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USING SYNTHETIC MODEL SYSTEMS TO UNDERSTAND CHARGE SEPARATION AND SPIN DYNAMICS IN PHOTOSYNTHETIC REACTION CENTERS

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## 1. Introduction

Over the past 20 years many biomimetic systems have been synthesized to model the photosynthetic reaction center (RC).(1) The purpose of these modeling studies is to use relatively simple electron donor-acceptor molecules with restricted donor-acceptor distances and orientations to probe the electronic interactions between photosynthetic pigments that lead to efficient, long-lived charge separation in photosynthetic reaction centers. These assemblies are designed to mimic several key properties of the RC protein: 1) multi-step 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. Most RC models fulfill only a subset of these criteria. Moreover, there is one key property of the RC primary photochemistry that has proven very difficult to mimic. It is the unique ability of the RP intermediate within the photosynthetic RC to yield, upon charge recombination, a triplet state that retains a memory of the precursor RP spin state, and exhibits the time-resolved EPR (TREPR) signal characteristic of this triplet state.

It is well recognized that singlet photochemistry governs charge separation in natural photosynthesis, while in model systems, both singlet and triplet channels are competitive and depend on several variables such as relative orientations, distances, and electronic couplings between the participating redox partners.(2) In addition, the solvent reorganization energy ( $\lambda_s$ ) due to solvent dipoles reorienting around the ion pair is of prime importance for tuning the energy levels of the charge-separated states, such that the branching ratio of the electron transfer rates, i.e., singlet- or triplet-initiated routes, can be controlled. Thus, to achieve the goal of mimicking natural photosynthesis by biomimetic supramolecular systems, it is essential to develop experimental methods to explicitly determine the energy levels of radical ion pair (RP)

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states. We show that this goal can be achieved by blending together molecular architecture, solvent properties, and fast EPR detection of paramagnetic transients.

Recent studies of intramolecular electron transfer (IET) illustrate the unique properties of liquid crystals (LCs) that make them interesting solvents in which to study covalently linked donor-spacer-acceptor systems.(3-6) Most importantly, the IET rates in these solvents are reduced by several orders of magnitude (from ps to ns), permitting the observation of IET processes on sub-microsecond time scales using time-resolved electron paramagnetic resonance (TREPR) spectroscopy.(3) This reduction of IET rates is due to the nematic potential associated with the alignment of the LC molecules, which restricts the isotropic molecular reorientation found in conventional solvents.(3,7,8) These inherent properties of LCs permit tuning the RP states into a time domain where the paramagnetic transients can be monitored over a wide temperature range.(3,9)

The powerful approach of coupling TREPR with LC solvents has permitted the elucidation of photochemical mechanisms that otherwise could not be observed. In particular, this technique recently permitted the first observation of the special spin-polarized triplet excited state in a multi-component model system generated by the same mechanism of back electron transfer observed in natural photosynthesis. (10,11) It is noteworthy that this model system consists of non-porphyrinoid entities and further studies of multistep ET processes within porphyrinoid systems dissolved in LCs would be valuable.

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

An attractive feature of nematic liquid crystals for the study of anisotropic charge transfer is the "nematic potential" associated with the reduced reorientational capability of the liquid crystalline solvent molecules in the presence of an ion pair, as compared to isotropic solvents.(9) This effect is associated with a high activation energy for reorientational motion in an aligned solvent and dramatically slows the rate of photoinduced charge recombination. Since intramolecular charge transfer in isotropic solvents frequently occurs on picosecond time scales, the nematic potential permits a wider variety of experimental techniques to be utilized since charge transfer lifetimes can be increased by 3-4 orders of magnitude.(9) In addition to the nematic potential, a second critical role that liquid crystals can play in spectroscopic applications is the control of LC director alignment as a function of the sign of the magnetic susceptibility of the LC molecules. LCs with positive susceptibilities align parallel to the magnetic field, while those with negative susceptibilities align perpendicular to the magnetic field. This has a large effect in the polarization dynamics observed in EPR and can assist in the assignment of the observed photoinduced state.

In the example given here, supramolecular systems were synthesized that model the photosynthetic reaction center (RC), as illustrated in Figure 1. They were designed to mimic several key properties of the RC protein: (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. Until this work, most RC models fulfilled only a subset of these criteria with very few reports employing time-resolved electron paramagnetic resonance spectroscopy (TREPR). We describe here TREPR results on a photosynthetic model system, 1, in a nematic LC that does not contain the natural pigments, yet closely mimics the spin dynamics of triplet state formation found only in photosynthetic RCs. The development of donor-acceptor systems that mimic photosynthetic mechanisms, and that are at the same time electronically and structurally simpler than the natural photosynthetic pigments, may aid our understanding of the mechanistic details of the radical pair dynamics. The design of supermolecule 1 followed criteria established for promoting high quantum yield charge separation in glassy media.

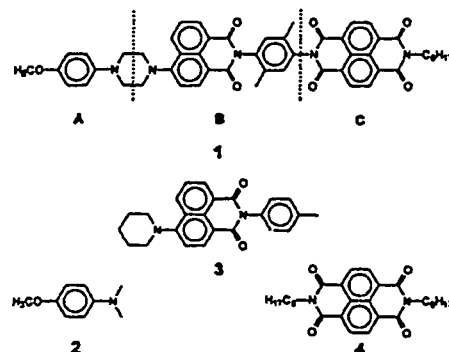


Figure 1. Supermolecule 1 and the control molecules are illustrated.

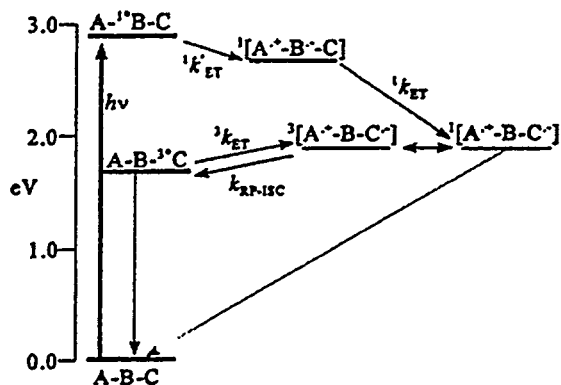
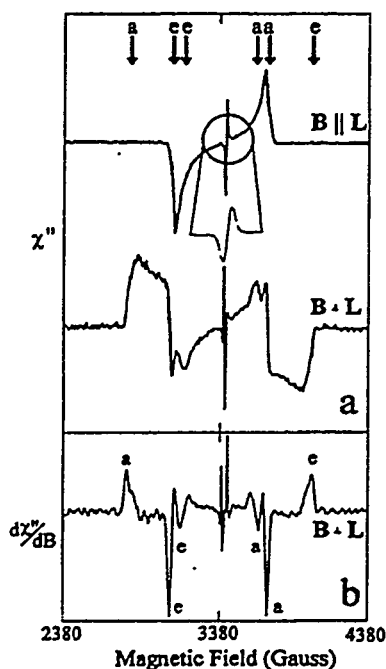


Figure 2. Energy level diagram of all relevant IET and ISC routes. The energies were determined in toluene.

Transient optical absorption spectroscopy carried out on 1 in toluene determined the nature of the intermediates and the rate constants for intramolecular electron transfer (IET) between the electronic states given in the energy level diagram in Figure 2. Laser excitation at 295K and 420 nm selectively excites chromophore B. The lowest excited singlet state of B accepts an electron from A with  $\tau = 8$  ps. A subsequent dark ET step with  $\tau = 430$  ps forms the final RP,  $^1[A^+-B-C^-]$ , 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 3). The line shapes of the broad spectra clearly suggest that they are due to a triplet state.

In all model systems reported thus far, triplet states observed by EPR are formed via a spin-orbit intersystem crossing (SO-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 and in green plant photosystems I and II. 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  $S-T^{\pm 1}$ ). Thus, SO-ISC results in mixed absorption (a) and emission (e) lines within a particular EPR transition, i.e.,  $T^i-T^0$  ( $i=\pm 1$ ), while in RP-ISC a mixed polarization pattern is impossible. Inspection of the



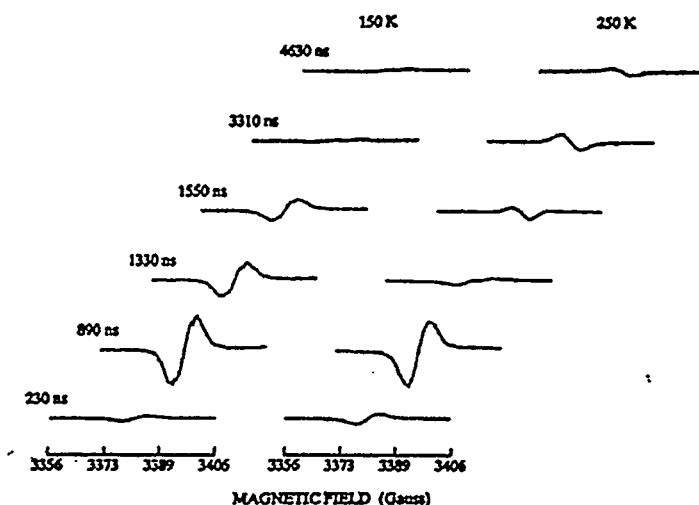
**Figure 3.** Direct detection CW-TREPR spectra of the triplet state  $A-B-^3C$  in a LC, at two orientations of the LC director,  $L$ , taken 700 ns after the laser pulse (420 nm) at 150K (the same spectra were recorded at lower temperatures down to 100K). The narrow spectrum is an expansion of the 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 (Figure 2). (b) Numerical differentiation of the B.LL spectrum.

triplet spectra (Figure 3) in the  $B \perp L$  and  $B \parallel L$  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. 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 4). The e,a spectrum must be assigned to the singlet-initiated RP,  $^1[A^+-B-C^-]$ , and because the intermediate RP is short-lived (430 ps), this polarization is due to the correlated RP mechanism. Zeeman and hyperfine induced interactions lead to  $S-T^0$  mixing between the two RP states, i.e.,  $^1RP-^3RP$ ; thus,  $^1[A^+-B-C^-]$  can decay via two routes (Figure 2). The first involves recombination to the ground state (from  $^1RP$ ), while the second, as discussed above, forms the triplet state,  $A-B-^3C$  (from  $^3RP$ ). This triplet state decays via a solvent-controlled secondary ET to repopulate  $^3RP$ , 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 4. The singlet-initiated e,a pattern is 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:

210 K  $\leftrightarrow$  263 K  $\leftrightarrow$  333 K  
 crystalline      soft-glass      nematic      isotropic



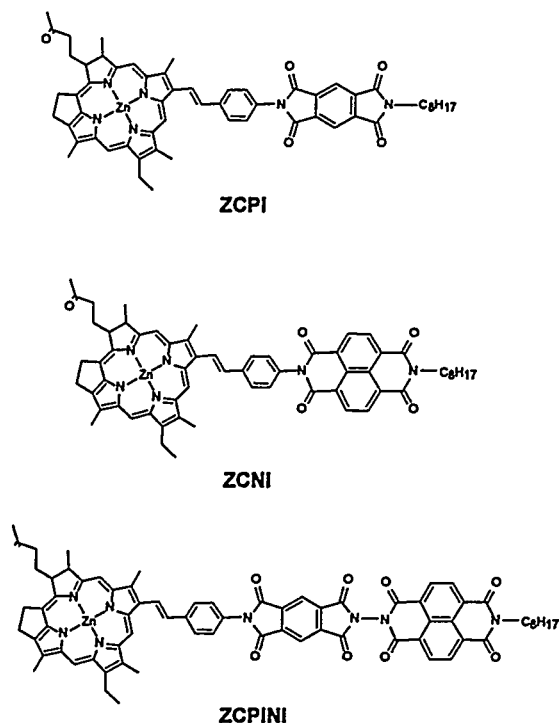
**Figure 4.** TREPR spectra of the spin-polarized RP,  $A^+-B-C^-$ , at two temperatures in the LC. The spectra are presented as a function of the time following the laser pulse (420 nm). Notice the signal phase change at 250 K. The g-factors of the (e,a) and (a,e) spectra are the same.

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.

### 3. Determination of Energy Levels of Radical Pair States in Photosynthetic Models Oriented in Liquid Crystals through Time-Resolved Electron Paramagnetic Resonance

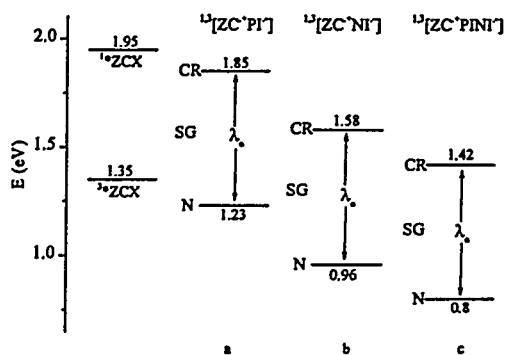
It is well recognized that singlet photochemistry governs charge separation in natural photosynthesis, while in model systems, both singlet and triplet channels are competitive and depend on several variables such as relative orientations, distances, and electronic couplings between the participating redox partners.<sup>(2)</sup> In addition, the solvent reorganization energy ( $\lambda_s$ ) due to solvent dipoles reorienting around the ion pair is of prime importance for tuning the energy levels of the charge-separated states, such that the branching ratio of the electron transfer rates, i.e., singlet- or triplet-initiated routes, can be

In the soft-glass regime, the solvent molecular motion is not frozen and is sufficient to allow ET to occur. 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  $A-B-^3C$  short-lived.



**Figure 5.** Photosynthetic model systems are illustrated.

ZCPINI, with D-to-A<sub>1</sub>, D-to-A<sub>2</sub> and D-to-A<sub>2</sub> center-to-center distances of ~ 11, ~ 11 and ~ 18 Å, respectively. These compounds, when oriented in different LCs, show photoinduced IET to produce charge-separated states that can be monitored by TREPR.



**Figure 6.** The temperature and phase dependent energy levels of the model systems are shown.

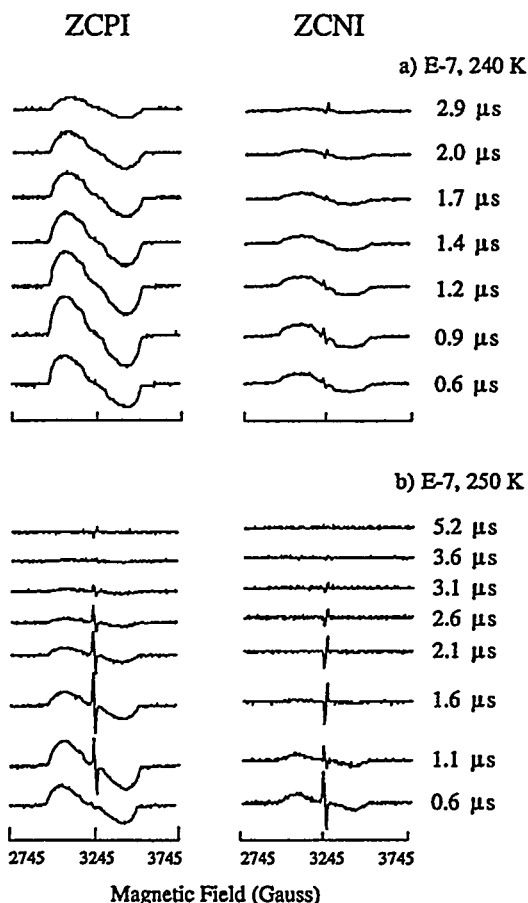
controlled. Thus, to achieve the goal of mimicking natural photosynthesis by biomimetic supramolecular systems, it is essential to develop experimental methods to explicitly determine the absolute values of the energy levels of RP states. We have shown that this goal can be achieved by blending together molecular architecture, solvent properties and fast EPR detection of paramagnetic transients.

The present work deals with a series of covalently linked compounds (Figure 5) containing a chlorophyll-like (chlorin) electron donor, D (ZC). Two electron acceptors are used with different reduction potentials, i.e., pyromellitimide, A<sub>1</sub> (PI) and 1,8:4,5 naphthalenediimide, A<sub>2</sub> (NI) to produce a series of molecules with small but deliberate differences of the ion-pair energies. The compounds investigated are ZCPI, ZCNI and

The origin of such a state and the spin dynamics associated with it strongly depend not only on λ<sub>s</sub>, but very substantially on the molecular architecture. Thus, while ZC<sup>•+</sup>-PI<sup>-</sup> and ZC<sup>•+</sup>-NI<sup>-</sup>, with short donor-acceptor distances, exhibit triplet radical pair (TRP) spectra, i.e., <sup>3</sup>[D<sup>•+</sup>-A<sup>-</sup>], the much longer donor-acceptor distance in the triad, ZC<sup>•+</sup>-PI-NI<sup>-</sup>, results in a correlated radical pair (CRP) spectrum, i.e., <sup>1,3</sup>[D<sup>•+</sup>-A<sub>1</sub>-A<sub>2</sub><sup>-</sup>]. These two types of spectra can be differentiated only by TREPR, via the dipolar and/or the exchange interactions, which strongly depend on the donor-acceptor distance. We further show



that the spectral analysis in terms of the energy states scheme in Figure 6, illustrating the different routes of triplet and RP states production, permits an accurate assignment of the energies of the RPs in the different phases of the LC solvents. This is the first demonstration of RP energy level determination for short-lived RPs by tuning the solvent reorganization energy through the different phases of LCs.



**Figure 7.** Direct-detection TREPR spectra (triplets and RPs), for different times after the laser pulse, of the photoexcited dyads in the soft glass of E-7 at a) 240K and (b) 250K.

#### 4. Conclusions

Our current work in modeling reaction center dynamics has resulted in the observation of each major spin-dependent photochemical pathway that is observed in reaction centers. The development of new, simpler model systems has permitted us to probe deeply into the mechanistic issues that drive these dynamics. Based on these results we

While space constraints limit complete discussion of these results, Figure 7 illustrates the main theme of this work. The spectra clearly illustrate that the ZCPI radical pair has a lower driving force for charge separation because the radical pair is only evident at the higher temperature, whereas the radical pair of ZCNI is present at both temperatures. Furthermore, the spectra illustrate the large increase in the solvation ability of the soft glass, as only a 10 K increase in temperature produces a strong signal from the ZCPI radical pair. In fact, as the temperature is increased through the soft glass region, approximately 0.65eV of solvent reorganization energy is gained. Thus, by observing the appearance of the radical pair signals at different temperatures, and considering the difference in the redox potentials of the molecules shown in Figure 5, accurate assignment of the radical pair energy levels can be achieved. Furthermore, polarization considerations leads to the assignment of the dyads as triplet radical pairs, the triad displays the CRP mechanism.

have returned to biomimetic chlorophyll-based electron donors to mimic these dynamics. Future studies will focus on the details of electronic structure and energetics of both the donor-acceptor molecules and their surrounding environment that dictate the mechanistic pathways and result in efficient photosynthetic charge separation.

## 5. Acknowledgment

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