EPR Investigation of Photoinduced Radical Pair Formation and Decay to a Triplet State in a Carotene−Porphyrin−Fullerene Triad

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Abstract: The photochemistry of a molecular triad consisting of a porphyrin (P) covalently linked to a carotenoid polyene (C) and a fullerene derivative (C_{60}) has been studied at 20 K by time-resolved EPR spectroscopy following laser excitation. Excitation of the porphyrin moiety yields $C-{}^1P-C_{60}$, which decays by photoinduced electron transfer to yield $C-P^{\bullet+}-C_{60}{}^{\bullet-}$. This state rapidly evolves into a final charge-separated state $C^{\bullet+}-P-C_{60}{}^{\bullet-}$, whose spin-polarized EPR signal was observed and simulated. There is a weak exchange interaction between the electrons in the radical pair ($J = 1.2$ G). The $C^{\bullet+}-P-C_{60}{}^{\bullet-}$ state decays to give the carotenoid triplet in high yield with a time constant of 1.2 μs. The spin polarization of ${}^3C-P-C_{60}$ is characteristic of a triplet formed by charge recombination of a singlet-derived radical pair. The kinetics of the decay of ${}^3C-P-C_{60}$ to the ground state were also determined. The photoinduced electron transfer from an excited singlet state at low temperature and the high yield of charge recombination to a spin-polarized triplet mimic similar processes observed in photosynthetic reaction centers.

Introduction

Supramolecular systems consisting of organic pigments covalently linked to electron donor and/or acceptor moieties can successfully mimic many of the major features of photosynthetic solar energy conversion, including absorption of visible light, singlet energy transfer between pigments, and photoinduced electron transfer from excited singlet states to give long-lived charge-separated states in high yield.[1−6] Mimicry of some other aspects of photosynthetic reaction centers has proven less facile. Photoinduced electron transfer in reaction centers occurs unabated at 4 K, whereas it is not observed at low temperatures with most model systems. In addition, natural reaction centers whose electron-transfer pathways have been blocked by reduction or removal of quinone electron acceptor moieties demonstrate charge recombination to yield chlorophyll and carotenoid triplet states whose spin polarization reflects that of their singlet-born radical pair precursor.[7−11] This phenomenon has not been observed in systems containing visible-absorbing pigments related to those found in photosynthetic reaction centers, although it has been detected in a UV-absorbing molecular triad based on aromatic imide chromophores.[12,13]

Most of the reaction center models of this type have employed quinones, porphyrins, or aromatic imides as electron acceptor moieties. It has recently been found that fullerenes can also function in this way. A variety of molecular dyads consisting of fullerenes linked to donor pigments demonstrate photoinduced electron transfer to the fullerene, yielding a charge-separated state.[14−25]

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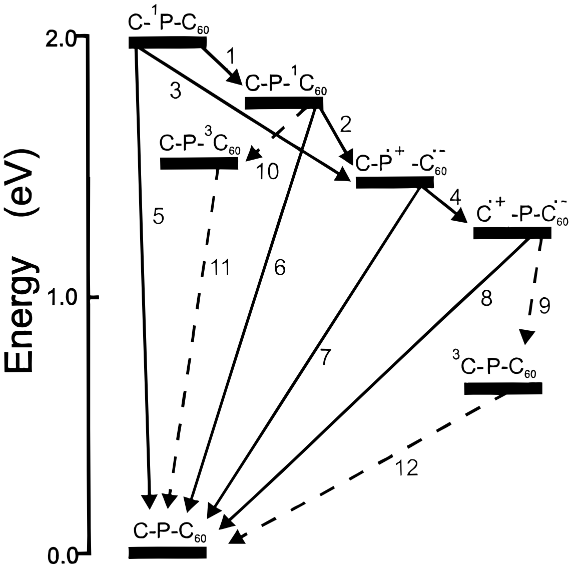

Figure 1. Transient states of triad **1** and relevant interconversion pathways. The energies of the various states have been estimated from spectroscopic and cyclic voltammetric data in polar solvents.[26]

Recently, the synthesis and photochemistry of carotenoid (C)−porphyrin (P)−fullerene (C_{60}) triad **1** was reported.[26] Time-resolved optical spectroscopic studies allowed deduction of the photochemistry shown in Figure 1. Excitation of the porphyrin moiety yields $C-{}^{1}P-C_{60}$. At 77 K in a 2-methyltetrahydrofuran glass, this state decays by a combination of photoinduced electron transfer to yield $C-P^{\bullet+}-C_{60}^{\bullet-}$ (step 3) and singlet energy transfer to the fullerene (step 1). The $C-P^{\bullet+}-C_{60}^{\bullet-}$ charge-separated state evolves by electron donation from the carotenoid to give the $C^{\bullet+}-P-C_{60}^{\bullet-}$ charge-separated species with an overall quantum yield of ∼0.10 (step 4). The $C^{\bullet+}-P-C_{60}^{\bullet-}$ state decays mainly by charge recombination to give the carotenoid triplet, rather than the ground state (step 9). The fullerene singlet state of the triad decays by normal intersystem crossing to give the triplet (step 10), which also decays normally. (The photochemical behavior of **1** in solution at ambient temperatures follows a slightly different course.[26]) Triad **1** demonstrates photoinduced electron transfer at low temperatures followed by charge recombination to a triplet state, similar to natural photosynthetic reaction centers. In the present study, we have used time-resolved EPR spectroscopy (TREPR) to observe the $C^{\bullet+}-P-C_{60}^{\bullet-}$, ${}^{3}C-P-C_{60}$, and $C-P-{}^{3}C_{60}$ states, their spin polarization, and their kinetic properties in order to compare the behavior of **1** with that of reaction centers and other model compounds.

Results

General Features of the Transient EPR Spectrum. Solutions of triad **1** in 2-methyltetrahydrofuran (∼0.01 M) were deaerated by several freeze−thaw cycles and sealed under vacuum. These were placed in the cavity of an X-band EPR spectrometer, cooled to 20 K where the solvent is a glass, and irradiated with 20 ns, 20−25 mJ pulses of light at 580 nm, where the porphyrin moiety absorbs strongly. The EPR experiment was conducted in time-resolved mode using direct detection (no field modulation), and spectra are shown in absorption mode. Figure 2 shows the EPR spectrum obtained 0.4 μs after laser excitation. The strong resonance in the center of the spectrum is characterized by an *aaa eee* polarization for the six transitions arising from the three canonical orientations of a triplet state randomly oriented relative to the spectrometer magnetic field in a glassy medium. This polarization pattern is one of those characteristic of formation of a triplet by normal spin−orbit-coupling promoted selective intersystem crossing from the singlet excited state.[8] The polarization pattern and D and E values ($|D| = 0.0099$ cm^{-1}, $|E| = 0.0014$ cm^{-1}) of this triplet are identical to those observed for model fullerene **2** (Figure 3c, dotted line) and previously reported.[27] Thus, it can be assigned to $C-P-{}^{3}C_{60}$.

The spectrum also features a weaker and broader (∼700 G) signal (Figure 2a) which overlaps with the $C-P-{}^{3}C_{60}$ spectrum only between 3300 and 3500 G (see spectra b and c in Figure 3 where a comparison of the EPR spectra from the triad and from model fullerene **2** is shown). Due to the small overlap of the two signals, which leaves the features at the canonical orientations clearly defined, the zero field splitting parameters of the broader spectrum can be extracted ($|D| = 0.0356$ cm^{-1}, $|E| = 0.0037$ cm^{-1}). These zero field splitting parameters are similar to those of a linear polyene with 9 double bonds,[28,29] allowing assignment of the signal to the carotenoid triplet state of **1**. As shown in spectra a and b in Figure 3, the polarization pattern of this triplet signal is *eaa eea*. This unusual pattern cannot arise from any spin−orbit-coupling promoted intersystem crossing path, and is characteristic of a triplet state with $D < 0$ populated exclusively in the T_0 high-field spin level, as discussed in more detail below.[8,30] A negative value for D is expected for rodlike molecules such as carotenoids in their triplet state.[31−33] A carotenoid triplet state having the polarization pattern *eaa eea* has been observed by TREPR in bacterial photosynthetic reaction centers.[11] Because this triplet is formed by triplet−triplet energy transfer from the primary donor bacteriochlorophyll dimer triplet state, it also has the radical-pair spin polarization pattern. A simulation of the carotenoid triplet state spectrum is shown in Figure 3c. It corresponds to a calculated powder triplet spectrum in the hypothesis of triplet population exclusively in the T_0 high-field spin level and with the ZFS parameters reported above.

Finally, a narrow (∼5 G) signal is observed in the center of the spectrum (Figure 2b). The kinetic behavior, polarization and line shape of this signal allow assignment to the $C^{\bullet+}-P-C_{60}^{\bullet-}$ radical pair state, as described in the Discussion section.

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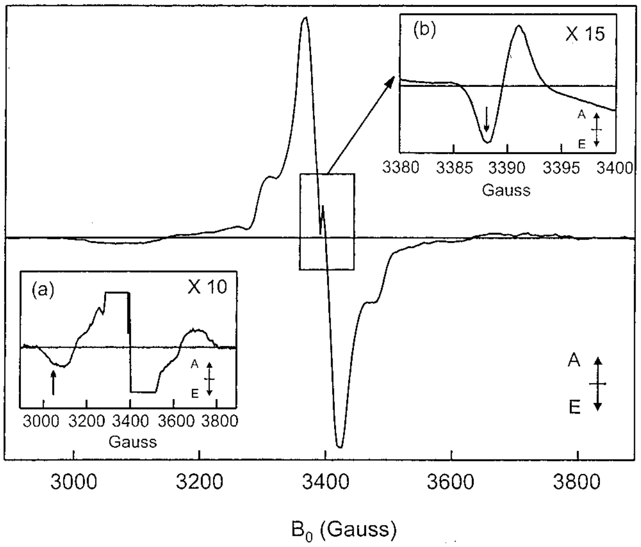


Figure 2. Time-resolved EPR spectrum of triad **1** in 2-methyltetrahydrofuran. The spectrum was obtained at 20 K 0.4 μs after the laser excitation pulse with 14.5 mW of microwave power and an integration time of 0.2 μs per point. The spectrum was obtained with direct detection, and appears in absorption (A) or emission (E), as indicated. (a) Expansion of the spectrum in the carotenoid triplet region. (b) Expansion of the spectrum of the $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}^{\bullet-}$ radical pair (1 G = 10^{-4} T).

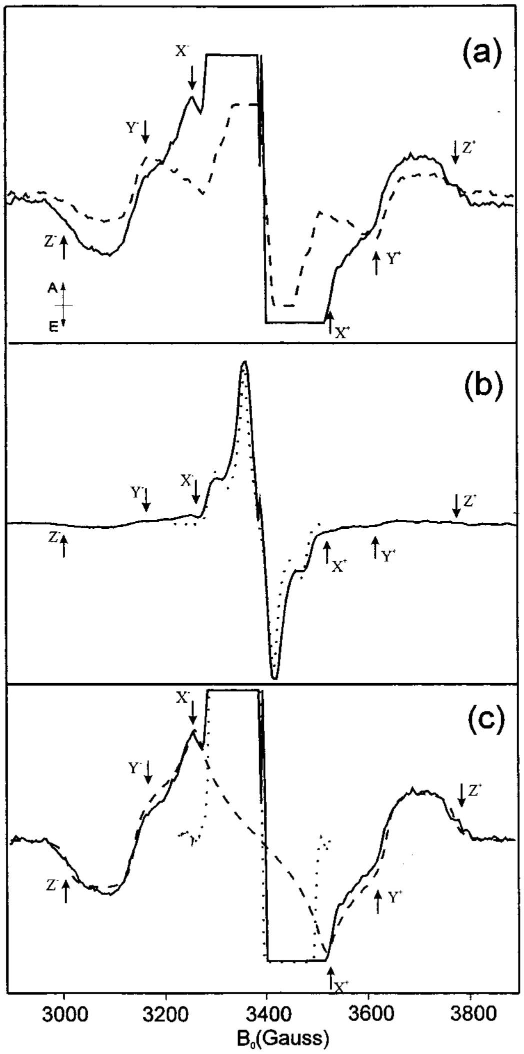


Figure 3. (a) Time-resolved EPR spectrum of the carotenoid triplet state of triad **1** in 2-methyltetrahydrofuran, taken under the conditions described for Figure 2: (—) 0.4 μs after the laser pulse, (- - -) 8.4 μs after the laser pulse. The arrows indicate the transitions arising from the three canonical orientations. (b) Comparison between the experimental spectrum of Figure 2 (—) and the spectrum of model compound **2** (···), taken under the same experimental conditions. The signals have been normalized at the field corresponding to the maximum. (c) Expansion of the spectra of part b. Also shown (- - -) is a simulation of the spectrum of the carotenoid triplet state populated by the radical pair mechanism (singlet precursor) using parameters reported in the text.

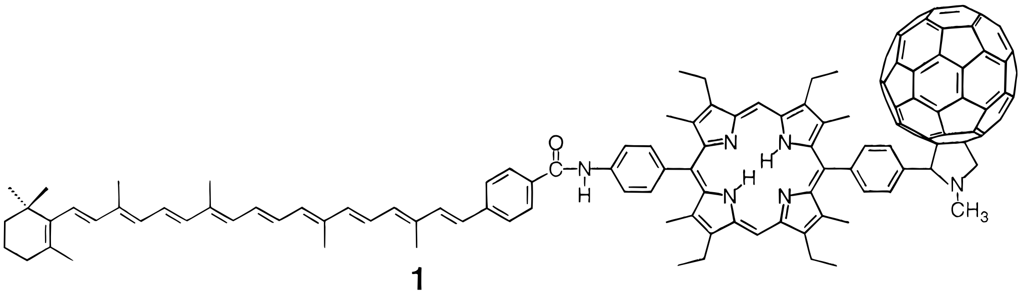
No EPR signal from a porphyrin moiety triplet state has been detected.

Time Evolution of the Spectrum. As suggested by Figure 3a, the EPR spectrum of triad **1** changes with time. It was possible to study this evolution for the three different signals on the nanosecond and microsecond time scales. Figure 4 shows the time course of the transient signals at 3050 and 3390 G. These signals correspond to the low-field transition for the canonical *z*-orientation of the carotenoid triplet state and the low-field emission peak of the $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}^{\bullet-}$ radical pair, respectively (see arrows in Figure 2). The analogous measurements for the high-field signals give the same results.

The rise and decay of these transient signals was simulated according to the kinetic scheme in Figure 1. The decay of the signal corresponding to the $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}^{\bullet-}$ radical pair and the rise of that due to $^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}$ are correlated, consistent with the assertion that the carotenoid triplet state is formed by charge recombination. Simulation of either kinetic process (solid lines in Figure 4) gives the same value for $k_9 + k_8$: $6.6 \times 10^5\ \mathrm{s}^{-1}$. This simulation was made neglecting spin−lattice and spin−spin relaxation and microwave-induced transitions. These approximations were validated by the invariability of the kinetic profiles with temperature in the range 10−40 K, and with microwave power up to the maximum employed (140 μW).

The rise of $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}^{\bullet-}$ is too rapid to be measured by the EPR experiment. Optical spectroscopic measurements provide information relevant to this point. Subpicosecond transient absorption measurements of **1** in 2-methyltetrahydrofuran at 298 K were performed by the pump−probe technique. Excitation of the sample with a 200 fs laser pulse at 590 nm was followed

Chart 1



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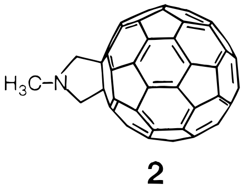

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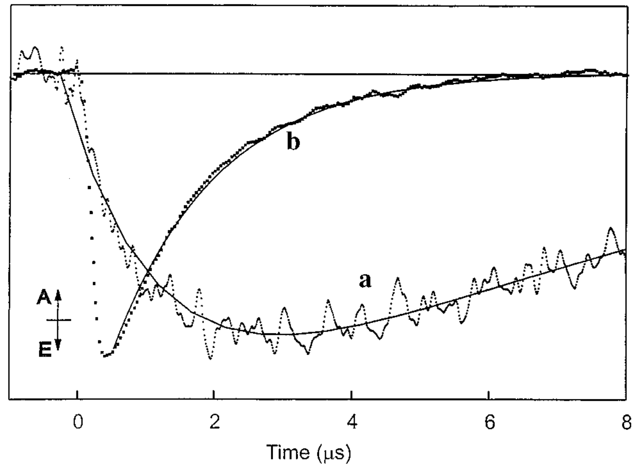

Figure 4. Time evolution of the EPR signals from triad **1** in 2-methyltetrahydrofuran solution at 20 K. The microwave power was 140 μW, and the sampling interval was 3 ns. The traces were obtained by subtraction of on- and off-resonance signals, and are averages of 1000 repetitions. (a) Low-field *z* transition of $^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}$ at 3050 G; (b) $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}{}^{\bullet-}$ radical pair at 3390 G; (—) Simulations using parameters reported in the text.

by detection of the transient absorbance at 948 nm, where the carotenoid radical cation has a large extinction coefficient and the fullerene radical anion also absorbs. The $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}{}^{\bullet-}$ state was found to form with a time constant of 65 ps. Thus, at 298 K the sum of k_4 and k_7 is $1.5 \times 10^{10}\ \mathrm{s}^{-1}$. The kinetic curves of Figure 4 have been calculated according to the scheme of Figure 1, taking into account that the decay rate of step 12 concerns in this case one triplet sublevel (k_z) and that only the T_0 triplet sublevel is populated by the radical pair mechanism.

The EPR signal decay of $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}{}^{\bullet-}$ is then given by:

$$S(t)_{[\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}{}^{\bullet-}]} \propto \exp[-(k_9 + k_8)t]$$

and the EPR signal of $[^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}]_z$ by

$$S(t)_{[^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}]_z} \propto \{\exp[-(k_9 + k_8)t] - \exp(-k_z t)\}/(k_z - k_9 - k_8)$$

In the same way it was also possible to measure the kinetics of the EPR signals of $^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}$ at values corresponding to the other two canonical transitions (*x*, *y*), as the contribution of the signal coming from $\mathrm{C}-\mathrm{P}-{}^3\mathrm{C}_{60}$ at these field values is negligible. The experimental curves and corresponding kinetic simulations for each of the three canonical orientations are shown in Figure 5, parts a, b, and c, respectively. The magnetic field strengths at which the three measurements were made are indicated in Figure 3a. The same value of the rate of formation of $^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}$ from $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}{}^{\bullet-}$ was used for all three simulations: $6.6 \times 10^5\ \mathrm{s}^{-1}$. Simulation of the data yielded the three rate constants shown below for decay of the carotenoid triplet signals corresponding to the three canonical orientations (step 12 in Figure 1):

$$k_x = 3.0 \times 10^5\ \mathrm{s}^{-1}; \qquad k_y = 3.0 \times 10^4\ \mathrm{s}^{-1}; \qquad k_z = 1.1 \times 10^5\ \mathrm{s}^{-1}$$

As discussed later, only the carotenoid T_0 level is populated through recombination of $\mathrm{C}^{\bullet+}-\mathrm{P}-\mathrm{C}_{60}{}^{\bullet-}$ in a high magnetic field. Since relaxation processes and microwave-induced transitions may be neglected under the conditions of the experiment, the kinetics of the processes in Figure 5 involve only this initially populated level. For external magnetic fields parallel to the *x*, *y*, and *z* zero-field axes (canonical orientations), the T_0 levels correspond to the unaltered *x*, *y*, and *z* zero-field levels, and the decay rates k_x, k_y, and k_z are thus the decay rates for the three carotenoid triplet sublevels at zero field. The differences in the decay constants for the three carotenoid triplet sublevels are responsible for the differences in the relative intensities of the signals in spectra taken at different times, as shown in Figure 3a.

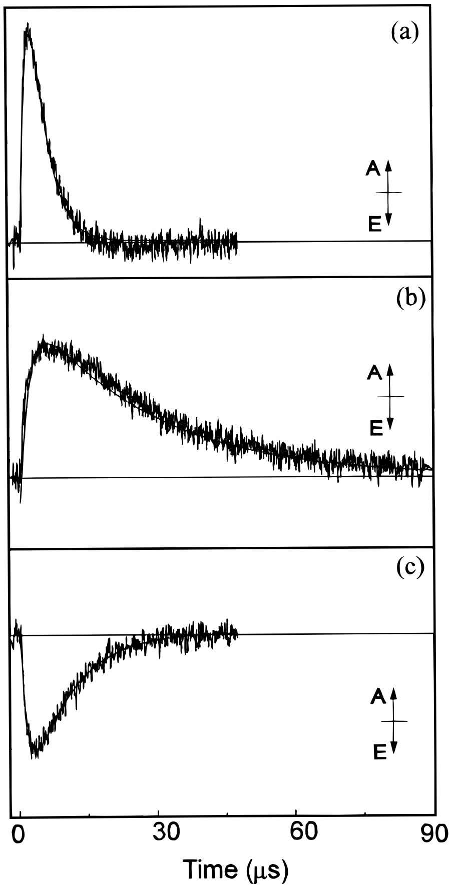

Figure 5. Time evolution of the EPR signals and corresponding kinetic simulations for $^3\mathrm{C}-\mathrm{P}-\mathrm{C}_{60}$ in 2-methyltetrahydrofuran solution at 20 K. The microwave power was 140 μW, and the sampling interval was 3 ns. The traces were obtained by subtraction of on- and off-resonance signals, and are averages of 1000 repetitions: (a) at the *x* canonical transition; (b) at the *y* transition; and (c) at the *z* transition.

The time evolution of the EPR signal assigned to $\mathrm{C}-\mathrm{P}-{}^3\mathrm{C}_{60}$ was also studied. Within experimental error, the results were identical to those obtained with model fullerene **2**. These results are consistent with formation of $\mathrm{C}-\mathrm{P}-{}^3\mathrm{C}_{60}$ by normal intersystem crossing.

Discussion

Kinetics of Charge Separation. Fluorescence experiments on **1** at 298 K in 2-methyltetrahydrofuran using the single photon timing technique show that the porphyrin first excited singlet state decays with a time constant of 10 ps by a combination of photoinduced electron transfer to yield $\mathrm{C}-\mathrm{P}^{\bullet+}-\mathrm{C}_{60}{}^{\bullet-}$ and singlet energy transfer to the fullerene ($k_1 + k_3 = 1.0 \times 10^{11}\ \mathrm{s}^{-1}$).[26] The fullerene first excited singlet state decays by photoinduced electron transfer to also give $\mathrm{C}-\mathrm{P}^{\bullet+}-\mathrm{C}_{60}{}^{\bullet-}$, with $k_2 = 3.1 \times 10^{10}\ \mathrm{s}^{-1}$. As the lifetimes of the porphyrin and fullerene excited singlet states in appropriate model compounds are several nanoseconds, the quantum yield of $\mathrm{C}-\mathrm{P}^{\bullet+}-\mathrm{C}_{60}{}^{\bullet-}$ is essentially unity. The subpicosecond transient absorption experiments mentioned above show that the final $C^{\bullet+}-P-C_{60}^{\bullet-}$ charge-separated state forms with a time constant of 65 ps, so that the sum of k_4 and k_7 is 1.5×10^{10} s^{-1}. The yield of $C^{\bullet+}-P-C_{60}^{\bullet-}$ is 0.14.

The kinetics of these formation steps have not been measured at lower temperatures. However, at 77 K, charge separation occurs from $C-{}^{1}P-C_{60}$ (but not $C-P-{}^{1}C_{60}$), and $C^{\bullet+}-P-C_{60}^{\bullet-}$ is produced with a yield of 0.12, based on light absorbed by the porhpyrin.[26] Electron transfer by step 3 must still be relatively fast at this temperature, as the lifetime of the porphyrin first excited singlet state in a model carotenoporphyrin is 7.2 ns at ambient temperatures. The EPR results indicate a high yield of $C^{\bullet+}-P-C_{60}^{\bullet-}$ even at 10 K, and at this temperature, the rise time of $C^{\bullet+}-P-C_{60}^{\bullet-}$ is too short to be measured by the EPR spectrometer (time resolution = 100 ns). Thus, the electron-transfer steps leading to the formation of $C^{\bullet+}-P-C_{60}^{\bullet}-$ are relatively insensitive to changes of temperature. This behavior is quite different from that observed with most porphyrin−quinone and similar dyad systems, where photoinduced electron transfer ceases at temperatures where the solvent becomes glassy,[2,3,6] but similar to that observed in photosynthetic reaction centers.

Kinetics of Charge Recombination. At 298 K in 2-methyltetrahydrofuran, optical measurements show that recombination of $C^{\bullet+}-P-C_{60}^{\bullet-}$ to give mainly ${}^{3}C-P-C_{60}$ occurs with $k_9 = 5.9 \times 10^6$ s^{-1} ($\Phi = 0.13$). At 77 K in a glass, the same processes occur. The carotenoid triplet state is formed with an overall quantum yield of ∼0.07, and $k_8 + k_9 = 6.7 \times 10^5$ s^{-1}.[26] Thus, reducing the temperature by 221 K and freezing the solvent reduces the charge recombination rate by only a factor of ∼9. As shown by the EPR results, additional cooling of the sample to 20 K does not change the radical pair recombination rate ($k_8 + k_9 = 6.6 \times 10^5$ s^{-1}). Thus, recombination is relatively insensitive to temperature in the 77 to 298 K region, and temperature independent at lower temperatures.

Although complete interpretation of the temperature dependence of charge recombination in **1** will have to await the results of a thorough temperature study, the few data obtained so far suggest a relatively weakly activated electron-transfer process at ambient temperatures which switches to a temperature-independent rate somewhere above 77 K. Phenomenologically, this is consistent with control of electron transfer by nuclear tunneling at low temperatures and charge recombination in the Marcus inverted region at higher temperatures.[34] Electrochemical measurements in polar solvents allow estimation of the energy of $C^{\bullet+}-P-C_{60}^{\bullet-}$ as 1.24 eV above the ground state. The energy of ${}^{3}C-P-C_{60}$ is about 0.63 eV.[35] The driving force for charge recombination of $C^{\bullet+}-P-C_{60}^{\bullet-}$ to the carotenoid triplet is expected to be more negative than −0.61 eV at 20K, since the small effective solvent dielectric constant in the glass should tend to destabilize the charge-separated state relative to polar solvents. The solvent reorganization energy at 20 K must be very small, and the internal reorganization energy of the triad is also expected to be substantially less than 0.61 eV. Thus, inverted behavior is expected. Charge recombination of $C^{\bullet+}-P-C_{60}^{\bullet-}$ to the ground state is therefore much more strongly inverted. This is consistent with the finding that charge recombination to yield the triplet is faster than recombination to the ground state.

Kinetics of Carotenoid Triplet Decay. The decay rate of ${}^{3}C-P-C_{60}$ has been determined by EPR spectroscopy, and by optical spectroscopy with laser flash photolysis.[26] In the EPR experiment, the measurement reports the decay of the zero-field triplet sublevel corresponding to the canonical direction chosen. The values obtained for these three rate constants, $k_x = 3.0 \times 10^5$ s^{-1}, $k_y = 3.0 \times 10^4$ s^{-1}, and $k_z = 1.1 \times 10^5$ s^{-1}, agree with those from recent TREPR measurements at 20 K on the same carotenoid moiety in a carotenoporphyrin dyad ($k_x = 2.2 \times 10^5$ s^{-1}, $k_y = 3.0 \times 10^4$ s^{-1}, $k_z = 1.5 \times 10^5$ s^{-1}).[36] In the dyad the carotenoid triplet state is populated by triplet−triplet transfer from the porphyrin moiety under photoexcitation. Even though the sublevel populations of the carotenoid triplet state are generated by a different mechanism with respect to those of the carotenoid triplet state in the triad, the decay rate constants are characteristic of the carotenoid only and are then expected to be the same in the two compounds.

The optical experiments reported earlier[26] measured the overall decay of the triplet population. At 298 K in 2-methyltetrahydrofuran and in the absence of oxygen, ${}^{3}C-P-C_{60}$ decays exponentially with $k_{12} = 2.0 \times 10^5$ s^{-1}. At 77 K, the decay at 550 nm (where the carotenoid triplet has a maximal extinction coefficient) could be fitted satisfactorily with two exponentials having time constants of 10 μs (87%, corresponding to ${}^{3}C-P-C_{60}$) and 83 μs (13%, corresponding to $C-P-{}^{3}C_{60}$). Carotenoid triplet states show slow thermal relaxation among triplet sublevels, compared to their lifetimes, up to 100−120 K, even in the absence of external magnetic fields.[37] The decay of the carotenoid triplet absorption at 77 K determined optically at 550 nm was simulated by using the rate constants and populations of the three zero-field levels derived from the EPR results and adding a fourth component (13%) corresponding to $C-P-{}^{3}C_{60}$ decay. Very good agreement between calculated and experimental decay curves was obtained, showing that the optical and EPR data are completely compatible. This also indicates that the rate constants for the decay of the three carotenoid triplet sublevels at 77 and 20 K are identical, and their average differs little from the value at 298 K. This is expected for a conventional activationless intersystem crossing process.

Spin Polarization. The spin polarization observed for the different species by transient EPR spectroscopy can yield important mechanistic information. In the current study, patterns were observed for three different species. For $C-P-{}^{3}C_{60}$, an *aaa eee* pattern was noted. This pattern is one of those characteristic of spin−orbit selective intersystem crossing from a singlet state.[8] Thus, this species originates from the fullerene first excited singlet state, and has nothing to do with the electron-transfer processes. With excitation of **1** at 580 nm, the porphyrin moiety absorbs about 80% of the light and the fullerene about 20%. The yield of intersystem crossing in fullerenes such as that in **1** is essentially unity.[27] This high yield and the small D value for $C-P-{}^{3}C_{60}$ explain the high intensity of the EPR signal for this species (Figure 2).

The carotenoid triplet EPR spectrum of **1** displays *eaa eea* polarization. As mentioned above, this pattern cannot arise through spin−orbit coupling, and is characteristic of triplets formed by charge recombination of a radical pair resulting from photoinduced electron transfer from an excited singlet state.[8,30] In this mechanism, the excited singlet state ($C-{}^{1}P-C_{60}$ in the present case) generates a singlet radical pair state. This state equilibrates with a nearly isoenergetic triplet sublevel (e.g., T_0)

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by dephasing of the weakly interacting electron spins promoted by the combined action of the exchange/dipolar and Zeeman/hyperfine interactions. Population of the other two triplet sublevels from the singlet or T_0 levels is not observed at high magnetic fields and low temperatures on the time scale of interest. Charge recombination from the T_0 level of the triplet radical pair yields the spin-polarized carotenoid triplet (^{3}C−P−C$_{60}$).

Finally, we consider the polarization of the signal that arises from the C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ radical pair, which is the progenitor of the carotenoid triplet state. Referring to Figure 1, the spin polarization might arise in either C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ or its precursor, C−P$^{\bullet+}$−C$_{60}$$^{\bullet-}$. Development of spin polarization in a radical pair by the mechanisms mentioned above requires several nanoseconds or longer. As mentioned above, the lifetime of C−P$^{\bullet+}$−C$_{60}$$^{\bullet-}$ in 2-methyltetrahydrofuran solution at 298 K is 65 ps. As the other electron-transfer rate constants in **1** are relatively insensitive to temperature, it is unlikely that the rates of steps 4 and 7 would decrease by the required amount at 20 K. In addition, photoinduced electron transfer from the carotenoid to the porphyrin radical cation in a closely related carotenoid−porphyrin−quinone triad occurs within a few tens of picosecond in solution.[38] Thus, we assume that the lifetime of C−P$^{\bullet+}$−C$_{60}$$^{\bullet-}$ is too short to allow significant polarization effects to develop. The polarization must arise within C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ due to spin dephasing by the mechanisms mentioned earlier.

This being the case, the signal pattern will depend on the g-factors and inhomogeneous line width differences between the carotenoid and fullerene radicals (the simulations are insensitive to the assumed homogeneous line widths as long as they are smaller than the inhomogeneous ones), and on the absolute values and signs of their exchange (J) and dipolar (D) interactions.[39] The basic description of the short-lived radical pair is a four level system with eigenfunctions and energies given by:[39]

$$\begin{array}{ll} |1\rangle = |T_{+1}\rangle & \omega_1 = \omega - J + D_{zz}/2 \\ |2\rangle = \cos\psi|S\rangle + \sin\psi|T_0\rangle & \omega_2 = \Omega - D_{zz}/2 \\ |3\rangle = -\sin\psi|S\rangle + \cos\psi|T_0\rangle & \omega_3 = -\Omega - D_{zz}/2 \\ |4\rangle = |T_{-1}\rangle & \omega_4 = -\omega - J + D_{zz}/2 \end{array}$$

with:

$$\omega = (\omega_A + \omega_B)/2$$

where (ω_A, ω_B) are the EPR frequencies of the two radicals in the absence of exchange and dipolar interactions;

$$D_{zz} = D(\cos^2\xi - 1/3)$$

with ξ the angle between the dipolar axis and the magnetic field direction;

$$\Omega^2 = (J + D_{zz}/2)^2 + (\omega_A - \omega_B)^2/4$$

and finally,

$$\tan 2\psi = \frac{(\omega_A - \omega_B)}{(2J + D_{zz})}$$

The J value describes the exchange contribution $-J(\boldsymbol{S}^2 - 1)$, and D_{zz} the magnetic dipolar contribution $(1/2)D_{zz}(3\boldsymbol{S_z}^2 - \boldsymbol{S}^2)$ to the Hamiltonian, the first being considered usually isotropic and the second being axially symmetric around the z line joining the two radicals as suitable for a point dipole interaction.

Since the initial population of the spin pair is concentrated in levels 2 and 3 with $M_S = 0$ (singlet precursor), the spectrum consists, for a given direction with respect to the magnetic field, and neglecting electron spin relaxation, of two doublets in antiphase.

The frequencies of the four EPR lines are:

$$\omega_{12} = \omega - \Omega - J + D_{zz}$$

$$\omega_{34} = \omega - \Omega + J - D_{zz}$$

$$\omega_{13} = \omega + \Omega - J + D_{zz}$$

$$\omega_{24} = \omega + \Omega + J - D_{zz}$$

corresponding to two doublets centered at $\omega \pm \Omega$ with splitting of $2(J - D_{zz})$. The spectrum of a randomly oriented radical pair is obtained by spherical averaging.

Note that a multiplicity of frequencies due to hyperfine structure would be necessary for a resolved spectrum; in our case, however, we may account for the unresolved hyperfine structure, in the following simulations, by using Gaussian line shapes for each doublet and assigning the corresponding widths which simulate each single radical spectrum.

The g-factors giving the ω_A and ω_B values and the peak-to-peak derivative line widths, ΔH_{pp}, which simulate the unresolved structure of the two radical moieties, can be taken from the literature EPR spectra for the corresponding radical ions in model carotenoids and fullerenes. They are $g = 2.0027$ and $\Delta H_{pp} = 20$ G for the carotenoid radical cation[40] and $g = 1.998$ and $\Delta H_{pp} = 1$ G for the fullerene anion.[41,42] The D value may be safely estimated by the point dipole approximation, given the large distance between the two radicals. Molecular mechanics calculations on **1** with the InsightII molecular-modeling package from Biosym Technologies yielded low-energy conformations with distances from the center of the carotenoid π-electron system to the center of the fullerene of ~36 Å. This in turn gives a D value of −0.6 G.

The remaining parameter necessary for the simulation of the radical pair spectrum is the value of J. Because the carotenoid radical cation has a large inhomogeneous line width, while that of the fullerene (with little hyperfine interaction due to protons) is much smaller, the doublet due to the carotenoid radical cation is practically undetectable in the spectrum. Figure 6 shows simulations for various $|D|/|J|$ ratios and various signs of J. The solid lines are the spectra obtained with no inhomogeneous broadening and show the complete expected polarization spherically averaged over the random molecular orientations. The dotted lines are the spectra convoluted with the Gaussian line shapes, which makes the carotenoid doublet disappear due to the hyperfine broadening.

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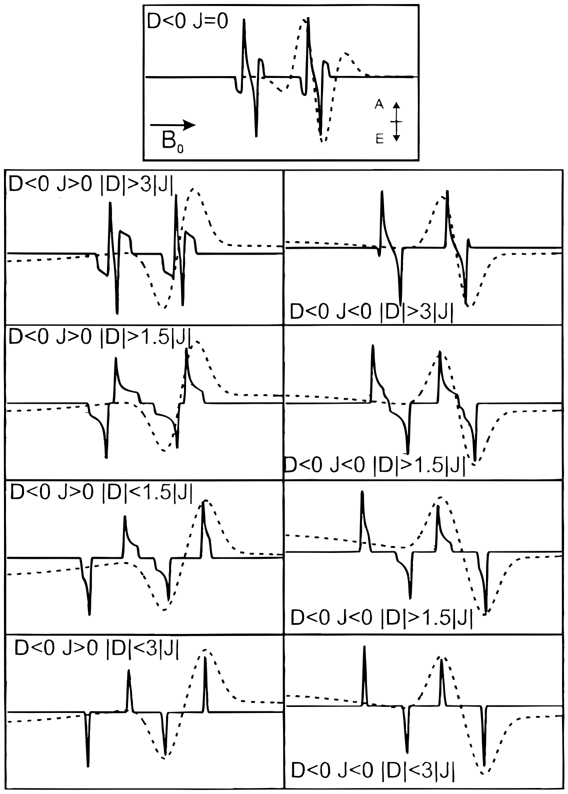

Figure 6. Simulated EPR spectra of the C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ radical pair for different values of the D/*J* ratio, using other parameters as discussed in the text: (—) $\Delta H_{pp} = 0.03$ G for both radicals; (- - -) $\Delta H_{pp} = 1$ G for C$_{60}$$^{\bullet-}$ and $\Delta H_{pp} = 20$ G for C$^{\bullet+}$.

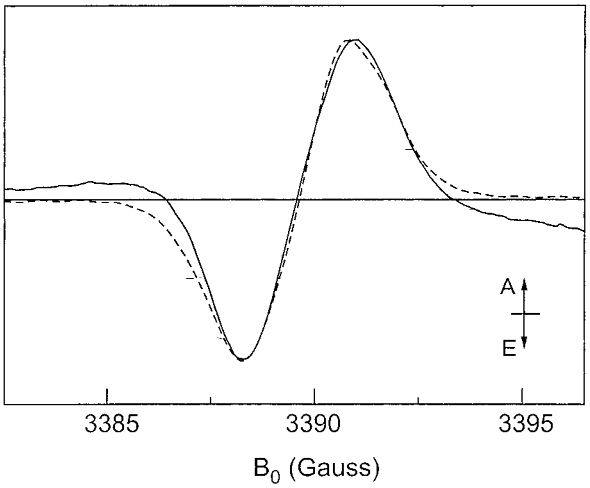

Figure 7. Experimental EPR spectrum of the C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ radical pair (—), and best-fit simulation with $D = -0.6$ G and $J = +1.2$ G (- - -).

As shown in Figure 6 the polarization pattern of the experimental spectrum cannot be reproduced for negative or zero *J* values. The best simulation gave a *J* value of +1.2 G. This spectrum and the experimental data are compared in Figure 7.

A positive value for *J* (triplet radical pair below singlet radical pair) is considered anomalous for untethered radical pairs, where the solvent cage keeps the two radicals at relatively short distances from one another during the encounter.[43] In linked systems such as the one under investigation and in donor−acceptor systems found in biological macromolecules, the two partners can be kept separated at much larger distances. In these cases, the sign of the exchange interaction is more difficult to predict.[44] In the case of **1**, where the carotenoid radical cation and fullerene radical anion are separated by a large distance (from the point of view of magnetic interactions), the nonzero value of *J* is indicative of an electronic interaction between the two moieties mediated by a superexchange mechanism involving the porphyrin ring.

Conclusions

The EPR studies on triad **1** are in complete accord with the results of the earlier optical studies. Excitation of the porphyrin moiety is followed by photoinduced electron transfer from the first excited singlet state to yield an intermediate C−P$^{\bullet+}$−C$_{60}$$^{\bullet-}$ charge-separated state. This species evolves into a final C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ radical pair state that can be detected by TREPR. The radical pair state decays to yield mainly the carotenoid triplet, ^{3}C−P−C$_{60}$, which then decays to the ground state. These events occur not only in solution at ambient temperatures, but also in a glass at temperatures as low as 10 K. The temperature dependence of the charge recombination reaction of C$^{\bullet+}$−P−C$_{60}$$^{\bullet-}$ is extremely weak.

The *eaa eea* spin polarization pattern of the carotenoid triplet EPR signal is characteristic of a triplet formed by recombination of a singlet-born radical pair, rather than normal spin−orbit coupling induced intersystem crossing. A related polarization, *aee aae*, is observed for chlorophyll triplets in photosynthetic reaction centers whose electron transport chain has been blocked. It is also due to radical pair recombination, but the pattern is inverted compared to that in **1** because the triplet sublevels of the chlorophyll are inverted ($D > 0$) with respect to those of the carotenoid ($D < 0$). Indeed, the polarization pattern *eaa eea* has been observed in the TREPR spectrum of carotenoid triplet states in carotenoid-containing bacterial reaction centers. In these reaction centers, the carotenoid triplet is formed by triplet−triplet energy transfer from the spin-polarized chlorophyll triplet, and thus inherits its polarization.[11]

In contrast to the natural photosynthetic system, the formation of spin-polarized local triplet states by a similar radical pair mechanism is very rare in synthetic systems. Triad **1** is the first example of a synthetic system that mimics such spin polarization when a pigment that also shows this phenomenon in natural reaction centers is used. Rapid formation of triplet states with unusual polarization through charge recombination of charge-shifted species has been observed in UV-absorbing molecular dyads where the donor and acceptor are nearly orthogonal π-electron systems, but the mechanism in this case is a special form of spin−orbit coupling.[46] Hasharoni and coworkers have observed spin-polarized triplet formation by radical pair recombination similar to that seen in **1** and natural reaction centers in an imide-based, UV-absorbing triad oriented in a nematic liquid crystal.[12,13]

All previous reaction center models employing pigments related to natural chlorophylls and carotenoids have demonstrated charge recombination to the ground state, rather than radical-pair induced triplet formation. In addition, the vast majority of these model systems fail to undergo photoinduced electron transfer in glasses at low temperatures. For example,

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a recently reported carotenoid−porphyrin−naphthoquinone triad undergoes photoinduced electron transfer in polar solvents from the porphyrin first excited singlet state to give C−P$^{•+}$−NQ$^{•-}$, which evolves into C$^{•+}$−P−NQ$^{•-}$. This triad has a carotenoid moiety identical to that in **1**, and the final charge-separated state has an energy of 1.23 eV above the ground state.[47,48] In **1**, the energy of C$^{•+}$−P−C$_{60}$$^{•-}$ in polar solvents is 1.24 eV. In the quinone-containing triad, the C$^{•+}$−P−NQ$^{•-}$ state recombines to the ground state, rather than the carotenoid triplet state, and photoinduced electron transfer does not occur in a glass at 77 K. Comparison of the results for **1** with those for this and other triads suggests that the unusual properties of **1** must derive from the fullerene moiety and associated reorganization and stabilization energies, rather than from differences in oxidation and reduction potentials and energies of excited states as measured in polar solvents.

Experimental Section

The synthesis of **1** has been reported.[26] Laser excitation at 580 nm was provided by a Lambda Physik LPX100 excimer laser (pulse width 20 ns, energy per pulse ∼180 mJ, repetition frequency 20 Hz) coupled to a modified FL2000 dye laser using Rhodamine 6G. The energy per pulse from the dye laser was 20−25 mJ. The EPR spectrometer was an X-band Bruker 200D equipped with a TM110 cavity and an Oxford Instruments flow cryostat. Time-resolved experiments were performed without field modulation with use of a wide-band preamplifier and sampling the signal either with a LeCroy 9361 oscilloscope (3 ns per point) or with an EG&G 162 boxcar averager.

Transient absorption measurements at ambient temperature on the subpicosecond time scale were made by using the pump−probe technique. The sample was dissolved in purified 2-methyltetrahydrofuran and the resulting solution was circulated by magnetic stirring in a cuvette having a 2-mm path length in the beam area. Excitation was at 590 nm with 150−200 fs, 30 μJ pulses at a repetition rate of 540 Hz. The signals from the continuum-generated white-light probe beam were collected by an optical spectrometric multichannel analyzer with a dual diode array detector head.[49]

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