

## Triplet States with Unusual Spin Polarization Resulting from Radical Ion Pair Recombination at Short Distances

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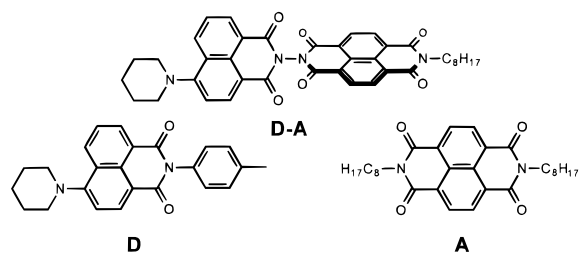
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Covalently bound electron donor–acceptor, [D–A], molecules that undergo photoinduced charge separation from a photoexcited singlet state to form radical ion pairs that subsequently undergo back electron transfer to yield a triplet state are very rare.<sup>1–3</sup> Apart from their importance in the general context of electron-transfer reactions, these molecules provide insights into the primary photochemistry of photosynthetic reaction centers.<sup>4–7</sup> Photoexcitation of [D–A] produces <sup>1</sup>[D–A], which undergoes rapid charge separation to yield <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>]. At [D<sup>•+</sup>–A<sup>•–</sup>] distances  $\geq 20$  Å, the exchange integral,  $J$ , between the two radicals is generally  $\leq 10^{-4}$  cm<sup>-1</sup>.<sup>1–3</sup> This weak interaction allows radical pair intersystem crossing (RP-ISC) within <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>] to occur, which leads to the formation of a spin-correlated radical pair <sup>3</sup>[D<sup>•+</sup>–A<sup>•–</sup>]. Radical ion pair recombination within <sup>3</sup>[D<sup>•+</sup>–A<sup>•–</sup>] then yields <sup>3</sup>[D–A]. In all of these reactions the spins remain correlated, which results in non-Boltzmann populations of the spin states within each intermediate. These intermediates exhibit spin polarized EPR spectra characteristic of the mechanism of their formation. In the two synthetic model systems reported to date that exhibit <sup>3</sup>[D–A] states which result from spin-correlated radical pairs, their  $\geq 20$  Å [D<sup>•+</sup>–A<sup>•–</sup>] distance is a consequence of two sequential electron-transfer steps. We report here the first example of a covalently bound [D–A] molecule in which a single electron-transfer step produces a [D<sup>•+</sup>–A<sup>•–</sup>] pair at a short 11 Å distance with a large  $J$  value that leads to efficient <sup>3</sup>[D–A] formation.

The donor–acceptor molecule, [D–A] uses a 4-(*N*-piperidinyl)-naphthalene-1,8-imide donor (D) and a 1,8:4,5-naphthalenediimide acceptor (A) and was prepared using methods detailed earlier.<sup>8</sup> Molecular mechanics calculations were used to determine that



the donor–acceptor distance within D–A is 11 Å, while the dihedral angle between the  $\pi$  systems of D and A is 86°. The energy of the lowest excited singlet state of D is 2.80 eV and its lifetime is 8.5 ns.<sup>10</sup> Femtosecond and nanosecond transient absorption spectroscopy of D–A in 2-methyltetrahydrofuran (MTHF) at 77 K were used to determine the rate constants for both photoinduced electron transfer from D to A within [D–A] and the subsequent radical ion pair recombination reaction.<sup>10</sup> The reduced electron acceptor A<sup>•–</sup> has a well-known optical absorption spectrum that exhibits an intense and narrow absorption band at 480 nm.<sup>11</sup> Selective excitation of D within [D–A] with 130 fs, 417 nm laser pulses produces the transient spectrum at 3 ps following the laser flash illustrated in Figure 1a, which clearly exhibits the spectral signature of A<sup>•–</sup>. The time constant for the formation of <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>] is  $\tau = 0.5$  ps, while the radical ion pair recombination occurs with  $\tau = 45$  ns (inset to Figure 1a). A much longer ( $> 1$   $\mu$ s) transient absorption signal is also observed.

The energy level of <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>] was determined to be 2.3 eV from the average of its weak charge-transfer absorption and emission features at 481 and 618 nm, respectively. The lifetime of emission due to radiative recombination within <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>] is 45 ns and agrees very well with the radical pair lifetime determined by transient absorption. Given that the lifetime of <sup>1</sup>D is 8.5 ns, the kinetic data show that selective excitation of D within [D–A] results in quantitative formation of <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>]. Phosphorescence spectra of <sup>3</sup>D, <sup>3</sup>A, and <sup>3</sup>[D–A] in MTHF at 77 K are shown in Figure 1b. When D is selectively excited, D, A, and [D–A] exhibit phosphorescence quantum yields of  $5.4 \times 10^{-5}$ ,  $3.9 \times 10^{-3}$ , and  $3.7 \times 10^{-3}$ , respectively, and phosphorescence lifetimes of 144, 62, and 66 ms, respectively. Localization of the triplet excitation on A within D–A, i.e., [D–<sup>3</sup>A], is indicated by the similar phosphorescence spectra, yields, and lifetimes of <sup>3</sup>A, and <sup>3</sup>[D–A]. The phosphorescence data combined with the transient absorption data strongly suggest that radical ion pair recombination within [D<sup>•+</sup>–A<sup>•–</sup>] produces [D–<sup>3</sup>A].

The 45 ns decay time of [D<sup>•+</sup>–A<sup>•–</sup>] is shorter than the time resolution of the time-resolved EPR (TREPR) experiments, so that direct observation of [D<sup>•+</sup>–A<sup>•–</sup>] is precluded in these experiments at 77 K. However, TREPR experiments can be used to observe the longer-lived triplet state [D–<sup>3</sup>A] that results from radical ion pair recombination within <sup>3</sup>[D<sup>•+</sup>–A<sup>•–</sup>]. At zero magnetic field, when  $J$  is very small, the nearly degenerate singlet spin state of <sup>1</sup>[D<sup>•+</sup>–A<sup>•–</sup>] and the three triplet sublevels of <sup>3</sup>[D<sup>•+</sup>–A<sup>•–</sup>] mix strongly. At 350 mT, typical of EPR experiments at X-band, the Zeeman interaction splits the triplet sublevels of <sup>3</sup>[D<sup>•+</sup>–A<sup>•–</sup>]. The principal axis system of <sup>3</sup>[D<sup>•+</sup>–A<sup>•–</sup>] is quantized along the magnetic field yielding T<sub>+1</sub> and T<sub>-1</sub> sublevels that are approximately 0.3 cm<sup>-1</sup> higher and lower, respectively, than the

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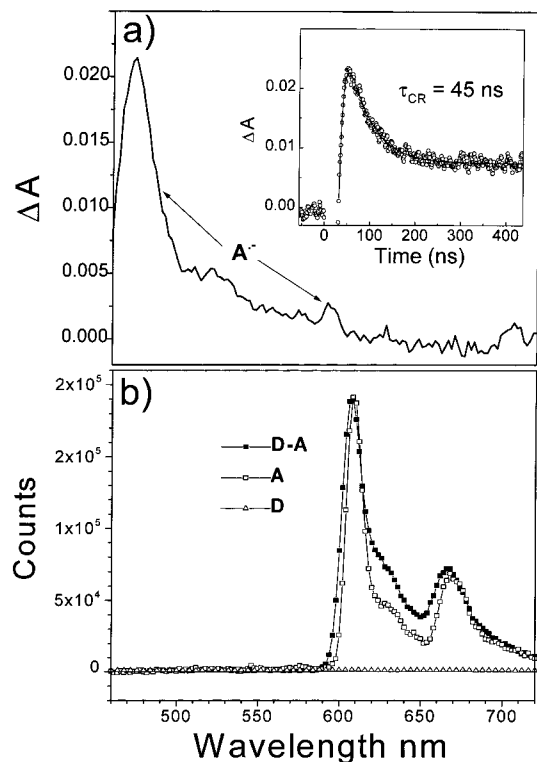
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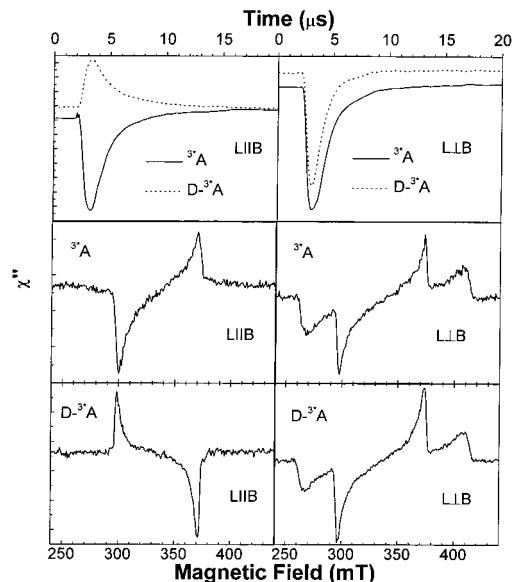
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**Figure 1.** (a) The transient absorption signal of  $[D^{*+}A^{*-}]$  in MTHF at 77 K is shown at 3 ps following 417 nm excitation with a 130 fs laser flash. The inset shows the transient absorption kinetics of  $[D^{*+}A^{*-}]$  recombination following 417 nm excitation with a 3 ns laser pulse. (b) Phosphorescence spectra of the D, A, and [D-A] molecules at 77 K in glassy MTHF are shown:  $^3A$  ( $\square$ ),  $^3D$  ( $\Delta$ ), and  $[D-^3A]$  ( $\blacksquare$ ).

field-independent  $T_0$  sublevel. As a consequence, preferential  $S-T_0$  mixing occurs within  $[D^{*+}A^{*-}]$  driven by differences between the Zeeman interactions of the two radicals and differences between the electron–nuclear hyperfine interactions within each radical. The resultant spin-correlated radical pair states are identified through the unique polarization of the EPR transitions that occur between these states.<sup>12–14</sup> The non-Boltzmann spin populations within the radical ion pair are transferred to the triplet state  $^3[D-A]$  that results from radical ion pair recombination within  $^3[D^{*+}A^{*-}]$ .<sup>15,16</sup> If  $J$  is large, as may be the case when the  $[D^{*+}A^{*-}]$  distance is small, mixing of the S state of the radical pair with either  $T_{-1}$  ( $J < 0$ ) or  $T_{+1}$  ( $J > 0$ ) may also occur, which results in different polarization of the EPR transitions relative to those that result from  $S-T_0$  mixing.

In control experiments the six-line powder pattern EPR spectra of the triplet states of D and A alone were recorded in the nematic liquid crystal E-7 (Merck) at 170 K.<sup>17</sup> The triplet state of D was not observed by EPR due to its low yield, while that of A exhibits an e,e,e,a,a,a polarization pattern (e = emission, a = absorption), which is consistent with its formation by a conventional spin–orbit intersystem crossing (SO–ISC) mechanism.<sup>16</sup> However, selective photoexcitation of D within [D-A] not only yields an intense phosphorescence signal (Figure 1b), but a correspondingly large triplet TREPR signal as well (Figure 2). As can be seen in Figure 2, the zero-field splitting parameters for  $^3A$  and the triplet generated by selective excitation of D within [D-A] are nearly identical, supporting the conclusion that the triplet state  $^3[D-A]$



**Figure 2.** TREPR kinetics (top two panels) and spectra (bottom four panels) obtained in the glassy liquid crystal E-7 at 170 K for  $^3A$  and  $D-^3A$ , where **L** is the director of the liquid crystal and **B** is the magnetic field.

is in fact  $[D-^3A]$ . However, the spin polarization patterns of  $[D-^3A]$  and  $^3A$  are different, with  $^3A$  having an e,e,e,a,a,a pattern typical of SO–ISC, while  $D-^3A$  has an e,e,a,e,a,a pattern. The polarization pattern of  $[D-^3A]$  is not consistent with either SO–ISC or RP–ISC resulting from  $S-T_0$  mixing alone. The latter is observed only in the photosynthetic reaction center and in biomimetic model systems having very small values of  $J$ .<sup>1–7</sup> The spin polarization pattern exhibited by  $[D-^3A]$  indicates that the close proximity of the electron spins within  $[D^{*+}A^{*-}]$  and the near orthogonality between the  $\pi$  systems of D and A creates the highly unusual balance in which  $J$  is large enough to permit both  $S-T_{-1}$  and  $S-T_0$  RP–ISC. This mixing is accompanied by strong anisotropic spin–lattice relaxation at the three canonical orientations of the principal axis system of the triplet state relative to the direction of the magnetic field. This anisotropy is readily apparent in Figure 2 by noting that the intensity of the low field line in the **L**||**B** EPR spectrum of  $^3A$  is greater than that of the high field line, while the opposite is true for  $[D-^3A]$ . This difference is also reflected in the EPR kinetic traces shown in the top two panels of Figure 2.

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**Supporting Information Available:** Experimental details for D-A (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) The zero field splitting values for  $[D-^3A]$  are the same in both MTHF at 77 K and in E-7 at 170 K. The liquid crystal solvent is used to align  $[D-^3A]$  relative to the external magnetic field to aid in clearly observing the six individual spin polarized EPR lines. The [D-A] molecule is oriented in the liquid crystal by slowly cooling a sample of [D-A] dissolved in the liquid crystal in the presence of the magnetic field.<sup>1,2</sup> Once the sample is frozen, it remains in its original orientation relative to the liquid crystal director **L**. The oriented, frozen sample can then be rotated relative to the magnetic field **B** to preferentially enhance particular canonical orientations of the triplet state.

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