

Biomimetic Modeling of Photosynthetic Reaction Center Function: Long-Lived, Spin-Polarized Radical Ion Pair Formation in Chlorophyll–Porphyrin–Quinone Triads

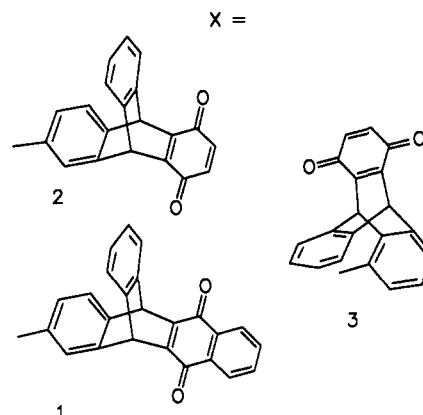
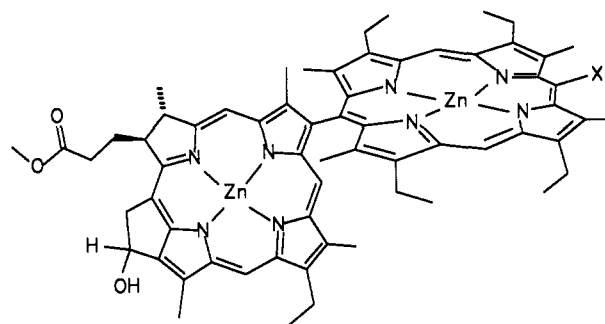
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Anisotropic spin–spin interactions within photogenerated radical ion pairs that possess restricted distances and orientations between the radical ions can be used to probe the structures of these pairs with EPR spectroscopy. A radical ion pair with an optimized free energy of recombination and a lifetime on the order of milliseconds should possess an electronic coupling matrix element $V < 0.001 \text{ cm}^{-1}$ ($\sim 10 \text{ G}$).^{1,2} 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.^{3,4} This mixing produces a non-Boltzmann population of the spin sublevels of the radical pair and often results in spin-polarized EPR spectra. Until very recently, the only systems that fulfilled these requirements were photosynthetic reaction centers.^{3,4} In 1990, we reported the EPR spectrum of a spin-correlated radical ion pair for the first time in a photosynthetic model system obtained with use of a phenylenediamine–porphyrin–quinone triad molecule dissolved in a glassy solid at low temperature.⁵ This molecule was designed to minimize the electronic interaction between the oxidized phenylenediamine and reduced quinone in the radical pair product state by carefully choosing the spacer groups that link the donor and acceptor and by using two electron-transfer steps to increase the distance between the separated charges as is done in natural photosynthesis.⁶ Several other groups have produced photosynthetic model systems possessing restricted radical pair distances that also undergo electron transfer at low temperatures.^{7–11} However, V for radical ion pair recombination is sufficiently small in only a few of these molecules to result in long-lived radical ion pairs with spin-polarized EPR spectra.^{10–12} We report here on 1–3, the first molecules based on a chlorophyll electron donor possessing sufficiently weak spin–spin interactions in the radical pair product state to exhibit both long lifetimes and spin-polarized EPR spectra analogous to those observed in photosynthetic reaction centers. The radical ion pairs produced within 1–3 directly probe how V changes with molecular structure when the orientation of the quinone relative to the chlorophyll is changed.

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Compounds 1–3 were synthesized by using methods that are an extension of those described previously^{13–16} and will be described in a future publication. The π system of the chlorophyll electron donor, ZC, in compounds 1–3 is restricted to a position $\sim 90^\circ$ to that of the adjacent porphyrin, ZP.¹⁷ The methyl groups surrounding the attachment positions in both macrocycles serve to restrict the geometry by providing steric constraints. The triptycenequinone moieties are also spatially restricted relative to the porphyrin. In 1 and 2, this results in about a $\sim 60^\circ$ angle between the quinone O–O axis and the chlorophyll macrocyclic plane, while in 3 the quinone O–O axis is parallel to the plane of the chlorophyll. The resulting structures place the ZC donors in 1, 2, and 3 at center-to-center distances of 20, 18, and 14 Å from the quinone acceptors, respectively.¹⁷

The free energy for the charge separation ${}^1\text{ZC}^+ \text{--} \text{ZP} \text{--} \text{XQ} \rightarrow \text{ZC}^+ \text{--} \text{ZP} \text{--} \text{XQ}^-$ in polar solvents neglecting the Coulombic interaction is $\Delta G = E_{\text{ox}} - E_{\text{red}} - E_s$, where E_s is the excited state energy, E_{ox} is the one-electron oxidation potential of the donor, and E_{red} is the one-electron reduction potential of the acceptor. Reduction of the chlorophyll ring E keto group to a hydroxyl in ZC produces two changes that combine to increase greatly the free energy available for charge separation in 1–3. First, the lowest excited singlet-state energy of the 9-hydroxychlorin increases to 2.00 from 1.86 eV in the 9-ketochlorin. Second, the 9-hydroxychlorin oxidizes at 0.39 V vs SCE, whereas the 9-ketochlorin oxidizes at 0.62 V.¹⁴ Thus, the total free energy available for photoinduced charge separation when using the 9-hydroxychlorin is 0.37 eV more negative than that available when using the 9-ketochlorin. The naphthoquinone in 1 reduces

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(16) Molecular weights of 1–3 were determined by laser desorption TOF mass spectrometry: for 1, 1458.8 calcd, 1459 found; for 2, 1408.8 calcd, 1409 found; for 3, 1408.8 calcd, 1409 found.

(17) The donor–acceptor distances and orientations were estimated from MM2 energy minimized structures.

at -0.61 V vs SCE in butyronitrile, while the benzoquinones in **2** and **3** reduce at -0.47 V.¹³ Thus, ΔG is -1.00 eV for **1** and -1.14 eV for **2** and **3** in polar solvents. In a low-temperature glass such as 2-methyltetrahydrofuran (MTHF), these values should decrease to about -0.2 and -0.3 eV, respectively.¹⁸

Transient absorption measurements^{14,15,19} with no applied magnetic field show that **1–3** undergo a single-step, photoinduced electron-transfer reaction, ${}^1\text{ZC-ZP-XQ} \rightarrow \text{ZC}^+-\text{ZP-XQ}^-$, with $\tau = 4.5, 3.3,$ and 2.0 ps, respectively, at 77 K. The quantum yields for charge separation in **1–3** are all $>99\%$ because the rate constants for charge separation are more than 1000 times faster than the ~ 5 -ns lifetime of ${}^1\text{ZC}$. The faster rate of reaction for **3** relative to **2** suggests that V for the charge separation reaction in **3** is somewhat larger than that in **2**. There is no evidence for participation of a distinct chemical intermediate involving the porphyrin within the 200-fs time resolution of the fastest measurements made on **1–3**. This is evidenced by the fact that the porphyrin Soret band does not show discernible bleaching at any time during the course of the photochemistry.^{14,15} Thus, the porphyrin may function as a virtual intermediate in a superexchange interaction between ZC^+ and XQ^- .^{15,20} This behavior is consistent with the fact that the energy level of $\text{ZC}^+-\text{ZP-XQ}^-$ is about 0.1 eV higher than that of ${}^1\text{ZC-ZP-XQ}$ in polar solvents and should be significantly higher than that of ${}^1\text{ZC-ZP-XQ}$ in the glassy solid. By comparison, the recombination reactions for **1–3**, $\text{ZC}^+-\text{ZP-XQ}^- \rightarrow \text{ZC-ZP-XQ}$, are *very slow*, occurring with 12.7, 8.4, and 2.5 ms time constants, respectively, at 77 K. The unusually long lifetimes of these ion pairs suggest that the electronic coupling V between ZC^+ and XQ^- is $<10^{-4}$ cm⁻¹.^{1,2}

The time-resolved EPR spectra of $\text{ZC}^+-\text{ZP-XQ}^-$ in **1–3** shown in Figure 1 confirm that long-lived photoinduced charge separation occurs in these molecules. The spectra are displayed in the first derivative mode. Irradiation of **1–3** produces intense EPR signals that consist of an emissive, E, low-field line and an absorptive, A, high-field line. At 30 K, the ZC^+ and XQ^- free radicals display Gaussian lines: ZC^+ , $g_{\text{iso}} = 2.0028$, fwhm = 10 G; NQ^- and BQ^- , $g_{\text{iso}} = 2.0047$, fwhm = 5 G. No EPR signals are observed in molecules related to **1–3** in which ZC or XQ are replaced by a *p*-tolyl group.

$S-T_0$ mixing of the radical pair energy levels occurs within $\text{ZC}^+-\text{ZP-XQ}^-$, producing mixed states that are overpopulated as a result of the single-state-derived electron-transfer reaction. Microwave-induced transitions between the overpopulated $S-T_0$ mixed states and the $T_{\pm 1}$ states of the radical pair result in spin-polarized EPR spectra. If $\text{ZC}^+-\text{ZP-XQ}^-$ is a correlated radical pair, a pair of partially overlapping antiphase doublets is expected.^{21–23} The polarization pattern observed, EAE, is similar to that observed for $\text{P700}^+-\text{A}_1^-$ in photosystem I of green plants^{3,4} and $\text{P865}^+-\text{Q}^-$ in bacterial reaction centers.^{3,4} Recently, theoretical models have been developed to simulate these spectra.^{24,25}

In $\text{ZC}^+-\text{ZP-XQ}^-$, the g -tensor of XQ^- is quite anisotropic because about 80% of the spin density in XQ^- is centered on the oxygen atoms.²⁶ The g -tensor for ZC^+ is much less anisotropic due to distribution of the spin primarily on carbon atoms but has not been measured precisely. The key parameters that were included in the simulations shown in Figure 1 are $2J = 0$ G for **1–3**, $D = -5$ G for **1**, -6 G for **2**, and -8 G for **3** and the orientation

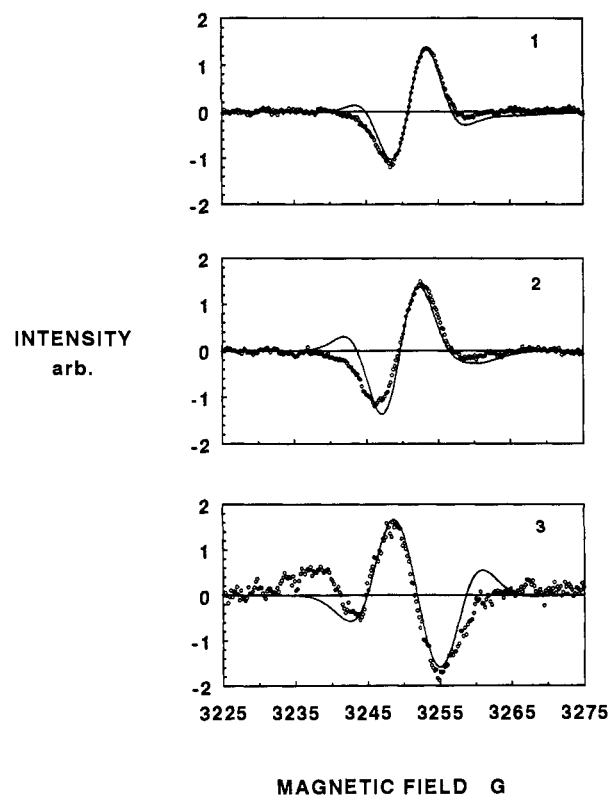


Figure 1. EPR signals of the spin-polarized radical ion pairs resulting from irradiation of 5×10^{-5} M **1**, **2**, and **3** in MTHF at 30 K using light > 600 nm, modulated at 500 Hz, with lock-in detection. Microwave power 5 mW, $\nu = 9.12$ GHz, Varian E-9 EPR spectrometer. The circles are the data points, and the solid lines are the simulations using the parameters given in the text.

of ZC relative to XQ in **1–3**. The dipolar couplings, D , for $\text{ZC}^+-\text{ZP-XQ}^-$ were calculated with use of the classical expression for the magnetic dipole-dipole interaction,²⁷ the ZC^+-XQ^- distance and orientation, and the spin distributions of ZC^+ and XQ^- . It is important to note that the distances and orientations between the XQ^- π system relative to that of ZC^+ used in the simulations were determined independently from the structures of **1–3**. The structural change in the quinone in going from **2** to **3** constitutes a rotation of the principal axis system of its anisotropic g -tensor relative to a vector joining the centers of the quinone and the primary electron donor ZC . Kinetic parameters for formation of the radical pair including the possible involvement of intermediate radical pairs have been excluded. 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 are probably due to the use of an isotropic g -value for ZC^+ . Nevertheless, the observed change in the overall shape of the EPR spectrum that results from rotating the quinone in **2** vs **3** is predicted accurately by theory. Our results strongly suggest that we can mimic the weak radical pair interactions found in natural photosynthesis by using **1–3**. With this knowledge, we will be able to design more complex biomimetic supermolecules that can be used to probe the influence of the surrounding medium on the charge separation process by using a combination of optical and magnetic resonance techniques.

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