Supporting Information for

Efficient Singlet Fission in an Orthogonal Anthracene Dimer Film

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Content

1. Crystal structures for 9-PhAn and 9,9'-BiAn

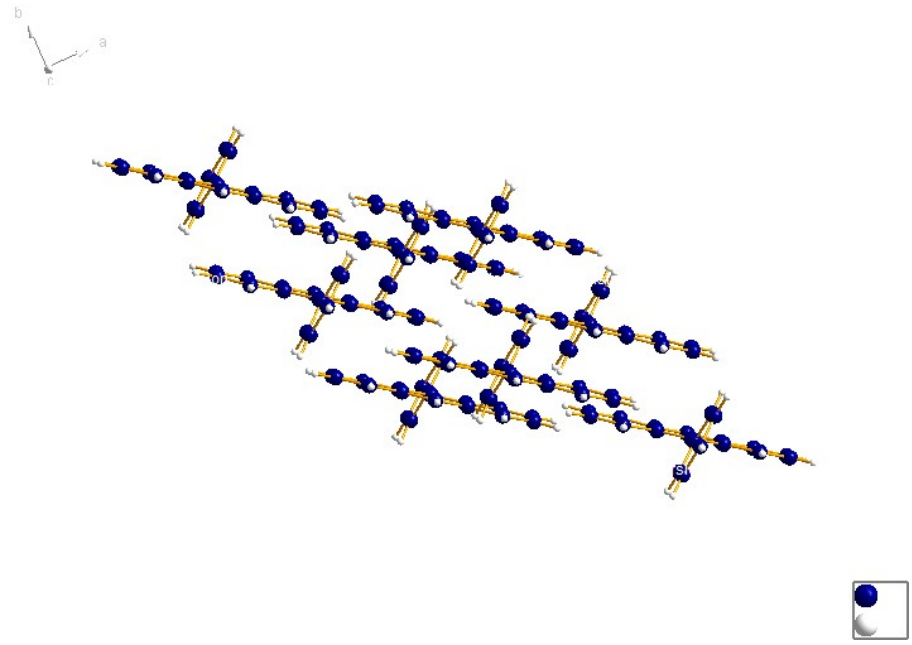

Figure S1. Crystal structure of 9-PhAn downloaded from the Cambridge Crystallographic Data Centre.[1]

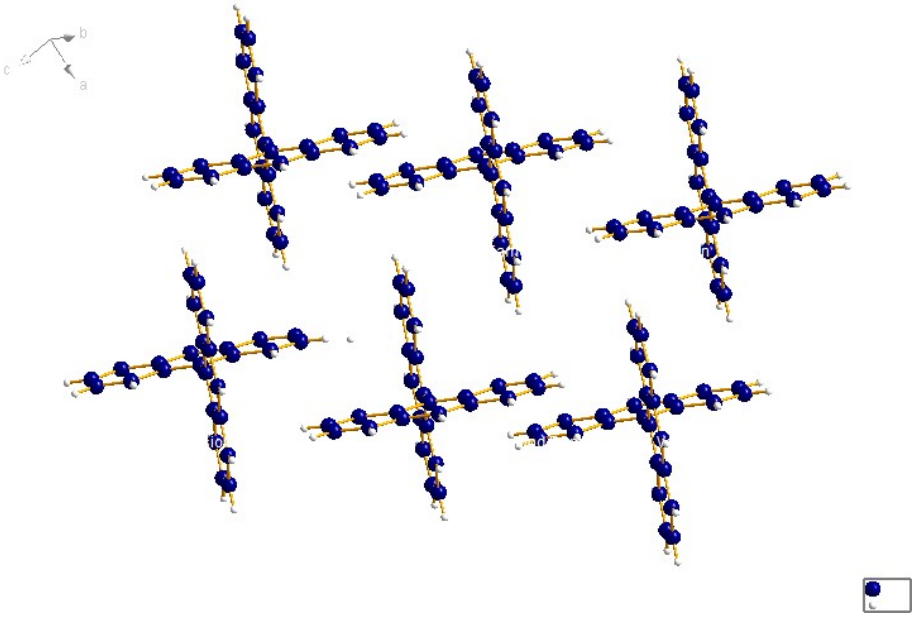

Figure S2. Crystal structure of 9,9'-BiAn.

Table S1. Crystallographic parameters for 9-PhAn and 9,9'-BiAn crystals.

	9-PhAn	9,9'-BiAn
Empirical	$C_{20}H_{14}$	C35 H26
Formula	254.310	446.56
Temperature/K	150.00	293
Crystal	triclinic	triclinic
Space	P-1	P-1
a/Å	6.247	10.5976
b/Å	10.259	11.4038
c/Å	10.779	11.6338
α/°	84.94	63.190
β/°	76.39	81.467
γ/°	77.39	85.013
Volume/Å3	654.7	1240.64
Z	2	2
ρcalc mg/cm-3	1.290	1.195
μ/mm-1	0.073	1.322
F(000)	268.0	472
2Θ range for data collection	6.648 to 141.08	3.178 to 51.928
Reflections collected	3981	9179
Independent reflections	2241[Rint = 0.0136, Rsigma = 0.0186]	5169 [R_{int} = 0.0953, R_{sigma} = 0.1525]
Data/restraints/parameters	2241/0/181	5169/0/521
Goodness-of-fit on F 2	1.038	1.303
Final R indexes [I>=2σ (I)]	R_1 = 0.1195, wR_2 = 0.2975	R_1 = 0.2047, wR_2 = 0.4605
Final R indexes [all data]	R_1 = 0.1213, wR_2 = 0.3042	R_1 = 0.3031, wR_2 = 0.5401
Largest diff. peak/hole /eÅ-	0.56/-0.46	1.00/-0.54

2. Comparison of XRD patterns between single crystal and solid film

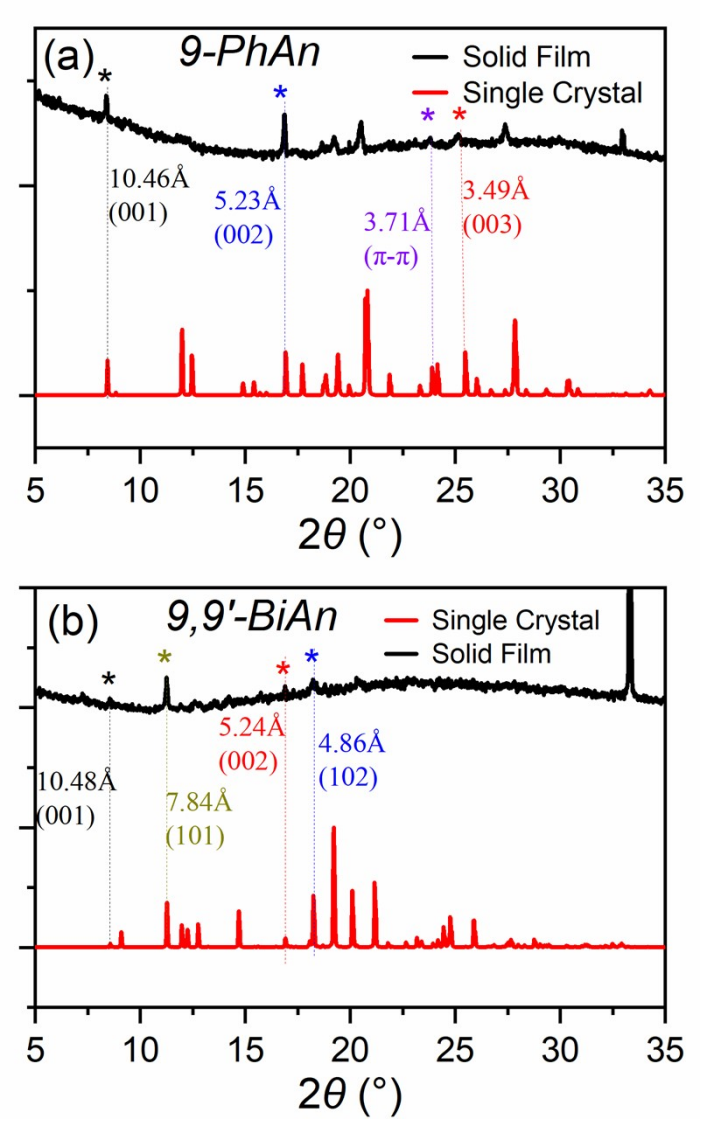

Figure S3. Comparison of XRD patterns between single crystal and solid film.

3. Fluorescence dynamics of 9-PhAn and 9,9'-BiAn in toluene

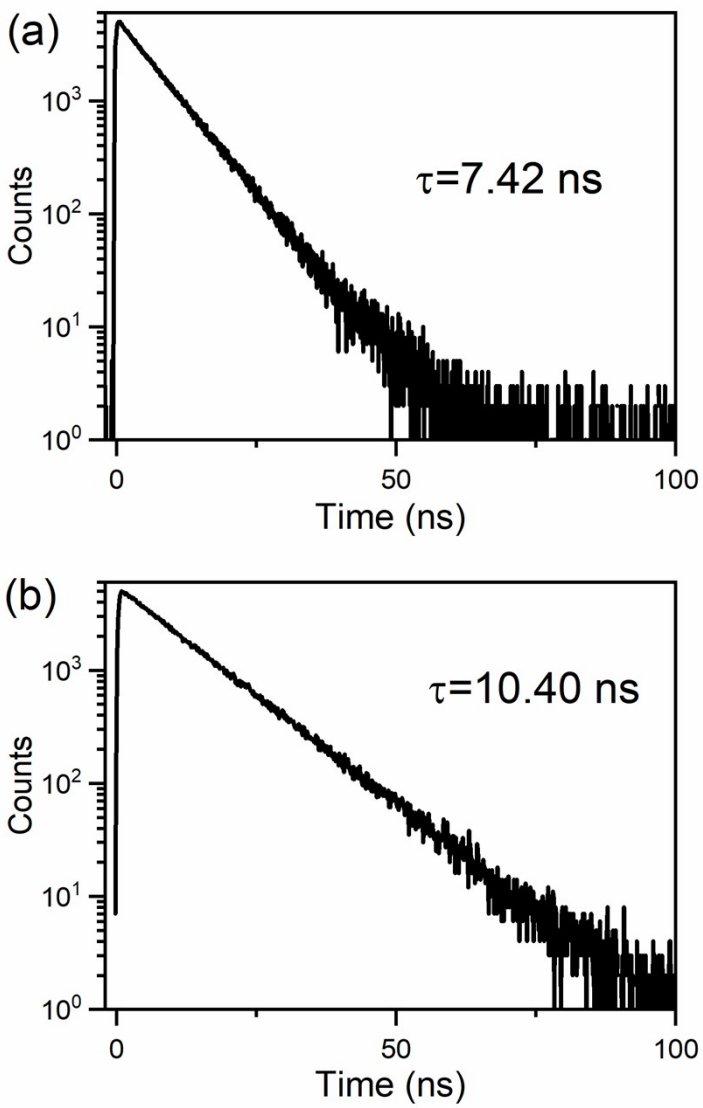

Figure S4. Fluorescence dynamics of 9-PhAn (a) and 9,9'-BiAn (b) monitored at the maximum emission peak in toluene.

4. *fs*-TA spectra of 9-PhAn in toluene

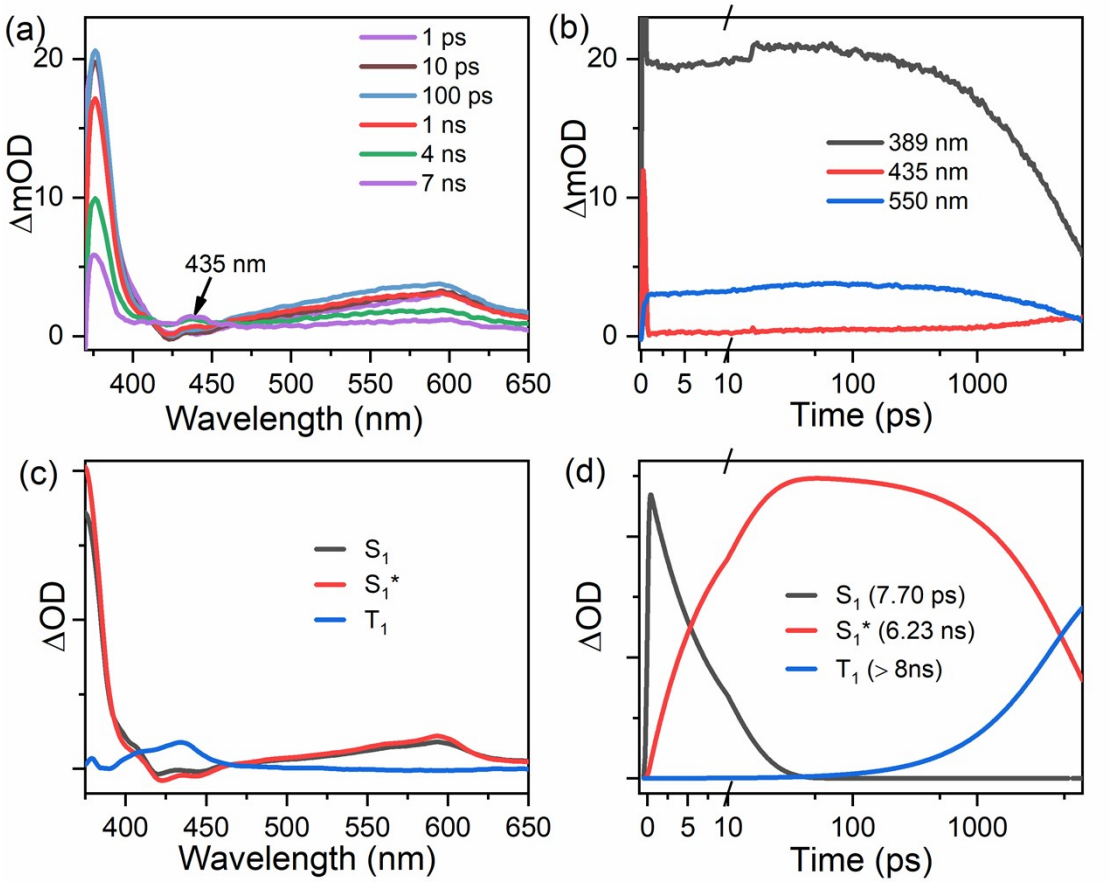

Figure S5. (a) *fs*-TA spectra of 9-PhAn in toluene. (b) Single-wavelength dynamics probed at different wavelengths. Species-associated spectra (c) and dynamics (d) obtained from global analysis.

In toluene, after photoexcitation, the TA spectra of 9-PhAn show immediately two photo-induced bleaching (PIB) bands corresponding to stimulated emission (SE) at 424 and 440 nm, and two excited-state absorption (ESA) associated to the singlet (S_1) state at 376 nm and 470-650 nm. As the time increases, the S_1 absorption intensity first increases slightly (Figure S5a), which should be caused by vibrational cooling and structural relaxation.[2] Then, the relaxated S_1 state (S_1*) decays gradually with a time constant of 6.23 ns (Figure S5c and S5d) and a small band of triplet (T_1) absorption is observed at 435 nm (this assignment is confirmed by the sensitization experiment. Figure S6). This slow conversion should be originated from intersystem crossing (ISC).

5. Sensitization experiment of 9-PhAn in solution and solid film

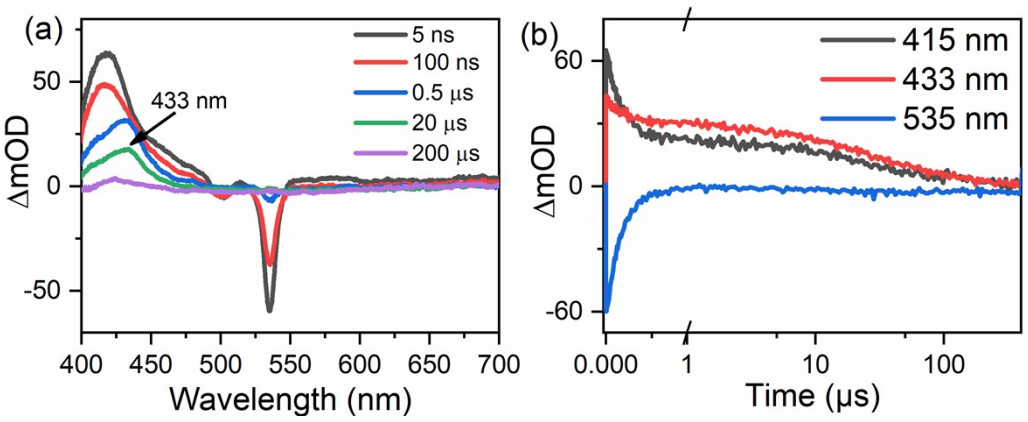

Figure S6. (a) *ns*-TA spectra for a mixture of 9-PhAn and PtOEP in toluene excited at 535 nm. (b) Single-wavelength dynamics probed at different wavelengths.

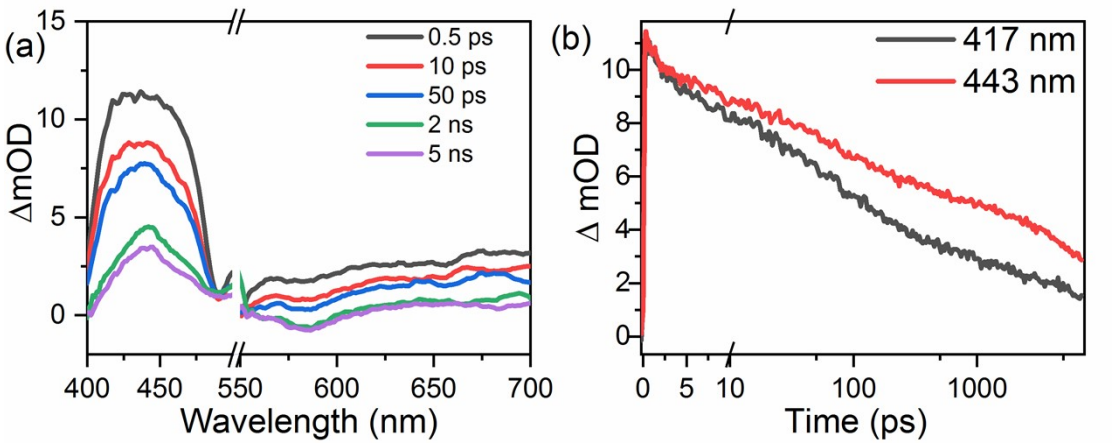

Figure S7. (a) *fs*-TA spectra for a doped film of 9-PhAn and PtOEP excited at 535 nm. (b) Single-wavelength dynamics probed at different wavelengths.

6. *fs*-TA spectra of 9,9'-BiAn in toluene

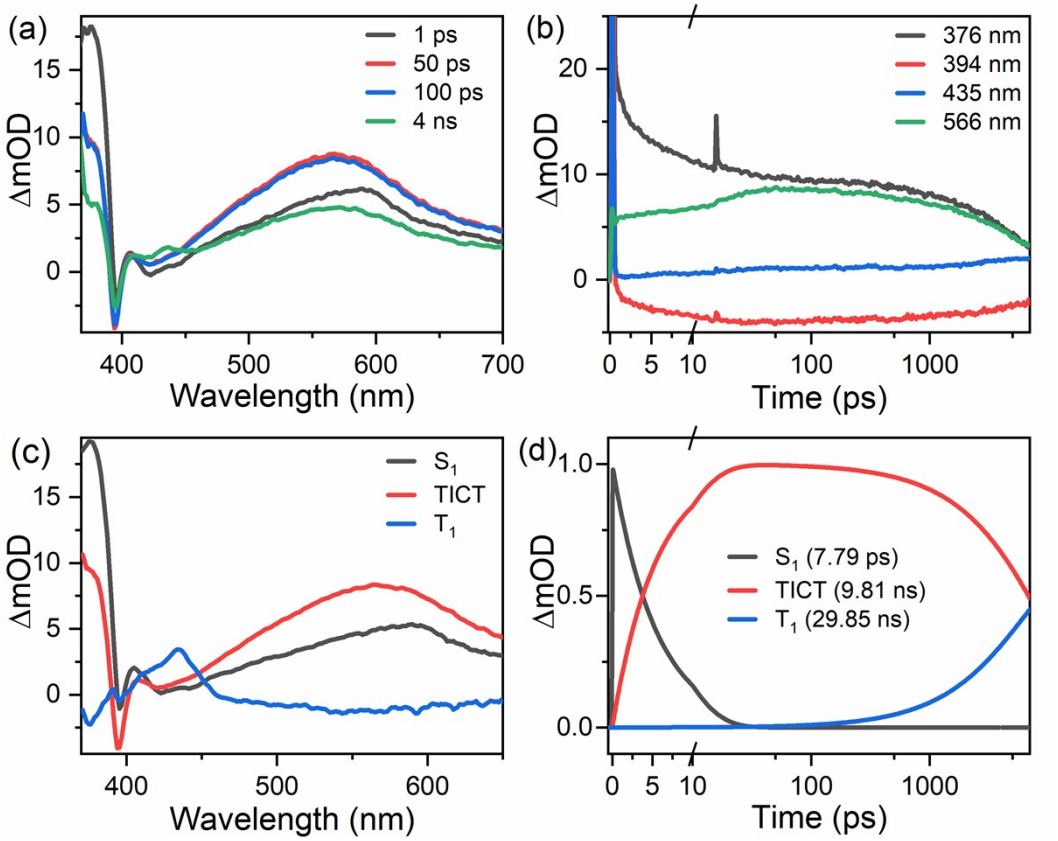

Figure S8. (a) *fs*-TA spectra of 9,9'-BiAn in toluene. (b) Single-wavelength dynamics probed at different wavelengths. Species-associated spectra (c) and dynamics (d) obtained from global analysis.

Upon photoexcitation, TA spectra of 9,9'-BiAn in toluene display immediately the GSB band at 394 nm, and the S_1 absorption at 376 nm and 450-650 nm (Figure S8a).with the decrease of S_1 absorption intensity at 376 nm, the initial S_1 absorption centered at 588 nm is blue-shifted to 569 nm along with an intensity increase (Figure S8a-S8b). This is ascribed to the formation of the TICT state and its generation time is 7.94 ps based on the global analysis (Figure S8c-S8d).

7. Sensitization experiment of 9,9'-BiAn in solution and solid film

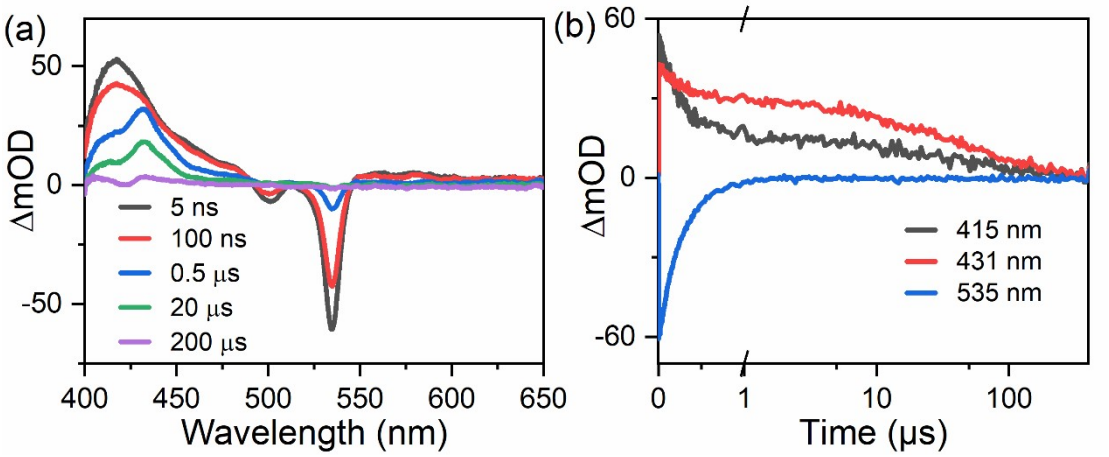

Figure S9. (a) *fs*-TA spectra for a mixture of 9,9'-BiAn and PtOEP excited at 535 nm in toluene. (b) Single-wavelength dynamics probed at different wavelengths.

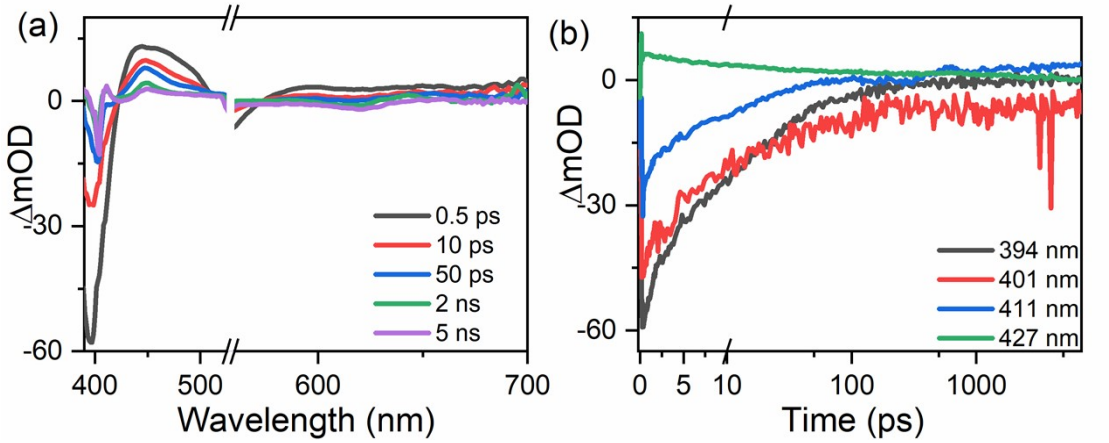

Figure S10. (a) *fs*-TA spectra for a doped film of 9,9'-BiAn and PtOEP excited at 535 nm. (b) Single-wavelength dynamics probed at different wavelengths.

8. Comparison of TA spectra between the raw data and fitting data

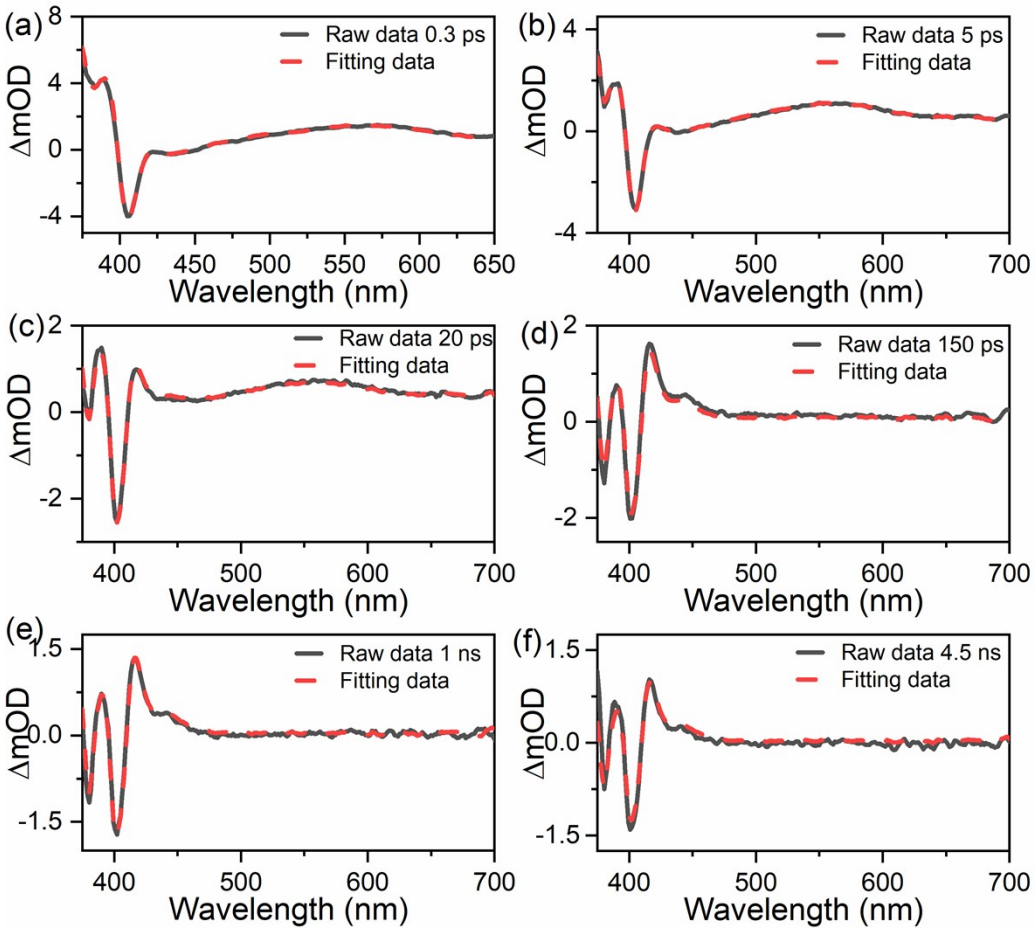

Figure S11. Comparison of TA spectra of 9,9'-BiAn film between the raw data and the fitting data using global analysis.

9. HOMO and LUMO distributions of 9-PhAn and 9,9'-BiAn

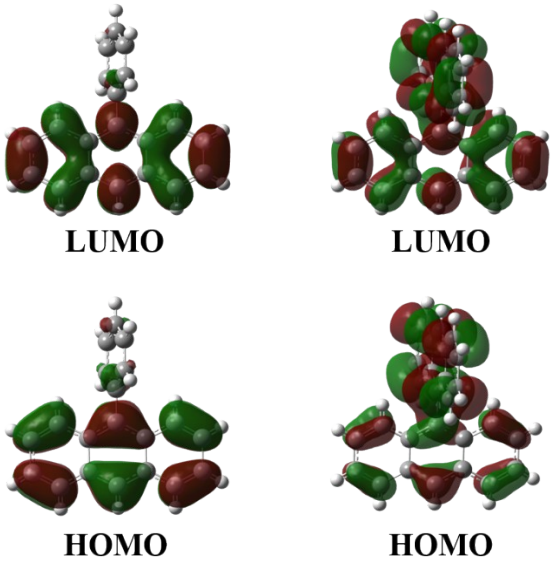

Figure S12 Lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO) of 9-PhAn and 9,9'-BiAn.

Table S2. Singlet and triplet energy of 9-PhAn and 9,9'-BiAn.

	9-PhAn	9,9'-BiAn
S_1 (eV)	3.66	3.61
T_1 (eV)	1.86	1.83

10. Absorption and fluorescence spectra of 9,9'-BiAn in solution and PMMA

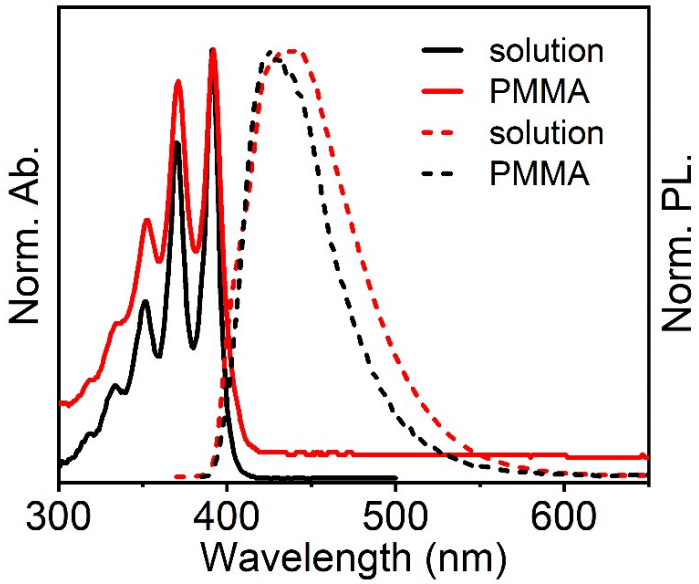

Figure 13 Absorption (solid line) and fluorescence (dash line) spectra of 9,9'-BiAn in toluene black line and PMMA (red line).

11. Triplet yield determination

The triplet yield was determined using the ground-state bleaching method according to the previous report.[3,4] The initial molecule concentration is assumed to be unity. The TA spectrum of an early time trace (0.3 ps) after photoexcitation was selected to represent the S_1 spectra for 9,9'-BiAn and 9-PhAn films. The S_1 concentration at the beginning is assumed to be C_1 whereas the T_1 concentration remains nearly 0.

The S_0 concentration ($C_t(S_0)$) at any time can be calculated following equation (1):

$$C_{t1}(S_0) = 1 - C_{t1}(S_1) - C_{t1}(T_1) \quad (1)$$

$$\Delta C_{t1}(S_0) = C_{t1}(S_0) - C_0(S_0) = 1 - C_{t1}(S_1) - C_{t1}(T_1) - 1 = 1 - C_1 - 0 - 1$$

$$= - C_{t1}(S_1) \quad (2)$$

The TA spectra at 325 ps and 460 ps were selected to represent the T_1 spectra of 9,9'-BiAn and 9-PhAn films, respectively. At these times, the S_1 state has decayed completely meanwhile the T_1 state was formed according to the species-associated dynamics obtained global analysis (Figure 4d and 5d in the main text).

$$C_{t2}(S_0) = 1 - C_{t2}(S_1) - C_{t2}(T_1) \quad (3)$$

$$\Delta C_{t2}(S_0) = C_{t2}(S_0) - C_0(S_0) = 1 - C_{t2}(S_1) - C_{t2}(T_1) - 1 = 1 - 0 - C_{t2}(T_1) - 1$$

$$= - C_{t2}(T_1) \quad (4)$$

The triplet quantum yield can be calculated by equation (5):

$$\Phi_T = \frac{C_{t2}(T_1)}{C_{t1}(S_1)} = \frac{\Delta C_{t2}(S_0)}{\Delta C_{t1}(S_0)} = \frac{GSB(t2)}{GSB(t1)} \quad (5)$$

The TA spectra show the superposition of GSB, S_1 absorption or T_1 absorption. Thus,

proper substration of the scaled GSB spectrum can reproduce the pure S_0, S_1, T_1 spectra. The specific operation is that only enough ground state absorption is added to the transient trace in order to remove the effect of the GSB band on the absorption (Figure S12 and S13). Therefore, the triplet yields of 9,9'-BiAn and 9-PhAn films can be determined.

For 9,9'-BiAn film:

$$\Phi_T = \frac{GSB(t2)}{GSB(t1)} = \frac{0.00945}{0.00575} = 164.3\% \pm 10\%$$

For 9-PhAn film:

$$\Phi_T = \frac{GSB(t2)}{GSB(t1)} = \frac{0.00329}{0.00735} = 44.8\% \pm 15\%$$

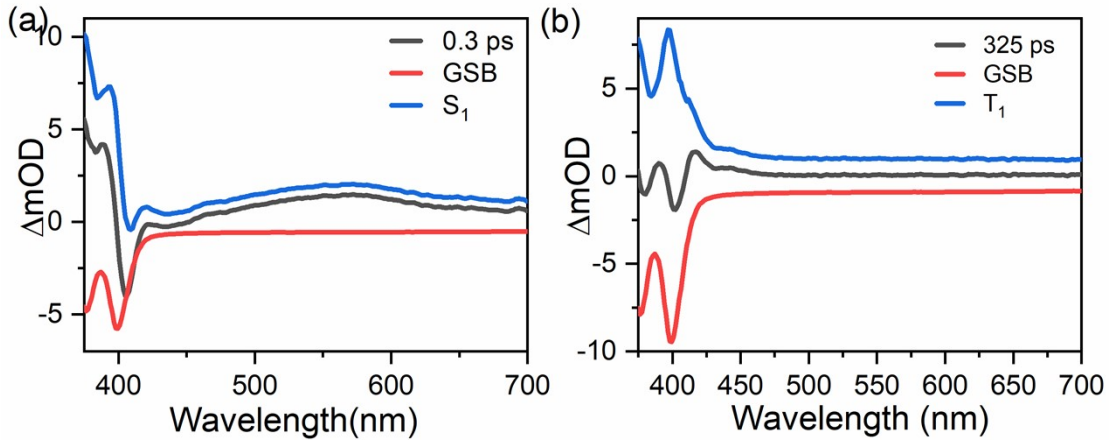

Figure S14. TA spectra and substration of the scaled steady state absorption spectra and resulting reconstructed absorption spectra of the pure singlet state (a) and triplet state (b) of 9,9'-BiAn film.

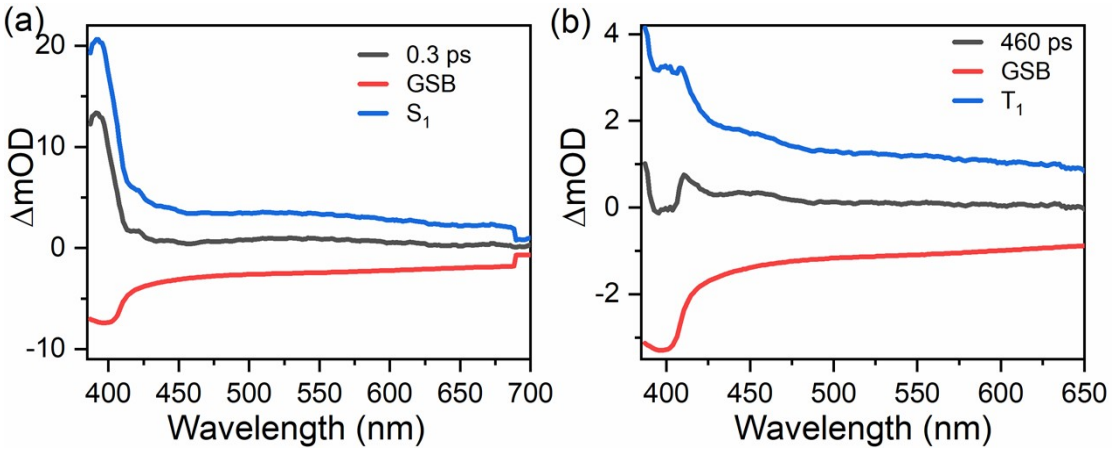

Figure S15. TA spectra and substration of the scaled steady state absorption spectra and resulting reconstructed absorption spectra of the pure singlet state (a) and triplet state (b) of 9-PhAn film.

Reference

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3 Y. Wu, K. Liu, H. Liu, Y. Zhang, H. Zhang, J. Yao, H. Fu, Impact of Intermolecular Distance on Singlet Fission in a Series of TIPS Pentacene Compounds, *J. Phys. Chem. Lett.* 2014, **5**, 3451-3455.

4 E.A. Margulies, Y.-L. Wu, P. Gawel, S.A. Miller, L.E. Shoer, R.D. Schaller, F. Diederich and M.R. Wasielewski, Sub-Picosecond Singlet Exciton Fission in Cyano-Substituted Diaryltetracenes. *Angew. Chem. Int. Ed*. 2015, **54**, 8679-8683.