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Electronic supplementary information

Modulated Emission from Dark Triplet Excitons in Aza-Acene Compounds: Fluorescence Versus Phosphorescence

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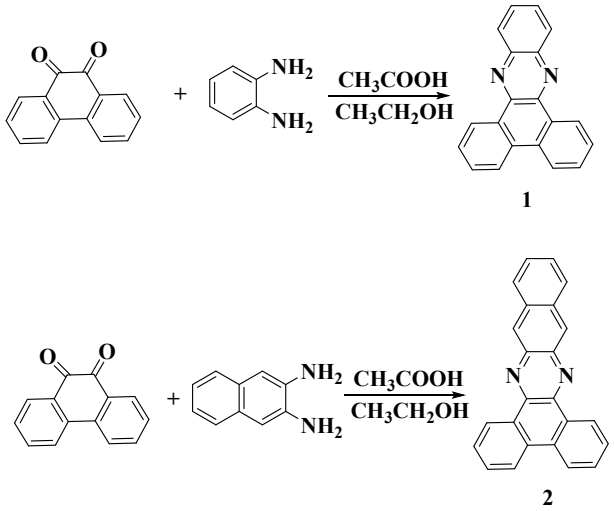
1. Synthesis and Compounds Data



Scheme S1. Synthetic pathway of the BP compounds.

Dibenzo[a,c]phenazine (1).

To a round bottom flask were added the phenanthrene-9,10-dione (1.04 g, 5 mmol), benzene-1, 2-diamine (0.60 g, 5.5 mmol), acetic acid (20 ml) and ethyl alcohol (40 ml). The reaction was heated and refluxed for 3h. After cooling to room temperature, the mixture was filtered under vacuum and washed with ethyl alcohol. The solid was dried under vacuum for 20 h, affording the faint yellow procedure **1** (1.34 g). Yield: 86 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (dd, *J* = 8.0, 1.2 Hz, 2H), 8.56 (d, *J* = 8.0 Hz, 2H), 8.35 – 8.29 (m, 2H), 7.86 (dt, *J* = 6.4, 3.2 Hz, 2H), 7.77 (tdd, *J* = 15.2, 10.4, 4.0 Hz, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ122.94, 126.30, 127.96, 129.48, 129.77, 130.33, 132.09, 142.23, 142.49. HRMS: calcd. for $C_{20}H_{12}N_2$ $[M+H]^+$ 281.1079; found 281.1059.

Tribenzo[a,c,i]phenazine (2).

To a round bottom flask were added the phenanthrene-9,10-dione (1.04 g, 5 mmol), naphthalene-2,3-diamine (0.87 g, 5.5 mmol), acetic acid (20 ml) and ethyl alcohol (40 ml). The reaction was heated and refluxed for 3h. After cooling to room temperature, the mixture was filtered under vacuum and washed with ethyl alcohol. The solid was dried under vacuum for 20 h, affording the faint yellow procedure **2** (1.67 g). Yield: 82 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (dd, *J* = 8.0, 1.2 Hz, 2H), 8.94 (s, 2H), 8.53 (d, *J* = 7.6 Hz, 2H), 8.20 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.79 (tdd, *J* = 15.2, 10.4, 4.4 Hz, 4H), 7.60 (dd, *J* = 6.4, 3.2 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ123.07, 126.56, 127.49, 128.17, 128.56, 132.43, 133.23, 134.09. HRMS: calcd. for $C_{24}H_{14}N_2$ $[M+H]^+$ 331.1235; found 331.1233.

2. Spectral Characterization and Photophysical Parameters

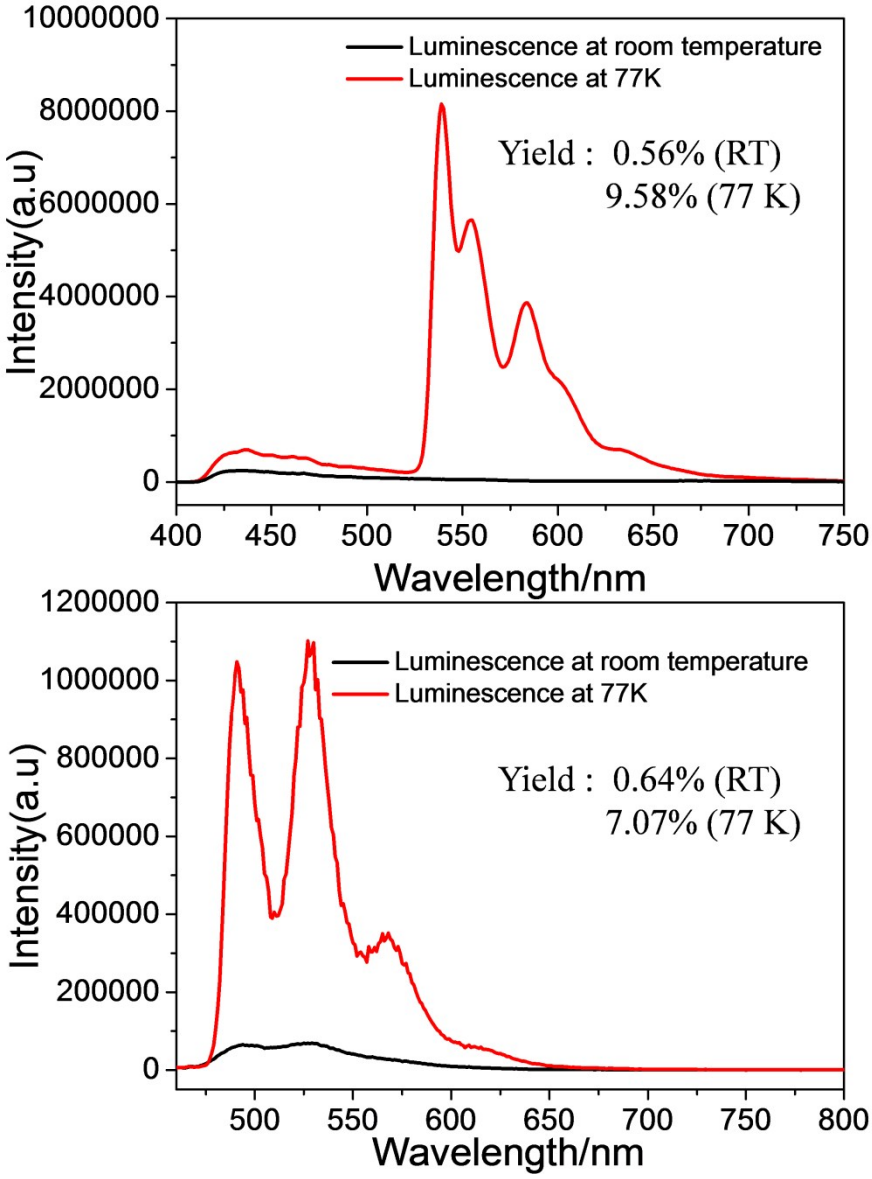


Fig. S1 Luminescence spectra at room temperature (black line) and at 77 K (red line) of DBP (up) and TBP (bottom) in Toluene (Tol) dilute solution, respectively. The absolute quantum yields were also presented at RT (room temperature) and 77 K.

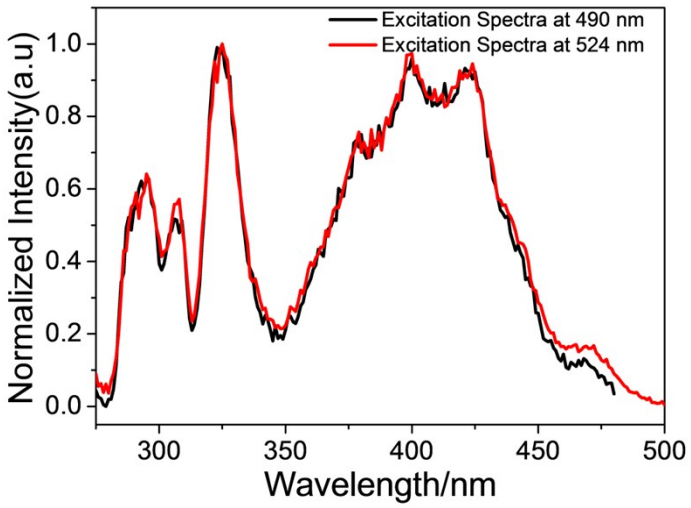


Fig. S2 Excitation spectra for TBP at 490 nm (black line) and 524 nm (red line), respectively.

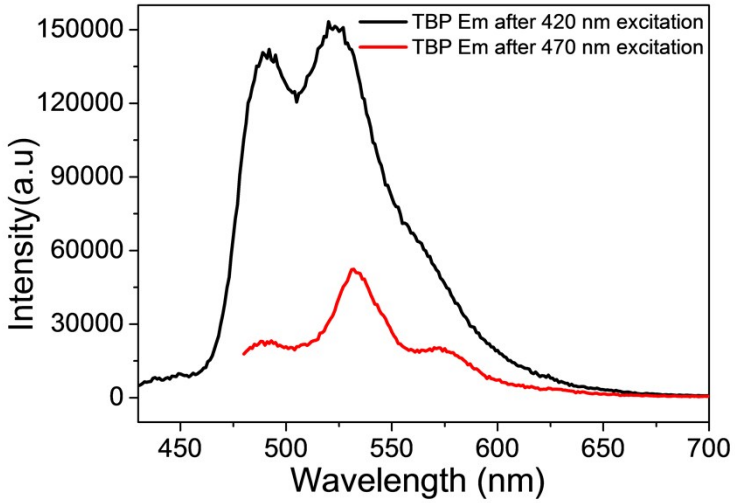


Fig. S3 Emission spectra for TDP in Tol dilute solution with excitation wavelength of 420 nm (black line) and 470 nm (red line), respectively.

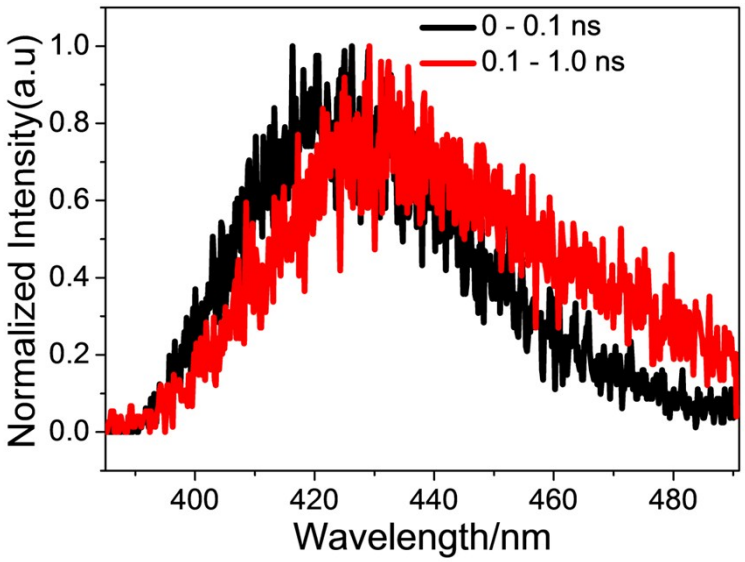


Fig. S4 Time-resolved fluorescence spectra for DBP at room-temperature integrated over 0 – 0.1 ns and 0.1 – 1.0 ns, respectively.

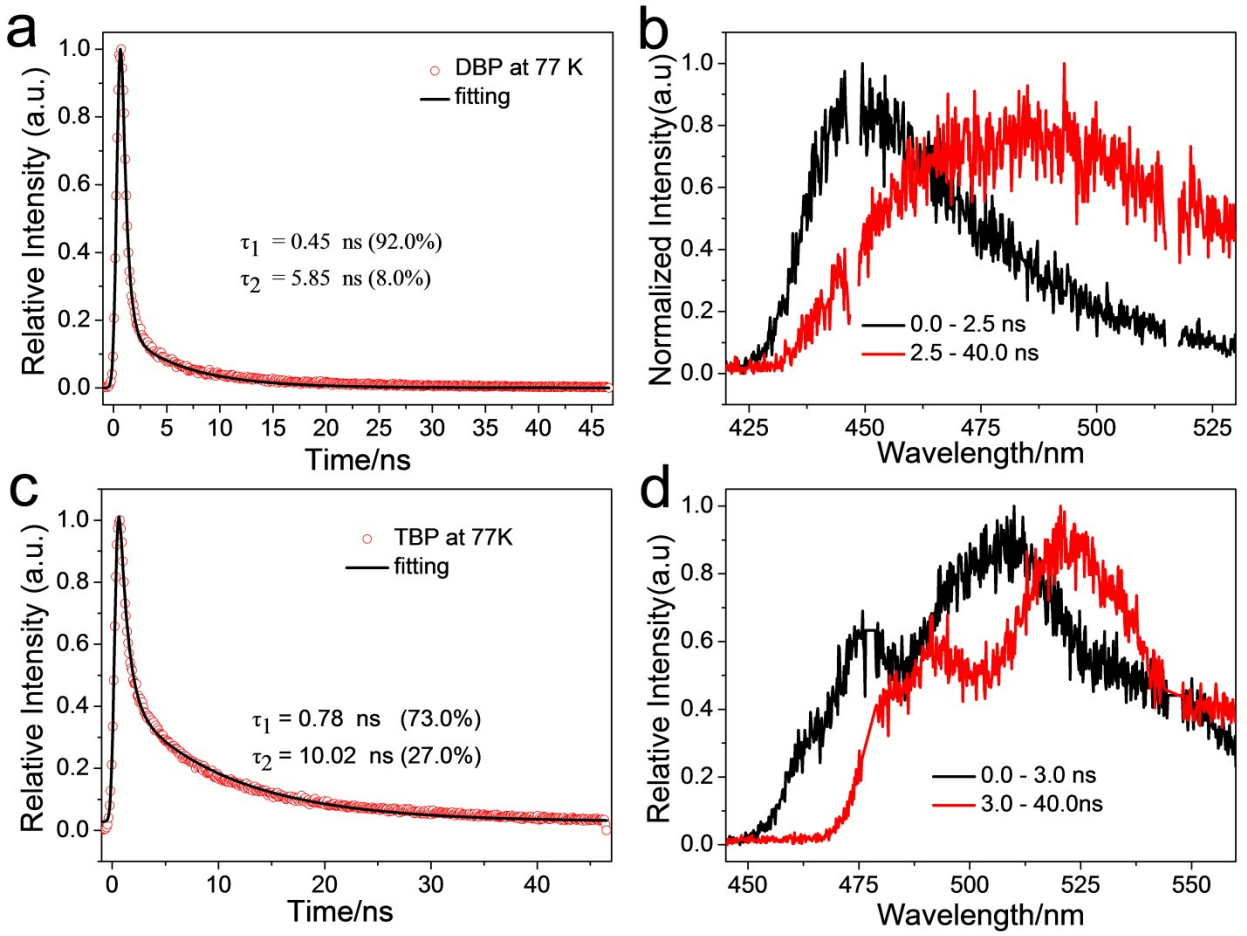


Fig. S5 Time-resolved fluorescence spectra decay transient of (a) DBT and (c) TBT in Tol dilute solution at 77 K with excitation wavelength of 400nm. (b) (d) represent the time-resolved fluorescence spectra for DBP and TBP at 77 K, respectively.

Nanosecond flash photolysis. The nanosecond flash photolysis system is based on the same mechanism as the femtosecond ultrafast transient absorption system. The THF output (355 nm) of the Nd:YAG laser (Continuum Surelite II, 7 ns fwhm) was used for pump pulse and the white light provided by a xenon arc lamp was used for the probe pulse. Samples in Tol solution (in a 1.0 cm quartz cell) were placed at the crossing point of the pump pulse and the probe pulse. The signals were detected by the Edinburgh LP920 and recorded on the Tektronix TDS 3012B oscilloscope and computer.

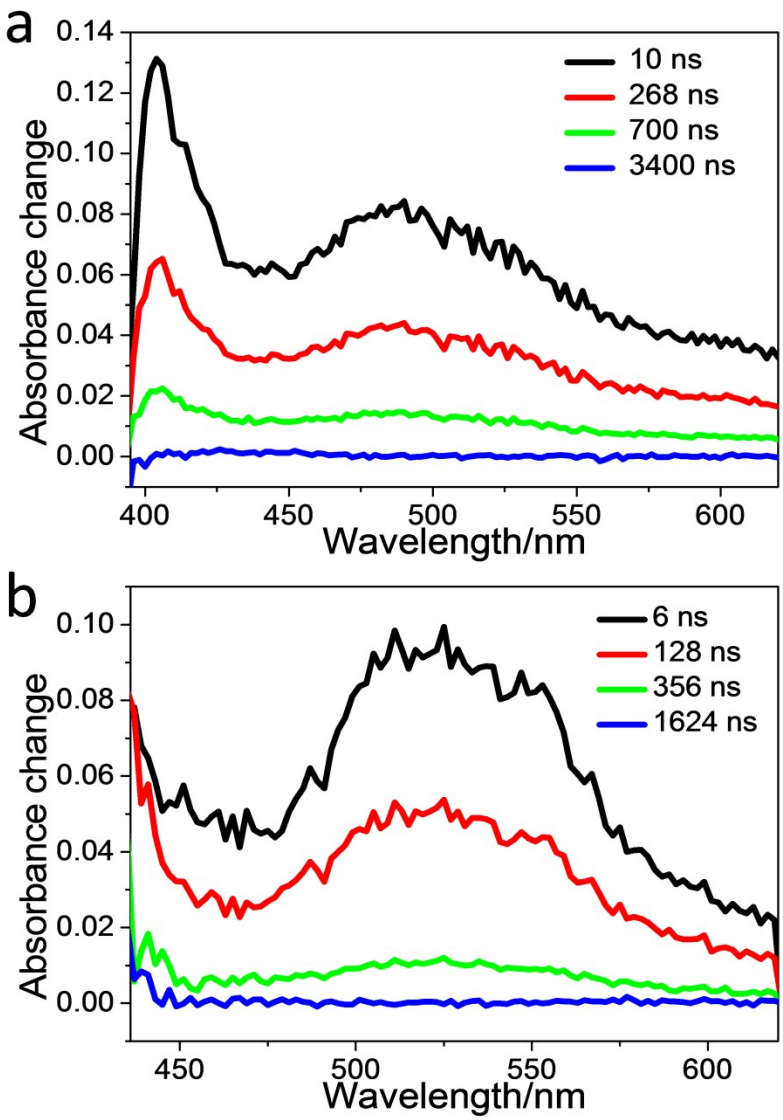


Fig. S6 (a) The nanosecond transient absorption spectra of DBP and (b) TBP in N_2-saturated Tol solutions using flash photolysis method upon excitation with 355 nm laser pulse at room temperature.

3. Computational data

Table S1 The calculated energy levels and the corresponding symmetry for the excited singlet and triplet states of DBP at b3lyp/6-311^{++}g** level.

Excited State	Singlet State			Triplet State		$\Delta E(T_n\text{-}S_1)$
	energy/ ev	symmetry	*f*		symmetry	
1	3.1878	B2	0.0182	2.2811	B1	
2	3.2565	B1	0.0012	2.4375	A1	
3	3.4060	A1	0.2410	2.6132	B1	
4	3.6199	B2	0.0012	2.7349	B2	
5	4.1930	A1	0.1578	3.1104	B2	-0.0774
6				3.4555	B2	0.2677
7				3.5883	A1	0.4005

Table S2 The calculated energy levels and the corresponding symmetry for the excited singlet and triplet states of TBP at b3lyp/6-311^{++}g** level.

Excited State	Singlet State			Triplet State		$\Delta E(T_n\text{-}S_1)$
	energy/ ev	symmetry	*f*	energy/ ev	symmetry	
1	2.5406	B2	0.0152	1.4818	B2	
2	3.0147	B1	0.0009	2.1894	A1	
3	3.0745	B2	0.0076	2.3276	B1	
4	3.1387	A1	0.2877	2.3383	B2	-0.2023
5	3.7998	B2	0.0041	2.6581	B2	0.1175
6	3.9451	A1	0.7955	3.0054	B2	0.4648
7				3.0882	A1	0.5476
8				3.1396	B2	0.5990
9				3.2898	B2	0.7492
10				3.3761	A1	0.8355
11				3.4879	B2	0.9473
12				3.5404	A2	0.9998
13				3.6887	A1	1.1481
14				3.8911	A1	1.3505
15				3.8976	B2	1.3570
16				3.9572	B2	1.4166