

## Solvent Control of Spin-Dependent Charge Recombination Mechanisms within Donor–Conjugated Bridge–Acceptor Molecules

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Progress toward molecular materials for solar energy conversion as well as electronics depends critically on finding molecules that exhibit efficient long-distance charge transport.<sup>1</sup> In addition, it is important to determine how neighboring molecules, whether they are other charge transport molecules or solvent, affect performance. We have shown recently that the oligomeric *p*-phenylene bridge within the PTZ–(Ph)<sub>*n*</sub>–PDI donor–bridge–acceptor system,<sup>2</sup> Figure 1, acts as a molecular wire in toluene, as shown by a change in the rate of radical ion pair (RP) recombination within PTZ<sup>+</sup>–(Ph)<sub>*n*</sub>–PDI<sup>•−</sup> from an exponential distance dependence to a linear distance dependence as the bridge becomes longer. The switch in mechanism occurs as the PTZ–(Ph)<sub>*n*</sub><sup>+</sup>–PDI<sup>•−</sup> bridge states come into near-resonance with PTZ<sup>+</sup>–(Ph)<sub>*n*</sub>–PDI<sup>•−</sup>, making thermally activated hopping a viable charge-transfer mechanism.

The RP population and its spin-selective recombination products are sensitive to the application of an external magnetic field, which in favorable cases can be used to directly measure the singlet–triplet splitting,  $2J$ , within a well-separated RP. The theory behind this magnetic field effect (MFE) and the relevant radical pair intersystem crossing (RP-ISC) mechanism is well-known to account for triplet production within RPs in photosynthetic reaction centers<sup>3–7</sup> and has been described in detail elsewhere.<sup>8,9</sup> The importance of the magnitude of  $2J$  within the RP lies in its inherent connection to the superexchange coupling matrix elements,  $V_{el}$ ,<sup>10–13</sup> which govern virtual excitations between the RP state and other energetically proximate states and serve as the nonadiabatic charge-transfer matrix elements.<sup>14,15</sup> The value of  $2J$  is a weighted sum of these matrix elements and, to a good approximation, directly proportional to  $V_{DA}^2$ , a one-electron quantity whose magnitude gives the effective coupling between the orbitals on the donor and acceptor sites.<sup>16</sup>

While the relationship between the magnitude of  $\Delta G_{CR}$  and the sign of  $2J$  has been discussed,<sup>9,17</sup> the MFE experiment monitors only  $|2J|$ . Moreover, the change in the RP population as a function of applied magnetic field does not depend on the sign of  $2J$ . The dependence of RP population on magnetic field, Figure 2, reveals the relative contributions of the singlet and triplet charge recombination (CR) pathways to overall RP decay. We have now observed an “inversion” of the MFE on the RP population within **1** and **2** upon a switch in solvent from nonpolar toluene to polar 2-methyltetrahydrofuran (MTHF). We interpret the inversion of the MFE as a switch in the relative importance of the singlet and triplet charge recombination (CR<sub>S</sub>, CR<sub>T</sub>) pathways from toluene to MTHF due to a stabilization of the RP state by the polar solvent, making CR<sub>S</sub> more energetically favorable. Previously, we have observed changes in RP dynamics in liquid crystal solvents.<sup>18</sup>

Synthesis, ground state, and transient absorption spectra of **1**, **2**, and their component chromophores have been previously reported.<sup>2</sup> Density functional theory geometry optimization<sup>19</sup> of **1** and **2** yields the donor–acceptor distances listed in Table 1. Details of the

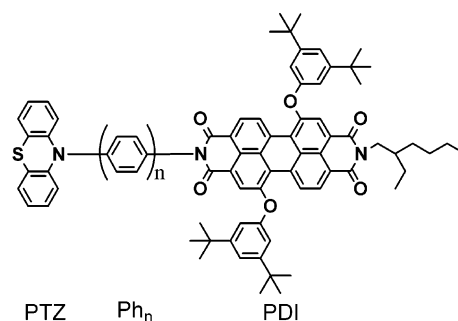


Figure 1. PTZ–(Ph)<sub>*n*</sub>–PDI, where *n* = 4 (**1**) and *n* = 5 (**2**).

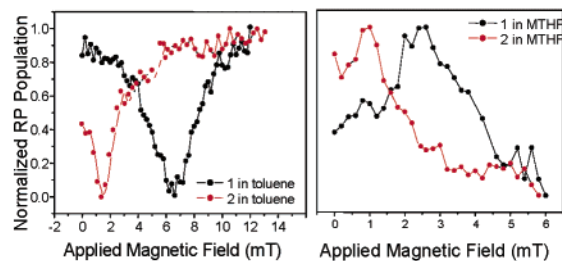


Figure 2. Plots of normalized RP population vs magnetic field for (left) **1** (black,  $2J = 6.4$  mT) and **2** (red,  $2J = 1.5$  mT) in toluene and (right) **1** (black,  $2J = 2.6$  mT) and **2** (red,  $2J = 1.0$  mT) in MTHF.

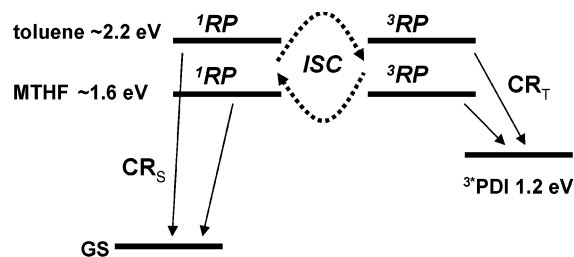
calculations for all values presented in Table 1, along with methodology for the nanosecond transient absorption and MFE experiments, a summary of redox potentials, and CR rates, can be found in Supporting Information and elsewhere.<sup>2</sup> The transient absorption of PDI<sup>•−</sup> at 50 ns following a 10 ns, 530 nm laser flash was monitored at 725 nm as a function of magnetic field to construct the plots in Figure 2. Values for  $2J$  are obtained directly from the minima/maxima of these plots, Table 1.

The RP population goes through a minimum at field value  $B_{2J}$  in toluene but through a maximum in MTHF. Thus, the MFE plots appear to be “inverted” in MTHF. The RP is born in the singlet state, as it comes from the singlet <sup>1</sup>\*PDI precursor.<sup>2</sup> If the triplet recombination pathway is favored over the singlet, then the increased efficiency of RP-ISC that leads to a maximum in triplet production at  $B_{2J}$  will also result in decreased RP population at this field, as the RP population experiences the more efficient CR pathway. Additionally, if the CR<sub>S</sub> pathway is favored, the RP population should go through a maximum at  $B_{2J}$ . One may then conclude that, in toluene, the CR<sub>T</sub> pathway leading to <sup>3</sup>\*PDI is faster and that, in MTHF, the singlet pathway leading to the ground state is faster.

What causes this effect? The simplest answer lies in the energetics, Figure 3. Table 1 lists the reorganization parameters ( $\lambda_I$ ,  $\lambda_S$ ) and driving forces ( $\Delta G_n = E_n - E_{RP}$ ) for singlet and triplet reactions for **1** and **2** in toluene and MTHF.  $E_{RP}$  is evaluated using

**Table 1.** Donor–Acceptor Center-to-Center Distances ( $r_{DA}$ ), Solvent ( $\lambda_S$ ), and Internal ( $\lambda_I$ ) Reorganization Energies, Reaction-Free Energies for Singlet ( $\Delta G_{CR,S}$ ) and Triplet ( $\Delta G_{CR,T}$ ) CR Processes, and  $2J$  Values for **1** and **2** in Toluene and MTHF

	$r_{DA}$ (Å)	$\lambda_S$ (eV)		$\lambda_I$ (eV)	$E_{RP}$ (eV) = $-\Delta G_{CR,S}$		$-\Delta G_{CR,T}$ (eV)		$ 2J $ (mT)	
		toluene	MTHF		toluene	MTHF	toluene	MTHF	toluene	MTHF
<b>1</b>	25.7	0.060	0.83	0.54	2.17	1.54	0.97	0.34	6.4	2.6
<b>2</b>	30.0	0.062	0.85	0.54	2.21	1.55	1.01	0.35	1.5	1.0

**Figure 3.** Energy levels of RP and recombination states in toluene and MTHF;  $\lambda = \sim 0.6$  eV (toluene) and  $\sim 1.4$  eV (MTHF).

the Weller expression for the energy of an RP in a solvent of arbitrary polarity.<sup>7</sup> In toluene, where  $\lambda = \sim 0.6$  eV, both the singlet ( $\Delta G_S = -2.2$  eV) and triplet ( $\Delta G_T = -1.0$  eV) CR processes are in the Marcus inverted region ( $| \Delta G | > \lambda$ ), but the energy gap for the triplet process is considerably smaller than that for the singlet process, resulting in a faster rate for  $CR_T$  than for  $CR_S$ . Thus, at  $B_{2J}$ , where RP-ISC is most efficient, the increased triplet RP population will be quickly depleted via the  $CR_T$  channel resulting in an overall decrease in the total RP population. On the other hand, in MTHF, the reorganization energy is considerably larger ( $\lambda = 1.4$  eV) and the RP is stabilized by the more polar medium. Therefore, although the singlet process ( $\Delta G_S = -1.6$  eV) is still inverted, it is situated much closer to the top of the energy gap law plot than the triplet process ( $\Delta G_T = -0.4$  eV), which has moved into the normal region. Consequently, at  $B_{2J}$ , where RP-ISC is most efficient, the increased population of triplet RP will result in an effective increase in the total RP population because  $CR_T$  is now slower than  $CR_S$ .

As shown in Figure 2 and Table 1, the measured singlet–triplet splittings ( $2J$ ) for the RPs within **1** and **2** are smaller in MTHF than in toluene. As the determination of singlet–triplet splittings from the coupling matrix elements and energy gaps is a complicated issue,<sup>2,8,9</sup> we will approach this issue more qualitatively here. The value of  $2J$  is the sum of the perturbations (to second order) of the singlet and triplet sublevels of the RP by surrounding states to which it is virtually excited.<sup>12</sup> The sign of the energy denominator determines whether the term is ferromagnetic or antiferromagnetic and its magnitude determines how much the term contributes to the sum. The states that must be considered in this analysis are the singlet precursor,  $1^*PDI$ , the triplet recombination product,  $3^*PDI$ , and the singlet ground state, GS. In toluene, the two dominant terms, the interaction with  $1^*PDI$ , which lowers the singlet RP, and the interaction with  $3^*PDI$ , which raises the triplet RP, result in a net antiferromagnetic interaction. However, in MTHF, the increased energy gap between the singlet RP and  $1^*PDI$  destabilizes the singlet RP at least as much as the decreased gap between the triplet RP and  $3^*PDI$  destabilizes the triplet RP, such that there is little net effect on the magnitude of  $2J$ . Moreover, the ferromagnetic interaction of the singlet RP with the singlet ground state is much

more significant. Consequently, the singlet–triplet gap is likely to be smaller in MTHF, and there is a good possibility of a ferromagnetic orientation of RP states, i.e., the triplet may lie below the singlet.

The stabilization of the RP states of **1** and **2** and the increased solvent reorganization energy in polar MTHF versus nonpolar toluene combine to change the relative efficiencies of the  $CR_S$  and  $CR_T$  pathways. In toluene, the triplet pathway is preferred, as evidenced by the minimum in the plot of RP population versus applied magnetic field at  $B_{2J}$ , where maximum singlet–triplet mixing occurs. In MTHF, the singlet pathway is more efficient, and the RP population is therefore maximized at  $B_{2J}$ . Future work will attempt to gain a systematic understanding of the contributions of various states to the perturbation of singlet and triplet RP levels needed for estimation of the electronic coupling matrix elements within these systems.

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**Supporting Information Available:** Computational and experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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