

Details on Monte Carlo simulation of torsional twisting motion of polyaromatic molecules

For the calculation of time evolution of the spin state, a Schrödinger equation with a time-dependent Hamiltonian was solved numerically for fine time step Δt as

$$|\psi_j(t + \Delta t)\rangle = \exp(-i\hat{H}(t)\Delta t)|\psi_j(t)\rangle \quad (1)$$

The Hamiltonian consists of time-independent and time-dependent part as

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_{2J}(t) \quad (2)$$

former of which includes the Zeeman interaction, effective hyperfine (HF) couplings between two nuclear spins ($I_1 = I_2 = 1/2$) and each of electron, and effective Hamiltonian for recombination reaction as

$$\hat{H}_0 = \frac{g_1\mu_B B_0}{\hbar} \hat{S}_{1Z} + \frac{g_2\mu_B B_0}{\hbar} \hat{S}_{2Z} + a_{1\text{eff}} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{I}}_1 + a_{2\text{eff}} \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{I}}_2 - ik_{\text{recS}} |S\rangle\langle S| - ik_{\text{recT}} |T\rangle\langle T| \quad (3)$$

$a_{1\text{eff}}$ and $a_{2\text{eff}}$ were calculated by Weller's equation (eq. 9 and 10 in the main text) from the reported HF couplings of PTZ cation and PDI anion radicals ($a_{1\text{eff}}/\gamma = 1.03$ mT, $a_{2\text{eff}}/\gamma = 0.24$ mT). The effective Hamiltonians for singlet and triplet recombination (5th and 6th terms) cause the same effect as respective Haberkorn operators for the Liouville equation (eq. 5 in the main text). The recombination rate constants for singlet and triplet manifolds were taken from reported values obtained by the kinetic simulation of the MFE on the PTZ-FL₂-PDI molecule ($k_{\text{recS}} = 6 \times 10^5$ s⁻¹, $k_{\text{recT}} = 1.2 \times 10^7$ s⁻¹)[1]. Only time-dependent interaction assumed here is the $2J$ coupling as

$$\hat{H}_{2J}(t) = -2J(t) \left(\frac{1}{4} + \mathbf{S}_1 \cdot \mathbf{S}_2 \right) \quad (4)$$

where $2J(t)$ was statistically sampled by Monte Carlo method as described later.

MARY spectra (Figure 4b in the main text) was simulated assuming the singlet electron spin state with the nuclear spin states j ($Z = 4$) as the initial spin state as

$$|\psi(0)\rangle = \frac{1}{Z} \sum_j |S_j\rangle \quad (5)$$

The yield of the excited triplet state generated by the recombination of the radical pair was calculated as

$$P_{\text{triplet}}(t) = \frac{1}{Z} \int_0^t k_{\text{recT}} \sum_j |\langle T | \psi_j(t) \rangle|^2 dt \quad (6)$$

For the calculation of the ST coherence (Figure 4c in the main text), the coherently mixed state was used as the initial spin state as

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}(|S\rangle + |T_{+1}\rangle) \quad (7)$$

The spin coherence at each time was evaluated as

$$\rho_{ST_{+1}}(t) = \langle S|\psi(t)\rangle\langle\psi(t)|T_{+1}\rangle \quad (8)$$

In this case, only the fluctuating $2J$ coupling (eq. 4) was used for the calculation, so that its effect on the spin state can be visualised.

The phenomenological ST dephasing term cannot be introduced into the present Schrödinger equation, but it is assumed to be induced by the fluctuation of the $2J$ coupling. Effect of conventional relaxation (T_1 and T_2) due to anisotropic HF interactions were also ignored. This is because the previous study with Liouville equation[1] indicates that the microsecond-order conventional relaxations do not affect the linewidth of the MARY spectra, and their effect is seen only in the high field region.

$2J(t)$ was calculated according to the eq. 22 in the main text from the fluctuating dihedral angles as

$$2J(t) = 2J_0 \cos^2 \theta_{DB}(t) \cos^2 \theta_{BA}(t) \prod_i^{N-1} \cos^2 \theta_{BB}^i(t) \quad (9)$$

where N is the number of the repeating bridge unit ($N = 2$ for PTZ-FL₂-PDI). Time evolution of the dihedral angles is calculated by Monte Carlo molecular dynamics (MD) simulation reported by Berlin et al.[2]. Change in the angle $\Delta\theta$ in the very fine time step Δt_{MD} is calculated by the motion equation

$$\Delta\theta = -\frac{D_{rot}}{k_B T} \frac{\partial U_{tor}(\theta)}{\partial \theta} \Delta t_{MD} + \Delta\theta_{diff} \quad (10)$$

where $\Delta\theta_{diff}$ is a random angle, the mean square value of which is described as

$$\Delta\theta_{diff}^2 = 2D_{rot} \Delta t_{MD} \quad (11)$$

The potential curves for θ_{DB} , θ_{BB} , and θ_{BA} were taken from the literature values for the same molecule obtained by DFT calculations.[3] U_{tor} for θ_{BB} and θ_{BA} respectively exhibit highest energy barriers of 0.15 and 0.5 eV in the totally flat conformation ($\theta = 0$ and π). A high potential barrier of ~ 3 eV was assumed for θ_{DB} . θ_{BB} exhibits a second barrier of ~ 0.1 eV at $\theta = \pi/2$ resulting in the potential minimum at $\theta \sim \pi/4$ and $3\pi/4$, whereas the second barriers for θ_{DB} and θ_{BA} are very small, and the potential minimum is at around $\theta \sim \pi/2$.

The MD simulation starts from a randomly sampled θ values assuming Boltzmann distribution. Small Δt_{MD} was used for the MD calculation so that $2D_{\text{rot}} \times \Delta t_{\text{MD}} = 0.002$. The product of $\cos^2 \theta$

$$f(t) = \cos^2 \theta_{\text{DB}}(t) \cdot \cos^2 \theta_{\text{BA}}(t) \cdot \cos^2 \theta_{\text{BB}}(t)$$

was calculated from the three θ trajectories, which gives the time dependent $2J$ coupling as $2J(t) = 2J_0 f(t)$. After coarse graining the $f(t)$ trajectory, $\Delta t = 40$ ps was used for the spin dynamics simulation since fluctuations at much higher frequency than the state-mixing frequency is unimportant. It turned out that statistical average for 1000 trajectories was enough to obtain well-converged results.

Figure S2-1 shows an example of single $f(t)$ trajectory for PTZ-FL₂-PDI at $D_{\text{rot}} = 5.0 \times 10^8 \text{ s}^{-1}$, which is the smallest value for the calculations in Figure 4c. However, the time scale of the modulation is very short, which likely results in motional narrowing of the $2J$ -resonance spectra. This feature is seen in Figure 4c in the main text, where larger D_{rot} results in slower ST-dephasing (narrower linewidth for MARY spectra).

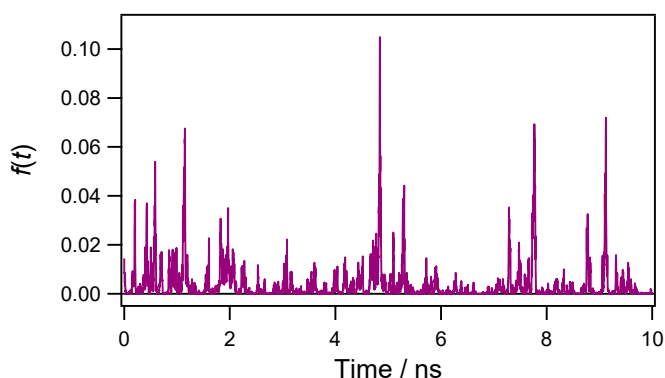


Figure S2-1. An example of trajectory for the product of $\cos^2 \theta$ at $D_{\text{rot}} = 5.0 \times 10^8 \text{ s}^{-1}$.

- [1] T. Miura, A. M. Scott, and M. R. Wasielewski, *J. Phys. Chem. C* **114** (48), 20370 (2010).
- [2] Y. A. Berlin, F. C. Grozema, L. D. A. Siebbeles, and M. A. Ratner, *J. Phys. Chem. C* **112** (29), 10988 (2008).
- [3] F. C. Grozema, Y. A. Berlin, L. D. A. Siebbeles, and M. A. Ratner, *J. Phys. Chem. B* **114** (45), 14564 (2010).