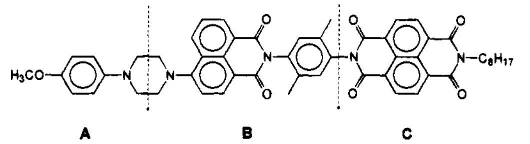
Mimicry of the Radical Pair and Triplet States in Photosynthetic Reaction Centers with a Synthetic Model

Kobi Hasharoni,[†] Haim Levanon,*[,†] Scott R. Greenfield,[‡]
David J. Gosztola,[‡] Walter A. Svec,[‡] and
Michael R. Wasielewski*[,‡,§]

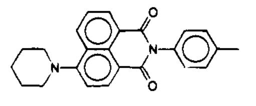
*Department of Physical Chemistry and
The Farkas Center for Light-Induced Processes
The Hebrew University of Jerusalem
Jerusalem 91904, Israel
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439
Department of Chemistry, Northwestern University
Evanston, Illinois 60208*

Received April 4, 1995

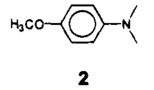
Supramolecular systems synthesized to model the photosynthetic reaction center (RC) are designed to mimic several key properties of the RC protein:[1] (1) multistep electron transfer (ET) to increase the lifetime of the radical pair (RP) product; (2) high quantum yield, fast formation, and slow recombination of the singlet-initiated charge separation; (3) temperature independent ET rates; and (4) spin polarization of the RP states. Thus far, most RC models fulfill only a subset of these criteria, with very few reports employing time-resolved electron paramagnetic resonance spectroscopy (TREPR).[2] Moreover, there is one key property of the RC primary photochemistry that has not been successfully mimicked by any model system until now. It is the ability of the RP intermediate within the photosynthetic RC to yield, upon charge recombination, a triplet state that retains a memory of the RP spin state and exhibits the TREPR signal characteristic of this triplet state. We now report TREPR results on a photosynthetic model system (**1**) in a nematic liquid crystal (LC) that does not contain the natural pigments, yet closely mimics the spin dynamics of triplet state formation found only in photosynthetic RCs. The advantages of employing LCs are given elsewhere.[3,4] The design of supermolecule **1** follows criteria established for promoting high quantum yield charge separation in glassy media.[5]



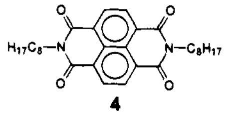
1



3



2



4

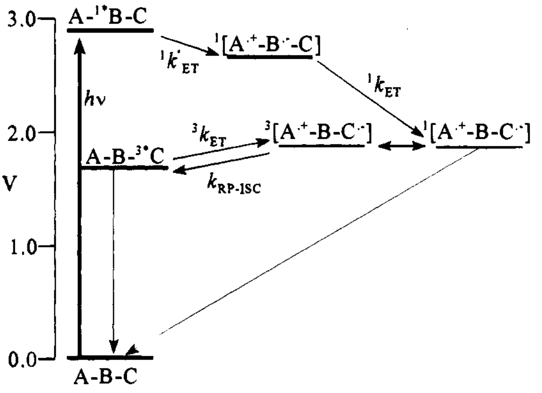


Figure 1. Energy level diagram of all relevant ET and ISC routes. The energies were determined in toluene.

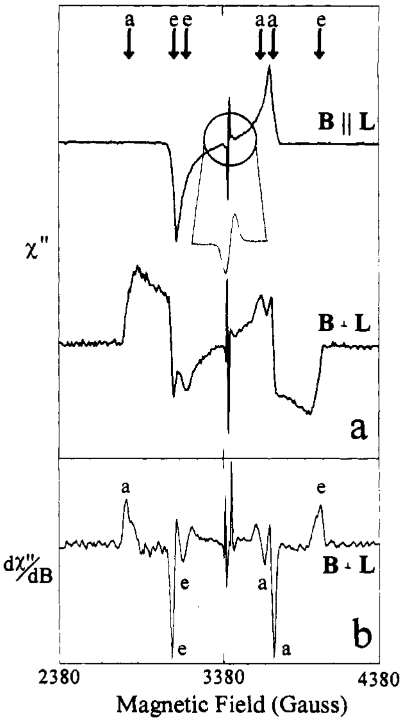


Figure 2. (a) Direct detection CW-TREPR spectra of the triplet state $A-B-{}^{3*}C$ in a LC, at two orientations of the LC director, **L**, taken 700 ns after the laser pulse (420 nm) at 150 K (the same spectra were recorded at lower temperatures down to 100 K). The narrow spectrum is an expansion of the RP signal, observed in the center of the triplet spectra at both orientations. At this temperature, the narrow spectrum is due to the primary ET route (Figures 1 and 3). (b) Numerical differentiation of the **B** ⊥ **L** spectrum.

Transient optical absorption spectroscopy carried out on **1** in toluene determined the nature of the intermediates and the rate constants for ET between the electronic states given in the energy level diagram in Figure 1. Laser excitation at 295 K and 420 nm selectively excites chromophore B. The lowest excited singlet state of B accepts an electron from A with τ = 8 ps. A subsequent dark ET step with τ = 430 ps forms the final RP, $^1[A^{\bullet+}-B-C^{\bullet-}]$, with a lifetime of 310 ns. Photoexcitation of **1** oriented in solid LC results in broad EPR spectra, at the two indicated orientations, with additional narrow lines superimposed at the center of the spectra (Figure 2). The line shapes of the broad spectra clearly suggest that they are due to a triplet state.[6]

In all model systems reported thus far, triplet states observed by EPR are formed via a spin–orbit intersystem crossing (SO-

---

[†] The Hebrew University of Jerusalem.

[‡] Argonne National Laboratory.

[§] Northwestern University.

(1) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(2) Wasielewski, M. R.; Gaines, G. L.; Wiederrecht, G. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1993**, *115*, 10442.

(3) (a) Hasharoni, K.; Levanon, H. *J. Phys. Chem.* **1995**, *99*, 4875. (b) Hasharoni, K.; Levanon, H.; Gätschmann, J.; Schubert, H.; Kurreck, H.; Möbius, K. *J. Phys. Chem.* **1995**, *99*, 7514.

(4) Levanon, H. *Rev. Chem. Intermed.* **1987**, *8*, 287.

(5) Gaines, G. L.; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719.

(6) Regev, A.; Levanon, H.; Murai, T.; Sessler, J. L. *J. Chem. Phys.* **1990**, *92*, 4718.

0002-7863/95/1517-8055$09.00/0

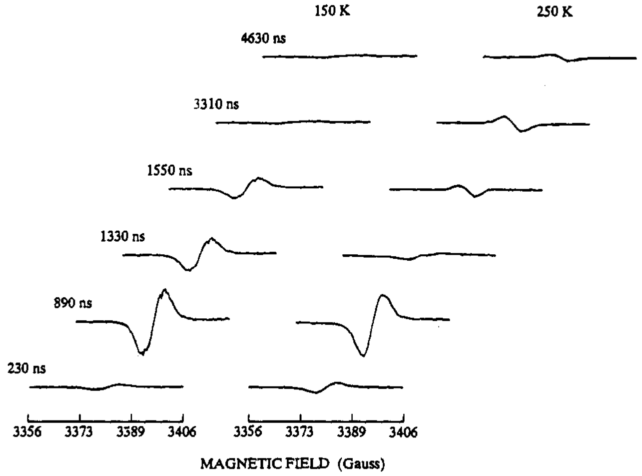


Figure 3. TREPR spectra of the spin-polarized RP, $A^{\bullet+}-B-C^{\bullet-}$, at two temperatures in the LC. The spectra are presented as a function of the time following the laser pulse (420 nm). Notice the signal phase change at 250 K. The *g*-factors of the (e,a) and (a,e) spectra are the same.

ISC) mechanism. Another possible mechanism is radical pair intersystem crossing (RP-ISC), which forms a triplet upon recombination within the RP, and which has been observed by TREPR only in bacterial[7] and in green plant photosystems I[8] and II.[9] These two mechanisms can be differentiated by the polarization pattern of the six EPR transitions at the canonical orientations. In SO-ISC, the three zero-field levels are selectively populated and this selectivity is carried over to the high-field energy levels. RP-ISC is also selective, but acts directly on the high-field triplet sublevels via singlet−triplet mixing, $S-T_0$ (or $S-T_{\pm1}$).[10,11] Thus, SO-ISC results in mixed absorption (a) and emission (e) lines within a particular EPR transition, i.e., $T_i \leftrightarrow T_0$ ($i = \pm1$), while in RP-ISC a mixed polarization pattern is impossible.[11] Inspection of the triplet spectra (Figure 2) in the $\mathbf{B} \perp \mathbf{L}$ and $\mathbf{B} \parallel \mathbf{L}$ orientations shows that the polarization pattern of a,e,e,a,a,e can only be attributed to a RP-ISC mechanism, as found for RC proteins.[7−9] This unique triplet state is found to be localized on C, and the triplet EPR spectrum of **4** exhibits identical zero-field splitting parameters, with polarization pattern of a,a,a,e,e,e, typical of SO-ISC.

Upon warming of the sample from 100 to 330 K, two observations are made. First, the triplet spectra are detectable only when the superimposed narrow line spectrum exhibits a time independent e,a pattern. This phenomenon occurs in the temperature range 100−240 K. Above 240 K the time-evolved narrow spectra exhibit phase inversion (Figure 3). The e,a spectrum must be assigned to the singlet-initiated RP, $^1[A^{\bullet+}-B-C^{\bullet-}]$, and because the intermediate RP is short-lived (430 ps), this polarization is due to the correlated RP mechanism.[12] Zeeman and hyperfine induced interactions lead to $S-T_0$ mixing between the two RP states, i.e., $^1\mathrm{RP} \leftrightarrow {}^3\mathrm{RP}$; thus, $^1[A^{\bullet+}-B-C^{\bullet-}]$ can decay via two routes (Figure 1). The first involves recombination to the ground state (from ^{1}RP), while the second, as discussed above, forms the triplet state, $A-B-{}^{3*}C$ (from ^{3}RP). This triplet state decays via a solvent-controlled secondary ET to repopulate ^{3}RP, or directly to the ground state. The existence of the secondary ET reaction, which is triplet initiated ($^3k_{ET}$), is evident from the phase change of the spectra in Figure 3. The singlet-initiated e,a pattern observed at short times after the laser pulse evolves at later times into a triplet-initiated a,e pattern. The temperature dependence of the secondary ET is consistent with the phase transition temperatures of the LC:[6]

$$\text{crystalline} \xleftrightarrow{210\text{ K}} \text{soft−glass} \xleftrightarrow{263\text{ K}} \text{nematic} \xleftrightarrow{333\text{ K}} \text{isotropic}$$

In the soft-glass regime, the solvent molecular motion is not frozen and is sufficient to allow ET to occur.[3] Thus, while the forward ET reaction seems to be independent of the LC phase (solid and fluid), the secondary ET becomes active only in the soft-glass and in the fluid nematic phases. The disappearance of the triplet spectrum, which occurs with the RP signal phase inversion, is probably due to a high quantum yield of the secondary (back) reaction, making $A-B-{}^{3*}C$ short-lived.

The observation of this triplet state in **1** by TREPR demonstrates that most of the electronic states found in the primary photochemistry of photosynthetic RCs can be mimicked successfully in synthetic models interacting with LCs.

Acknowledgment. This was supported by a U.S.−Israel BSF, the Deutsche Forschungsgemeinschaft, Volkswagen Stiftung grants (H.L.), and the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. DOE under Contract W-31-109-ENG-38 (M.R.W.). S.R.G. is supported by a Distinguished Postdoctoral Fellowship from the U.S. DOE. A grant of the Erna and Victor Hasselblad Foundation (H.L.) is highly acknowledged. The Farkas Center is supported by the Minerva Gesellschaft für die Forschung, GmbH, München, FRG. Discussions with Prof. J. R. Norris are highly acknowledged.

Supporting Information Available: Synthesis and optical characterization of **1−4** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951078W

---

[7] Dutton, P. L.; Leigh, J. S.; Seibert, M. *Biochem. Biophys. Res. Commun.* **1972**, *46*, 406.

[8] Regev, A.; Nechushtai, R.; Levanon, H.; Thornber, J. P. *J. Phys. Chem.* **1989**, *93*, 2421.

[9] Rutherford, A. W.; Paterson, D. R.; Mullet, J. E. *Biochim. Biophys. Acta* **1981**, *635*, 205.

[10] Thurnauer, M. C.; Katz, J. J.; Norris, J. R. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3270.

[11] Levanon, H.; Norris, J. R. *Chem. Rev.* **1978**, *78*, 185.

[12] (a) Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307. (b) Closs, G. L.; Forbes, M. D. E.; Norris, J. R. *J. Phys. Chem.* **1987**, *91*, 3592.