A First High-Field EPR Study of Photoinduced Electron Transfer in a Base-Paired Porphyrin−Dinitrobenzene Supramolecular Complex

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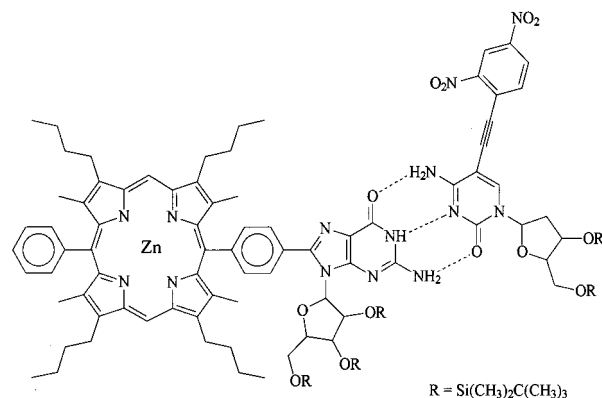
Since the discovery of photoinduced electron transfer (ET) between bacteriochlorophyll and cytochrome,[1] many of the more hotly debated issues in the realm of biological ET have involved questions of how long-range ET events proceed through various noncovalently linked protein pathways.[2−5] To answer such questions, different spectroscopies have been applied to the study of biomimetic model systems wherein the donor (D) and acceptor (A) molecules are tethered together noncovalently via either electrostatic interactions[6] or hydrogen bonds.[7,8] These studies, in conjunction with work on covalently linked models,[9−12] have broadened our knowledge of structure−function relationships associated with ET processes. Still, many facets of ET processes remain poorly understood, in particular the role of noncovalent interactions. Work on proteins served to establish that specific hydrogen-bonding interactions are critical in achieving long-range D−A electronic coupling.[13−15] Furthermore, studies on model systems revealed that the electronic coupling for ET through hydrogen bonds may be larger than that for comparable processes, mediated by either σ- or π-bonding networks.[16]

In the present Communication, we report on a first study that combines time-resolved X-band (9.5 GHz, 0.33 T) and W-band (95 GHz, 3.3 T)[17] EPR of a photoexcited Watson−Crick base-paired D−A complex, which demonstrates how the

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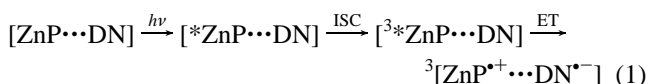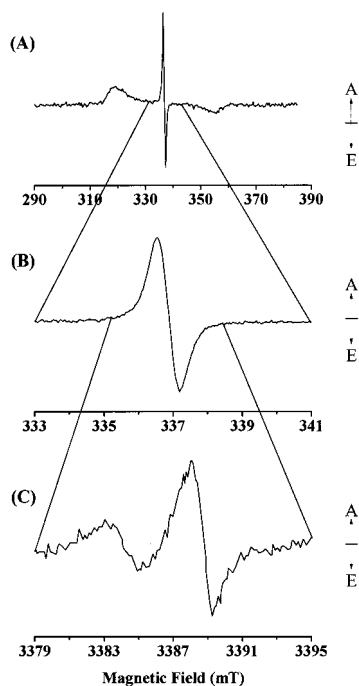
Chart 1

R = Si(CH₃)₂C(CH₃)₃

critical supramolecular geometry and, moreover, the ET pathways are stabilized by multiple hydrogen-bonding interactions. EPR experiments at such high Zeeman fields, with significantly improved spectral and time resolution, allow us to directly identify the partners of the charge-separated radical pair (RP) generated by selective light excitation and to determine unambiguously the genesis of the spin-correlated radical pair (SCRP) in the ET reaction.

Previously,[7,8] we reported X-band time-resolved EPR (TREPR) studies of photoinduced ET within hydrogen-bonded D−A complexes, embedded in two nematic liquid crystals (LC) whose director orientations differ by $\pi/2$. In the present study, we concentrate on W-band TREPR (continuous wave, direct detection, i.e., without field modulation) experiments on a base-paired system (Chart 1). This system consists of a guanine-functionalized zinc(II) porphyrin (ZnP) linked to a cytosine-functionalized dinitrobenzene (DN) via noncovalent base-pairing interactions [ZnP···DN].[8,18]

Selective pulsed laser excitation (532 nm, 2mJ, 5 ns) of the porphyrin part in [ZnP···DN] results in long-range, triplet-initiated ET to the dinitrobenzene, ~18 Å apart in the nematic phase of the LC.[7,8]

$$[\text{ZnP···DN}] \xrightarrow{h\nu} [\text{*ZnP···DN}] \xrightarrow{\text{ISC}} [^3\text{*ZnP···DN}] \xrightarrow{\text{ET}}$$
$$^3[\text{ZnP}^{\bullet+}\text{···DN}^{\bullet-}] \quad (1)$$

The transient paramagnetic species in eq 1 are EPR detected in their absorption (A) or emission (E) modes shortly (nanoseconds to microseconds) after the laser pulse in order to detect them in their spin-polarized states. Figure 1A shows the X-band TREPR broad and narrow spin-polarized signals, which were ascribed to ^{3}*(ZnP) and to the radical pair $^3[\text{ZnP}^{\bullet+}\text{···DN}^{\bullet-}]$, respectively.[8] The narrow derivative-like A/E signal (Figure 1B) was assigned to a weakly coupled, but still spin-correlated, RP, originating from photoinduced triplet-initiated (eq 1) ET. This assignment was based on SCRP theory of a weakly coupled RP.[19,20] For small values of D (zero-field splitting) and J (exchange) parameters, as compared to its EPR line width, a derivative-like signal is predicted for X-band EPR whose phase pattern, absorption or emission, should depend on the molecular orientation of the RP

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(A)

(B)

(C)

Figure 1. (A) X-band A/E TREPR spectra of [^{3}ZnP⋯DN] and the superimposed RP ^{3}[ZnP$^{\bullet+}$⋯DN$^{\bullet-}$] (narrow signal), taken in the nematic phase of the liquid crystal E-7 at 298 K, 450 ns after the laser pulse.[8] (B) Expanded X-band TREPR spectrum of the RP.[8] (C) W-band TREPR spectrum of the RP, taken 250 ns after the laser pulse at 280 K in E-7. Note that the TREPR signals are recorded in A/E mode of detection and not as first field derivatives.

with respect to the magnetic field.[19,20] Thus, when changing the direction of the LC axis and, thereby, the radical pair molecular orientation by $\pi/2$, it was, indeed, observed that the phase pattern changed from A/E to E/A, which is typical for the SCRP case. Such findings are in contrast to the strongly coupled triplet radical pair case with relatively large D and J values.[20]

The above method for differentiating between weak and strong exchange coupling is admittedly rather indirect and asks for an independent, more direct experimental confirmation. Also, the question remained open whether the derivative-like line consists of contributions from both radicals of the pair or from only one. To identify the partners of the RP and their interactions and clarify the origin of the narrow spin-polarized signal, W-band high-field EPR experiments (10 ns time resolution) were carried out. Figure 1C shows the spin-polarized radical pair W-band EPR spectrum with two resolved A/E features. In fact, for a weakly coupled RP in disordered samples, SCRP theory predicts,[19,20] as for the general case, a pair of derivative-like lines. The pair separation is field dependent and determined, at a given $\mathbf{B}_0$ field, by the difference in g-factors of the two radicals in the SCRP, while the splitting of the antiphase components of the individual derivative-like lines is defined by the dipolar and exchange interactions. The isotropic g-factors of ZnP$^{\bullet+}$ and DN$^{\bullet-}$ are 2.0025 ± 0.0003[21] and 2.0049 ± 0.0003,[22] respectively. At X-band, their Δg corresponds to a line separation of 0.42 mT that remains unresolved because of the larger dipolar coupling (D = 0.47 mT for [ZnP$^{\bullet+}$⋯DN$^{\bullet-}$]) and larger inhomogeneous line widths.[8] At W-band, however, for a weakly coupled SCRP such as the present one, it is expected

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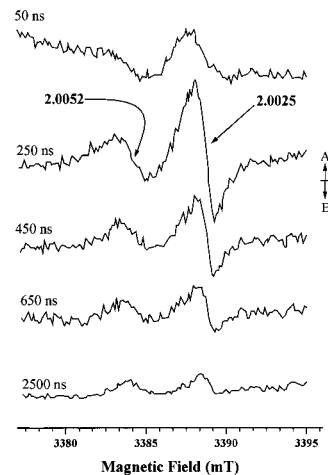

Figure 2. W-band EPR time evolution of the spin-polarized radical pair spectra at different delay times after the laser pulse (280 K, in E-7). The different g-factors are indicated.

that two well-resolved, A/E lines, separated by 4.2 mT, would be observed. For a strongly coupled triplet pair, on the other hand, only one line would be expected, even at high field. As can be seen from Figure 1C, a weakly coupled RP spectrum with two separated A/E features of both radicals is, indeed, observed for the ensemble studied. This confirms that light-induced ET proceeds in the steps postulated by eq 1.

Figure 2 depicts the time evolution of the W-band TREPR spectra. At early times after the laser pulse, two derivative-like A/E lines are observed centered around 2.0052 ± 0.0001 and 2.0025 ± 0.0001. This is in close agreement with the literature values cited above and exactly what SCRP theory predicts for a weakly coupled [ZnP$^{\bullet+}$⋯DN$^{\bullet-}$] radical pair; i.e., the low-field A/E line corresponds to the spin-polarized spectrum of DN$^{\bullet-}$ and the high-field A/E line to the spin-polarized spectrum of ZnP$^{\bullet+}$. The different signal amplitudes are due to different line widths of the two radicals. The larger line width of DN$^{\bullet-}$ is caused by its larger g-anisotropy, reflecting the orientational distribution of this guest molecule in the liquid crystal.

At sufficiently long times after the laser pulse, the A/E lines turn into features characteristic of an absorption spectrum (Figure 2). This evolution is ascribed to the SCRP undergoing relaxation to a state of thermal equilibrium, with a spin−lattice relaxation time T_1 of approximately 100 ns. This relaxation, therefore, competes with the building-up of the TREPR spectrum with an ET time constant of approximately 50 ns. This means that back ET must be slower than several microseconds.

To summarize, we have demonstrated that high-field time-resolved EPR opens a new direction in straightforward elucidation of complex photochemical ET reactions, where different paramagnetic states and species are involved. This conclusion applies not only to base-paired donor−acceptor supramolecular ensembles as described here but also to the large ET proteins, such as photosynthetic reaction centers,[23,24] and their covalently linked D−A model systems.[11]