Electronic Supplementary Material (ESI) for RSC Advances

Ultrafast photoexcitation dynamics of π-conjugated bodipy-anthracene-radical triad system: electron transfer, energy transfer and charge-separated ion-pair state toward a uniquely electron-polarized photo-excited quartet state

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Supplementary Information

We here present the time-resolved ESR data, pump-probe experimental data, and time-resolved PL data of the bodipy- anthracene-radical triad system (**1**) or its model compounds as supplementary information.

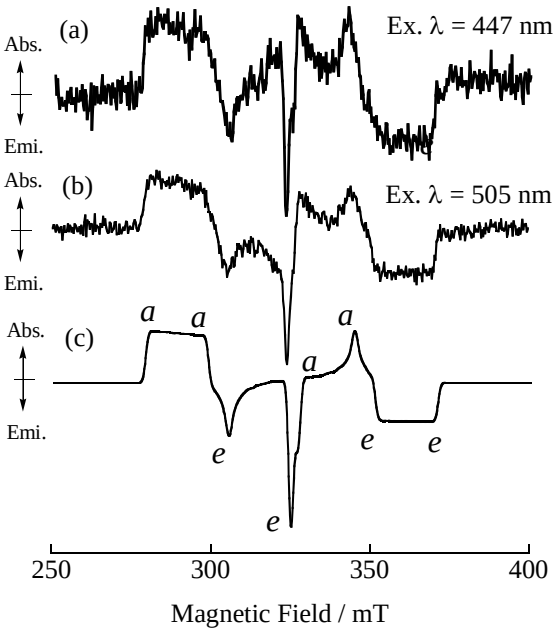

Fig. S1. Typical TRESR spectra of **1** at 30 K in a glass matrix and simulation.[S1] (a) TRESR spectra at 0.3 μs after excitation with λ = 447 nm, (b) λ = 505 nm, and (c) simulation. Spectral simulations were carried out using the hybrid eigenfield/exact diagonalization method, taking DEP into account. The spin Hamiltonian parameters of **1** were determined to be $S = 3/2$, $g = 2.0035$, $D = 0.0215$ cm^{-1}, and $E = 0.001$ cm^{-1} by spectral simulation (Figure S1c). The DEP phase pattern of **1** aeeaae (e/a: emission/absorption of microwave), is different to that of the parent π-radical, aaaeee. (not shown). This unique DEP was generated by attachment of the bodipy functional group. The spectral simulation (Figure S1(c)) was carried out assuming selective populations both for the *zero-field* and *high-field* wave-functions (zero-field:high-field = 0.36:0.64). The latter pattern can be reasonably explained by the mechanism through an quantum-mixed doublet-quartet state.[S2] According to the resonance field, the central peak at 325 mT is a superimposition of the polarized ground-state signal, which is included in the simulation. Thus, competition between the spin-orbit ISC (SO-ISC) and other mechanisms occurs in **1**. Similar competition between SO-ISC and radical-pair (RP) mechanisms have been observed only in photo-system I and II reaction centers,[S3] and in their model systems through the ion pair (IP) state.[S4]

[S1] a) Teki, Y.; Tamekuni, H.; Takeuchi, J.; Miura, Y.; *Angew. Chem.* **2006**, 118, 4782; *Angew. Chem. Int. Ed.,* **2006**, 45, 4666; b) Teki, Y.; Tamekuni, H.; Haruta, K.; Takeuchi, J.; Miura, Y.; *J. Mater. Chem.* **2008**, 18, 381.

[S2] Teki, Y.; Matsumoto, T.; *Phys.Chem. Chem.Phys.*, 2011, **13**, 5728.

[S3] Levanon, H.; Norris, J. R.; *Chem. Rev.* 1978, **78**, 185.

[S4] a) Hasharoni, K.; Levanon, H.; Greenfield, S. R.; Gosztola, D. J.; Svec, W. A.; Wasielewski, M. R.; *J. Am. Chem. Soc.* 1995, **117**, 8055; b) Hasharoni, K.; Levanon, H.; Greenfield, S. R.; Gosztola, D. J.; Svec, W. A.; Wasielewski, M. R.; *J. Am. Chem. Soc.* 1996, **118**, 10228

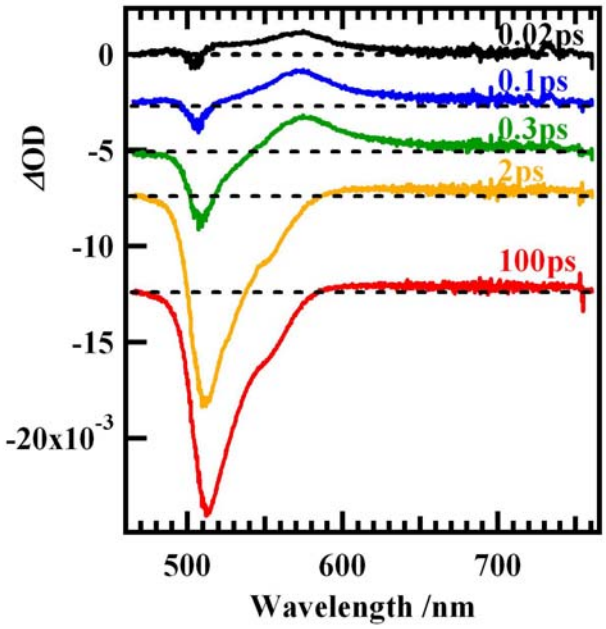

Fig. S2. Typical transient absorption spectra (*Δ*OD) of **1** in toluene upon excitation at λ = 390 nm at room temperature. The transient spectra were recorded after 0.02, 0.1, 0.3, 2 and 100 ps after photoexcitation. The horizontal broken lines represent baselines for each spectrum.

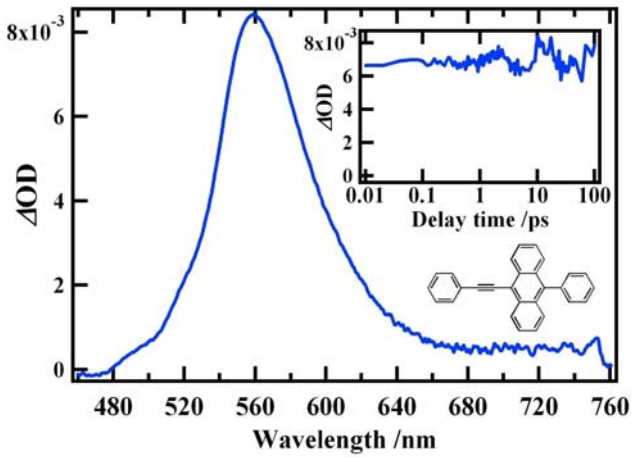

Fig. S3. A typical fs-pump-probe spectrum of a model donor molecule (control compound of **1**), 9-phenyl-10-phenylethynyl-anthracene in butyronitrile measured at room temperature. The center peak at 560 nm corresponds to the transient absorption signal from singlet excitons of the anthracene moiety. The inset indicates a time profile measured at 560 nm. This demonstrates that the decay of the singlet is almost negligible in this time scale.

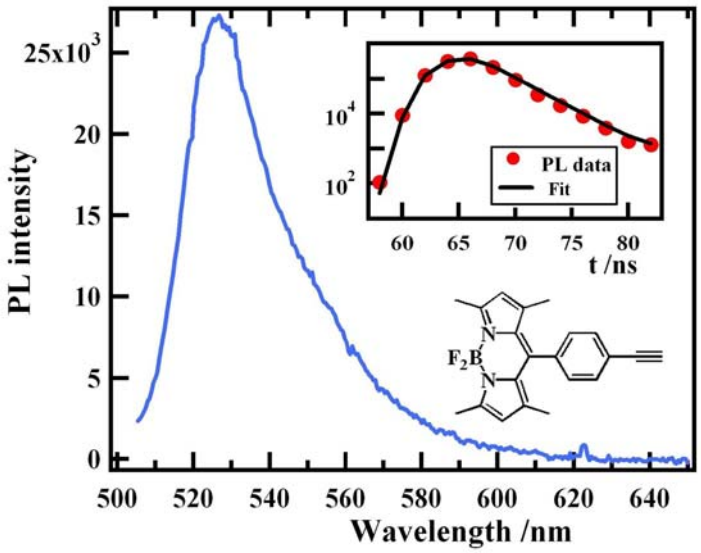

Fig. S4 A typical fluorescence spectrum of a model acceptor molecule, 4,4-Difluoro-1,3,5,7-tetramethyl-8-(*p*-ethynylphenyl)-4-bora-3a,4a-diaza-s-indacene in butyronitrile measured at room temperature. The excitation wavelength was 505 nm. The inset indicates the time profile of the fluorescence recorded at 525 nm (filled circles). The time profile was analyzed by considering the time profile of the excitation laser. The result of the analysis is shown by the solid curve in the inset and determined the decay time constant to be 2.5 ns.