Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2017

Supporting Information

Two bilayer metal−organic frameworks with rare trinuclear heterometal clusters and tunable photoluminescence

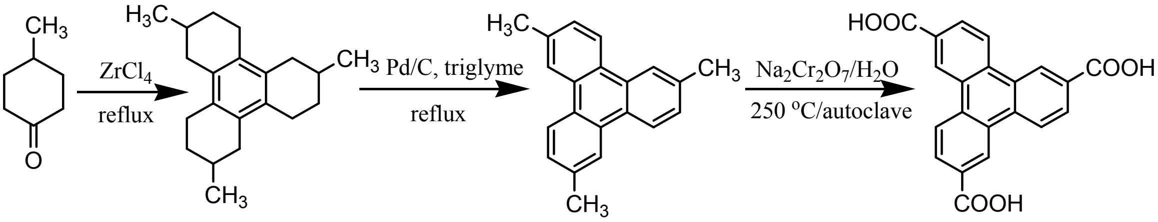
Yun-Nan Gong,* Xue-Wen Wei, Lv-Heng He, Ya-Qiong Wen, Ya-Wen Ren,
Yong-Rong Xie, Di-Chang Zhong*

Experimental Section

Materials and Methods

All of the chemicals are commercially available and used without further purification. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer. The thermogravimetric analysis (TGA) was carried out on Netzsch TG-209 Thermogravimetry Analyzer in N_2 atmosphere. UV-vis spectra were recorded on a Shimadzu UV-2501PC spectrophotometer.

Synthesis of H_3TTCA. a) 4-Methylcyclohexanone (40 g, 0.35 mol) was refluxed with zirconium tetrachloride (4 g, 17 mmol) for 12 h. After cooling to room temperature, hot chloroform (200 mL) was added and the gumlike solids were filtered off. The solvent was distilled off, and the product was recrystallised from butanol. White crystals of 2,6,10-trimethyl-dodecahydrotriphenlene were collected by filtration (19.59 g, yield: 58 %); b) The mixture of dodecahydro isomers (5 g, 18 mmol) was refluxed with 10 % Pd/C (0.5 g, 0.47 mmol) in 20 mL of triglyme under argon for 24 h. After cooling to room temperature, chloroform (200 mL) was added and the mixture was heated to reflux to redissolve the partially precipitated product. The mixture was filtered hot, the chloroform was evaporated and the product was recrystallised from butanol. White crystals of 2,6,10-trimethyltriphenylene were collected by filtration (3.29 g, yield: 69 %). c) The mixture of 2,6,10-trimethyltriphenylene (0.2 g, 0.74 mmol) and $Na_2Cr_2O_7 \cdot 2H_2O$ (0.7 g, 2.35 mmol) in 3.0 mL of distilled water was sealed in a Teflon-lined autoclave (20 mL) and heated at 250 ºC for 6 h. After cooling to room temperature, the autoclave contents were washed out with water, the green chromium salts were filtered off and the formed of triphenylene-2,6,10-tricarboxylic acid (H_3TTCA) was precipitated by addition of hydrochloric acid (0.054 g, yield: 20 %).



Scheme S1. Synthetic route for preoaration of H_3TTCA

Synthesis of $(Me_2NH_2)_3[Pb_2K(TTCA)_2Cl_2]$ (1)

A mixture of $PbCl_2$ (0.028 g, 0.1 mmol), H_3TTCA (0.018 g, 0.05 mmol), KCl (0.0074 g, 0.1 mmol), hydrochloric acid (2 drop) and DMF (8.0 mL) was heated at 155 °C for 72 h in a sealed Teflon-lined autoclave. After the autoclave cooled to room temperature, colorless block-shaped crystals of **1** were collected by filtration. Yield: 35%. Anal. Calcd for $C_{48}H_{42}O_{12}N_3Cl_2Pb_2K$ (**1**): C, 41.86; H, 3.07; N, 3.05 %; Found: C, 42.31; H, 2.85; N, 3.42 %.

Synthesis of $(Me_2NH_2)_5[Cd_2Na(TTCA)_2(HTTCA)_2]\cdot 4DMF\cdot 2H_2O$ (2)

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.034 g, 0.15 mmol), H_3TTCA (0.018 g, 0.05 mmol), NaCl (0.006 g, 0.1 mmol) and DMF (8.0 mL) was heated at 140 °C for 72 h in a sealed Teflon-lined autoclave. After the autoclave cooled to room temperature, colorless block-shaped crystals of **2** were collected by filtration. Yield: 12%. Anal. Calcd for $C_{106}H_{110}N_9Cd_2NaO_{38}$ (**2**): C, 53.81; H, 4.69; N, 5.33 %; Found: C, 54.23; H,4.85; N, 5.51 %.

Crystal Structures Determination for 1 and 2

The single-crystal data of **1** and **2** were collected on Agilent Technologies Gemini A Ultra system, with Mo Kα radiation (λ = 0.71073 Å) and Cu Kα radiation (λ = 1.54178 Å), respectively. All empirical absorption corrections were applied using the SCALE3 ABSPACK program.[1] The structures were solved by direct method and refined by full-matrix least-squares analysis on F^2 using the SHELX program package. All non-hydrogen atoms were refined anisotropically. The final formulas were calculated from the elemental analysis data and TGA data. All calculations were performed using the SHELXTL system of computer program.[2] Crystallographic data and refinement details are displayed in table 1. Selected bond lengths and angles are given in table 2.

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. **1** and **2** were prepared by filtration and drying at 180 ^{o}C for 2 h. The wavelength of the exciting light was run from low to high wavelength at increments of 10 nm between 200 and 420 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 410 and 400 nm, respectively.

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

	1	**2**
Formula	$C_{48}H_{42}Cl_2KN_3O_{12}Pb_2$	$C_{106}H_{110}N_9Cd_2NaO_{38}$
Formula weight	1377.22	2365.85
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C2/c
a (Å)	9.9175(5)	17.546(2)
b (Å)	10.0625(4)	21.3217(10)
c (Å)	13.4072(7)	35.974(2)
α (°)	107.383(2)	90
β (°)	108.957(2)	99.105(9)
γ (°)	91.213(3)	90
V (Å^3)	1197.20(10)	13288.6(19)
Z	1	4
D_c (g·cm^{-3})	1.910	0.938
Reflections/ Unique	10094 / 5386	20673 / 10869
R(int)	0.0249	0.0965
GOF on F^2	1.049	1.142
$R_1[I \geq 2\sigma(I)]^a$	0.0371	0.1299
$wR_2[I \geq 2\sigma(I)]^b$	0.0831	0.3795

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [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 **1** and **2**.

1					
Pb1-Cl1	2.624(3)	Pb1-O4#1	2.826(5)	K1-O2	2.725(4)
Pb1-O1	2.703(5)	Pb1-O5#2	2.635(5)	K1-O4#1	2.654(5)
Pb1-O2	2.788(5)	Pb1-O6#2	2.687(6)	K1-O2#5	2.725(4)
Pb1-O3#1	2.675(5)			K1-O4#3	2.654(5)
O3#4-Pb1-O4#1	82.65(15)	O2-K1-O4#1	66.82(14)	O3#1-Pb1-O5#2	127.38(17)
O5#2-Pb1-O6#2	48.77(15)	O1-Pb1-O3#4	100.98(17)	O3#1-Pb1-O6#2	78.88(16)
O3#4-Pb1-O5#2	99.64(15)	O2-Pb1-O3#1	110.86(14)	O3#1-Pb1-O3#3	72.04(13)
O3#4-Pb1-O6#2	90.23(16)	O2-Pb1-O4#1	63.68(13)	O4#1-Pb1-O5#2	173.29(15)
O1-Pb1-O2	47.21(16)	O2-Pb1-O5#2	121.72(13)	O4#1-Pb1-O6#2	125.23(15)
O1-Pb1-O3#1	156.61(18)	O2-Pb1-O6#2	167.66(14)	O2-K1-O2#5	180.00
O1-Pb1-O4#1	110.55(16)	O4#1-K1-O4#3	180.00	O2#5-K1-O4#3	66.82(14)
O1-Pb1-O5#2	75.32(17)	O2-Pb1-O3#4	99.88(15)	O2#5-K1-O4#1	113.18(14)
O2-K1-O4#3	113.18(14)	O3#1-Pb1-O4#1	47.22(16)	O1-Pb1-O6#2	124.08(16)
2					
Cd1-O1	2.495(8)	Cd1-O3#6	2.587(9)	Na1-O8	2.465(9)
Cd1-O2	2.428(9)	Cd1-O4#6	2.322(9)	Na1-O10#5	2.390(9)
Cd1-O7	2.591(12)	Cd1-O9#7	2.299(11)	Na1-O2#8	2.267(7)
Cd1-O8	2.283(10)	Cd1-O10#7	2.578(10)	Na1-O8#8	2.465(9)
Na1-O2	2.267(7)	Na1-O10#7	2.390(9)	O4#6-Cd1-O10#7	141.1(3)
O1-Cd1-O2	52.2(3)	O3#6-Cd1-O8	98.8(3)	O8-Na1-O10#5	108.5(3)
O8-Cd1-O10#7	71.5(3)	O4#6-Cd1-O8	137.6(3)	O8-Na1-O10#7	71.5 (3)
O1-Cd1-O7	85.2(3)	O3#6-Cd1-O7	88.8(3)	O2#8-Na1-O8	101.0(4)
O1-Cd1-O8	117.7(3)	O4#6-Cd1-O7	92.2(4)	O2#8-Na1-O10#5	82.8(3)
O1-Cd1-O3#6	126.7(3)	O2-Cd1-O4#6	126.4(3)	O2-Cd1-O8	79.5(3)
O1-Cd1-O4#6	74.4(3)	O2-Cd1-O9#7	97.9(4)	O4#6-Cd1-O9#7	89.6(4)
O1-Cd1-O9#7	102.9(3)	O9#7-Cd1-O10#7	53.2(3)	O2-Na1-O8	79.0(4)
O1-Cd1-O10#7	120.5(3)	O8-Cd1-O9#7	122.6(4)	O2-Na1-O10#5	97.2(3)
O3#6 -Cd1-O4#6	52.9(3)	O2-Cd1-O10#7	75.9(3)	O2-Na1-O10#7	82.8(3)
O3#6 -Cd1-O9#7	86.0(3)	O7-Cd1-O10#7	122.9(3)	O2-Na1-O8#8	101.0(4)
O2-Cd1-O7	87.4(3)	O3#6 -Cd1-O10#7	107.0 (3)	O7-Cd1-O8	52.2(3)

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

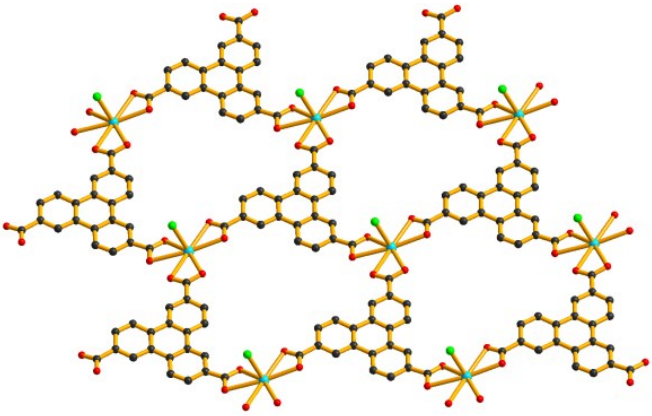


Fig. S1 View of the 2D monolayer structure constructed by Pb(II) ions, Cl^- anions and $TTCA^{3-}$ ligands in **1**.

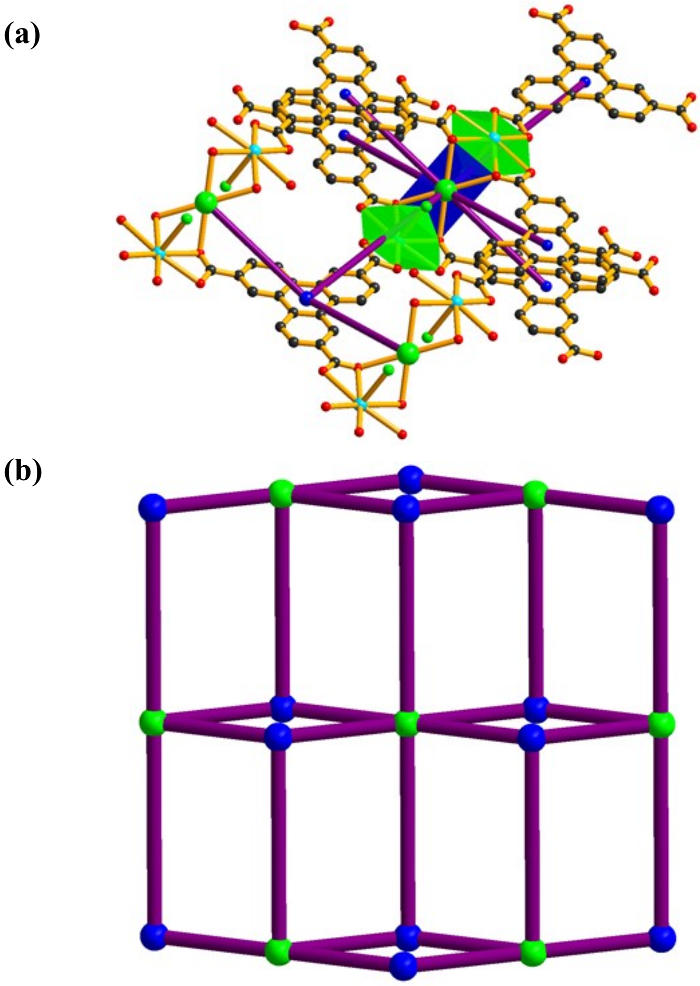


Fig. S2 (a) The six-connected heterometal trinuclear cluster and three-connected $TTCA^{3-}$ ligand in **1**. (b) View of the (3,6)-connected topological network of **1**.

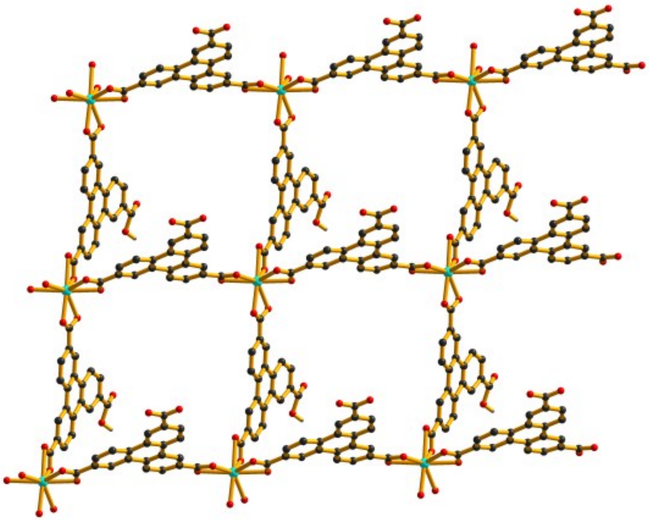


Fig. S3 View of the 2D monolayer structure constructed by Cd(II) ions, TTCA^{3-} and HTTCA^{2-} ligands of **2**.

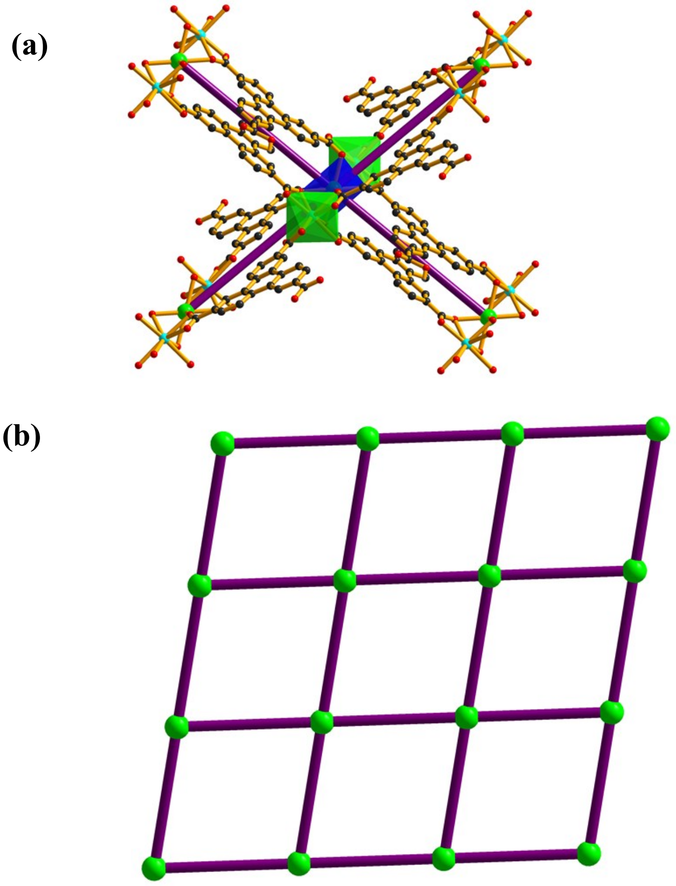


Fig. S4 (a) The four-connected heterometal trinuclear cluster; (b) View of the 4-connected topological network of **2**.

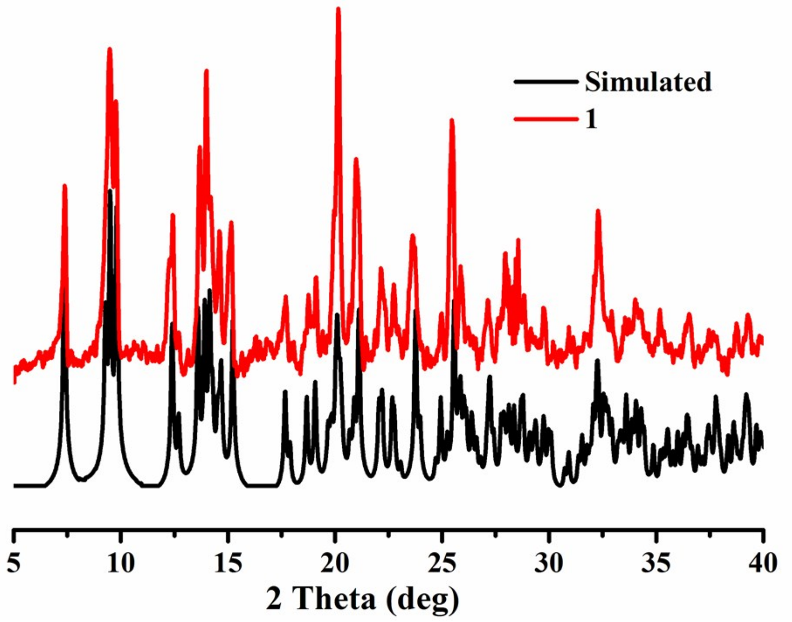


Fig. S5 The simulated and measured PXRD patterns of **1**.

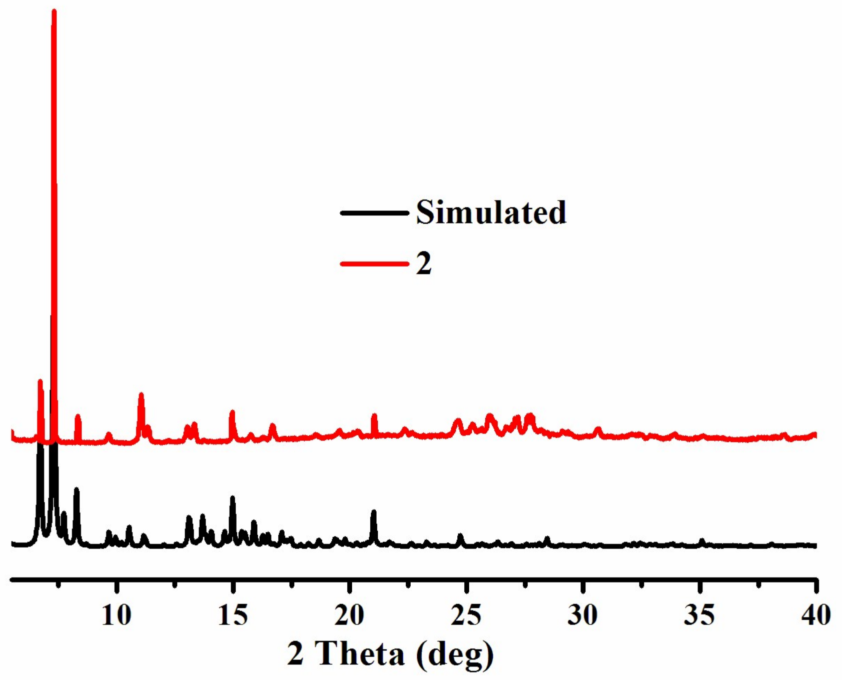


Fig. S6 The simulated and measured PXRD patterns of **2**.

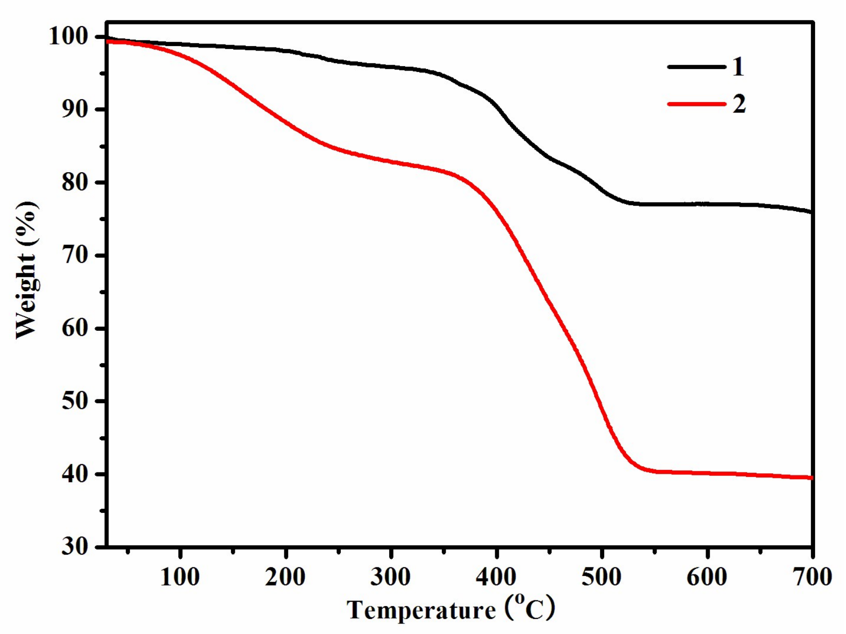


Fig. S7 TGA curves for **1** and **2**.

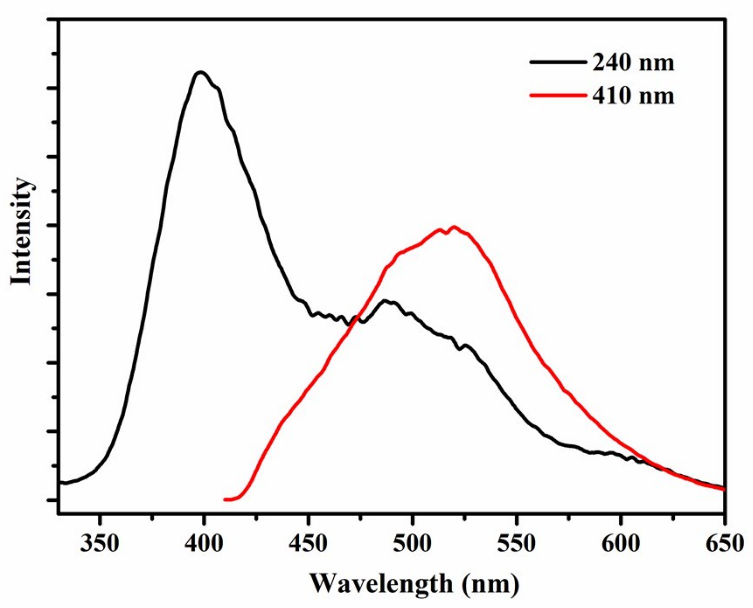


Fig. S8 Solid-state PL spectra of H_3TTCA by variation of excitation light.

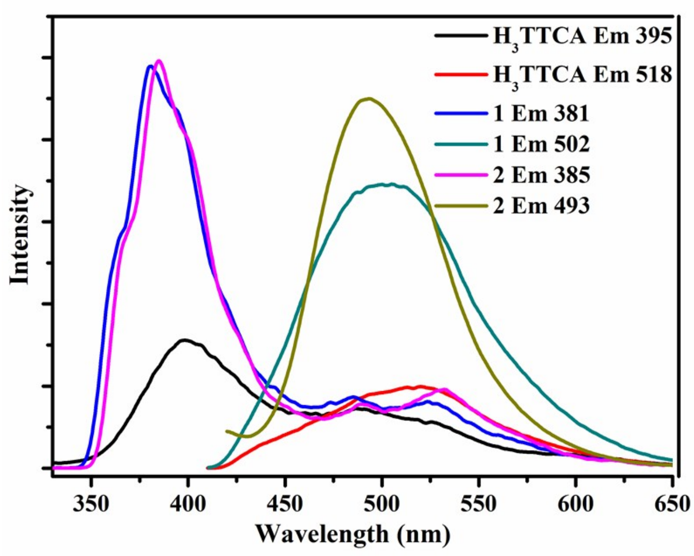


Fig. S9 Solid-state PL spectra of H_3TTCA, **1** and **2** (Em = emission).

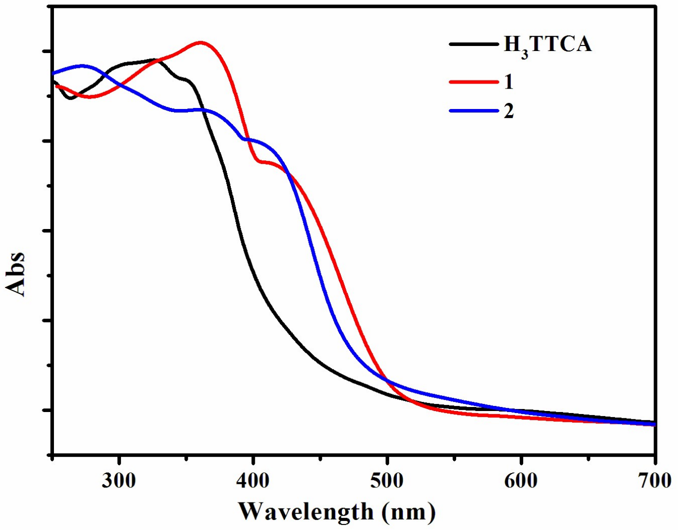


Fig. S10 The UV-vis diffuse-reflectance spectra of H_3TTCA, **1** and **2**.

References

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

2. Sheldrick, G. M. SHELXS 97, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, 1997.