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Manipulating Photogenerated Radical Ion Pair Lifetimes in Wirelike Molecules Using Microwave Pulses: Molecular Spintronic Gates

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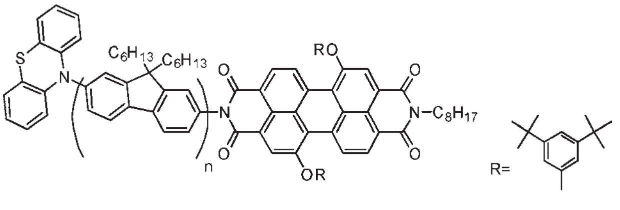
S Supporting Information

ABSTRACT: We have studied spin-dependent charge transfer dynamics in wirelike donor−bridge−acceptor (D−B−A) molecules comprising a phenothiazine (PTZ) donor, an oligo(2,7-fluorene) (FL$_n$) bridge, and a perylene-3,4:9,10-bis(dicarboximide) (PDI) acceptor, PTZ−FL$_3$−PDI (**1**) and PTZ−FL$_4$−PDI (**2**), dissolved in the magnetic field-aligned nematic phase of 4-cyano-4′-*n*-pentylbiphenyl (5CB) at 295 K. Time-resolved EPR spectroscopy using both continuous wave and pulsed microwaves shows that the photogenerated radical pairs (RPs), PTZ$^{+\bullet}$−FL$_3$−PDI$^{-\bullet}$ and PTZ$^{+\bullet}$−FL$_4$−PDI$^{-\bullet}$, recombine much faster from the singlet RP manifold than the triplet RP manifold. When a strong resonant microwave π pulse is applied following RP photogeneration in **1** and **2**, the RP lifetimes increase about 50-fold as indicated by electron spin−echo detection. This result shows that the RP lifetime can be greatly extended by rapidly switching off fast triplet RP recombination.

It is important to elucidate and control the factors that determine the lifetimes of photogenerated charge separated states in donor-bridge-acceptor (D−B−A) molecules for solar energy conversion[1] and molecular electronics[2] and spintronics.[3] Most charge transfer reactions in molecular systems occur by the exponentially distance-dependent superexchange mechanism,[4] while nearly distance-independent thermal charge hopping is ideal for long-range "wirelike" transport.[5] The hopping mechanism requires the energy level of the reactant state to be nearly resonant with the oxidized or reduced bridge states.[5a] Thus, the energy levels of the charge separated states are an important controlling factor for bridge-mediated electron transfer, one that is typically tuned by changing solvent dielectric constant. For example, both the efficiency and the direction of electron transfer can be controlled by the anisotropic dielectric properties of liquid crystals.[6]

For charge recombination (CR) reactions, the spin dynamics of the radical ion pairs (RPs) must also be considered.[4b,7] Following rapid charge separation, the initially formed singlet RP, $^1(D^{+\bullet}{-}B{-}A^{-\bullet})$, undergoes radical-pair intersystem crossing (RP-ISC)[8] induced by electron−nuclear hyperfine coupling within the radicals to produce the triplet RP, $^3(D^{+\bullet}{-}B{-}A^{-\bullet})$. The CR reactions take place spin selectively from these RP states, so that interconversion between the singlet and triplet RP states can be a kinetic bottleneck for the overall CR process.[9] Modification of the spin dynamics by an applied magnetic field has been shown to dramatically change the spin-selective RP reaction yields.[9,10] These magnetic field effects (MFEs) allow control over the CR lifetime, so that the spin-dependent CR pathways as well as the RP spin−spin exchange interaction $2J = E_S - E_T$, where E_S and E_T are spin state energies for the singlet and triplet RP states, respectively, can be probed. The value of $2J$ is exponentially distance dependent and directly reflects the donor−acceptor electronic coupling (V_{DA}).[11] It is also possible to control the RP spin dynamics on a nanosecond time scale by photogenerating the RP in an applied magnetic field, then applying a resonant microwave (MW) pulse that inverts the spins of the RP, thus controlling spin-selective CR and the yield of singlet and triplet products. This technique is known as reaction-yield-detected magnetic resonance (RYDMR).[12] For example, MW irradiation has been shown to increase the photogenerated singlet RP lifetime in bacterial photosynthetic reaction center proteins by 1−2 orders of magnitude.[13]

At the ~350 mT magnetic field characteristic of time-resolved EPR (TREPR) measurements at X-band, the triplet sublevels of $^3(D^{+\bullet}{-}B{-}A^{-\bullet})$ undergo Zeeman splitting, and are best described by the T_{+1}, T_0, and T_{-1} eigenstates that are quantized along the applied magnetic field, while the $^1(D^{+\bullet}{-}B{-}A^{-\bullet})$ (S) energy is unaffected.[14] When intra-RP distances are $\gtrsim$15 Å, $2J$ is generally <10 mT, so that the S and T_0 spin states are close in energy and mix, while the T_{+1} and T_{-1} states are energetically far removed from T_0 and do not mix with S.[14] The two RP states that result from S−T_0 mixing are preferentially populated due to the initial population of S, so that the four EPR transitions that occur between these states and T_{+1} and T_{-1} are spin polarized.[8] The resulting TREPR spectrum consists of two antiphase doublets, centered at the *g*-factors of the individual radicals that comprise the pair. The splitting in each doublet is determined by $2J$ and D, the dipolar interaction between the radicals. The subsequent charge recombination process is spin selective; i.e. $^1(D^{+\bullet}{-}B{-}A^{-\bullet})$ recombines to the singlet ground state, while $^3(D^{+\bullet}{-}B{-}A^{-\bullet})$ recombines to yield the triplet $^{3*}(D{-}B{-}A)$.[15]



PTZ-FL$_n$-PDI , **1** (n = 3) and **2** (n = 4).

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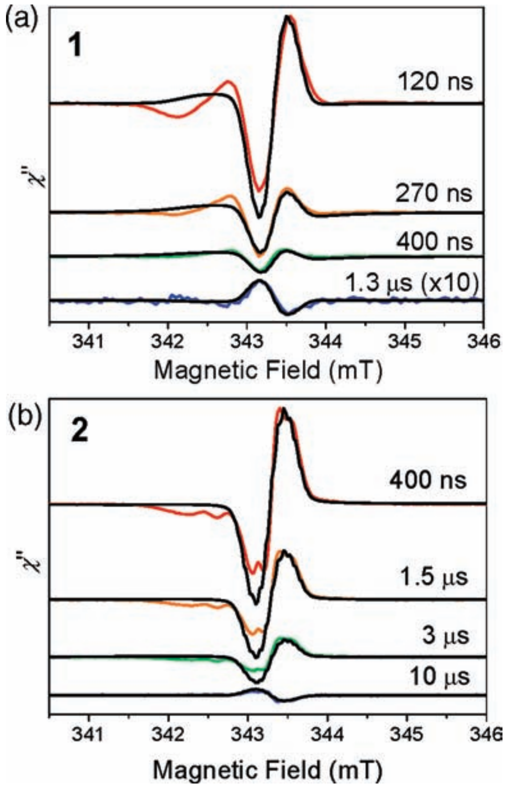

Figure 1. TREPR spectra at 295 K in 5CB. (a) and (b) are SCRP spectra for **1** and **2**, respectively, at the indicated observation times after a 7 ns, 532 nm laser pulse. Black lines are simulated SCRP spectra using the kinetic model described in the Supporting Information.

Here we report on the spin and charge transfer dynamics of D−B−A molecules comprising a phenothiazine (PTZ) donor, an oligo(2,7-fluorene) (FL_n) bridge, and a perylene-3,4:9,10-bis(dicarboximide) (PDI) acceptor, PTZ−FL_3−PDI (**1**) and PTZ−FL_4−PDI (**2**)[5a,9,16] dissolved in the room temperature nematic liquid crystal 4′-cyano-4-*n*-pentylbiphenyl (5CB).[6a] Placing 5CB in the ~350 mT magnetic field (B) used for the TREPR experiments at 295 K aligns the director of 5CB (L) parallel to the field ($L \| B$). In turn, 5CB preferentially aligns the long axes of **1** and **2** parallel to L as indicated by the EPR spectra of ^{3*}PDI formed by CR (See Supporting Information). TREPR using continuous-wave (CW) microwave irradiation and pulsed EPR-detected RYDMR are used to characterize and control the CR processes in **1** and **2**. The synthesis of **1** and **2** is described elsewhere.[5a] Each molecule was dissolved in 5CB, then loaded into a 4 mm OD × 2 mm ID quartz tube and degassed by 4−5 freeze−pump−thaw cycles. The experimental setup for TREPR and pulsed EPR at X-band was described previously.[4b,17] The PDI chromophore in the samples was selectively excited with 7 ns, 532 nm, 2 mJ laser pulses from a frequency-doubled Nd:YAG laser. The total instrument response time is ~50 ns for TREPR.

The TREPR spectra for **1** and **2**, (a and b in Figure 1, respectively) in 5CB at room temperature show narrow spin polarized signals assigned to the $PTZ^{+\bullet}$−FL_n−$PDI^{-\bullet}$ spin correlated radical pair (SCRP).[14c] These spectra also show a time-dependent inversion of their polarization patterns from *E*/*A* to *A*/*E* (*E* = emission, *A* = enhanced absorption). This phase inversion is not observed in toluene. The polarization pattern of the SCRP is determined by the sign rule: $\Gamma = \Delta P \cdot \mathrm{sign}[2J - D(3\cos^2\xi - 1)] = (+)$ gives *E*/*A* or (−) gives *A*/*E*, where ξ is the angle between the magnetic field and the vector that connects the two radicals, and the second-order polarization $\Delta P = P_{S-T0} - P_{T\pm1}$, where P_{S-T0} and $P_{T\pm1}$ are the populations of the S−T_0 mixed states and $T_{\pm1}$ states, respectively.[8a,18] The second term is usually independent of the observation time, so that the phase inversion indicates a change in the sign of ΔP.

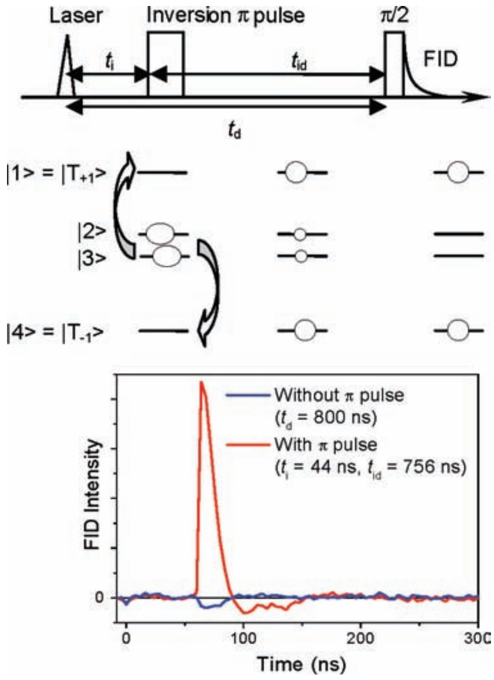

Figure 2. Enhancement of the FID signal of **1** by irradiation with a π MW pulse at 44 ns after the laser pulse. The pulse sequence and the schematic diagram of the spin dynamics are shown. The initial population on the reactive S−T_0 mixed states (|2> and |3>) is transferred to nonreactive T_{+1} and T_{-1} states by the π pulse resulting in the large population and the strong FID at even the late time. The time for FID is defined as the time after the detection $\pi/2$ pulse (at $t_d = t_i + t_{id}$ after the laser). The FID signal without laser irradiation is subtracted from the traces. The signal before 60 ns cannot be observed due to the dead time of the spectrometer.

Time-dependent polarization inversion in SCRPs has been reported previously[19] and is mostly likely a consequence of dominant CR from the RP singlet sublevel at early times followed by transfer of a small population to the $T_{\pm1}$ states at later times by slow spin relaxation (k_{rlx}). Since CR does not occur from the $T_{\pm1}$ states, overpopulation of these states is seen at later times. We have carried out spectral simulations based on the kinetic model presented earlier,[19b] assuming that spin selective recombination occurs from the singlet and triplet manifolds with rate constants k_{CRS} and k_{CRT}, respectively (see Supporting Information). The time-resolved spectra are qualitatively well simulated with very small values of 2*J* (<0.1 mT), when $k_{CRS} \gg k_{CRT}, k_{rlx}$. The value of 2*J* for a weakly coupled RP depends on its electronic coupling to energetically accessible CS precursor and CR product states by

$$2J = \left[\sum_n \frac{|\langle \psi_{RP}|V_{RP-n}|\psi_n\rangle|^2}{E_{RP} - E_n - \lambda}\right]_S - \left[\sum_n \frac{|\langle \psi_{RP}|V_{RP-n}|\psi_n\rangle|^2}{E_{RP} - E_n - \lambda}\right]_T \tag{1}$$

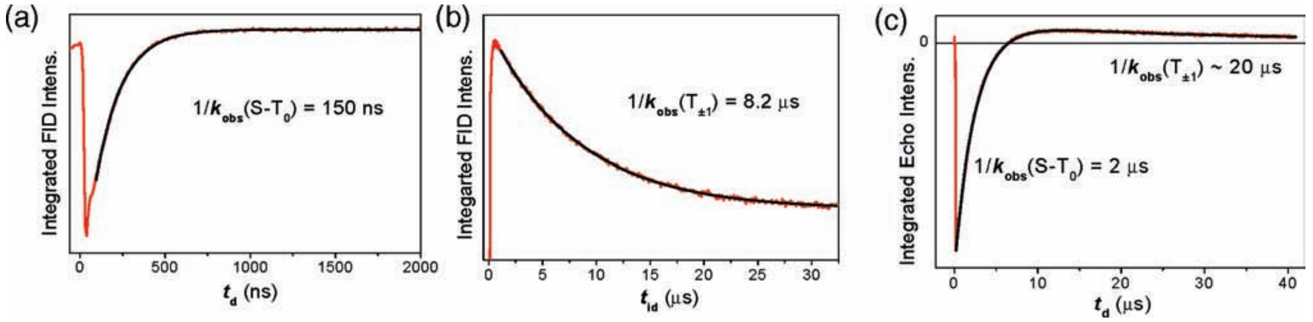

Figure 3. RP population kinetics for **1** (a, b) and **2** (c) recorded by pulsed EPR at the center magnetic field. (a) Laser-$t_D$$-$$\pi/2$-FID pulse sequence for monitoring $\Delta P \approx P_{S-T0}$. (b) Laser-$t_i$(=44 ns)$-\pi-t_{id}-\pi/2$-FID sequence for monitoring $\Delta P \approx P_{T\pm1}$. (c) Laser-$t_D-\pi/2-T$(=108 ns)$-\pi$-echo sequence for monitoring ΔP. The integration gate for the FID/echo (8 ns width) is placed where the maximum signal is observed and shifted in synchronization with the detection pulse. Black lines in (a) and (b) are single exponential fits, whereas for (c) the fit is obtained by two-state kinetics simulation.

where the indicated matrix elements couple the singlet and triplet RP states to states n, E_{RP}, and E_n are energies of these states, respectively, and λ is the total nuclear reorganization energy of the CR reaction.[11] The $2J$ values for **1** and **2** in 5CB are at least 10 times smaller than those in toluene, indicating that V_{DA} is smaller and/or there are larger energy differences between the coupled states.[5a] The latter is more likely, given the large difference in static dielectric constants between toluene (ε = 2.38) and 5CB ($\varepsilon_{\|}$ = 18, $\varepsilon_{\perp}$ = 6).[20]

The polarization inversion mechanism mentioned previously[19b] can be confirmed by RYDMR experiments.[21] In this technique, applying a resonant MW pulse to the RP transfers population from the mixed S$-$T$_0$ levels to the nearly empty T$_{\pm1}$ levels, which permits observation of the "lifetime" of the T$_{\pm1}$ states. This change in population results in changes in the relative yields of singlet and triplet CR products, which are usually detected optically. In our case, however, it is very difficult to observe transient absorption signals due to scattering from the nematic phase of 5CB at room temperature. As an alternative to the optically detected RYDMR experiment, after the initial MW pulse that creates the overpopulated T$_{\pm1}$ RP levels, we have detected transitions between these levels and the mixed RP S$-$T$_0$ levels using either the free induction decay (FID) following a $\pi/2$ pulse or electron spin echo (ESE) detection using the two-pulse sequence $\pi/2-T-\pi$ (Figure 2).[22] The transverse spin relaxation time T_2 of the RP resulting from restricted motion of **1** and **2** in the aligned nematic phase of 5CB is sufficiently long to permit ESE experiments to be performed in this medium at 295 K. We observed nearly a 20-fold enhancement of the FID signal of **1** following the π inversion pulse (Figure 2) (determination of the MW flip angle is based on transient nutation experiments, see Supporting Information). This effect is a result of population pumping from the reactive S$-$T$_0$ states ($|2\rangle$ and $|3\rangle$, Figure 2) to the nonreactive T$_{\pm1}$ states. A similar effect is also observed on the ESE signal from **2**. These observations strongly support the conclusion from the TREPR experiments using CW MW irradiation that $k_{CRS} \gg k_{CRT}$, k_{rlx}.

The decay kinetics of the S$-$T$_0$ mixed states and T$_{\pm1}$ states are observed separately by several pulse-delay experiments. The kinetics without the π inversion pulse is obtained by the simple pulse sequence of laser-$t_D-\pi/2$-FID for **1** as shown in Figure 3a. The signal tracks the time evolution of the second order polarization ΔP. The value of ΔP without the initial inversion π pulse reflects the population of the S$-$T$_0$ mixed states because T$_{\pm1}$ states have negligible population, i.e. $k_{rlx} \ll k_{CRS}$, k_{CRT}. When $2J$ is small, the observed decay rate for the S$-$T$_0$ population at high field, can be approximated as

$$k_{obs}(S - T_0) = k_{CRS}/2 + k_{CRT}/2 \approx k_{CRS}/2 \qquad (2)$$

because S$-$T$_0$ mixing is much faster ($\geq 10^8$ s^{-1}) than k_{CRS} and k_{CRT} and $k_{CRS} \gg k_{CRT}$ as indicated by the TREPR results using CW MWs. Thus, the observed 150 ns decay for **1** yields k_{CRS} = 1.3 × 10^7 s^{-1}. On the other hand, the kinetics in the presence of the π inversion pulse are recorded by using the pulse sequence laser$-t_i-\pi-t_{id}-\pi/2-$FID, where t_{id} is varied (Figure 3b). In this case, one can observe the time evolution of the T$_{\pm1}$ states, which are populated by the inversion pulse. The decay of the T$_{\pm1}$ states is governed by triplet CR and/or relaxation to the S$-$T$_0$ mixed states followed by the fast CR from the mixed states, which is approximated by

$$k_{obs}(T_{\pm1}) = k_{CRT} + k_{rlx} \qquad (3)$$

The 8.2 μs decay time for **1** yields k_{obs}(T$_{\pm1}$) = 1.2 × 10^5 s^{-1},[19b,23] which means that the RP lifetime is extended by about a factor of 50 by the MW pulse as has been observed for the photosynthetic reaction center.[13] However, the experiment does not separate k_{CRT} and k_{rlx}.

The kinetics for **2** without the initial inversion π pulse is observed by the laser-$t_d-\pi/2-T-\pi$-echo pulse sequence, where t_d is varied (Figure 3c). The kinetics show a fast 2 μs decay component, which is followed by a distinct population inversion and a very slow decay of the inverted signal (>20 μs); the two components are assigned to k_{obs}(S$-$T$_0$) and k_{obs}(T$_{\pm1}$), respectively. The trace is fit by simple two-state kinetics (Supporting Information), which give k_{CRS} = 7 × 10^5 s^{-1} and k_{rlx} = 3×10^4 s^{-1}. The simulation is not sensitive to k_{CRT}, but an upper limit of k_{CRT} < 7 × 10^4 s^{-1} is obtained. The very slow relaxation is indicative of very slow molecular motion of the RP in the nematic liquid crystal. The value of k_{rlx} is unlikely to depend significantly on the number of FL units, given that the relaxation is mainly induced by fluctuations in the anisotropies of the magnetic parameters of each radical by local rotational motions.[24] If that is the case, we can use the value of k_{rlx} determined from **2** (3 × 10^4 s^{-1}) to determine k_{CRT} for **1**: $k_{CRT} = k_{obs}(T_{\pm1}) - k_{rlx}$ = 9 × 10^4 s^{-1}, which is somewhat larger than that for **2**.

The dramatic change in the lifetimes of RPs by the initial MW π-pulse for the D−B−A molecules could be used as way to produce molecular spintronic gates controlled by both visible and MW pulses. Molecules **1** and **2** in 5CB are formally AND gates, if the number of charge carriers at late times $(1/k_{\mathrm{CRS}} \ll t \ll 1/k_{\mathrm{T}\pm1})$ is regarded as the output signal.

In conclusion, we have succeeded in elucidating and controlling the spin-selective CR dynamics in wirelike PTZ−FL$_n$−PDI molecules oriented in 5CB by TREPR and pulse-EPR-detected RYDMR. The large increase in the lifetime of the RPs by the initial MW pulse manifests the importance of spin dynamics in prolonging charge separation for solar energy conversion, molecular electronics, and spintronics applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detail regarding the simulation of RP TREPR spectra, pulsed EPR kinetics, TREPR kinetics, and transient nutation experiments for pulsed EPR. This material is available free of charge via the Internet at http://pubs.acs.org.

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