Electronic Supplementary Information

Colour-tunable ultralong organic phosphorescence upon temperature stimulus

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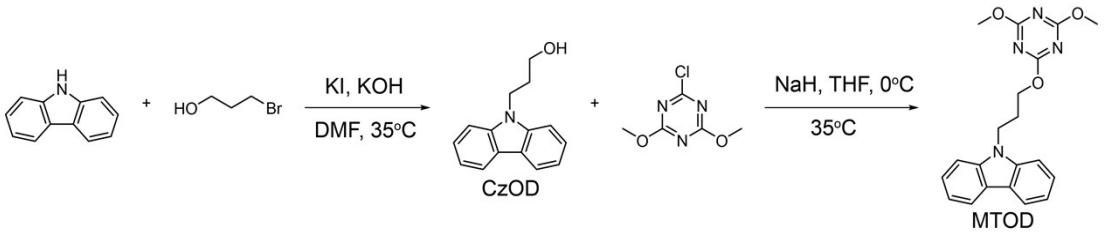
Experimental

Reagents and materials

Carbazole, 2-chloro-4,6-dimethoxy-1,3,5-triazine, potassium hydroxide, potassium iodide, sodium hydride, N,N-Dimethylformamide were purchased from commercial sources without further purification. Tetrahydrofuran (THF) was dried by sodium through distillation, with benzophenone as chromogenic reagent.

Measurements

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were determined on a Bruker Ultra Shield plus 400 MHz spectrometer in $CDCl_3$. Tetramethylsilane (TMS) was used as the internal standard of chemical shifts. And resonance patterns were signed with the notations s (singlet), d (double), t (triplet), q (quartet), and m (multiplet). Steady-state photoluminescence and phosphorescence spectra were measured using Hitachi F-4600 under ambient condition. The lifetime and time-resolved emission spectra were obtained on Edinburgh FLSP920 fluorescence spectrophotometer equipped with a nanosecond hydrogen flash-lamp (nF920), and a microsecond flash-lamp (μF900), respectively. Photoluminescence quantum yields were measured by Hamamatsu Absolute PL Quantum Yield Spectrometer C11347. The photographs were taken using a Cannon EOS 700D camera with a hand-held 365 nm ultraviolet lamp switched on and off. The measurements at 77 K were achieved in the liquid nitrogen. X-ray crystallography was achieved using a Bruker SMART APEX-II CCD diffractometer with graphite monochromated Mo-Kα radiation. Cambridge Crystallographic Data Centre (CCDC) 1912663 at 293 K and 1912664 at 100 K contain the supplementary crystallographic data for this paper. These data can be acquired free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The 77 K test environment was achieved in liquid nitrogen, and other sub-zero temperatures were achieved in a mixture of ethanol and liquid nitrogen.



Scheme S1. Synthetic routes of MTOD.

Synthesis

CzOD: Carbazole (3 g, 17.94 mmol), potassium iodide (1.47 g, 8.86 mmol) and potassium hydroxide (6.06 g, 108.00 mmol) were dissolved in 100 mL DMF. The solution was stirred at 35°C to dissolve carbazole. Then 3-bromo-1-propanol (0.37 g, 2.66 mmol) was added into the solution to react for 3 hours. After the reaction, DMF was extracted with dichloromethane and water to collect the organic phase, CH_2Cl_2 was removed by rotary evaporation. White solid is obtained with a high yield of 49.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dt, 2H), 7.56 – 7.48 (m, 4H), 7.33 – 7.27 (m, 2H), 4.48 (t, 2H), 3.61 (t, 2H), 2.13 (p, 2H), 1.70 (s, 1H).

MTOD: CzOD (0.5 g, 2.22 mmol) was dissolved in 4mL DMF then sodium hydride (0.15 g, 6.25 mmol) was added into the solution and stirred at room temperature for 30 minutes. 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.39g, 2.22mmol) was dissolved in 60mL DMF. Put the solution at 35 °C to keep temperature in the oil bath pot. Then the above CzOD sodium salt solution was slowly added into the reaction solution, and the reaction under 35°C more than 10 hours. After the reaction, THF in the reaction solution was removed by rotary evaporation. The resulting solid was extracted with CH_2Cl_2 and water for three times, and the organic phase was collected. After the removal of dichloromethane by rotary evaporation, the resulting solid was purified by flash column chromatography to give white powder with a high yield of 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, 2H), 7.45 (d, 4H), 7.32 – 7.27 (m, 1H), 7.25 (d, 1H), 4.56 (t, 2H), 4.36 (t, 2H), 3.99 (d, 6H), 2.50 – 2.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.52, 172.99, 140.32, 125.75, 122.97, 120.40, 119.05, 108.57, 65.21, 55.36, 39.28, 27.94.

MCzT: The materials were synthesized through two-step reactions according to our previous report.[1]

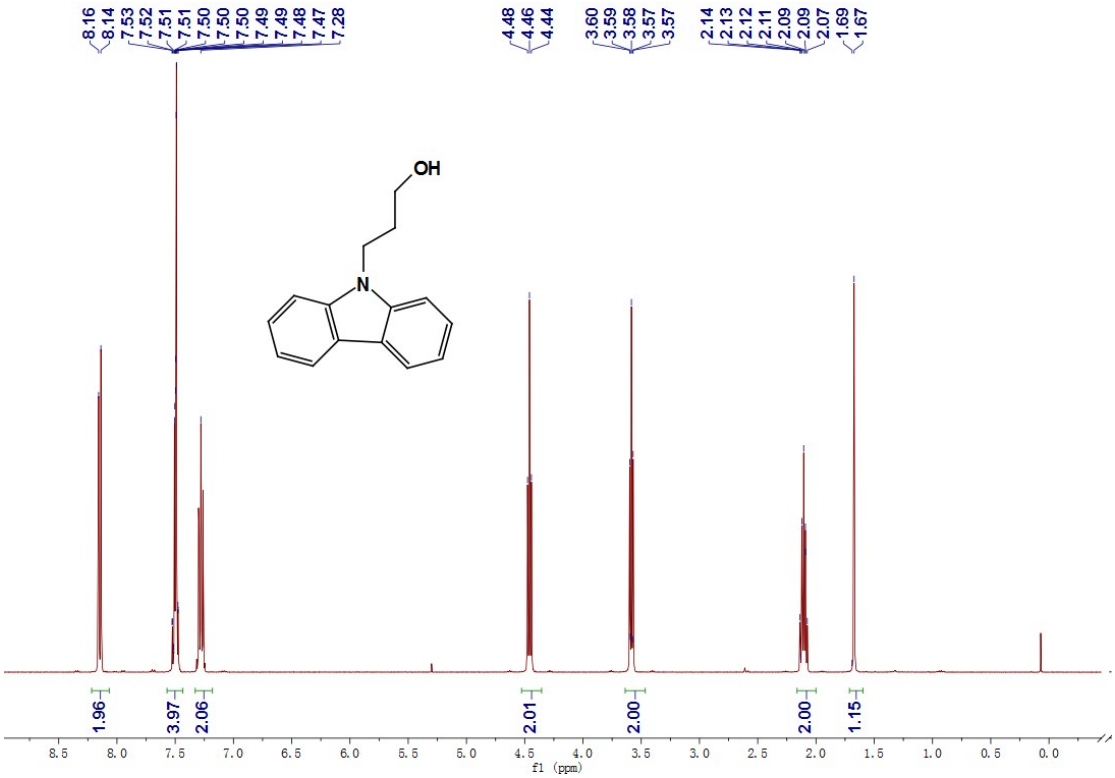


Figure S1. ^{1}H NMR spectrum of CZOD in $CDCl_3$.

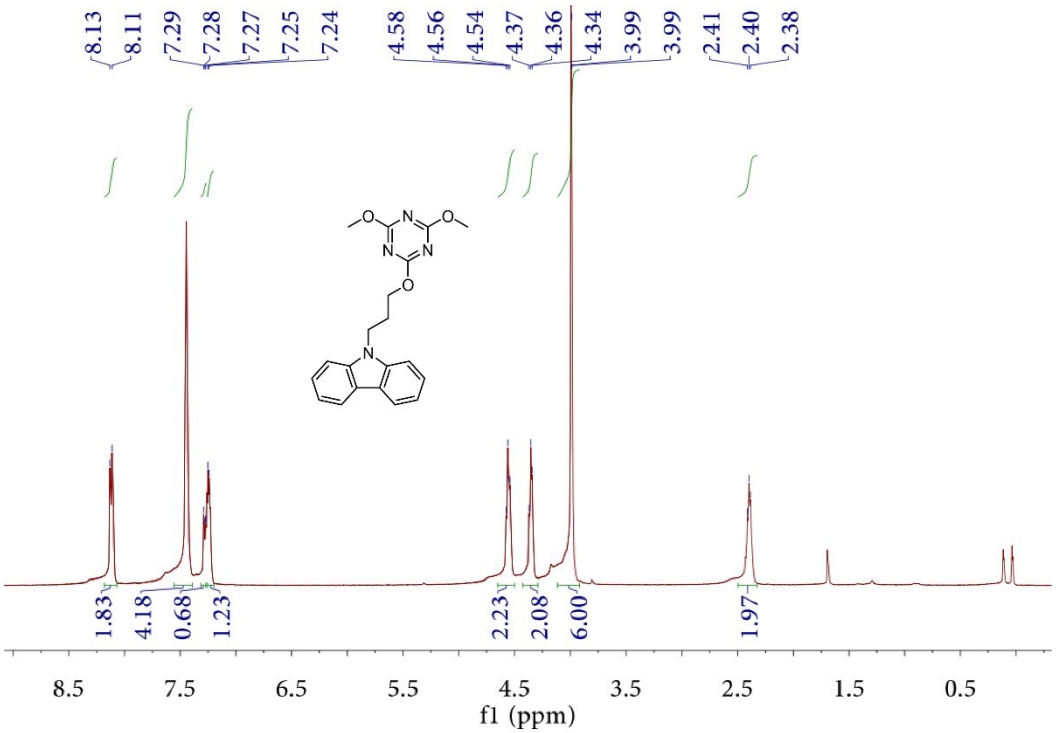


Figure S2. ^{1}H NMR spectrum of MTOD in $CDCl_3$.

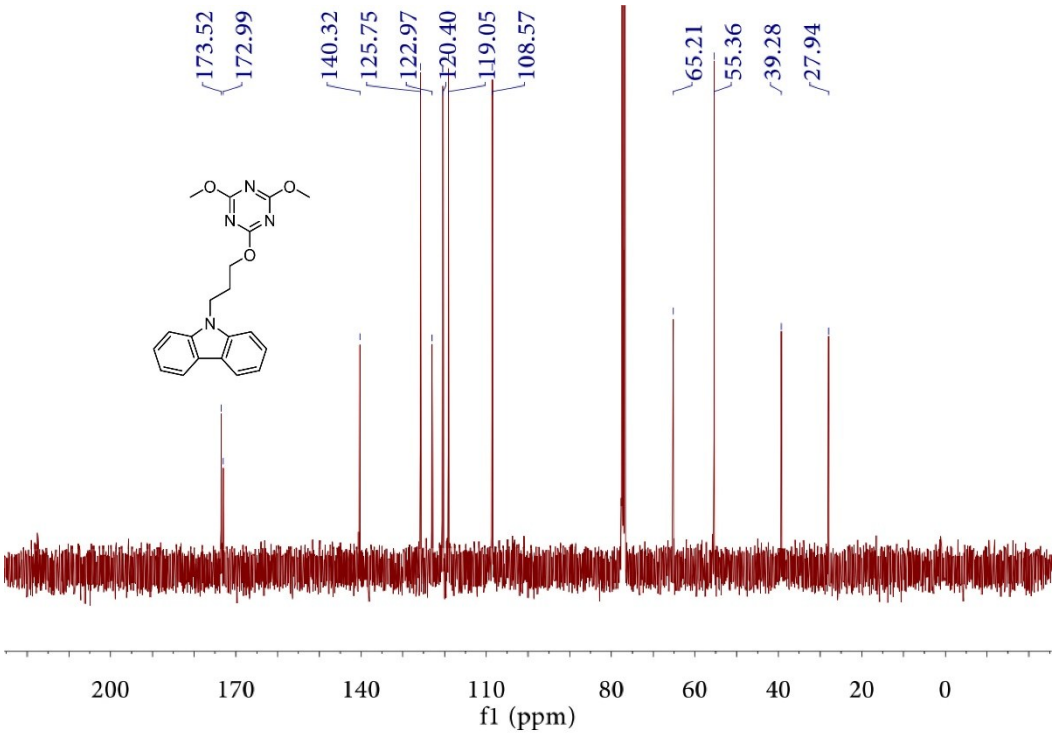


Figure S3. ^{13}C NMR spectrum of MTOT in $CDCl_3$.

Results and Discussion

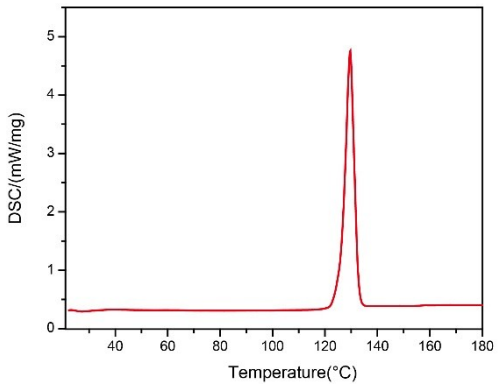


Figure S4. Differential scanning calorimetry curves of the MTOD.

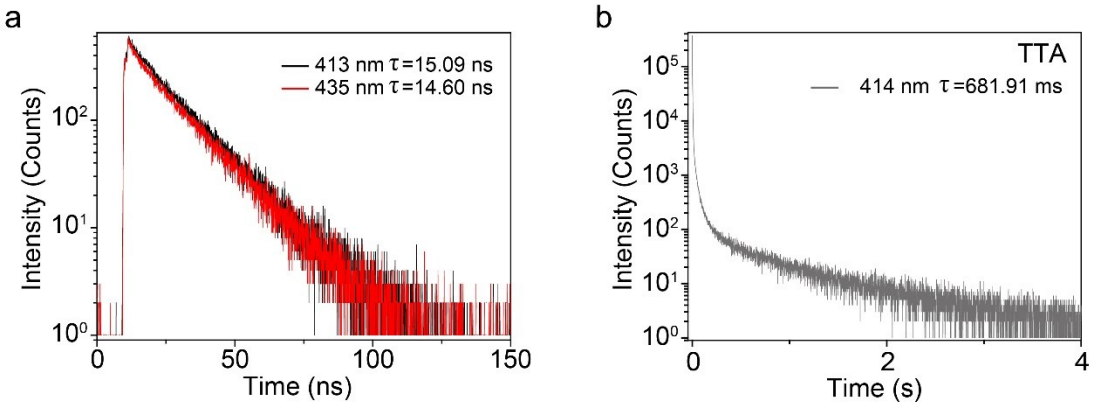


Figure S5. Lifetime decay profiles of a) the fluorescence emission bands at 413 (black curve) and 435 nm (red curve) and b) the TTA emission bands at 414nm.

Table S1. Fluorescence lifetimes of MTOD crystals.

Wavelength (nm)	**Fluorescence**			
	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
413	15.09	100	-	-
435	14.60	100	-	-

Table S2. Ultralong lifetimes of crystalline MTOD at RT and 77 K.

Temperature	**Wavelength (nm)**	**Ultralong luminescence**							
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ_4 (ms)	A_4 (%)
At room temperature	414	2.19	38.29	11.00	24.67	53.18	20.42	681.91	16.62
	556	2.56	1.74	26.98	1.90	353.35	7.72	860.56	88.64
	600	10.58	1.21	159.42	5.06	860.59	93.73		
At 77 K	478	10	0.92	100	10.52	403.50	34.18	2535.28	54.38
	553	8.51	2.54	214.66	22.89	1248.63	74.58		
	597	5.48	3.17	100.00	12.50	1138.30	84.33		

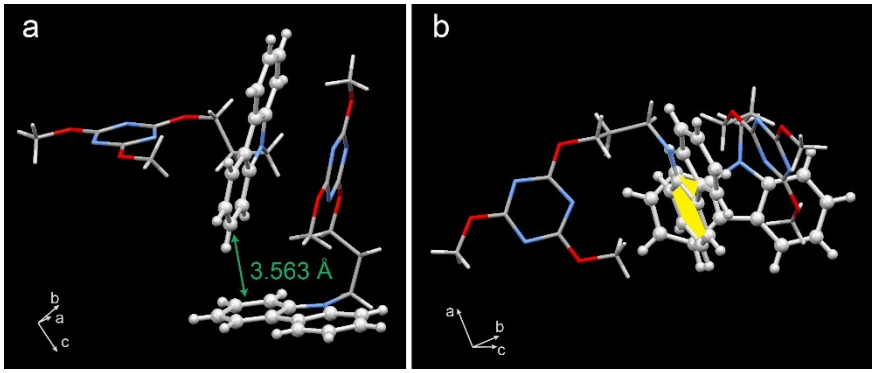


Figure S6. Molecular packing of the dimers of MTOD crystals. Yellow areas show the π-π overlap of carbazoles.

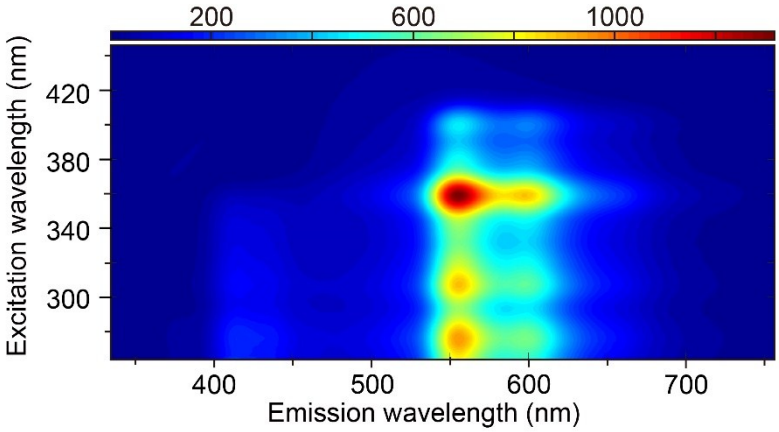


Figure S7. Excitation-phosphorescence mapping of the MTOD crystal.

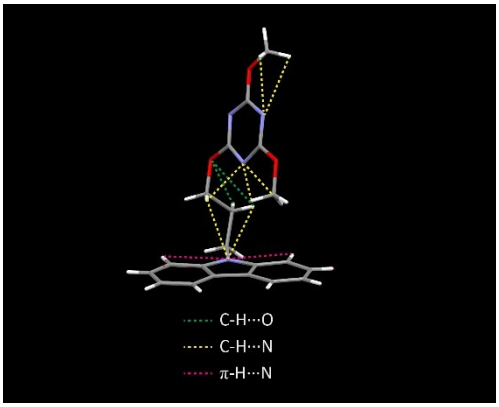


Figure S8. Intramolecular interaction of MTOD.

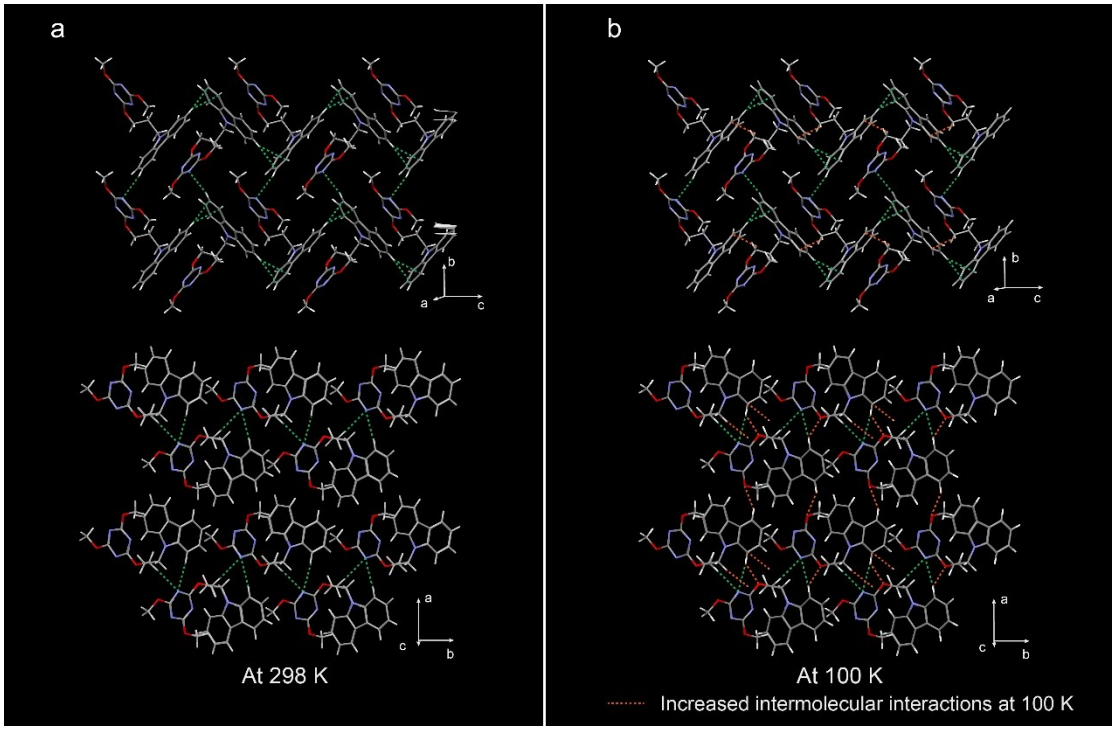


Figure S9. Molecular arrangement of MTOD (a) at room temperature and (b) at 100 K.

Table S3. Molecular interactions in crystalline MTOD at different temperatures

Types of Interactions		MTOD (298 K)	MTOD (100 K)
Intramolecular interactions (Å)	C-H···O	2.612, 2.622	2.632, 2.675
	C-H···N	2.347, 2.532, 2.587, 2.589, 2.650, 2.702, 2.722	2.549, 2.588, 2.666, 2.678, 2.687, 2.770, -
	π-H···N	2.765, 2.771	2.780, 2.782
Intermolecular interactions (Å)	C-H···N	2.681	2.598
	C-H···π	-	2.872, 2.880
	π-H···O	-	2.702, 2.710
	π-H···π	2.791, 2.876	2.719, 2.827
	π-H···N	2.703, 2.711	2.640, 2.657

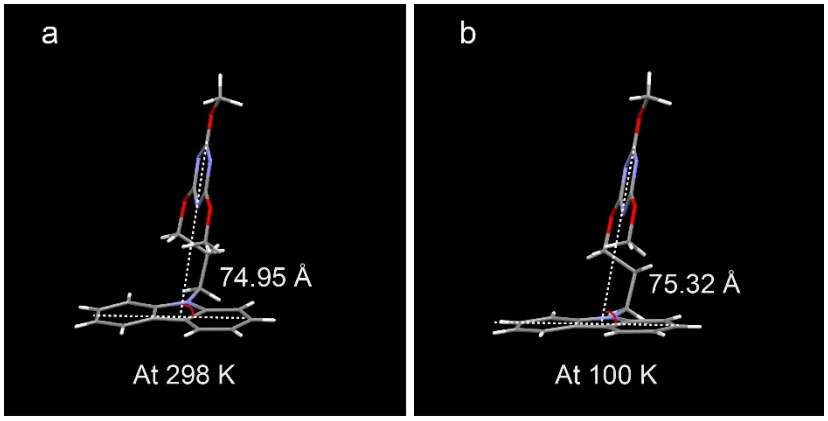


Figure S10. Dihedral angles between triazine and carbazole groups of MTOD crystals (a) at RT and (b) 100 K

References

1. L. Gu, H. Shi, M. Gu, K. Ling, H. Ma, S. Cai, L. Song, C. Ma, H. Li, G. Xing, X. Hang, J. Li, Y. Gao, W. Yao, Z. Shuai, Z. An, X. Liu and W. Huang, *Angew Chem Int Ed.*, 2018, **57**, 8425.