exchange interaction, J, between radicals within a charge separated ion pair is sufficiently weak that differences in local magnetic fields surrounding each radical result in S-T$_0$ mixing of the radical pair spin sublevels.[3] 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. Such spectra have been reported extensively for both bacterial and green plant reaction centers,[4-6] but have not been observed previously in rigid model systems.

In order to observe the structurally important anisotropic spin-spin interactions within radical pairs and to prevent spin lattice relaxation from destroying the spin polarization it is necessary to examine the radical pairs in the solid state at low temperatures. Photosynthetic model systems based on chlorophyll or porphyrin electron donors have the interesting, but unfortunate property that the efficiency of their light-initiated electron transfer reactions, which proceed from the lowest excited singlet state, is negligibly low whenever they are dissolved in solid solutions. Put more precisely, the decay rates of chlorophyll and porphyrin excited singlet states are much shorter than the rates of electron transfer from these donors to most electron acceptors in the solid state.

It is well known that polar solvents stabilize ions very well in the liquid state. Placing an ion in a polar solvent causes the solvent dipoles to re-orient so that the energy of the ion within the solvent decreases. On the other hand, if an ion is produced within a polar solvent that is frozen, the solvent dipoles can no longer re-orient, and thus, cannot stabilize the ion. In the solid state the energy level of the ion pair is much higher than that in the liquid. In fact, it may be so high that it lies above the energy of the excited state. In that case electron transfer cannot occur in the solid state.



1: M □ Zn, 2: M = 2H



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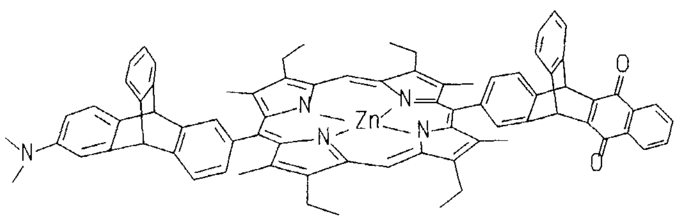

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Recently, we developed criteria for achieving high quantum yield charge separation in porphyrin-based donor-acceptor systems at cryogenic temperatures.[7] Using this information as a predictive model we synthesized compound **1**, TAPD-ZP-NQ, which undergoes two-step, sequential charge separation at 5 K to yield a radical ion pair which possesses an overall 23 Å center-to-center distance[8], *a 4 ms lifetime*, and *spin-polarization* as indicated by EPR.

RESULTS

Compounds **1** and **2** were prepared as follows: 2-formyltriptycenenaphthoquinone,[9] 3,3'-diethyl-4,4'-dimethyldipyrrylmethane,[10] and 5-formyl-N-(p-nitrophenyl)-isoindoline[11] were condensed in CH_2Cl_2 using BF_3-Et_2O catalyst[12] to yield the statistical mixture of porphyrinogens. The porphyrinogens were oxidized to porphyrins with chloranil at room temperature and separated on silica gel. The nitro group was reduced with $SnCl_2$/HCl, and dimethylated with $NaBH_3CN/CH_2O$[13] to give **2** in 15% overall yield based on the starting aldehydes. (mass spec: FAB calcd. 1047 found M+4 1051). The porphyrin was metalated quantitatively with $ZnOAc_2$ in $CHCl_3$/MeOH to yield **1**. Compound **3** was prepared in 11% overall yield by a procedure analogous to that used for **1** by replacing the quinone aldehyde with p-tolualdehyde. Compound **4** was prepared by quantitative Zn insertion into the corresponding free base synthesized previously.[14]

The energetics of electron transfer within **1** at room temperature in butyronitrile were determined from electrochemical measurements of its redox potentials and the fluorescence spectrum of ZP.[15] The ion-pair energy levels at room temperature in liquid butyronitrile are estimated from the sum of the one-electron oxidation potential of the donor and the one-electron reduction potential of the acceptor. At room temperature the energies of TAPD-^{1*}ZP-NQ, TAPD-ZP$^+$-NQ$^-$, and TAPD$^+$-ZP-NQ$^-$ in butyronitrile are about 2.15, 1.29, and 0.84 eV, respectively. Dielectric continuum theory is used to estimate that the energy of the initial ion-pair, TAPD-ZP$^+$-NQ$^-$, is destabilized by about 0.7 eV in solid butyronitrile relative to its energy in liquid butyronitrile, while the energy of the final ion-pair, TAPD$^+$-ZP-NQ$^-$, is destabilized by about 1.0 eV. The validity of this treatment has been demonstrated experimentally.[7] We estimate that the corresponding energy levels in solid butyronitrile are about 2.15, 1.99, and 1.84 eV, respectively. Picosecond transient absorption and emission measurements[16] with no applied magnetic field show that the primary reaction, TAPD-^{1*}ZP-NQ -> TAPD-ZP$^+$-NQ$^-$, occurs in τ = 5 ps, while the secondary reaction, TAPD-ZP$^+$-NQ$^-$ -> TAPD$^+$-ZP-NQ$^-$, occurs with τ = 530 ps. Charge recombination within the long-lived ion-pair, TAPD$^+$-ZP-NQ$^-$, occurs with a 4 ms time constant. The thermodynamic and kinetic parameters for TAPD-ZP-NQ following excitation are summarized in Figure 1.

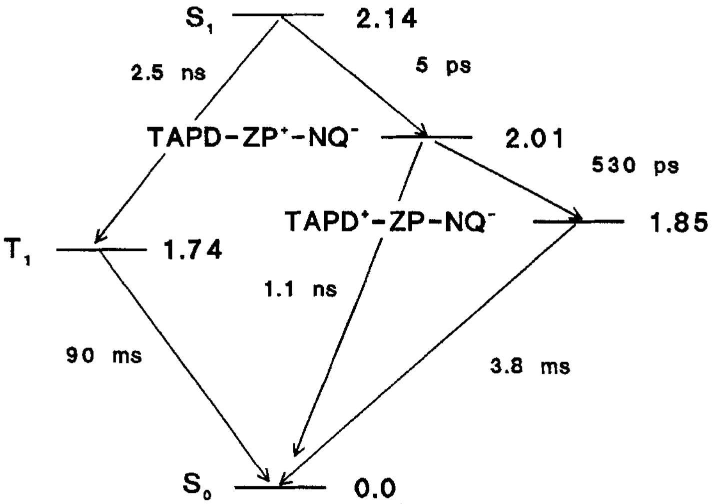

FIGURE 1. Energy levels and kinetics of intermediates produced following excitation of TAPD-ZP-NQ.

The EPR spectrum of $TAPD^+$-ZP-NQ^- is shown in Figure 2. This spectrum is displayed in the first derivative mode so that the low field line emissive, *E*, while the high field line is absorptive, *A*. Extensive control experiments were performed to assign the origin of this signal. At 5 K the $TAPD^+$ and NQ^- free radicals display gaussian lines: $TAPD^+$, g_{iso} = 2.0030, FWHM = 35 G; NQ^-, g_{iso} = 2.0047, FWHM = 5 G. Removing the Zn atom from the porphyrin in **1** makes the initial electron transfer reaction endergonic in the solid state. Thus, excitation of the porphyrin in **2** results only in formation of its lowest excited triplet state which shows a strong EPR signal with zero field splitting parameters $|D| = 0.0451$ cm^{-1} and $|E| = 0.0041$ cm^{-1}. Replacement of the NQ in **1** by a p-tolyl group, **3**, results in no observed electron transfer reactions at 5 K. Replacing the TAPD moiety by N,N-dimethylaniline in **4** also results in no photoinduced EPR signals. Since the N,N-dimethylaniline moiety oxidizes at 0.78 V *vs* SCE,[14] the secondary electron transfer in **4** is endergonic.

DISCUSSION

The spectrum in Figure 2 can be attributed to 2 radicals, $TAPD^+$ with a broad linewidth at lower *g*-factor and NQ^- with a narrow linewidth at higher *g*-factor. Polarization is observed on a millisecond time scale because the spin-lattice relaxation times of the radicals are long at 5 K. Spin polarization of $TAPD^+$-ZP-NQ^- can result from two mechanisms. The first mechanism is the usual radical pair mechanism, RPM, of CIDEP[17]. S-T_0 mixing in

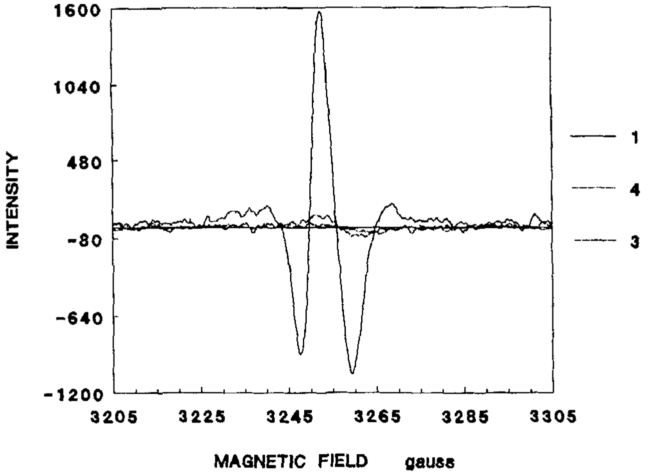

FIGURE 2. First derivative EPR signals resulting from 540 nm, 500 Hz modulated irradiation of 5 x 10^{-5} M solutions of 1, 3, and 4 at 5K in PrCN.

TAPD-ZP^+-NQ^- is followed by polarization transfer to a non-interacting radical pair $TAPD^+$-ZP-NQ^-, i.e. $J = 0$. The second mechanism assumes that $TAPD^+$-ZP-NQ^- is itself an interacting spin correlated radical pair, i.e. $|J| \sim 0.1 - 10$ G.[18-20] In this case S-T_0 mixing in $TAPD^+$-ZP-NQ^- can also produce polarized spectra.

If spin polarization in $TAPD^+$-ZP-NQ^- results from the RPM of CIDEP, all polarization produced from differences in hyperfine interactions within the precursor radical TAPD-ZP^+-NQ^- is lost, and only "net" polarization due to Δg differences between ZP^+ and NQ^- remains. Thus, since $J < 0$, $\Delta g > 0$, and the initial state radical pair state is a singlet, the RPM of CIDEP predicts that the NQ^- signal should be absorptive, while the $TAPD^+$ signal should be emissive. However, the polarization pattern of the lines within the spectrum in Figure 2 do not support this mechansim. The RPM of CIDEP also requires that the initial radical pair lives sufficiently long for polarization to develop. The 0.5 ns lifetime of TAPD-ZP^+-NQ^- is probably too short for this to occur.[17]

On the other hand, if the correlated radical pair mechanism is operative, a pair of partially overlapping anti-phase doublets is expected.[18-20] This mechanism in combination with *g* anisotropies within the radical pair will result in an *E A E* polarization pattern for the signal at 9 GHz. This polarization pattern is similar to that observed for $P700^+$ - A_1^- in Photosystem I of green plants,[4] and $P865^+$-Q^- in bacterial reaction centers.[5] Since the spin-polarized EPR signal from $TAPD^+$-ZP-NQ^- closely resembles those from photosynthetic organisms, and since we know the structure of 1, the magnitudes of the spin-spin interactions and the relative orientations of the donors and acceptors in the proteins should be similar to those in **1**. We are preparing derivatives of **1** in which the orientation of TAPD$^+$ relative to NQ$^-$ is changed. This will allow us to investigate the dependence of the spin-polarized signal on the anisotropic spin-spin interactions between the radicals. Additional work is currently in progress on deuterated derivatives of **1** to narrow the TAPD$^+$ signal in order to aid in simulating the spectrum based on a new approach to describing the EPR spectra of correlated radical pairs.[21]

CONCLUSIONS

Our results show that it is now possible to study charge separation over fixed distances and orientations using magnetic resonance as well as optical studies. These studies should give us a direct measure of the electronic coupling between an electron donor-acceptor pair as a function of structure and environment and may lead to a better understanding of electron transfer in photosynthesis.

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