Supplementary Information

Modulating the triplet chromophore environment to prolong the emission lifetime of ultralong organic phosphorescence

Guohui Yang+, Anqi Lv+, Zixuan Xu, Zhicheng Song, Kang Shen, Chongyang Lin, Guowei Niu, Huili Ma, Huifang Shi,*Zhongfu An*

G. Yang, A. Lv, Z. Xu, Z. Song, K. Shen, C. Lin, G. Niu, H. Ma, Z. An, H. Shi. Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing
E-mail: iamhfshi@njtech.edu.cn; iamzfan@njtech.edu.cn
[+] These authors are the co-first authors of this work

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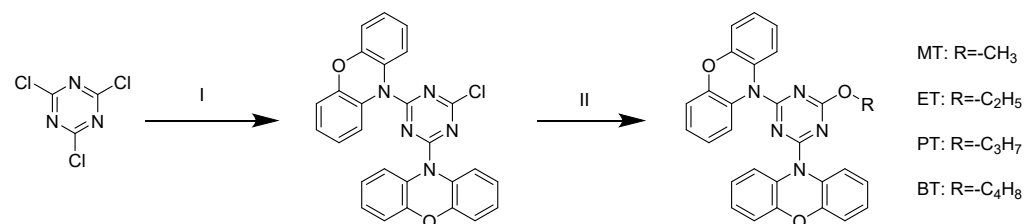**II. Additional photophysical properties of the materials in solution and crystal states**

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I. Experimental section

General procedures for synthesis of organic phosphorescence materials.

Scheme S1. Synthetic routes of target molecules MT, ET, PT, and BT. (I) 2.1 equiv. *n*-BuLi, phenoxazine, 35 °C, 12 h; (II) 1.1 equiv. Na, alkyl-alcohols, room temperature, 30 min.

Molecule Synthesis.

10,10'-（6-chloro-1, 3, 5-triazine-2, 4-diyl）bis(10H-phenoxazine) (TDX).

The target molecule is synthesized through a two-step reaction. Into a 500 mL round-bottom flask, tetrahydrofuran (THF) solution (100 mL) with 10H-phenoxazine (1.9 g, 10.8 mmol) was placed, and 1.6 Mn-butyllithium/hexane solution (7.1 mL) was slowly added to the stirred solution at 0 °C. Then the mixture was stirred at room temperature for 60 min. Then, the solution was slowly added to 2,4,6-trichloro-1,3,5-triazine (1.0 g; 5.4 mmol) at 35 °C for 4 h, the reaction mixture was extracted with CH_2Cl_2 for three times. Then the organic layer was collected and dried with Na_2SO_4. The solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography with PE/DCM (1: 6), affording a white solid was obtained (2.58 g, 50 %).

10, 10'-（6-methoxy-1, 3, 5-triazine-2, 4-diyl）bis(10H-phenoxazine) (MT).

Sodium (0.023 g, 1.0 mmol) was dissolved in 1 mL methanol to form sodium methylate, which was slowly added to a stirred solution of TDX (0.3 g, 0.67 mmol) in 10 mL THF. After the solution was stirred for 60 min at room temperature, the solvent was removed by rotary evaporation and the crude product was collected and extracted with CH_2Cl_2 for three times. The solvent was removed by rotary evaporation to give MT (0.2 g, 70.0 %) as a white solid. ^{1}H NMR (Chloroform-d) δ 7.65 (d, *J* = 8.2, 1.1 Hz, 4H), 7.15 (ddd, *J* = 7.6, 6.8, 1.4 Hz, 4H), 7.11 – 6.99 (m, 8H), 3.85 (d, *J* = 0.6 Hz, 3H). ^{13}C NMR (Chloroform-d) *δ* 170.91, 165.52, 151.39, 129.31, 127.36, 126.20, 122.89, 116.59, 54.65. Elemental analysis: Calcd for $C_{28}H_{19}N_5O_3$, C,71.03; H.4.04; N,14.79; O,10.04. Found: C,70.92; H.3.712; N,14.87.

10, 10'-（6-ethoxy-1, 3, 5-triazine-2, 4-diyl）bis(10H-phenoxazine) (ET).

Sodium (0.023 g, 1.0 mmol) was dissolved in 1 mL ethanol to form sodium ethoxide, which was slowly added to a stirred solution of TDX (0.3 g, 0.67 mmol) in 10 mL THF. After the solution was stirred for 60 min at room temperature, the solvent was removed by rotary evaporation and the crude product was collected and extracted with CH_2Cl_2 for three times. The solvent was removed by rotary evaporation to give ET (0.22 g, 67.4 %) as a white solid. ^{1}H NMR (Chloroform-d) δ 7.65 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.15 (ddd, *J* = 8.2, 7.2, 1.6 Hz, 4H), 7.11 – 7.00 (m, 8H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (Chloroform-d) δ 165.54, 151.41, 129.38, 127.37, 126.15, 122.88, 116.57, 63.54, 14.34. Elemental analysis: Calcd for $C_{29}H_{21}N_5O_3$, C,71.45; H.4.34; N,14.37; O,9.85. Found: C,71.28; H.4.09; N,14.42.

10, 10'-（6-propoxy-1, 3, 5-triazine-2, 4-diyl）bis(10H-phenoxazine)(PT).

Sodium (0.023 g, 1.0 mmol) was dissolved in 1 mL propanol to form sodium propoxide, which was slowly added to a stirred solution of TDX (0.3 g, 0.67 mmol) in 10 mL THF. After the solution was stirred for 60 min at room temperature, the solvent was removed by rotary evaporation and the crude product was collected and extracted with CH_2Cl_2 for three times. The solvent was removed by rotary evaporation to give PT (0.22 g, 65.5 %) as a white. ^{1}H

NMR (400 MHz, Chloroform-d) δ 7.65 (dd, J = 8.1, 1.5 Hz, 4H), 7.15 (ddd, J = 8.4, 7.1, 1.5 Hz, 4H), 7.11 – 6.97 (m, 8H), 4.18 (t, J = 7.1 Hz, 2H), 1.72 (q, J = 7.3 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 170.63, 165.53, 151.40, 129.40, 127.39, 126.13, 122.88, 116.57, 69.20, 22.02, 10.26. Elemental analysis: Calcd for $C_{30}H_{23}N_5O_3$, C,71.84; H.4.62; N,13.96; O,9.57. Found: C,71.63; H.4.844; N,13.93.

10, 10'-（6-butoxy-1, 3, 5-triazine-2, 4-diyl）bis(10H-phenoxazine)(BT).

Sodium (0.023 g, 1.0 mmol) was dissolved in 1 mL butanol to form sodium butoxide, which was slowly added to a stirred solution of TDX (0.3 g, 0.67 mmol) in 10 mL THF. After the solution was stirred for 60 min at room temperature, the solvent was removed by rotary evaporation and the crude product was collected and extracted with CH_2Cl_2 for three times. The solvent was removed by rotary evaporation to give BT (0.26 g, 75.2 %) as a white solid.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (dd, J = 8.1, 1.5 Hz, 4H), 7.15 (td, J = 7.7, 7.2, 1.4 Hz, 4H), 7.11 – 7.00 (m, 8H), 4.23 (t, J = 7.0 Hz, 2H), 1.68 (p, J = 7.2 Hz, 2H), 1.44 – 1.32 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.63, 165.54, 151.41, 129.41, 127.38, 126.13, 122.88, 116.57, 67.53, 30.73, 19.07, 13.82. Calcd for $C_{31}H_{25}N_5O_3$, C,72.22; H.4.89; N,13.58; O,9.31. Found: C,71.91; H.4.945; N,13.45.
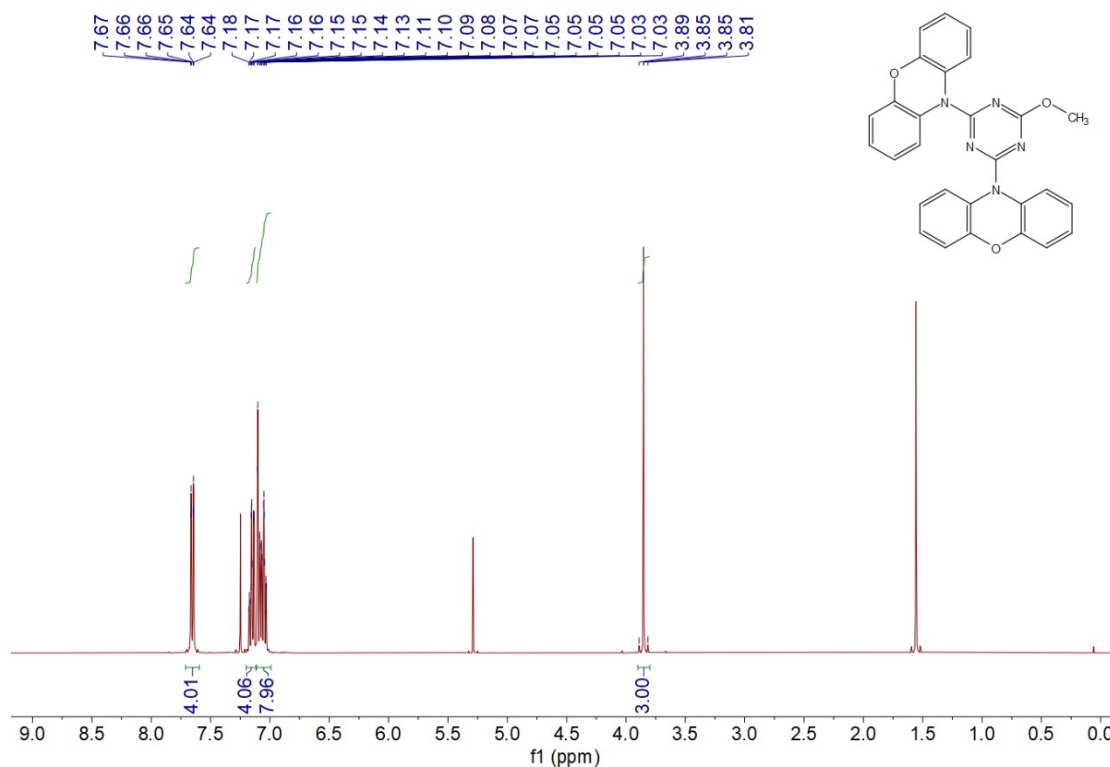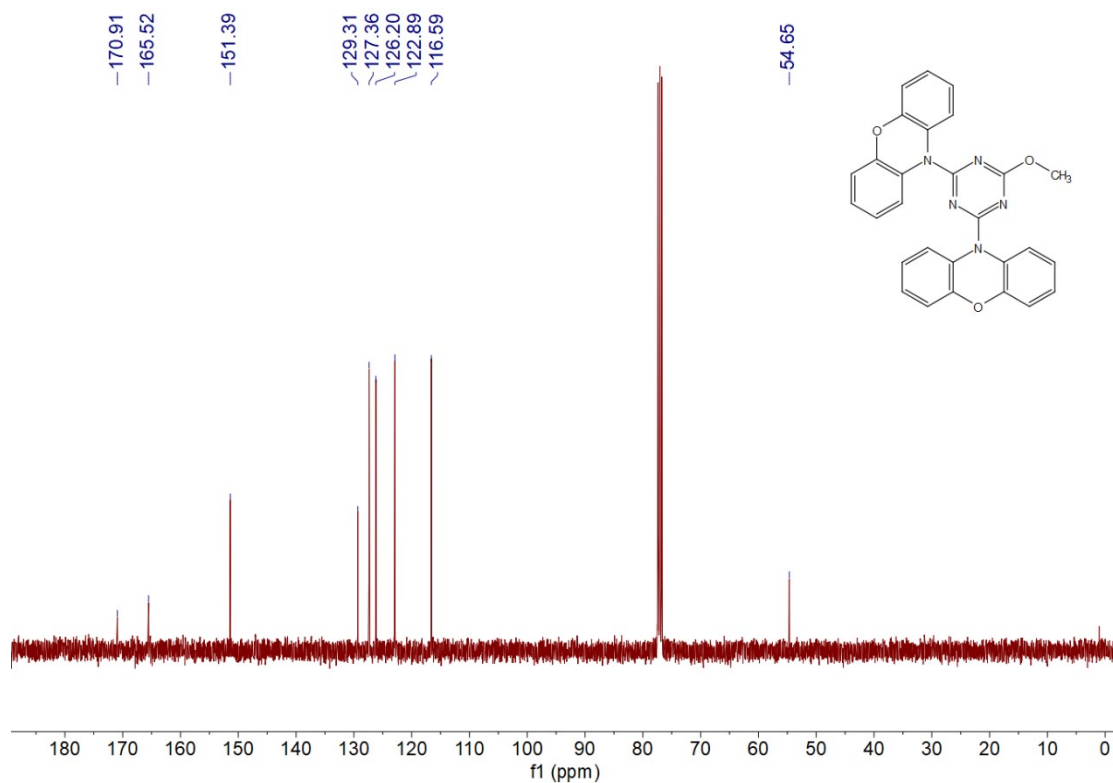

Figure S1. ^{1}H NMR spectrum of MT in CDCl$_3$.

Figure S2. ^{13}C NMR spectrum of MT in CDCl$_3$.
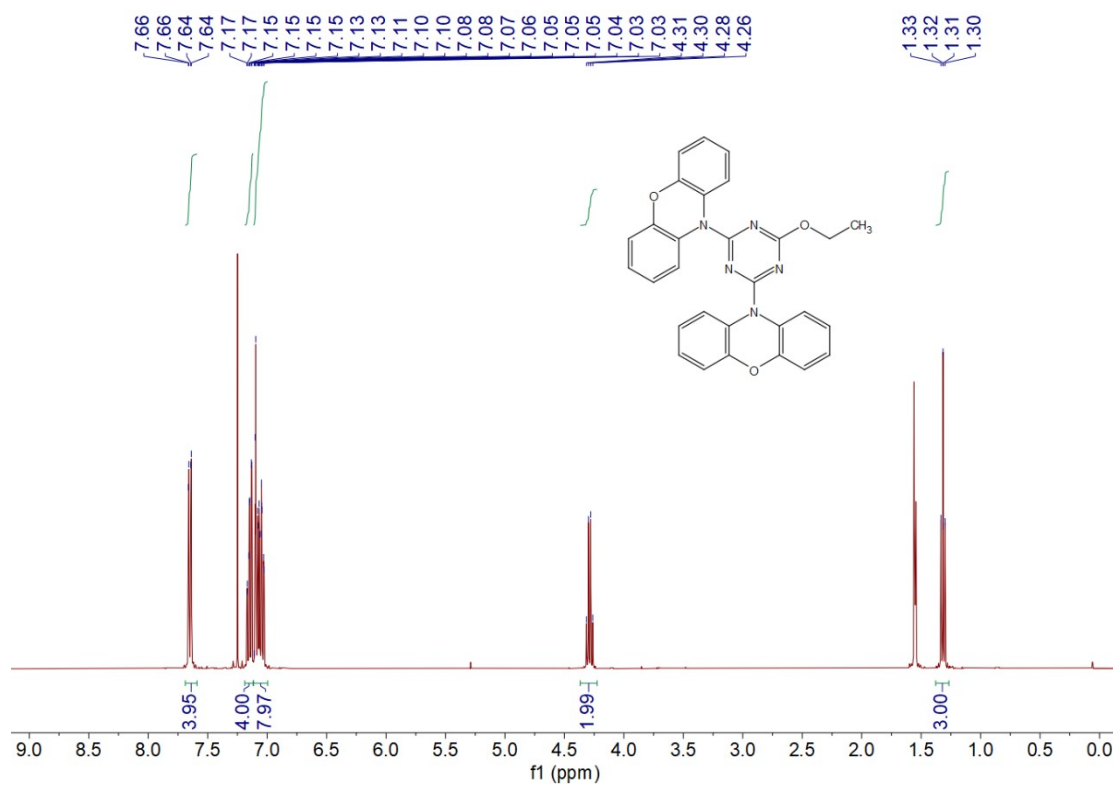
Figure S3. ^{1}H NMR spectrum of ET in CDCl$_3$.
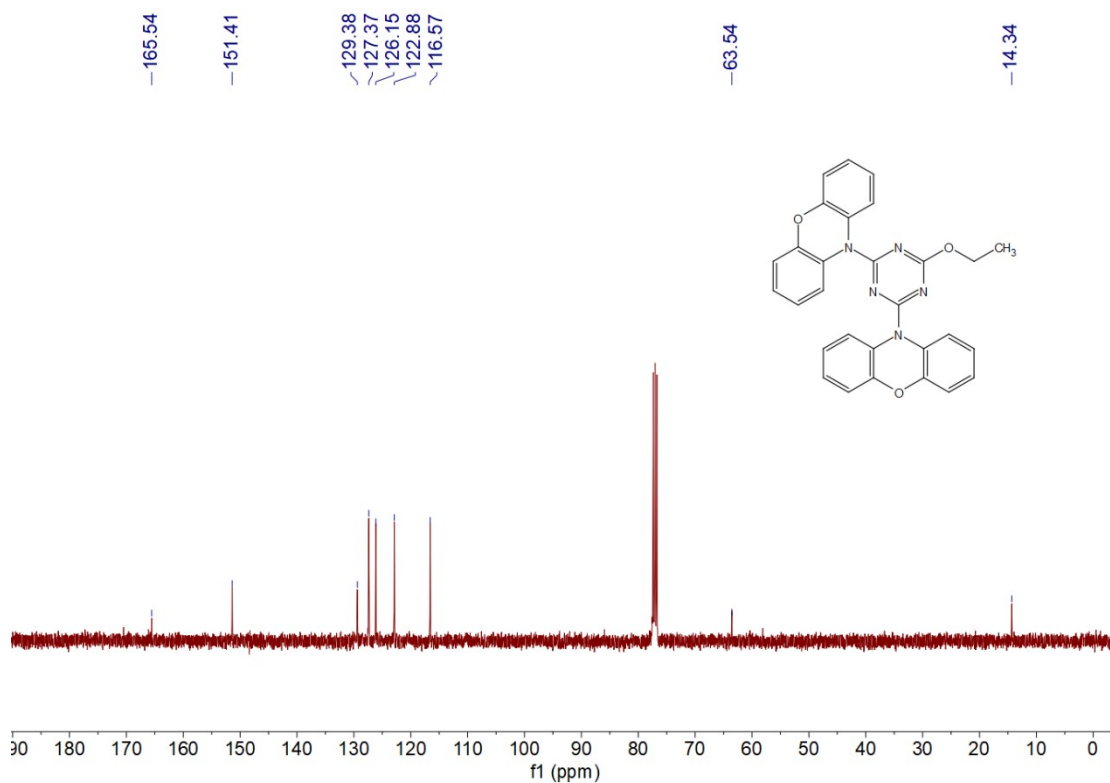
Figure S4. ^{13}C NMR spectrum of ET in CDCl$_3$.
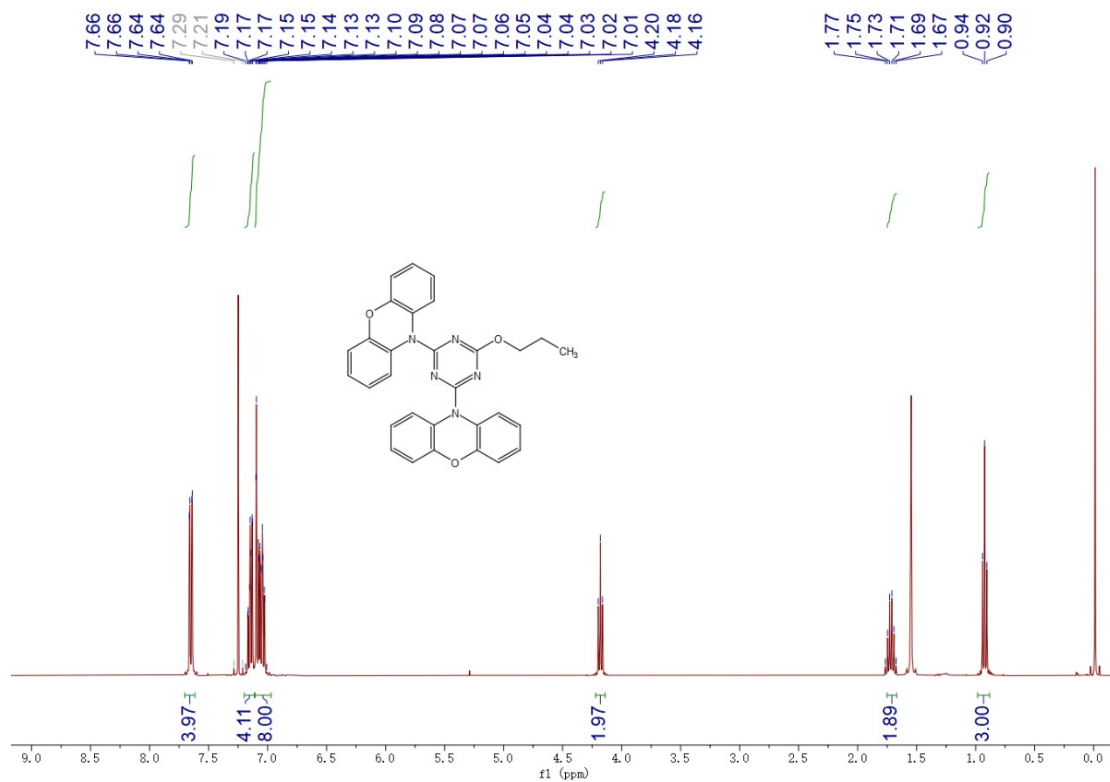
Figure S5. ^{1}H NMR spectrum of PT in CDCl$_3$.
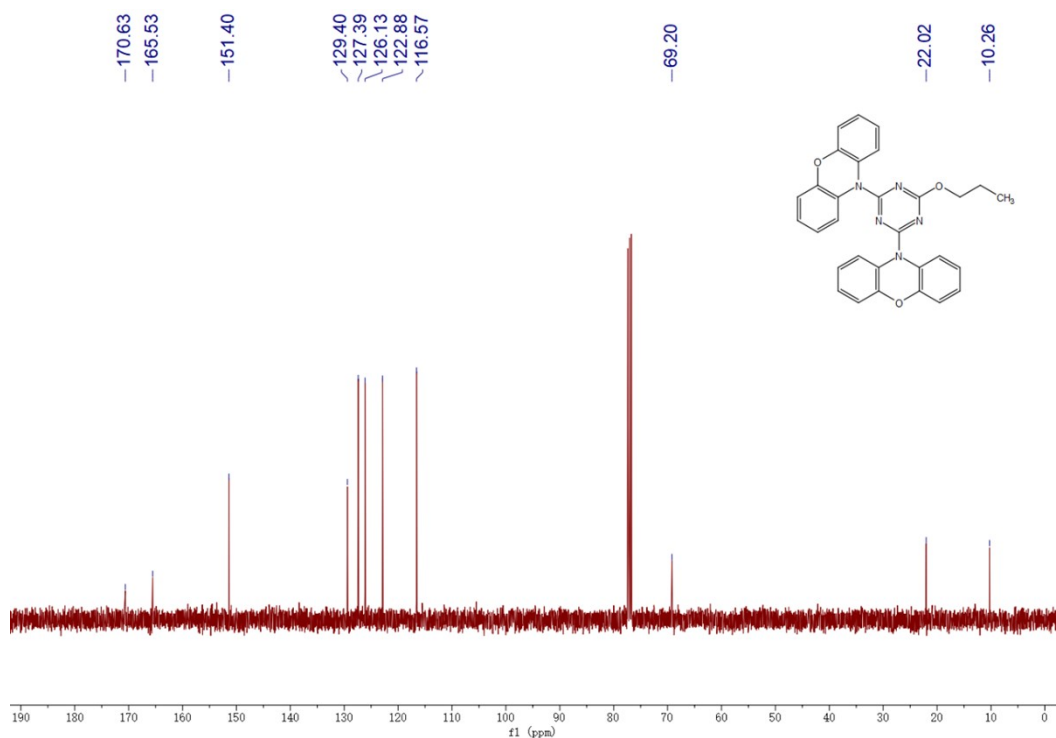
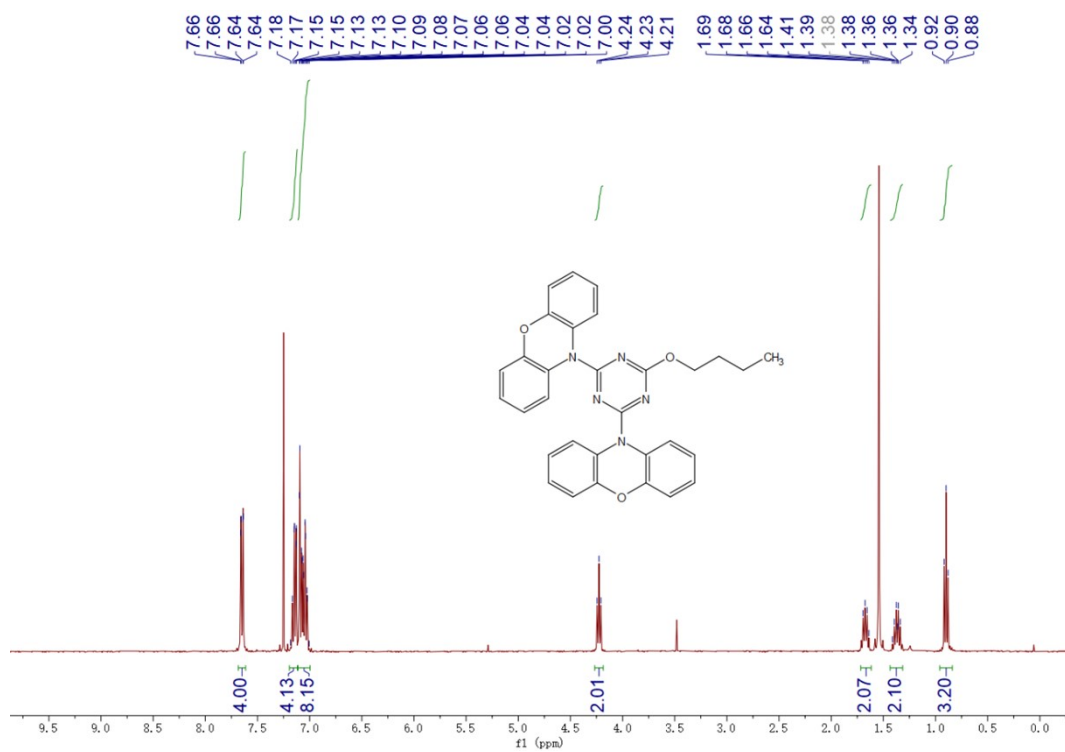**Figure S6**. ^{13}C NMR spectrum of PT in CDCl$_3$.

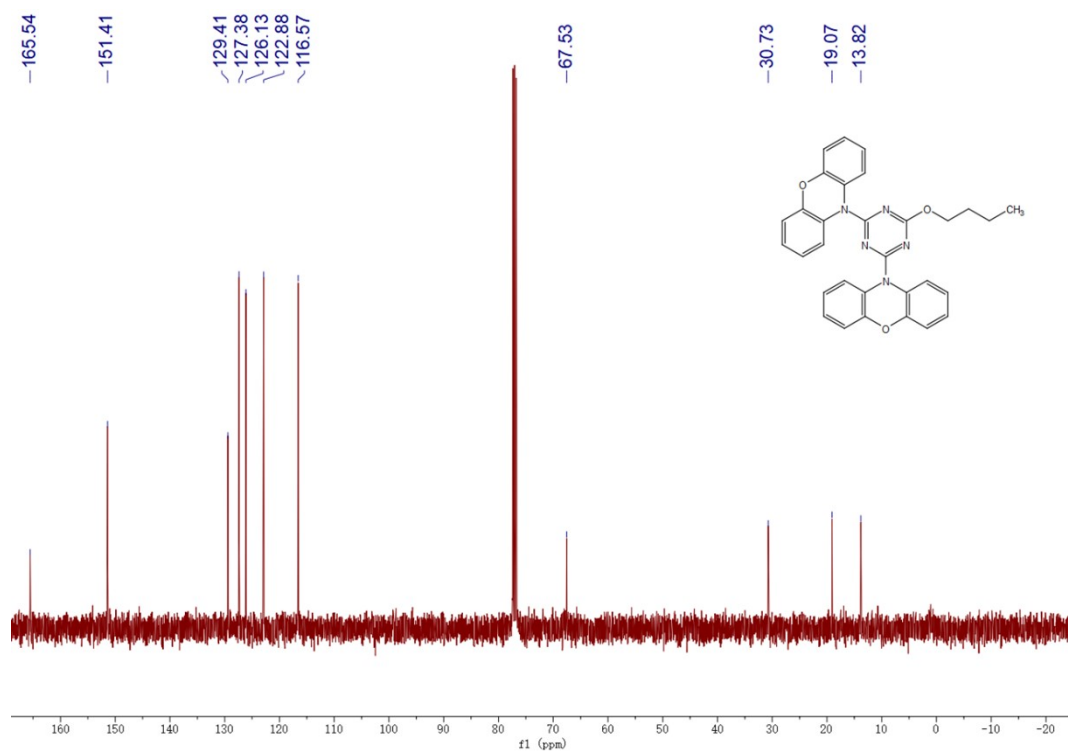

Figure S7. ^{1}H NMR spectrum of BT in CDCl$_3$.

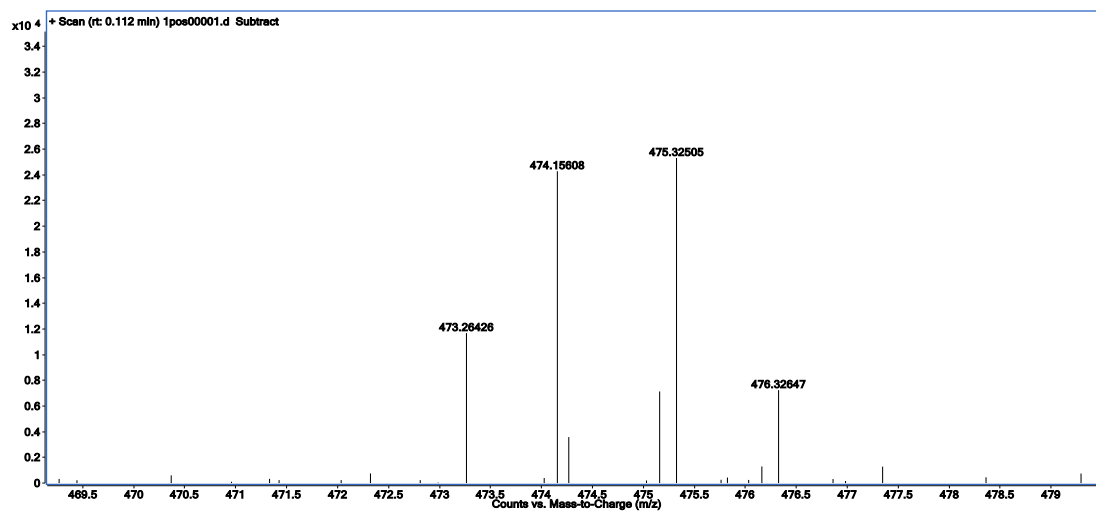**Figure S8.** ^{13}C NMR spectrum of BT in CDCl$_3$.
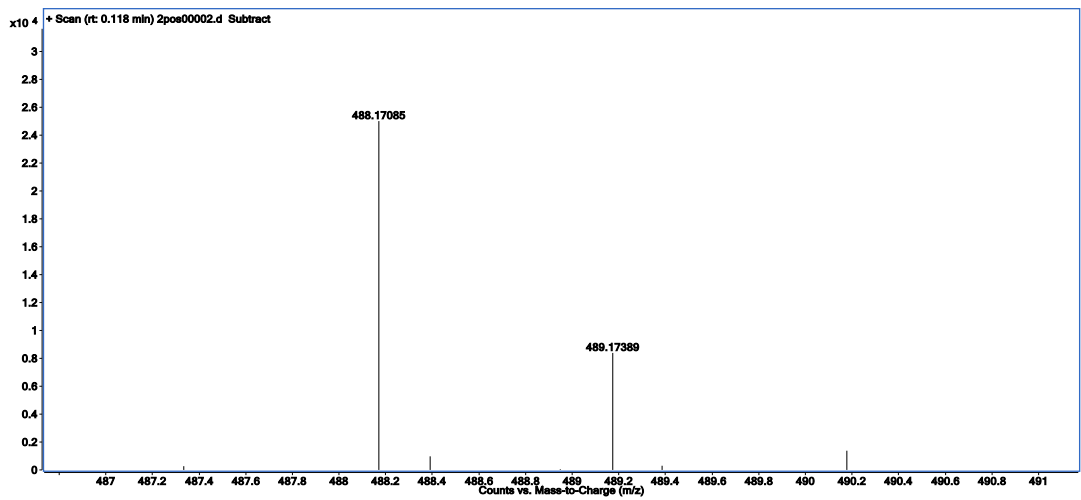

Figure S9. HRMS of MT.
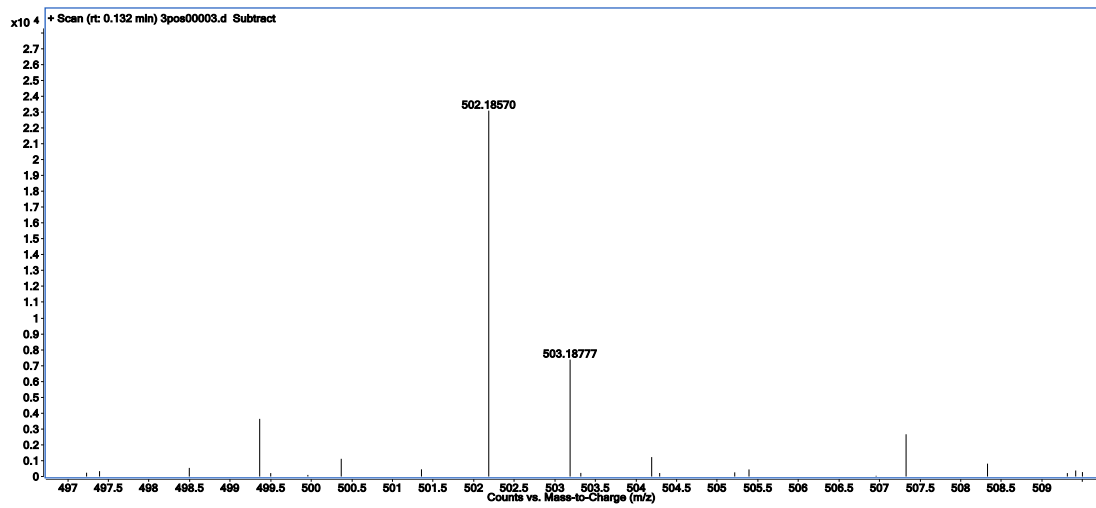
Figure S10. HRMS of ET.
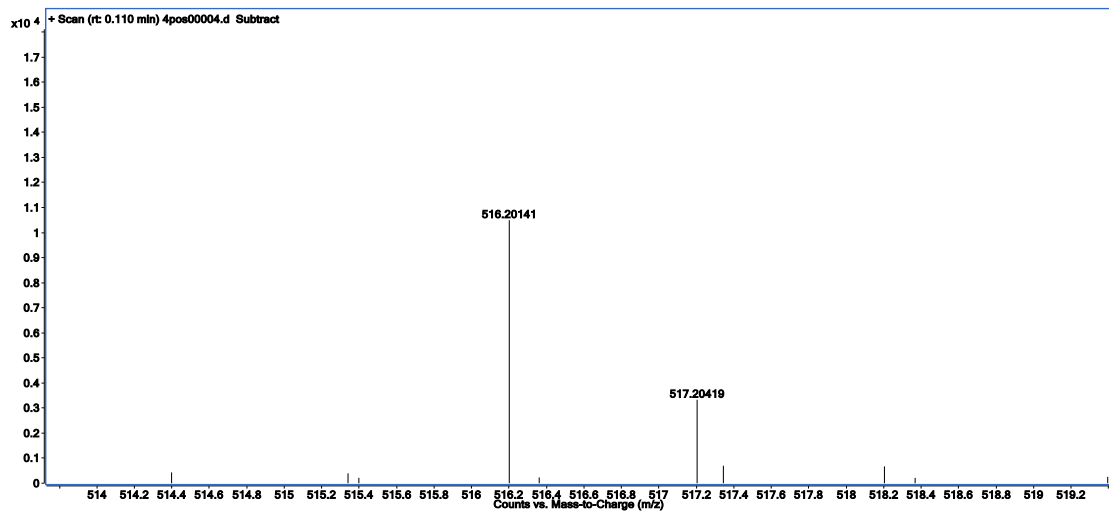

Figure S11. HRMS of PT.

Figure S12. HRMS of BT.

Ⅱ. Additional photophysical properties of the materials in solution and crystal states

Table S1. Photoluminescence (PL) and phosphorescence efficiency of four compounds in crystal under ambient conditions

Compounds	φ_{PL} (%)	$\varphi_{Phos}/\varphi_{PL}$(%)	φ_{Phos} (%)
MT	46.1	4.4	2.0
ET	21.7	77.6	16.8
PT	22.6	57.8	13.1
BT	13.6	74.4	10.1

The PL quantum efficiency is measured by a Hamamatsu C11347 absolute PL quantum yield spectrometer with an integrating sphere under ambient conditions. The PL quantum efficiency is measured by a Hamamatsu C11347 absolute PL quantum yield spectrometer with an integrating sphere under ambient conditions. The phosphorescence quantum yields of the compounds were obtained from the following equation:

$$\phi_{phos} = \frac{B}{A} \times \phi_{PL}$$

where A and B represent the integral areas of total photoluminescence and phosphorescence spectra, respectively. The phosphorescence was separated from the total PL spectrum on the basis of the phosphorescence spectrum.
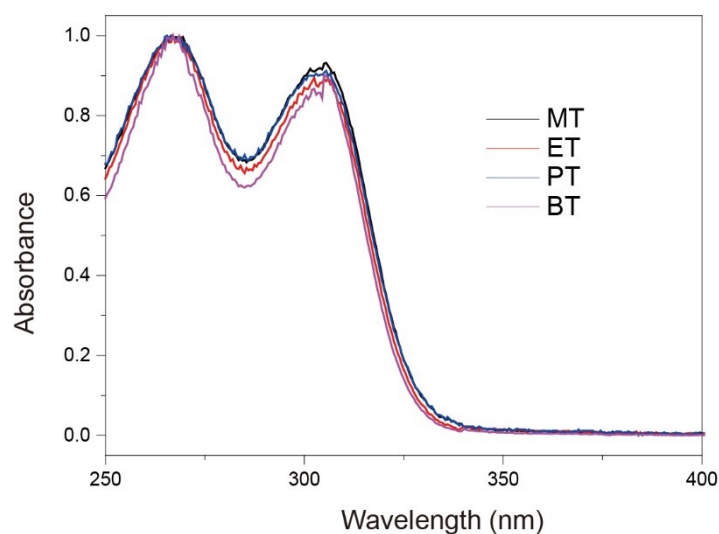
Figure S13. Normalized UV absorption spectra of MT, ET, PT and BT in dichloromethane (1.0×10⁻⁵ M) under ambient conditions.
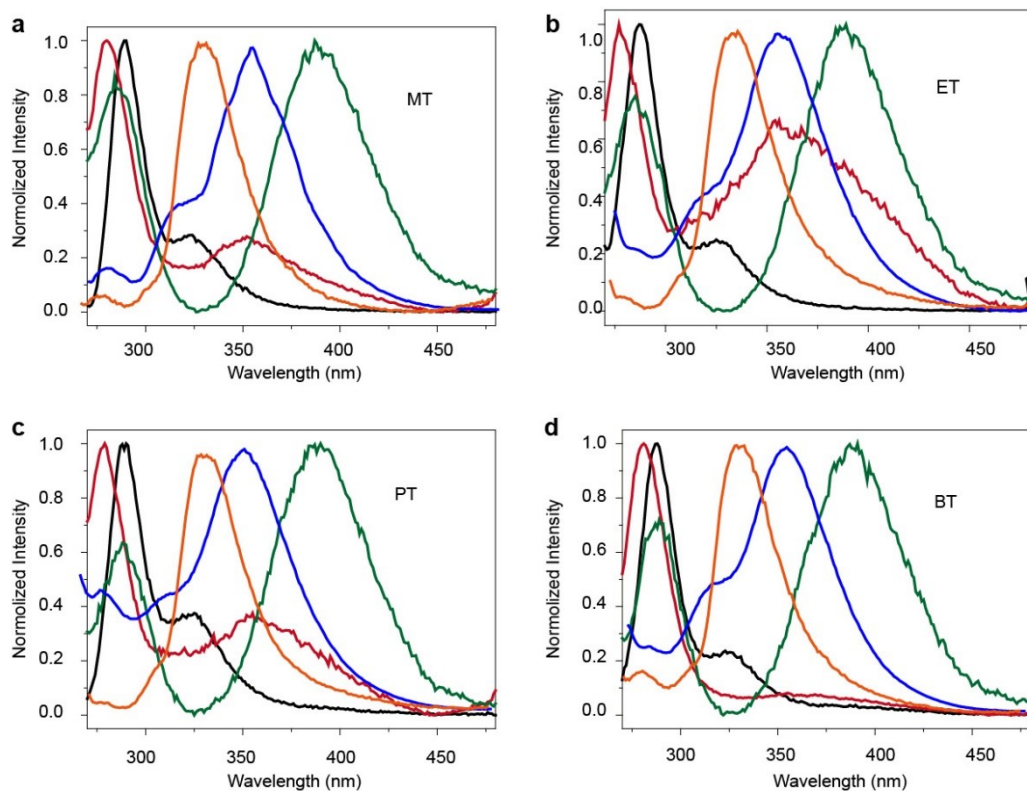
Figure S14. Normalized steady-state PL spectra of (a) MT, (b) ET, (c) PT and (d) BT in different solvents (1.0×10^{-5} M). black line-toluene, orange line-dichloromethane, red line-trichloromethane, blue line-tetrahydrofuran, green line-N, N-dimethylformamide.
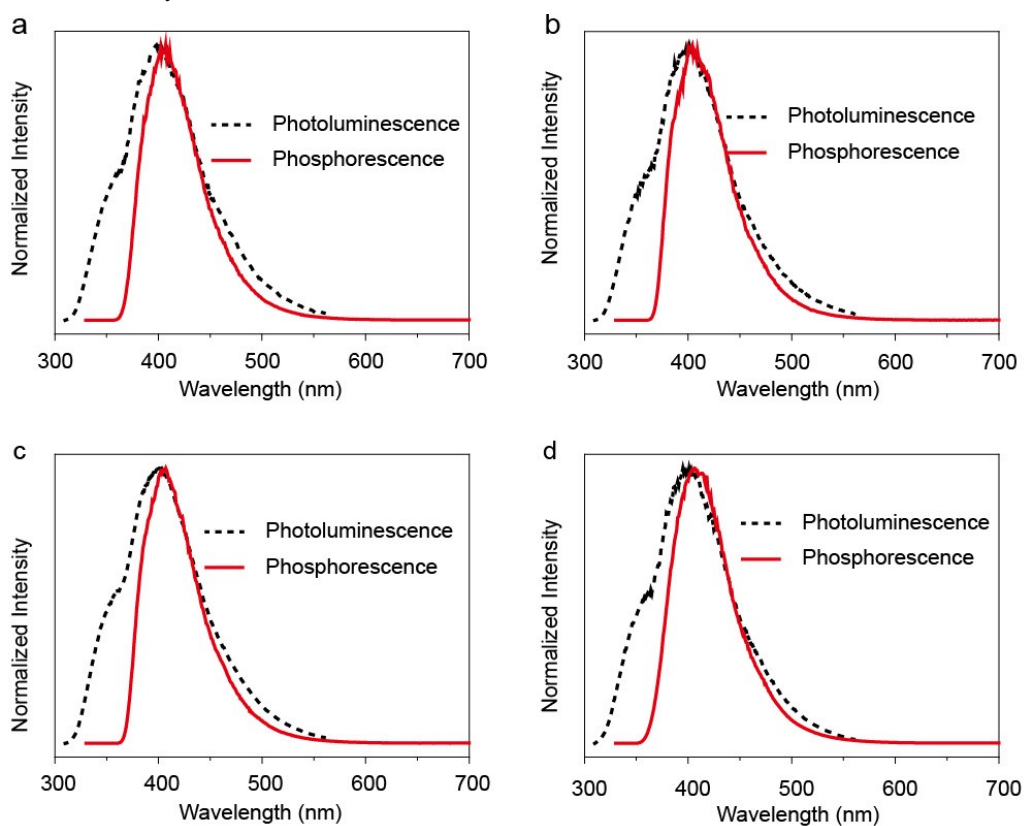
Figure S15. Steady-state PL and phosphorescence spectra of (a) MT, (b) ET, (c) PT and (d) BT in 2-methyltetrahydrofuran (1.0×10^{-5} M) at 77 K.
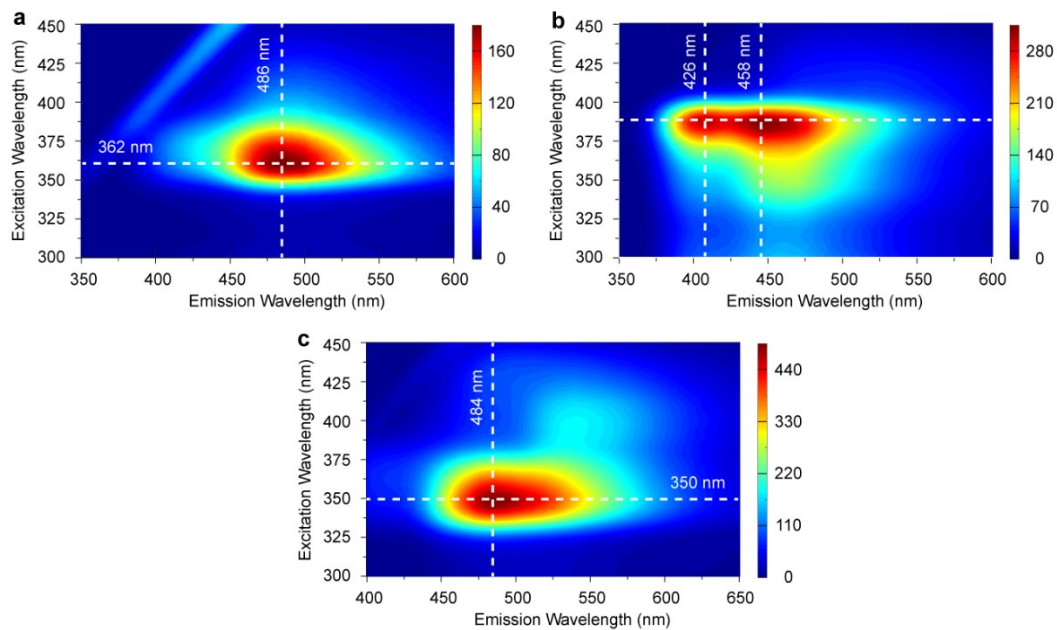
Figure S16. Excitation-phosphorescence mapping of (a) ET, (b) PT and (c) BT crystals under ambient conditions.
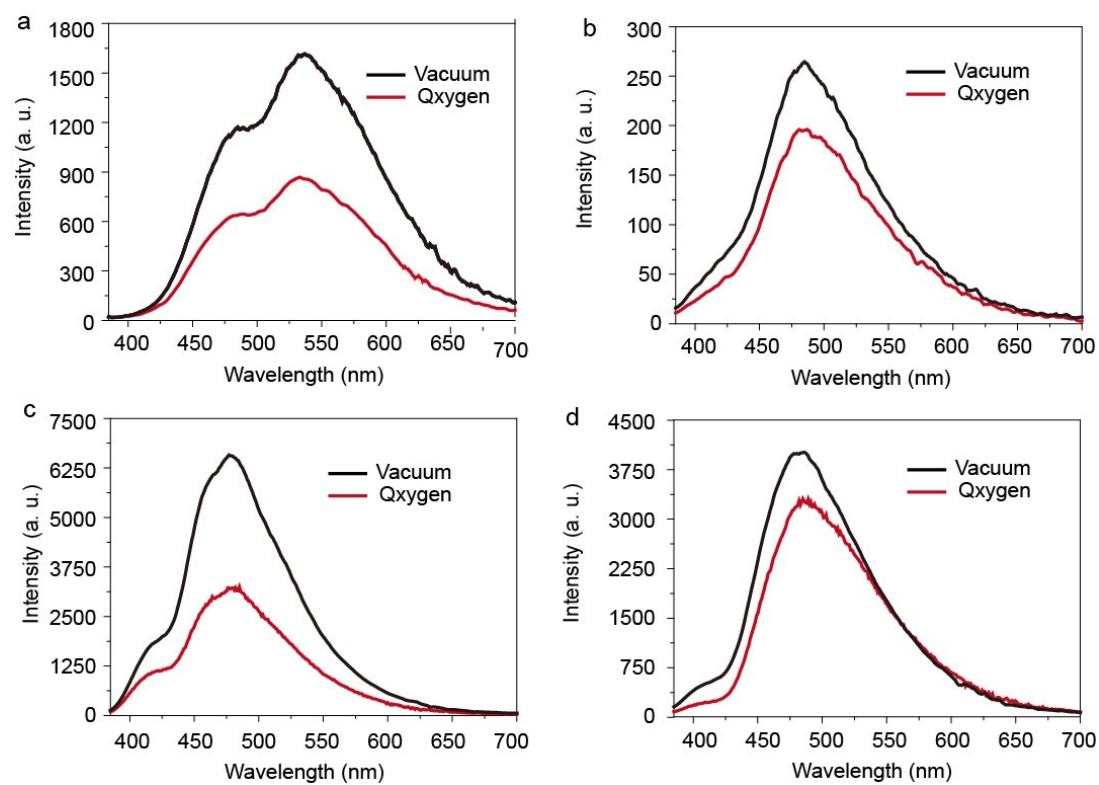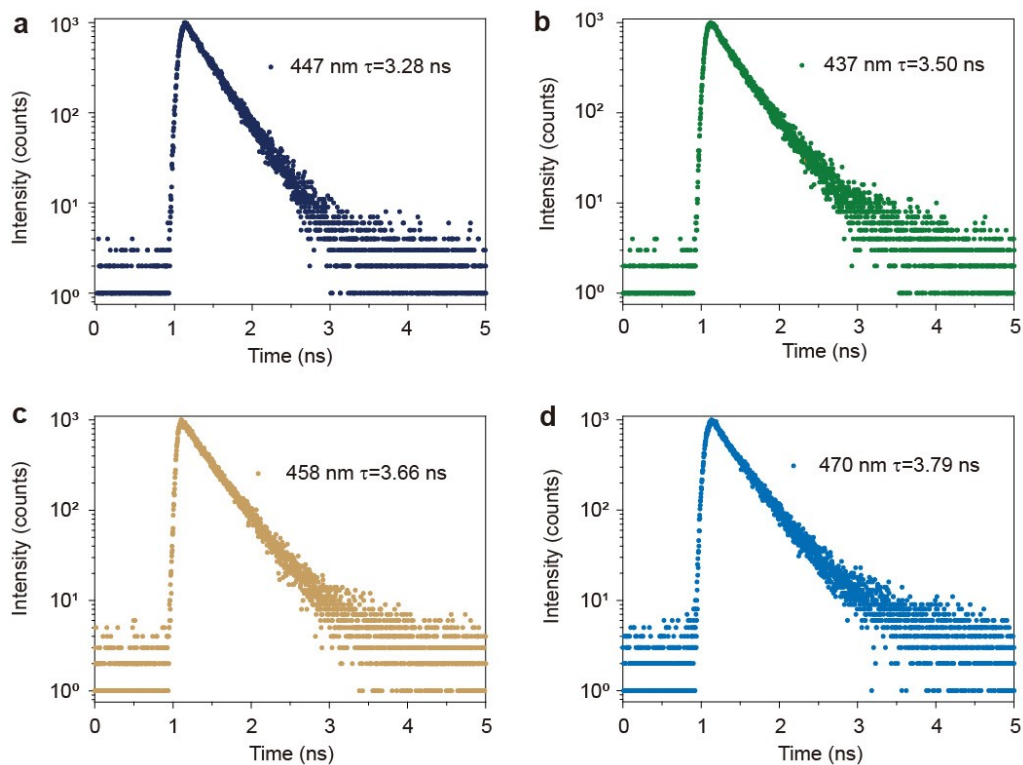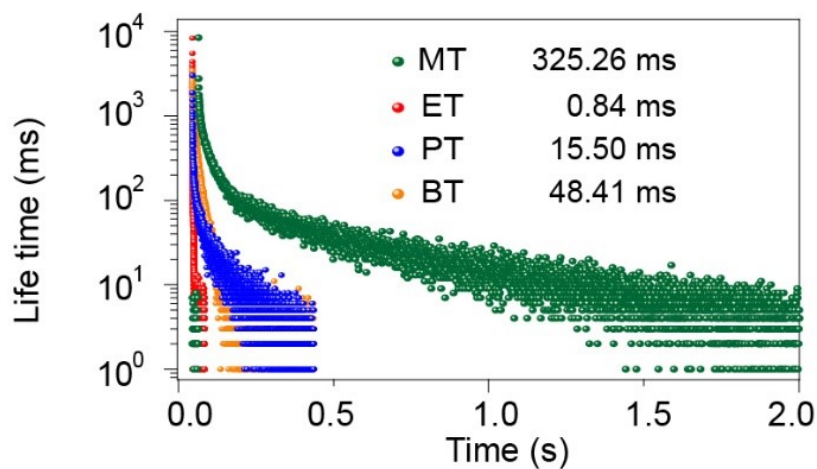

Figure S17. Phosphorescence spectra of (a) MT (b) ET (c) PT and (d) BT crystals excited by 350 nm in vacuum and oxygen, respectively.

Figure S18. Lifetime decay profiles of the fluorescence of (a) MT (b) ET (c) PT and (d) BT crystals under ambient conditions.

Table S2. Lifetimes of crystalline MT\ET\PT and BT at different emission wavelengths under ambient conditions

Compound	Wavelength	Fluorescence					Phosphorescence						
		τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ (ns)	τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ (ms)
MOTX	447	3.28	100			3.28							
	540						5.32	10.2	47.327	15.37	426.5	74.43	325.26
EOTX	437	3.5	100			3.5							
	482						0.25	20.19	0.99	79.81			0.84
POTX	458	3.66	100			3.66	2.69	14	10.7	49.86	27.081	36.14	15.5
BOTX	470	3.79	100			3.79							
	484						4.37	26.27	64.1	73.73			48.41

Figure S19. Lifetime decay profiles of the phosphorescence of (a) MT (b) ET (c) PT and (d) BT crystals under ambient conditions.

$$k_r^{Fluo} = \Phi_{Fluo} / \tau_{Fluo} \qquad (a)$$

$$\Phi_{isc} = 1 - \Phi_{Fluo} - \Phi_{ic} \approx 1 - \Phi_{Fluo} \qquad (b)$$

$$\tau_{Fluo} = \frac{1}{k_r^{Fluo} + k_{nr}^{Fluo} + k_{isc}};$$

$$\Phi_{isc} = \frac{k_{isc}}{k_r^{Fluo} + k_{nr}^{Fluo} + k_{isc}} = k_{isc} \times \tau_{Fluo};$$

$$k_{isc} = \frac{\Phi_{isc}}{\tau_{Fluo}} \qquad (c)$$

$$\tau_{Phos} = \frac{1}{k_r^{Phos} + k_{nr}^{Phos}};$$

$$\Phi_{Phos} = \frac{\Phi_{isc} \times k_r^{Phos}}{k_r^{Phos} + k_{nr}^{Phos}} = \Phi_{isc} \times k_r^{Phos} \times \tau_{Phos};$$

$$k_r^{Phos} = \frac{\Phi_{Phos}}{\Phi_{isc} \times \tau_{Phos}} \qquad (d)$$

$$k_{nr}^{Phos} = \frac{1}{\tau_{Phos}} - k_r^{Phos} \qquad (e)$$

Where, k_r^{Fluo}, k_{isc}, k_r^{Phos}, k_{nr}^{Phos} are the radiative rate constant of prompt fluorescence, rate constant of inter system crossing (ISC), radiative rate constant of phosphorescence and nonradiative rate constant of phosphorescence.

Table S3. Dynamic photophysical parameters of organic phosphorescence.

Comound	$\tau_{F,c}$	$\tau_{P,c}$	$\Phi_{F,c}$	$\Phi_{P,c}$	k_r^{Fluo}	Φ_{isc}	k_{isc}	k_r^{Phos}	k_{nr}^{Phos}
	[ns]	[ms]	[%]	[%]	[s^{-1}][a]	[%][b]	[s^{-1}][c]	[s^{-1}][d]	[s^{-1}][e]
MT	3.28	325.26	46.1	0.02	1.41E+08	53.9	1.64E+08	1.14E-03	3.07E+00
ET	3.5	0.84	21.7	0.17	6.20E+07	78.3	2.24E+08	2.58E+00	1.19E+03
PT	3.66	15.5	22.6	0.13	6.17E+07	77.4	2.11E+08	1.08E-01	6.44E+01
BT	3.79	48.41	13.6	0.10	3.59E+07	86.4	2.28E+08	2.39E-02	2.06E+01

Table S4. Single crystal data.

Compound	MT	ET	PT	BT
Formula	$C_{28}H_{19}N_5O_3$	$C_{29}H_{21}N_5O_3$	$C_{30}H_{23}N_5O_3$	$C_{31}H_{25}N_5O_3$
Volume	2252.7(6)	4845.3(6)		
Space Group	P 2$_1$/c	P b c a	P 2$_1$/c	P -1
Cell Lengths (Å)	a 16.635(2)，	a 12.4579(9)，	a 12.1825(9)，	a 10.425(3)，
	b 10. 2469(15)，	b 19.4130(14)，	b 9.3177(7)，	b 11.248(4)，
	c 13.4933(19)	c 20.0349(14)	c 21.9525(16)	c 11.536(4)
Cell Angles(Å)	a 90，	a 90，	a 90，	a 75.358(9)，
	b 101.646(4)，	b 90，	b 100.055(2)，	b 76.789(8)，
	g 90	g 90	g 90	g 80.503(7)
Cell Volume(Å^3)	2252.68	4845.34	2453.62	1265.87
Z	4	8	4	2
Density (g/cm^2)	1.396	1.326	1.358	1.353

| F(000)	984	2000.0	1048.0	540.0
h_{max}, k_{max}, l_{max},	22,14,18	18,28,28	19,15,36	16,17,17
T_{mix}, T_{max}	0.989,0.991	0.989,0.991	0.989,0.991	0.991,0.991
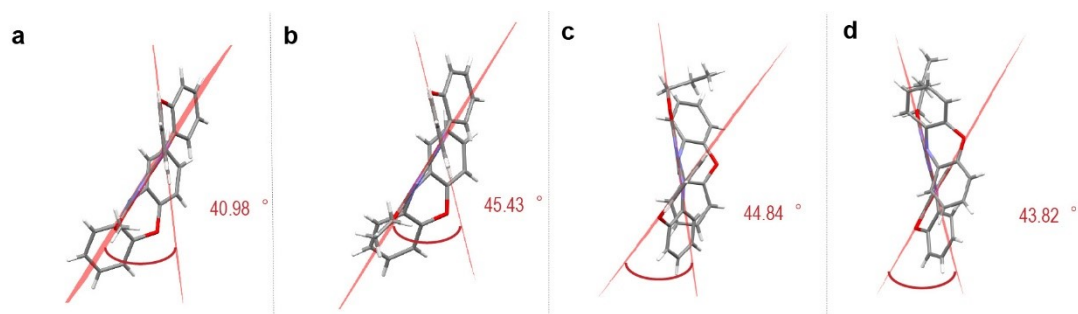
Figure S20. The angle between the (a) MT, (b) ET, (c) PT and (d) BT triazine ring and the benzene ring on one side of the phenoxazine near the alkyl chain.
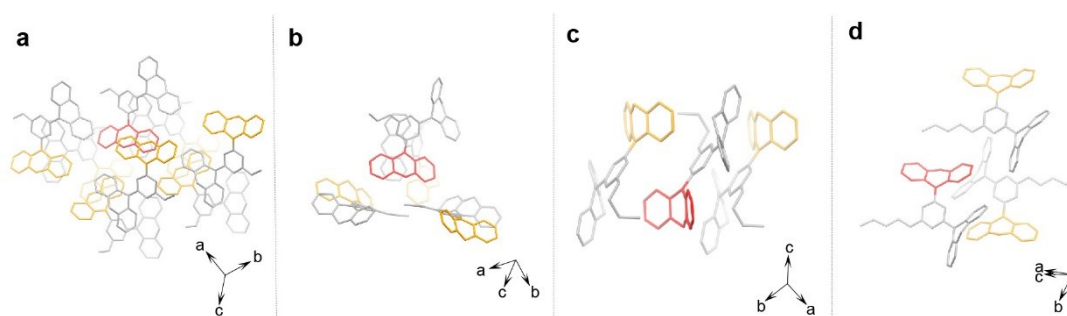

Figure S21. The surrounding environment of a triplet chromophore of (a) MT, (b) ET, (c) PT and (d) BT molecules.

By analyzing the stacking of triplet chromophores in the dimer, we found that the triplet chromophores of the MT dimer were stacked in parallel, with a vertical distance of 3.420 Å and a centroid distance between two parallel benzene rings of 4.524 Å. For ET presents a tilted stacking mode with the shortest distance between the triplet excited chromophores of 4.015 Å, and the farthest is 7.340 Å. It can be seen that the interaction between the triplet excited chromophores in the longer-lived molecular dimer is closer together. (Figure S22a, Figure S22b). Next, we found that the triplet-excited chromophores of the longer-lived MT molecule interacted with C-H···π of 2.857 Å and 2.889 Å, head-to-head connection and the shortest lifetime ET molecules are completely separated by non-triplet chromophores, there is no obvious interaction between them (Figure S22c, Figure S22d).
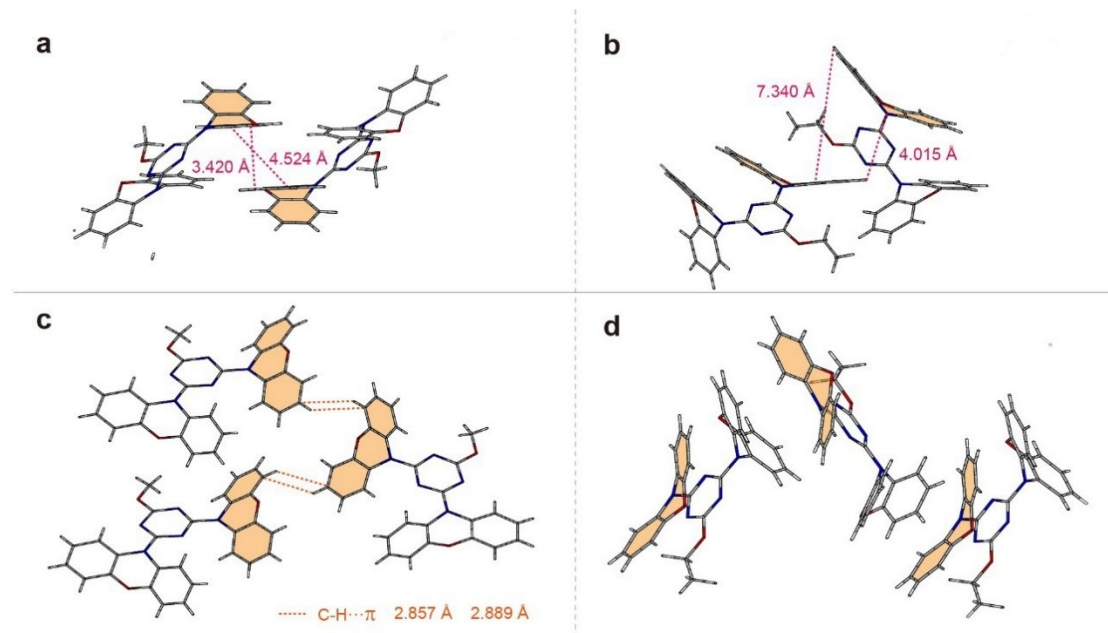
Figure S22. Molecular stacking of dimers and trimers from the single crystal of MT (a) (c) and ET (b) (d).
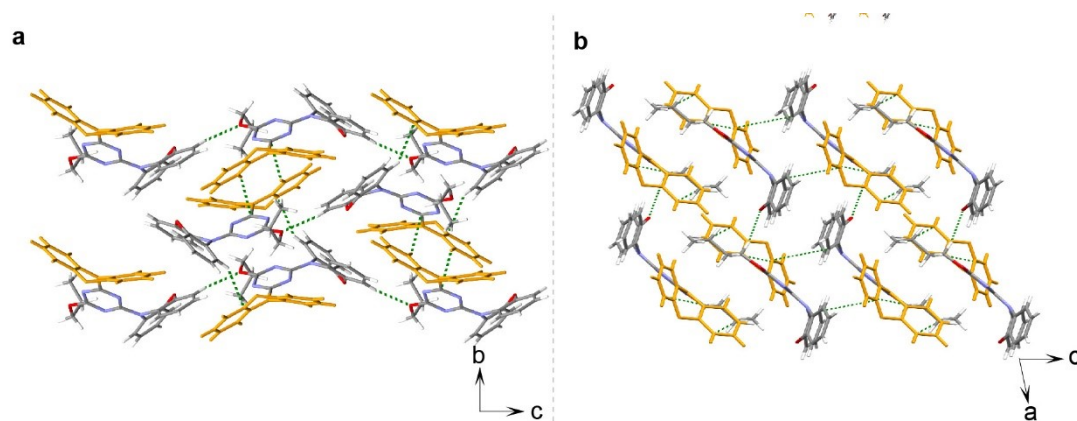
Figure S23. The packing modes of the PT (a) and BT (b) crystals.

Table S4: The forces and types of interaction on MT and ET molecules

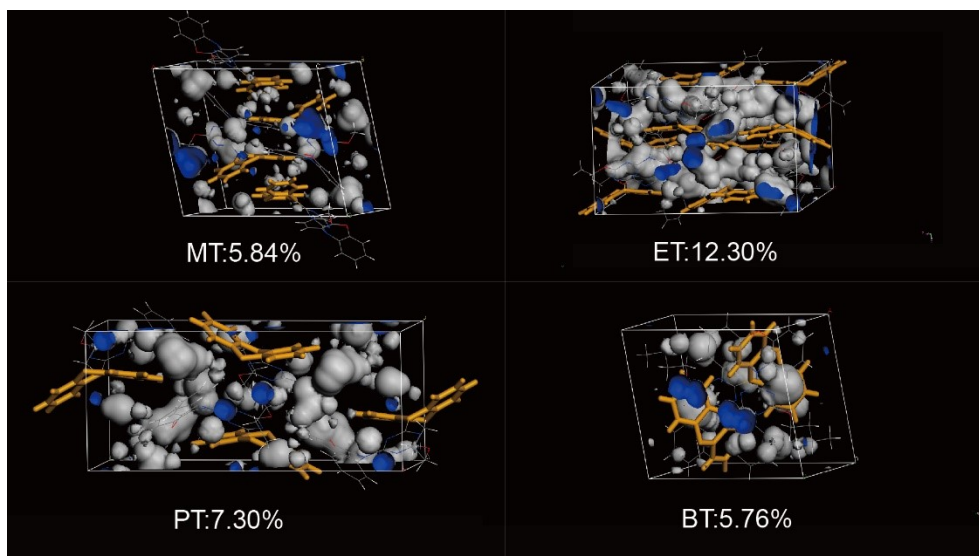| Style	Length（Å）	Amount	Style	Length（Å）	Amount
MT			ET		
C-H---O	2.579	2	C-H---π	2.789	2
C-H---π	2.826	2	C-H---N	2.742	2
	2.891	2	C-H---O	2.585	2
	2.857	2	π---π	3.310	2
	2.889	2		3.294	2
	2.865	2			
	2.794	2			
C-H---H-C	2.343	2			
C---C	3.389	2			
C-H---N	2.690	2			

IV. Theoretical calculation

Figure S24. The calculated free volume region in the single crystal cells of MT, ET, PT, BT.
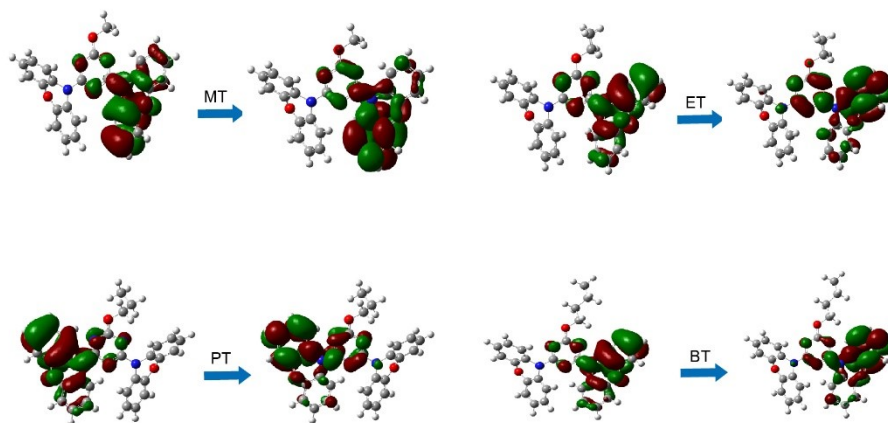

Figure S25. The NTOs of the low-lying excited state for MT/ET/PT/BT in crystal at the B3LYP/6-31G* level.
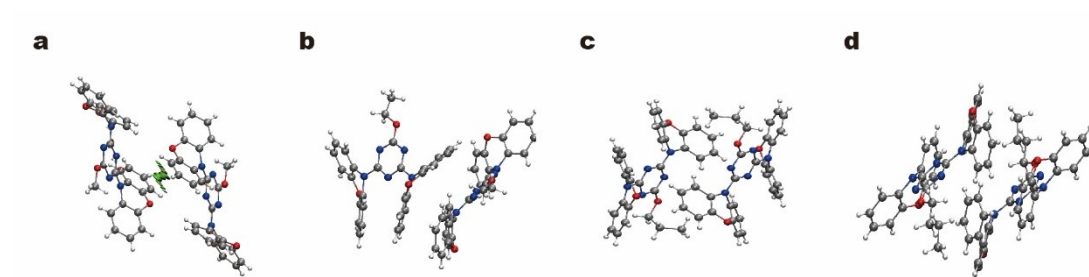

FigureS26. The reduced density gradient (RDG) isosurface the intermolecular interaction (Eint) between triplet chromophores in MT (a), ET (b), PT (c), and BT (d) dimer.