Supporting Information

Photochromism, photoluminescence modulation and selective recognition of small molecules of two highly stable dynamic metal-organic frameworks

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Experimental section

Materials and instrumentation

All of the chemicals are commercially available and used without further purification. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The thermogravimetric analyses (TGA) were carried out on Netzsch TG-209 Thermogravimetry Analyzer in N_2 atmosphere. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer. The ESR spectra were measured on a Bruker ER-420 spectrometer with a 100 KHz magnetic field in *X* band and an electronic field of 9655.448 MHz at room temperature.

Synthesis

Preparation of 1, 1a-1e. $[Tb(TTCA)(DMA)(H_2O)]\cdot 7DMA\cdot 9.5H_2O$ (**1**), $[Tb(TTCA)(MeOH)_2(H_2O)]\cdot 27MeOH$ (**1a**), $[Tb(TTCA)(EtOH)(H_2O)]\cdot 17.5EtOH$ (**1b**), $[Tb(TTCA)(PrOH)(H_2O)]\cdot 11PrOH$ (**1c**) and $[Tb(TTCA)(BuOH)(H_2O)]\cdot 6.33BuOH$ (**1d**) were prepared according to the reported method.[1] To further prepare the guest-exchanged sample $[Tb(TTCA)(BZA)_{1.25}(H_2O)_{0.75}]\cdot 2BZA\cdot 2DMA\cdot 2H_2O$ (**1e**), crystals of **1** were immersed in benzyl alcohol (BZA) for 7 days, and the guest solutions refreshed two times daily. Anal. Calcd for $C_{51.75}H_{58.50}O_{14}N_2Tb$ (**1e**): C, 56.96; H, 5.36; N, 2.57 %; Found: C, 56.53; H, 5.06; N, 2.35 %. Anal. Calcd for $[Tb(TTCA)(BZA)_{1.25}(H_2O)_{0.75}]\cdot 2BZA$ ($C_{43.75}H_{36.50}O_{10}Tb$): C, 59.60; H, 4.14; N, 0.00 %; Found: C, 59.95; H, 3.96; N, 0.04 %.

Synthesis of $[Eu(TTCA)(DMA)(H_2O)]\cdot 1.5DMA\cdot 19H_2O$ (2). A mixture of $Eu(NO_3)_3\cdot 6H_2O$ (0.045 g, 0.1 mmol), H_3TTCA (0.018 g, 0.05 mmol), triethylamine (1 drop) and DMA (8.0 mL) was heated at 110 °C for 72 h in a sealed Teflon-lined autoclave. The autoclave was cooled to room temperature. Colorless block-shaped crystals of **2** were collected by filtration. Yield: 25 %. Anal. Calcd for $C_{31}H_{71.5}N_{2.5}O_{28.5}Eu$ (**2**): C, 34.24; H, 6.58; N, 3.22 %; Found: C, 34.68; H, 6.23; N, 3.05 %.

Preparation of 2a. Crystals of **2** were exposed to the atmosphere for 2 hours to produce the crystals of $[Eu(TTCA)(DMA)_2]\cdot 0.5DMA\cdot 15H_2O$ (**2a**). Anal. Calcd

for $C_{31}H_{61.5}N_{2.5}O_{23.5}Eu$ (**2a**): C, 37.33; H, 6.17; N, 3.51 %; Found: C, 37.83; H, 6.31; N, 3.26 %.

X-ray Crystallography

The single-crystal data of **1e**, **2** and **2a** were collected on Agilent Technologies Gemini A Ultra system, with Cu/Kα radiation (λ = 1.54178 Å). All empirical absorption corrections were applied using the SCALE3 ABSPACK program.[2] The structure was solved by direct methods and refined by full-matrix least-squares analysis on F^2 using the SHELXL-2017/1 program package. All non-hydrogen atoms were refined anisotropically. The electron density of disordered solvent molecules in **1e**, **2** and **2a** were treated as a diffuse contribution using the program SQUEEZE.[3] The final formula was calculated from the SQUEEZE results combined with elemental analysis data and TGA data. All calculations were performed using the SHELXTL system of computer programs. The crystallographic data for **1e**, **2** and **2a** are summarized in Table S1, and the selected bond lengths and angles are listed in Table S2.

Fluorescence measurements

Photoluminescence of H_3TTCA, **1** and **2** were investigated in the solid state at room temperature on a Perkin-Elmer LS 55 fluorescence spectrometer. The wavelength of the exciting light was run from low to high wavelength at increments of 10 nm between 200 and 410 nm. Emission spectra was collected in the range of 300-700 nm, with a scan speed of 100 nm/min, and the slits was set at 10. The fluorescence quantum yields for **1** and **2** were determined using C9920-02G fluorescence spectrometer, excited by light at 320 and 350 nm, respectively. The fluorescence lifetimes for **1** and **2** were determined using FLS 920 fluorescence spectrometer, excited by light at 320 and 350 nm, respectively.

Table S1. Crystal Data and Structure Refinements for **1e**, **2** and **2a**.

	1e	**2**	**2a**
Formula	$C_{51.75}H_{58.5}O_{14}N_2Tb$	$C_{31}H_{71.5}N_{2.5}O_{28.5}Eu$	$C_{31}H_{61.5}N_{2.5}O_{23.5}Eu$
Formula weight	1091.09	1086.78	996.28
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	C2/c
a (Å)	26.3408(9)	25.683(3)	27.329(2)
b (Å)	14.8489(5)	16.2849(15)	13.2671(14)
c (Å)	27.2678(14)	26.745(2)	26.0537(19)
α (˚)	90	90	90
β (˚)	113.459(5)	112.951(12)	113.565(9)
γ (˚)	90	90	90
V (Å^3)	9783.8(8)	10300.5(17)	8658.8(14)
Z	8	8	8
D_c (g·cm^{-3})	1.074	0.792	1.018
Reflections/ Unique	19818/ 8516	19279 / 8565	14902 / 7101
R(int)	0.045	0.071	0.046
GOF on F^2	1.060	0.965	0.984
$R_1[I \geq 2\sigma(I)]^a$	0.0639	0.0703	0.0524
$wR_2[I \geq 2\sigma(I)]^b$	0.1955	0.2036	0.1508

[a] $R_1 = \Sigma \mid\mid F_o \mid - \mid F_c \mid\mid / \Sigma \mid F_o \mid$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Selected Bond Distances (Å) and Angles (°) for **1e**, **2** and **2a**.

1e					
Tb1-O1	2.493(4)	Tb1-O7	2.391(5)	Tb1-O4#2	2.275(4)
Tb1-O2	2.388(4)	Tb1-O1AA	2.40(3)	Tb1-O5#3	2.430(6)
Tb1-O1AB	2.423(10)	Tb1-O3#1	2.256(5)	Tb1-O6#3	2.400(5)
O1-Tb1-O2	53.35(15)	O1AA-Tb1-O3#1	94.6(8)	O2-Tb1-O5#3	109.71(18)
O3#1 -Tb1-O7	76.58(17)	O1-Tb1-O5#3	124.97(15)	O3#1-Tb1-O4#2	90.62(16)
O1-Tb1-O1AB	75.1(3)	O1AA-Tb1-O4#2	151.7(7)	O2-Tb1 -O6#3	79.92(18)
O4#2-Tb1-O7	80.41(17)	O1-Tb1-O6#3	71.40(16)	O3#1-Tb1-O5#3	155.19(15)
O1-Tb1-O7	143.20(17)	O1AA-Tb1-O5#3	82.8(8)	O3#1-Tb1-O6#3	148.39(16)
O5#3-Tb1-O7	79.02(18)	O1AA-Tb1-O6#3	71.8(8)	O1AB-Tb1-O7	76.4(3)
O1-Tb1-O1AA	81.6(7)	O2-Tb1-O1AB	127.9(3)	O4#2 -Tb1-O5#3	80.96(17)
O6#3-Tb1-O7	123.55(19)	O2-Tb1-O7	151.91(17)	O3#1-Tb1-O1AB	85.7(3)
O1-Tb1-O3#1	78.60(15)	O1AA-Tb1-O2	132.7(7)	O4#2-Tb1-O6#3	115.13(18)
O1-Tb1-O4#2	126.69(15)	O2-Tb1-O3#1	90.24(17)	O1AB-Tb1-O4#2	156.7(3)
O1AB-Tb1-O6#3	77.3(3)	O2 -Tb1-O4#2	74.97(15)	O1AB-Tb1-O5#3	92.9(3)
O1AA-Tb1-O7	73.8(7)	O5#3-Tb1-O6#3	53.59(16)		
2					
Eu1-O1	2.473(5)	Eu1-O8	2.360(5)	Eu1-O3#6	2.473(7)
Eu1-O2	2.437(6)	Eu1-O6#4	2.308(6)	Eu1-O4#6	2.475(6)
Eu1-O7	2.357(8)	Eu1-O5#5	2.329(6)	O3#6-Eu1-O6#4	148.0(2)
O1-Eu1-O2	53.53(18)	O2-Eu1-O7	131.3(2)	O7-Eu1-O8	76.9(3)
O4#6-Eu1-O8	77.5(2)	O4#6 -Eu1-O6#4	158.35(18)	O6#4 -Eu1-O7	78.1(3)
O1-Eu1-O7	80.1(2)	O2-Eu1-O8	150.8(2)	O5#5-Eu1-O7	148.4(2)
O1-Eu1-O8	155.6(2)	O3#6-Eu1-O5#5	130.2(2)	O3#6-Eu1-O7	76.8(3)
O1-Eu1-O6#4	78.44(18)	O2-Eu1-O6#4	103.3(2)	O4#6-Eu1-O7	114.1(3)
O1-Eu1-O5#5	117.8(2)	O4#6 -Eu1-O5#5	80.7(2)	O6#4 -Eu1-O8	88.8(2)
O1-Eu1-O3#6	78.01(19)	O2-Eu1-O5#5	76.35(19)	O5#5-Eu1-O8	79.7(2)
O1-Eu1-O4#6	120.12(17)	O2-Eu1-O3#6	79.4(2)	O3#6-Eu1-O8	104.4(2)
O5#5-Eu1-O6#4	80.4(2)	O3#6 -Eu1-O4#6	53.2(2)	O2-Eu1-O4#6	82.37(19)
2a					
Eu1-O1	2.485(5)	Eu1-O8	2.378(5)	Eu -O6#6	2.415(5)
Eu1-O2	2.438(5)	Eu1-O4#7	2.325(5)	Eu1-O3#8	2.310(5)
Eu1-O7	2.363(7)	Eu1-O5#6	2.506(4)	O4#7-Eu1-O7	77.8(2)
O1-Eu1-O2	52.84(16)	O5#6-Eu1-O6#6	53.30(16)	O5#6-Eu1-O7	82.7(2)
O1-Eu1-O7	113.1(2)	O2-Eu1-O4#7	147.25(17)	O6#6-Eu1-O7	131.8(2)
O3#8-Eu1-O8	79.2(2)	O2-Eu1-O5#6	79.73(16)	O3#8-Eu1-O7	147.4(2)
O1-Eu1-O8	77.15(18)	O3#8-Eu1-O5#6	115.63(17)	O4#7-Eu1-O8	89.21(19)
O1-Eu1-O4#7	159.38(16)	O2-Eu1-O6#6	76.94(17)	O5#6 -Eu1-O8	157.02(19)
O1-Eu1-O5#6	120.66(16)	O3#8-Eu1-O6#6	77.71(16)	O6#6-Eu1-O8	149.60(19)
O1-Eu1-O6#6	80.21(16)	O2-Eu1-O3#8	130.88(18)	O2-Eu1-O7	76.7(2)
O4#7-Eu1-O5#6	76.93(16)	O7-Eu1-O8	76.4(2)	O2-Eu1-O8	104.3(2)
O1-Eu1-O3#8	81.82(17)	O3#8-Eu1-O4#7	80.47(18)	O4#7-Eu1-O6#6	106.09(17)

Symmetry codes: #1 1 - x, y, 3/2 - z; #2 x, 1 - y, 1/2 + z; #3 1/2 - x, 1/2 + y, 3/2 - z; #4 - x, y, 1/2 - z; #5 x, 1 - y, -1/2 - z; #6 1/2 - x, -1/2 + y,1/2 - z ; #7 -1/2 + x, - 1/2 + y, z; #8 1/2 - x, 3/2 - y, - z.

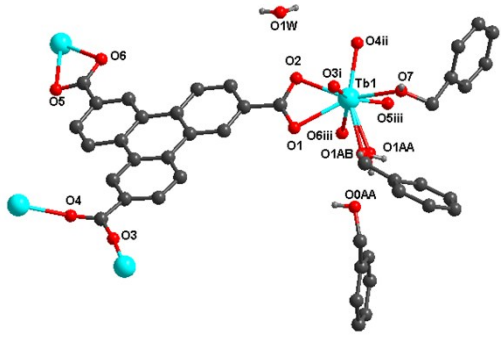

Fig. S1 The coordination environments of Tb^{3+} and $TTCA^{3-}$ in **1e** (symmetry operations: i: 1 - x, y, 3/2 - z; ii: x, 1 - y, 1/2 + z; iii: 1/2 - x, 1/2 + y, 3/2 - z).

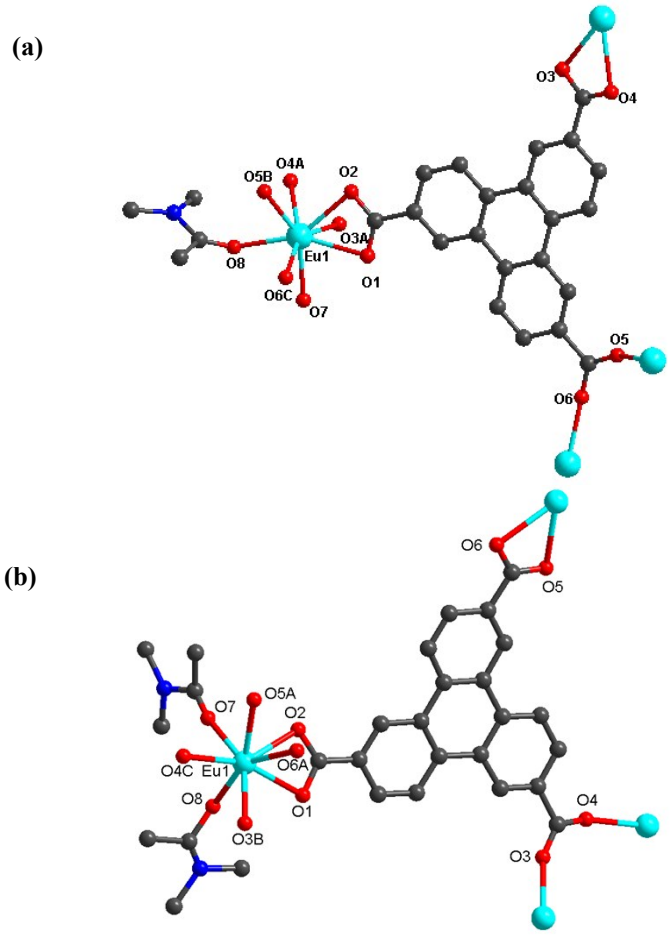

Fig. S2 (a) The coordination environments of Eu^{3+} and $TTCA^{3-}$ in **2** (symmetry operations: A: 1/2- x, -1/2 + y, 1/2 - z; B: x, 1 - y, -1/2 - z; C: - x, y, 1/2 - z). (b) The coordination environments of Eu^{3+} and $TTCA^{3-}$ in **2a** (symmetry operations: A: 1/2 - x, -1/2 + y, 1/2 - z; B: 1/2 - x, 3/2 - y, - z; C: -1/2 + x, -1/2 + y, z).

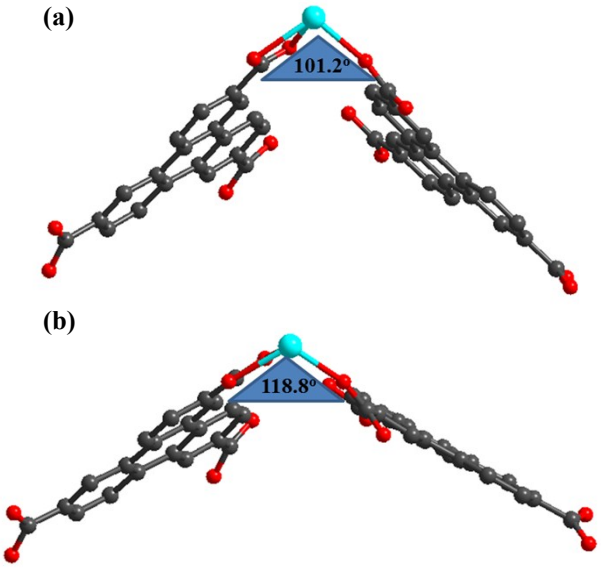

Fig. S3 The dihedral angles between neighbor TTCA ligands of **2** (a) and **2a** (b).

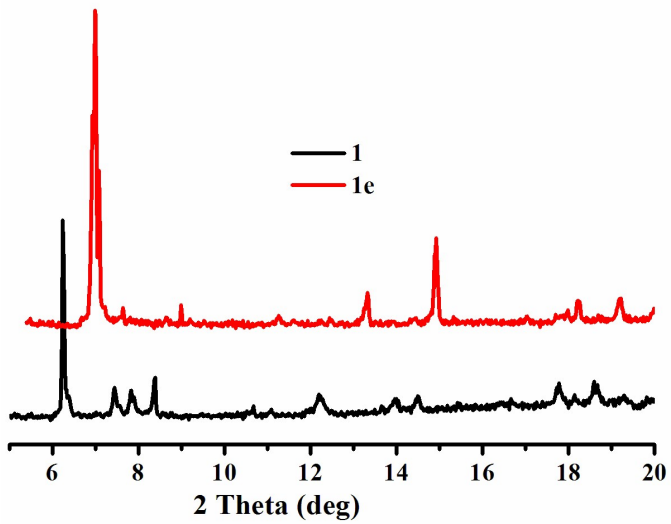

Fig. S4 PXRD patterns of **1** and **1e**, showing that the position of the peak at 6.25° in **1** moved to higher angles in **1e**.

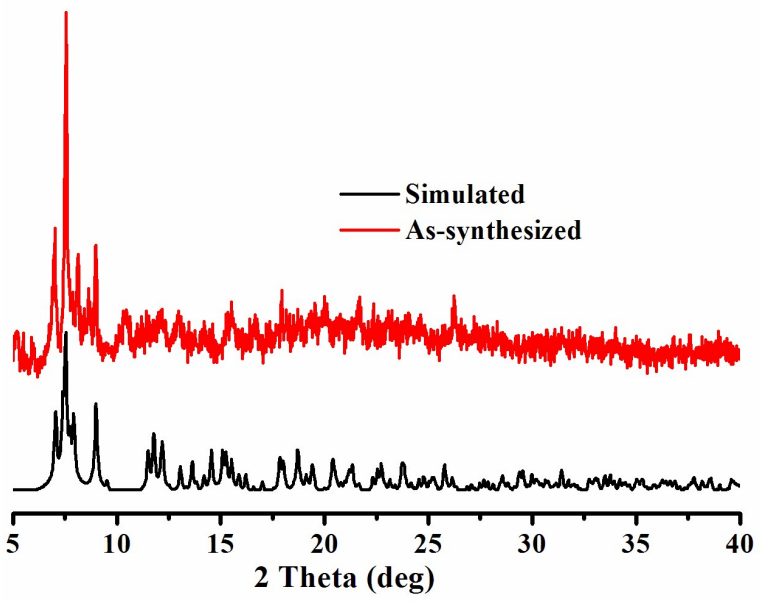

Fig. S5 The simulated and measured PXRD patterns of **2a**.

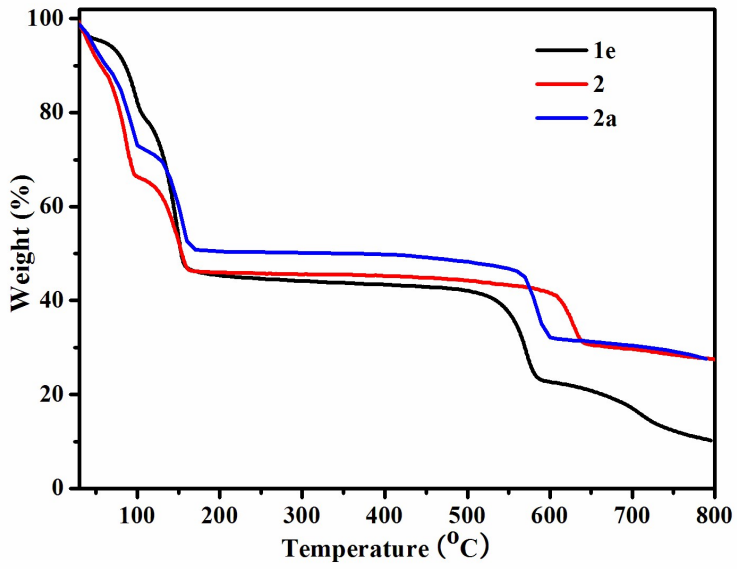

Fig. S6 TGA curves for **1e**, **2** and **2a**.

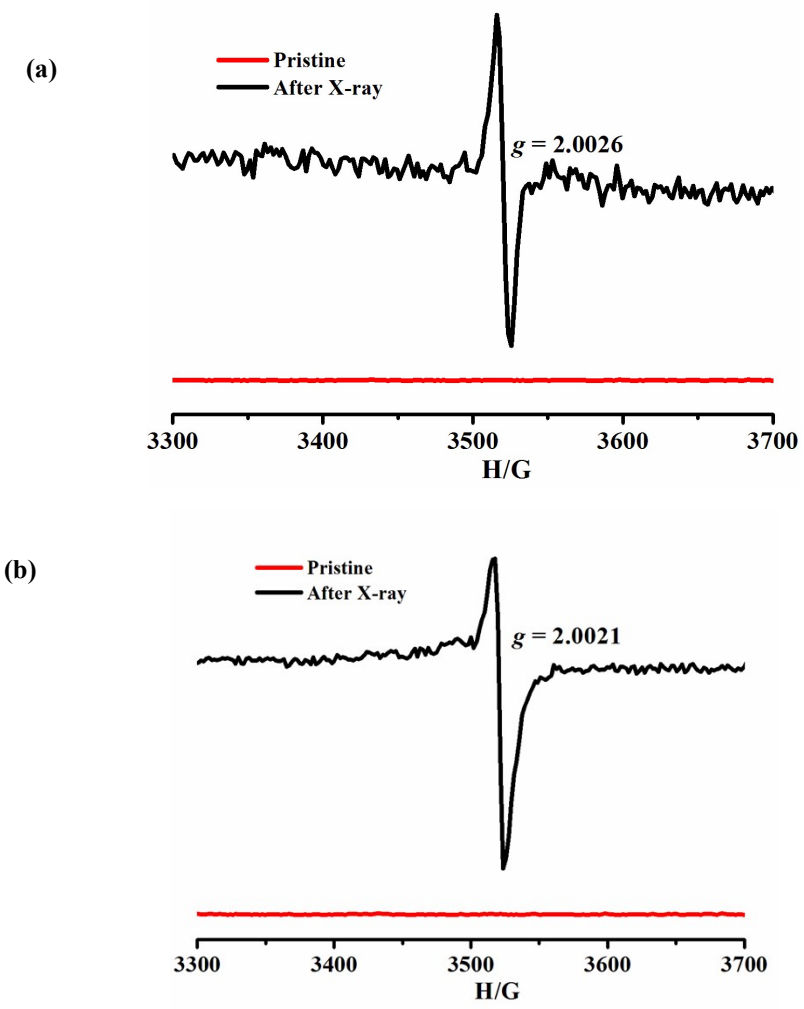

Fig. S7 Reversible ESR spectras for **1** (a) and **2** (b) before (red line) and after (black line) irradiation with X-ray light for 12 h, respectively.

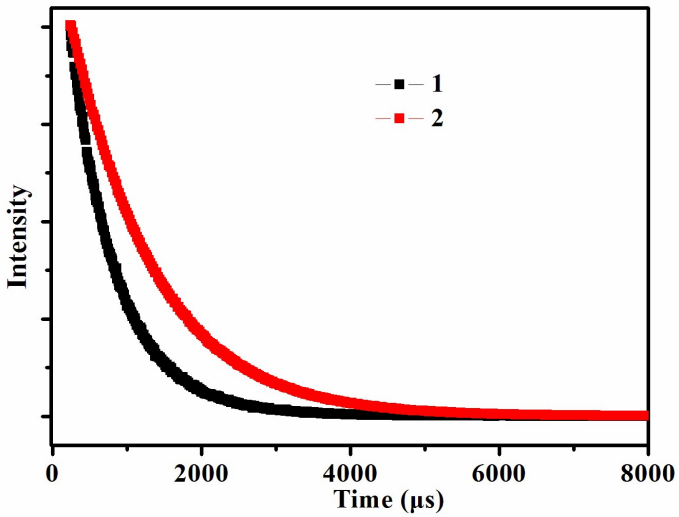

Fig. S8 Photoluminescence decay profiles for **1** and **2** at room temperature.

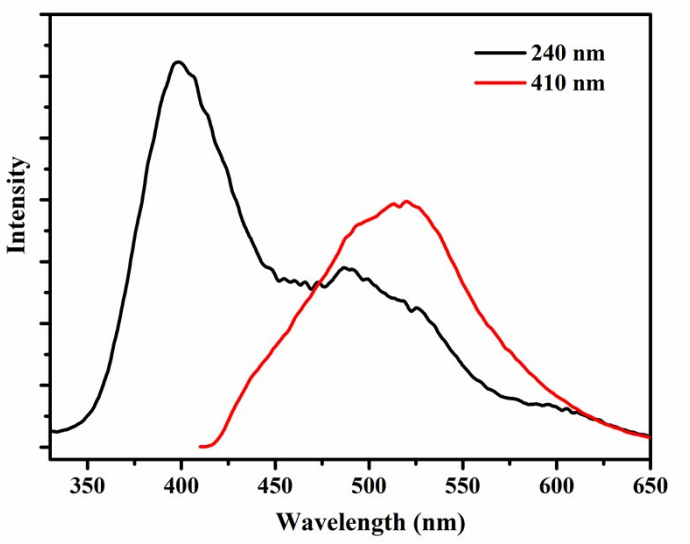

Fig. S9 Solid-state PL spectra of H_3TTCA by variation of excitation light.

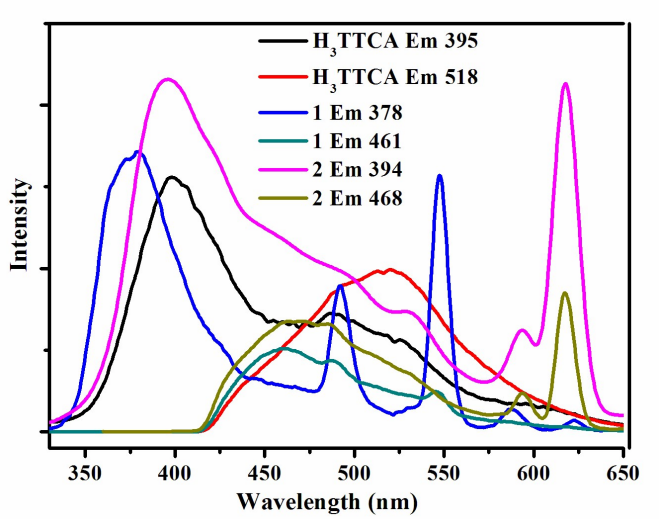

Fig. S10 Solid-state PL spectra of H_3TTCA, **1** and **2** (Em = emission).

References

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2 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, 1996.

3 A. Spek, *Acta Cryst.,* 2015, **C71**, 9.