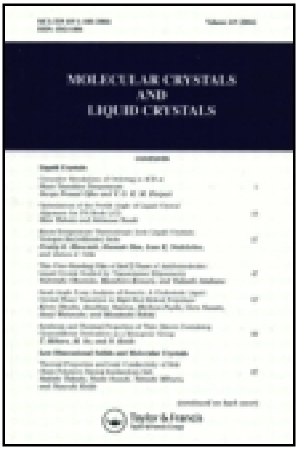

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Reaction Center Models in Liquid Crystals: Identification of Paramagnetic Intermediates

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REACTION CENTER MODELS IN LIQUID CRYSTALS: IDENTIFICATION OF PARAMAGNETIC INTERMEDIATES

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Photoinduced charge separation and recombination to the triplet state in a carotene (C) porphyrin (P) fullerene (C_{60}) triad have been followed by time-resolved electron paramagnetic resonance (EPR). The electron transfer process has been studied at different temperatures in both a glassy isotropic matrix (2-methyltetrahydrofuran) and uniaxial liquid crystal (E-7). In both media, the triad undergoes two-step photoinduced electron transfer, with the generation of a long-lived charge separated state ($C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$), and charge recombination to the triplet state, localized in the carotene moiety. The carotenoid triplet state is initially polarized according to the mechanism of recombination of a radical pair with singlet precursor. Both the photoinduced spin-correlated radical pair and the carotene triplet are observed in E-7 starting from the glass to the liquid crystal phase. The exchange interaction between the electrons in the radical pair ($J = 1.2$ Gauss) has been evaluated by simulation of the EPR spectrum in the isotropic glass and comparison with the corresponding spectrum in the oriented medium.

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Keywords: photosynthetic model system; electron transfer; liquid crystals; EPR

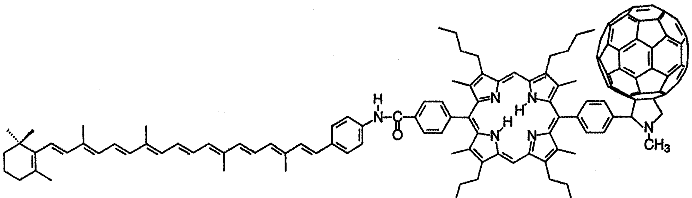
INTRODUCTION

Supramolecular systems consisting of organic pigments covalently linked to electron donor and/or acceptor moieties have long been investigated as models for photoinduced electron transfer in photosynthetic reaction centers [1–3]. Most of the reaction center models have employed quinones, porphyrins or aromatic imides as electron acceptors. In more recent times fullerene derivatives have been found to be excellent acceptor components in such supramolecular systems [4,5].

The synthesis and photochemistry of three different carotene (C) porphyrin (P) fullerene (C_{60}) triads have been reported [6–8]. The apparently small structural differences between them lead to significant changes in electronic coupling and driving force, affecting the rates and yields of the photoinduced electron-transfer reactions. These molecular triads mimic several aspects of photosynthetic electron transfer, including photoinduced electron transfer in a glass at low temperature, charge recombination to the triplet state and photoprotection by a triplet energy transfer relay mechanism [9]. For the first synthesized C-P-C_{60} triad (triad **1**, see Liddell et al. [6]), the exchange interaction between the electrons in the $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ radical pair and the triplet recombination mechanism have been determined by electron paramagnetic resonance experiments [10].

The second C-P-C_{60} triad (triad **2**), differing from the previous one mainly by the reversal of the amide linkage joining the carotenoid and the porphyrin moieties, has been studied and compared to triad **1** in terms of its photoinduced electron-transfer behaviour, as a function of temperature and solvent, by time-resolved optical spectroscopy [7]. At low temperature (77 K), in 2-methyltetrahydrofuran (2-MeTHF) glass, excitation of the porphyrin moiety leads to photoinduced electron transfer from the porphyrin first excited singlet state to the fullerene, yielding the C-$P^{\bullet+}$-$C_{60}{}^{\bullet-}$ charge separated state. The latter evolves by electron donation from the carotenoid to give the $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ long-lived charge separated state which decays mainly by charge recombination to give the carotenoid triplet (^{3}C-P-C_{60}), rather than the ground state. Direct excitation of the fullerene moiety yields the C-P-$^1C_{60}$ state, which, at low temperatures, is not quenched by electron transfer but decays by intersystem crossing to give C-P-$^3C_{60}$. At ambient temperature, the C-P-$^1C_{60}$ state also undergoes photoinduced electron transfer to yield the C-$P^{\bullet+}$-$C_{60}{}^{\bullet-}$ charge separated state.

The photochemistry of triad **2** in 2-MeTHF has also been studied by time-resolved electron paramagnetic resonance (TREPR) and, in a preliminary work [11], the assignment of all the observed paramagnetic species ($C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$, ^{3}C-P-C_{60}, C-P-$^{3}C_{60}$) was made. In the present study we compare the photochemistry of this triad in the glassy 2-MeTHF matrix and in the uniaxial liquid crystal (E-7). Time-resolved EPR spectroscopy is used to characterize both the radical pair and the recombination triplet state in terms of their spin polarization and kinetic properties, in the isotropic matrix and in the different phases of E-7.



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EXPERIMENTAL

Time-resolved EPR spectra were obtained using a pulsed laser light guided into an X-band EPR spectrometer (Bruker ER 200D) equipped with a low-Q TE_{011} cavity and a nitrogen flow-system or with a TE_{102} cavity and a helium flow cryostat (Oxford ESR 900). The time–resolution of the TREPR spectrometer is ~180 ns. Laser excitation at 580 nm was provided by a Lambda Physik LPX 100 excimer laser pumping a modified FL 2000 dye laser using Rhodamin 6G (pulse bandwidth 20 ns, repetition frequency 20 Hz, energy per pulse from the dye laser ~ 10 mJ). Excitation at 580 nm yields mostly C-^{1}P-C_{60}. No field modulation or phase-sensitive detection was used. The transient signals were sampled with a Lecroy 9361 oscilloscope (3 ns per point).

The synthesis of triad **2** has been reported [7]. Solutions of triad **2** in 2-MeTHF (~1 mM) were deaerated by several freeze-thaw cycles and sealed under vacuum. The liquid crystal samples (~1 mM) were prepared by dissolving triad **2** in toluene solution, evaporating the solvent and then introducing E-7; samples were degassed and sealed as described above. The alignment of the liquid crystal samples was carried out in the nematic phase under an external high magnetic field (8000 Gauss) for 10 min and, if required, by fast cooling down to the crystalline phase in the high magnetic field conditions [12].

RESULTS AND DISCUSSION

TREPR in 2-MeTHF

Figure 1 shows the spin-polarized EPR powder spectrum at 0.5 μs after the laser pulse of triad **2** in 2-MeTHF glass. The EPR spectrum is very similar to the one previously reported for triad **1** in the same experimental conditions [10].

The strong resonance in the center of the spectrum can be assigned to the fullerene triplet state (C-P-$^3C_{60}$). The polarization pattern and the D and E values ($|D| = 0.0090\,\mathrm{cm}^{-1}$, $|E| = 0.0014\,\mathrm{cm}^{-1}$) of this triplet are those observed for a model fullerene compound [13]. Also the kinetic behaviour of this triplet EPR signal is identical to that obtained for the model fullerene (results not shown), showing that the C-P-$^3C_{60}$ is formed by normal intersystem crossing and is only a side product of the photoprocess. At 580 nm, in fact, ~20% of the absorbed light excites the fullerene moiety directly.

The broader signal, which overlaps with the C-P-$^3C_{60}$ spectrum (see the expansion of the spectrum in Fig. 1a) can be assigned to the carotenoid

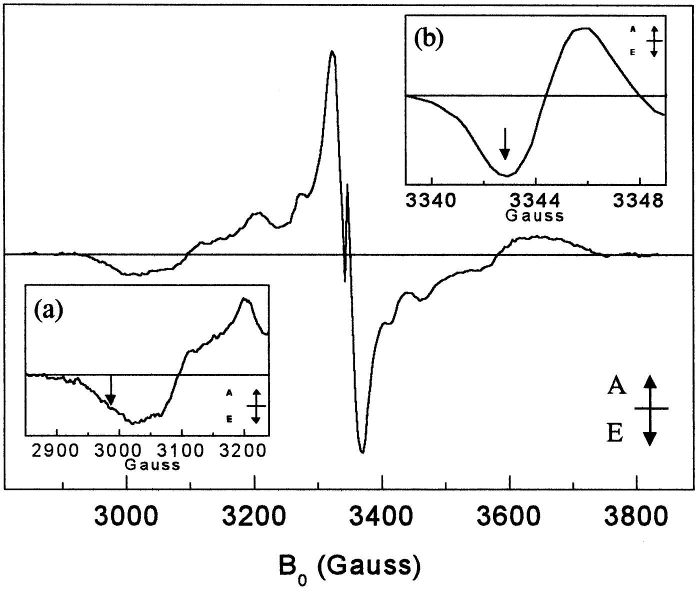

FIGURE 1 Time–resolved EPR spectrum of triad **2** in 2-MeTHF at 0.5 μs after the laser flash. Experimental conditions: T = 20 K, $\nu_{mw} = 9.4$ GHz, $P_{mw} = 2$ mW. (a) Expansion of the spectrum in the carotenoid triplet low-field region. (b) Expansion of the spectrum of the $C^{\bullet +}$-P-$C_{60}{}^{\bullet -}$ radical pair. A = absorption, E = emission.

triplet state (^{3}C-P-C$_{60}$). Only the low-field region of the spectrum is shown, given the symmetry of the lines with respect to the central field. The zero field splitting parameters ($|D| = 0.0358\,\mathrm{cm}^{-1}$, $|E| = 0.0032\,\mathrm{cm}^{-1}$) are similar to those of a linear polyene with 9 double bonds [14]; the spin polarization pattern (*eaa eea*) observed is characteristic of a triplet state with $D < 0$ (rodlike molecules) populated exclusively in the T_0 high-field sublevel. This polarization pattern cannot arise from a spin-orbit coupling promoted intersystem crossing and it is produced by charge recombination of a singlet born radical pair.

The narrow signal (peak to peak 2.8 Gauss) observed in the center of the spectrum (Fig. 1b) can be assigned to the C$^{\bullet+}$-P-C$_{60}{}^{\bullet-}$ radical pair state both in terms of the kinetic behaviour and spin polarization, as will be discussed in the next paragraphs.

Figure 2 shows the time evolution of the EPR signals corresponding to the low-field transition for the canonical z-orientation of the carotenoid triplet state and the low-field emission peak of the C$^{\bullet+}$-P-C$_{60}{}^{\bullet-}$ radical pair signal. The transient signals have been normalized at their maxima to facilitate comparison of the kinetics. The field positions at which the transient EPR signals have been recorded are shown with arrows in Figs. 1a and 1b. The narrow C$^{\bullet+}$-P-C$_{60}{}^{\bullet-}$ EPR signal decay is correlated with the growth of the carotenoid triplet state, consistent with both the assignment of the EPR signals and the assertion that the carotenoid triplet state is formed by charge recombination. The time evolution of the high-field signals gives the same result.

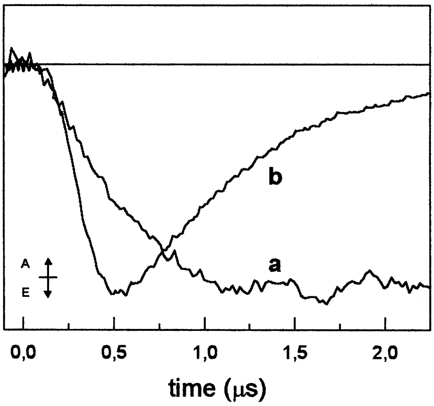

FIGURE 2 Time evolution of the EPR signals from triad **2** in 2-MeTHF. (a) Low-field z-transition of the^{3}C-P-C$_{60}$ at 2970 G (b) C$^{\bullet+}$-P-C$_{60}{}^{\bullet-}$ radical pair at 3343 G. Experimental conditions: $T = 20$ K, $\nu_{mw} = 9.4$ GHz, $P_{mw} = 2$ mW, sampling interval = 10 ns. A = absorption, E = emission.

Simulations of the radical pair EPR spectrum have been performed, in the framework of P. Hore [15], in order to extract the important mechanistic information contained in the spin polarization pattern. The best-fit simulation is shown together with the experimental EPR spectrum taken at 0.25 μs from the laser pulse in Figure 3. The narrow EPR signal can be in this way definitively assigned to the long-lived charge separated state $C^{\bullet +}$-P-$C_{60}{}^{\bullet -}$: the polarization pattern is consistent with a correlated radical pair mechanism with a singlet precursor, in which the exchange interaction is positive and it is the main contribution to the splitting of the signal ($J = 1.2$ Gauss). While the exchange parameter has been derived from the best-fit simulation, the zero-field splitting parameter ($D = -0.6$ Gauss) has been estimated in the point-dipole approximation, given the large distance between the two radicals (center to center ~36 Å). All the other parameters for the simulation are the same as the ones used in the previous TREPR study on triad **1** [10].

As in the case of the triad **1**, a positive value for the exchange interaction between the electrons has been found. Given the large separation between the carotenoid radical cation and the fullerene radical anion, the non-zero value of J is indicative of an electronic interaction between the two moieties mediated by a superexchange mechanism involving the porphyrin ring. The result of the simulation shows also that the exchange interaction does not change upon reversal of the amide linkage joining the carotenoid to the porphyrin.

In order to confirm the results of the simulation of the spin-correlated radical pair, we have also performed time-resolved EPR on triad **2** in the

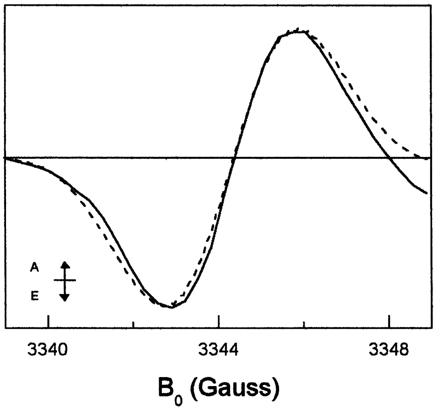

FIGURE 3 Experimental EPR spectrum of the $C^{\bullet +}$-P-$C_{60}{}^{\bullet -}$ in 2-MeTHF at 0.25 μs after the laser flash (—) and best-fit simulation (- - -) with $D = -0.6$ G and $J = 1.2$ G. Experimental conditions as in Figure 1. A = absorption, E = emission.

oriented matrix of E-7. Liquid crystal solvents are convenient media, both for the advantage of slowing down the rates of intramolecular electron transfer and also in terms of orientational effects on the EPR spectrum [16,17].

TREPR in E-7

Figure 4 shows the spin-polarized EPR spectrum at 0.5 μs after the laser pulse of triad **2** in the nematic phase of E-7, at ambient temperature. Contributions from all the three paramagnetic species (^{3}C-P-C_{60}, $C^{\bullet +}$-P-$C_{60}{}^{\bullet -}$, C-P-$^3C_{60}$) are recognizable in the EPR spectrum. Furthermore, a high degree of ordering of the liquid crystal sample is apparent when comparing the EPR spectrum to the corresponding one in 2-MeTHF glass (see Fig. 1): the lineshape and polarization of the EPR signals of both carotenoid (see Figure 4a) and fullerene triplets are those of a partially ordered rather than a powder type spectrum.

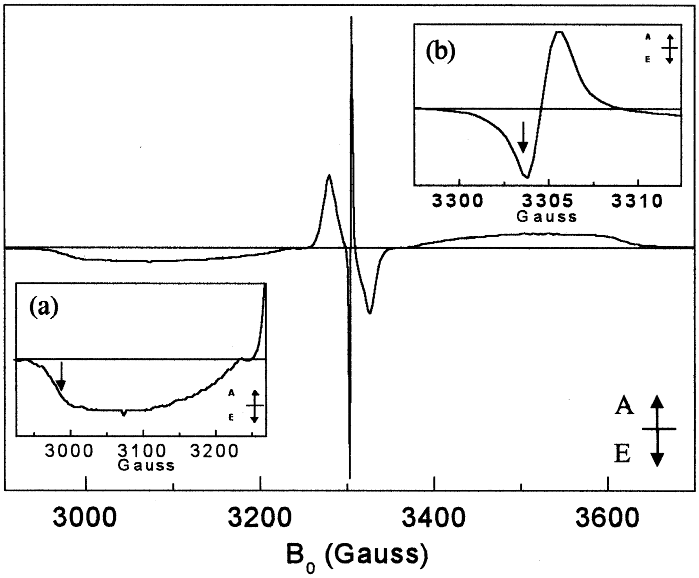

FIGURE 4 Time–resolved EPR spectrum of triad **2** in the nematic phase of E-7 at 0.5 μs after the laser flash. Experimental conditions: T = 295 K, ν_{mw} = 9.3 GHz, P_{mw} = 2 mW. (a) Expansion of the spectrum in the carotenoid triplet low-field region. (b) Expansion of the spectrum of the $C^{\bullet +}$-P-$C_{60}{}^{\bullet -}$radical pair. A = absorption, E = emission.

The main contribution to the spectrum is not, as in the case of 2-MeTHF, the fullerene triplet but the narrow EPR signal at the center, whose enlargement is shown in Figure 4b. This signal has been attributed also in this case to the $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ radical pair. The assignment is based on the kinetic behaviour and on the lineshape features, as it will be explained in the next paragraphs.

Figure 5 shows the time evolution of the EPR signals corresponding to the low-field transition for the canonical *z*-orientation of the carotenoid triplet state and the low-field emission peak of the $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ radical pair signal, in the nematic phase of E-7 (T = 295 K). The field positions at which the transient EPR signals have been recorded are shown with arrows in the Figures 4a and 4b.

As in 2-MeTHF, the $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ EPR signal decay is accompanied by the rise of the carotenoid triplet state, proving the assignment of the paramagnetic species and that the generation of a long-lived charge separated state followed by recombination to the triplet state are observed also in the nematic phase of the uniaxial liquid crystal solvent at ambient temperature.

The time evolution of both the radical pair and the carotenoid triplet signals shows some differences in the nematic phase of E-7 (Fig. 5) with respect to 2-MeTHF (Fig. 2). The radical pair kinetic curve is characterized by a polarization phase inversion, which is not found in the 2-MeTHF glass. This inversion likely corresponds to the activation of the triplet initiated route for producing the radical pair state in the nematic phase of E-7. The

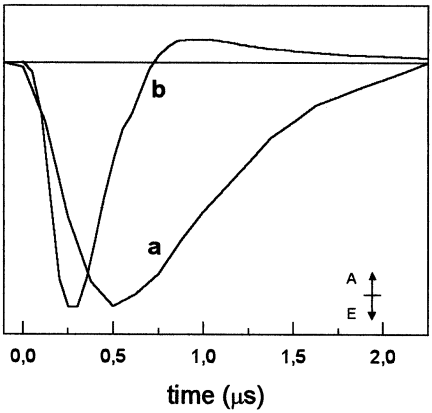

FIGURE 5 Time evolution of the EPR signals from triad **2** in the nematic phase of E-7. (a) Low-field *z*-transition of the ^{3}C-P-C_{60} at 2987 G and (b) $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ radical pair at 3303.5 G. Experimental conditions: T = 295 K, ν_{mw} = 9.3 GHz, P_{mw} = 2 mW, sampling interval = 50 ns. A = absorption, E = emission.

carotenoid triplet decay kinetics are accelerated in the nematic phase of E-7 compared to 2-MeTHF glass. This effect can be probably ascribed to magnetic relaxation effects which became active only at ambient temperature.

Further experiments show that the $C^{\bullet +}$-P-$C_{60}^{\bullet -}$ radical pair is formed also in the glass phase of E-7, allowing a direct comparison in the glass phase of both the isotropic and anisotropic solvents, and the possibility to vary the angle of the ordering director of the mesophase (**L**) with the external magnetic field (**B**). In this way, also the orientation dependence of the spectra can be investigated.

The $C^{\bullet +}$-P-$C_{60}^{\bullet -}$ radical pair signals at 0.25 µs from the laser pulse in both the glass (T = 150 K) and the nematic phases of E-7 and in 2-MeTHF (T = 20 K) are compared in Figure 6. The spectral positions have been superimposed and the spectra have been normalized at their maxima. The spectrum corresponding to the glass phase of E-7 has been recorded at the perpendicular orientation of the director **L** relative to the magnetic field. It has been obtained by rotation of the sample in the cavity by π/2 about an axis perpendicular to the external magnetic field. The radical pair spectrum corresponding to a parallel orientation of **L** relative to **B** has not been superimposed because for this orientation the stronger fullerene triplet contribution modifies the radical pair lineshape to the point that it cannot be used for comparison with the other spectra. In the fluid nematic phase (see Fig. 4), where the director is aligned parallel to the external magnetic

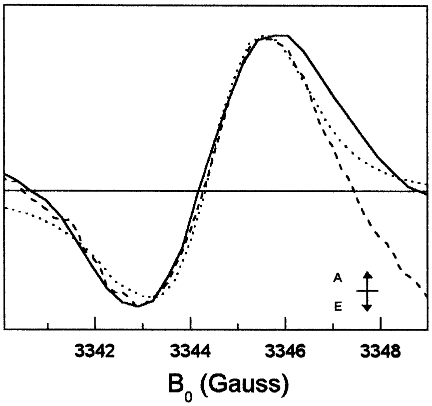

FIGURE 6 Time-resolved EPR spectra of the $C^{\bullet +}$-P-$C_{60}^{\bullet -}$radical pair at 0.25 µs from the laser flash in different media and temperatures: (—) in 2-MeTHF at T = 20 K, (---) in the glass phase of E-7 ($\mathbf{L} \perp \mathbf{B}$) at T = 150 K, (···) in the nematic phase of E-7 ($\mathbf{L} \parallel \mathbf{B}$) at T = 295 K. Experimental conditions as in Figs. 1 and 4. A = absorption, E = emission.

field, the fullerene triplet does not affect the radical pair lineshape given its small intensity as compared to the $C^{\bullet+}$-P-$C_{60}{}^{\bullet-}$ signal. Therefore, comparison of the radical pair EPR signal between the parallel and perpendicular orientation of the director relative to the magnetic field must be made using the glass data for the perpendicular orientation and the nematic phase data for the parallel orientation.

The carotenoid and fullerene partially ordered triplet spectra can be used to estimate the distribution function of the oriented sample in the liquid crystal. In particular, the emissive spin-polarization pattern of the carotenoid triplet low-field region indicates that the long molecular axis is parallel to both $\mathbf{L}$ and $\mathbf{B}$.

On the contrary, as it can be clearly seen in Figure 6, no significant spectral changes in the radical pair spectrum are produced by the orientational effect induced on the system by the liquid crystal medium or by the variation of the liquid crystal phase. The small differences in lineshape are due to a slightly different contribution of the fullerene triplet to the spectrum.

This result supports the evaluation of the exchange interaction parameter J as derived from the simulation of the radical pair EPR spectrum in 2-MeTHF glass (see Fig. 3). Even if the peak-to-peak width is not expected to be strongly affected by the orientation of the medium because the inhomogeneous hyperfine broadening is the dominant feature of the lineshape, effects should be visible when going from a $\mathbf{L} \parallel \mathbf{B}$ to a $\mathbf{L} \perp \mathbf{B}$ configuration in terms of the phase of the EPR signal as predicted by the correlated radical pair sign rule [15]. Inversion of the polarization when going from a $\mathbf{L} \parallel \mathbf{B}$ to a $\mathbf{L} \perp \mathbf{B}$ configuration is expected in the case where the dipolar interaction is the main contribution to the splitting of the spectrum. Invariance of the phase of the spectrum is instead predicted in the case where the exchange interaction is the main contribution, as it has been derived from the simulation of the spectrum. Therefore, the EPR experiments in the oriented liquid crystal medium, confirming the result of the radical pair EPR spectrum simulations, provide evidence for superexchange electronic interactions between the carotenoid and the fullerene, mediated by the porphyrin ring connecting the two moieties. The role of the bridge and the invariance of the exchange interaction when reversing the chemical linkage joining the carotenoid and the porphyrin are still under investigation.

CONCLUSIONS

The time-resolved EPR study of the molecular triad **2** in 2-MeTHF supports the photochemical scheme suggested by Kuciauskas et al. [7]: the generation of a long-lived charge separated state by photoinduced electron transfer and the formation in high yield of the carotenoid triplet state by charge recombination, in the glass at low temperatures. These photochemical processes are reminiscent of the primary events of photosynthesis, making this molecular triad a good model for artificial photosynthetic reaction centers.

The mimicry of the long-lived radical pair and triplet recombination by triad **2** is observed also in the uniaxial liquid crystal solvent, both in the crystalline and nematic phases.

The use of the liquid crystal medium allows us to follow the radical pair recombination kinetics of triad **2** over a wide temperature range, up to ambient temperature. A detailed kinetic study is in progress in order to derive recombination rates as a function of the temperature and discuss the results in the context of the electron transfer theory, taking into account the important role played by the fullerene moiety in terms of reorganization and stabilization energies.

Simulations of the spin-polarized radical pair EPR spectrum have given a non-zero, positive value for the exchange interaction between the electrons in the radical pair. The result is consistent with the one previously found for triad **1** and it is confirmed by the invariance of the radical pair spectra of triad **2** in the liquid crystal medium. No phase inversion of the radical pair spectrum has been observed when going from a $\mathbf{L} \parallel \mathbf{B}$ to a $\mathbf{L} \perp \mathbf{B}$ configuration, in accordance with the values for the exchange and dipolar interaction parameters derived from the best-fit simulation.

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