# Modulation of Radical Ion Pair Lifetimes by the Presence of a Third Spin in Rodlike Donor−Acceptor Triads

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Controlling the lifetimes of photogenerated radical ion pairs (PRPs) is a major goal in the quest for practical artificial photosynthetic systems and for molecule-based spintronics. It is well known that the molecular structure of a donor−acceptor system can be changed to optimize the electronic coupling between the PRPs, resulting in favorable charge separation (CS) and charge recombination (CR) rates. It would be far more convenient to avoid extensive synthetic modifications to the structure to achieve the same ends by perturbation of the electronic properties of the PRP. The CR kinetics within weakly interacting radical ion pairs in rodlike covalent donor−acceptor molecules have been shown to be spin-selective and thus very sensitive to the application of weak magnetic fields.[1,2] Stronger internal magnetic fields provided by the presence of a stable radical interacting with the PRP can also modulate the spin-selective CR dynamics.[3−7] We present here results on PRPs within rodlike donor−acceptor molecules having a covalently attached stable 2,2,6,6-tetramethylpiperidinoxyl radical (T•). The distances and orientations between all three radicals are highly restricted by the intervening molecular structure, making it possible to directly measure both the CR dynamics and the spin−spin exchange interaction, $2J_{PRP}$, between the radicals within the PRPs. The structures of the molecular triads, **1a**, D−C−PI, **1b**, D−C−PI−T•, **2a**, D−C−NI, and **2b**, D−C−NI−T•, are shown below, where D = *p*-methoxyaniline, C = 4-(*N*-piperidinyl)-naphthalene-1,8-dicarboximide, NI = naphthalene-1,8:4,5-bis(dicarboximide), and PI = pyromellitimide. The molecules with terminal *n*-octyl groups, **1a** and **2a**, have been characterized previously using femtosecond and nanosecond transient absorption spectroscopy as well as measurements of $2J_{PRP}$ using magnetic field effects on the triplet state yield resulting from CR.[1,2]
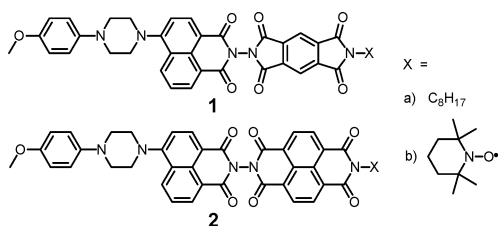
The syntheses, redox potentials, and rate constants of both CS and CR for **1a** and **2a** have been reported previously.[1] The syntheses of **1b** and **2b** are given in the Supporting Information, and the redox potentials for **1b** and **2b** are unchanged by the addition of T•. Thus, the radical ion pair energies of **1a,b** and **2a,b** in toluene are 2.24 eV for D+•−C−PI−•−X and 1.97 eV for D+•−C−NI−•−X, where X = C8H17 or T•, while the energies of the localized triplet states 3*NI, 3*PI, and 3*C are 2.03, 2.45, and 2.05 eV, respectively, Figure 1.[8,9] Excitation of **1a,b** and **2a,b** at 420 nm gives 1*C, from which CS occurs in a few picoseconds to yield the initial singlet PRPs: [1(D+•−C−•)−PI−X] and [1(D−C+•−NI−•)−X].[1,8] Subsequent sub-
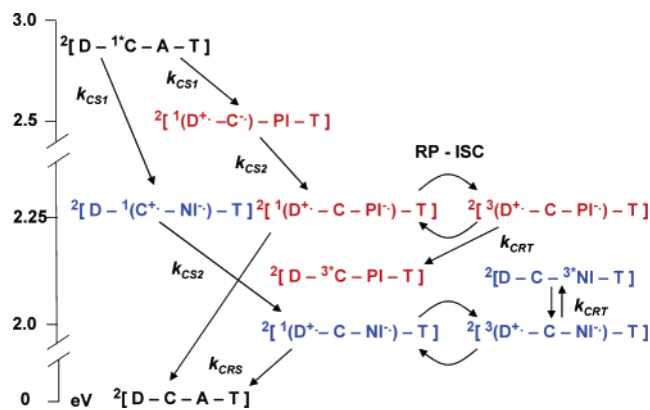

Figure 1. Electron-transfer pathways for **1b** and **2b**, where A = PI or NI. The quartet states are not included for reasons explained in the text.

nanosecond charge shift reactions yield [1(D+•−C−PI−•)−X] and [1(D+•−C−NI−•)−X]. However, when X = T•, the overall triradical is a doublet state denoted 2[1(D+•−C−Y−•)−T•], where Y = NI or PI. Charge recombination within 2[1(D+•−C−Y−•)−T•] produces the doublet ground state 2[D−C−Y−T•] (k_{CRS}), while radical pair intersystem crossing[4,10−14] (RP-ISC) leads to a triplet PRP, which in the presence of T• produces a pair of doublet states and a quartet state: 2,4[3(D+•−C−Y−•)−T•]. Charge recombination of the triplet PRP (k_{CRT}) produces the neutral doublet and quartet states 2,4[D−3*C−PI−T•] and 2,4[D−C−3*NI−T•] having two unpaired spins localized on C and NI, respectively.[9,15]

The total reorganization energy of the CR process in **1a,b** and **2a,b** is approximately 0.3 eV,[8] so that for 2,4[3(D+•−C−PI−•)−T•] → 2,4[D−3*C−PI−T•], $\Delta G = -0.19$ eV and lies near the top of the Marcus rate versus free energy profile.[16] However, for 2,4[3(D+•−C−NI−•)−T•] → 2,4[D−C−3*NI−T•], $\Delta G = 0.06$ eV, so that an equilibrium between 2[3(D+•−C−NI−•)−T•] and 2[D−C−3*NI−T•] is established and the observed yield of 3*NI is relatively small with or without T• attached.[15] In all cases, recombination from the singlet PRP to ground state with k_{CRS} lies deep within the Marcus inverted region and is therefore expected to be relatively slow.

The PRP lifetime of **1b** ($\tau_{CR} = 10.5$ ns) is about 40% shorter than that of **1a** ($\tau_{CR} = 16.6$ ns), Figure 2, and the yield of the 3*C recombination product relative to the initial PRP yield increases significantly upon addition of the T• radical ($\Delta A_{3*C}/\Delta A_{RP} = 0.35$ for **1b**, Figure 2, and =0.04 for **1a**, not shown). As noted above, based on energetic considerations, k_{CRT} is much larger than k_{CRS} for **1a,b**. Due to their close proximity, the spin−spin exchange interaction between T• and PI−• is large and increases the efficiency of RP-ISC, an effect referred to as enhanced ISC or EISC.[3,6,7,17] Because the PRP is initially formed in the singlet state, EISC increases the rate at which triplet PRP is produced, so that a larger PRP population accesses the more efficient triplet recombination
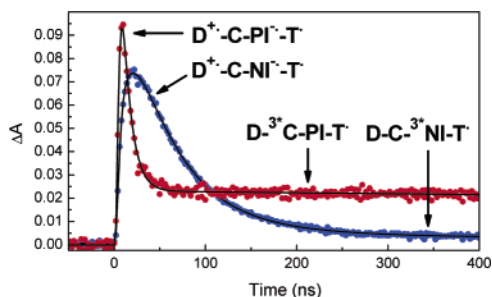
Figure 2. Kinetic traces following a 7 ns laser flash at 420 nm: (red ●) **1b**, 710 nm probe, and (blue ●) **2b**, 470 nm probe (both in toluene).
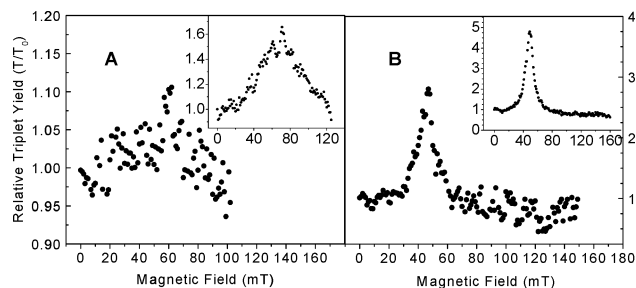

Figure 3. Magnetic field effects measured in toluene for (A) **1b**; inset, **1a**; (B) **2b**; inset, **2a**. $T/T_0 = \Delta A/\Delta A_0$ at 400 ns after the laser pulse.

pathway, leading to both an increased CR rate and an increased yield of ^{3*}C.

In contrast, the PRP lifetime of **2b** ($\tau_{CR} = 49.9$ ns) is almost double that of **2a** ($\tau_{CR} = 28.5$ ns), Figure 2. Given that the PRP is nearly isoenergetic with ^{3*}NI for both **2a** and **2b**, the PRP state and ^{3*}NI are in equilibrium,[9] so that the net decay rate out of the triplet PRP is slower than that from the singlet PRP. Thus, the yield of ^{3*}NI recombination product remains low relative to the initial yield of the PRP ($\Delta A_{3*NI}/\Delta A_{RP} = 0.08$ for **2b**, Figure 2, and $=0.05$ for **2a**, not shown). EISC has the opposite effect on the PRP lifetime of **2b** than it does on that of **1b** because the population shift toward the triplet PRP state in **2b** presents a bottleneck to overall PRP decay due to the fact that ^{3*}NI is slightly higher in energy than the triplet PRP.

A plot of the effect of an applied magnetic field on the yield of ^{3*}C, Figure 3A, shows only a small shift in the position of the $2J_{PRP}$ resonance between **1a** ($2J_{PRP} = 66$ mT) and **1b** ($2J_{PRP} = 60$ mT). However, EISC reduces the influence of the applied magnetic field on the RP dynamics.[6] The magnetic field due to T$^\bullet$ is most likely considerably larger than the field at which the $2J_{PRP}$ resonance occurs, and, therefore, the yield of triplet RP becomes less sensitive to the external magnetic field. Figure 3B shows the corresponding data for **2a** and **b** in which there is no significant shift in the $2J_{PRP}$ resonance between **2a** ($2J_{PRP} = 47.5$ mT) and **2b** ($2J_{PRP} = 47$ mT). Thus, the presence of T$^\bullet$ does not appreciably influence the exchange coupling between unpaired spins of the PRP, although, once again, the magnitude of the resonance decreases in the presence of T$^\bullet$.

In addition to EISC, the presence of T$^\bullet$ introduces the possibility that the three-spin system may intersystem cross to the quartet state via the doublet-precursor radical−triplet pair mechanism (DP-RTPM).[5,17−24] However, the energy gap between the doublet and quartet states should be reasonably large because it is approximately equal to the exchange energy between the spin on the acceptor radical anion and that on T$^\bullet$. As the spin−spin exchange interaction depends exponentially on radical−radical distance, this energy gap is observed to be very small for the PRPs D$^{+\bullet}$−C−PI$^{-\bullet}$ and D$^{+\bullet}$−C−NI$^{-\bullet}$ at 14.9 and 14.7 Å, respectively, and should be prohibitively large for both the NI$^{-\bullet}$−T$^\bullet$ and the PI$^{-\bullet}$−T$^\bullet$ pairs at 8.6 Å.[5] Thus, intersystem crossing due to RTPM is very unlikely. Additionally, the RTPM mechanism is rate determining in systems where it accelerates ISC into or out of an unreactive quartet state. The quartet state in our systems, $^4[^3(D^{+\bullet}-C-Y^{-\bullet})-T^\bullet]$, where Y = PI or NI, is a charge-separated state and may therefore recombine to $^4[D-^{3*}C-PI-T^\bullet]$ or $^4[D-C-^{3*}NI-T^\bullet]$, respectively, so that doublet-quartet ISC should have little or no impact on the CR dynamics of our systems.

In summary, the dependence of the ^{3*}NI and ^{3*}C yield on an applied external magnetic field shows a distinct resonance from which $2J_{PRP}$ is determined directly. The presence of a third spin does not, however, perturb the magnitude of $2J_{PRP}$. We find that T$^\bullet$ enhances radical pair intersystem crossing, resulting in an increase or decrease in the PRP lifetime depending on the relative ordering of the energy levels of the PRP and the local neutral triplet states. This is especially pronounced when the PRP is nearly isoenergetic with the neutral triplet state, as is the case for **2b**. We are currently examining whether pulsed-EPR techniques can be used to manipulate the spin states of T$^\bullet$ to directly control CR events in these systems.

Supporting Information Available: Synthetic and spectroscopic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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