

Supporting Information

Microporous heterometal-organic framework as a sensor for BTEX with high selectivity

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Experimental Section

1. Materials and Methods

H₆TTHA was prepared by the literature method,¹ and the other chemicals purchased were of reagent grade and used without further purification. Analyses for C, H, and N were carried out on a Perkin-Elmer 240 CHN elemental analyzer. Powder X-ray diffraction measurements were recorded on a Rigaku D/Max-2500 X-ray diffractometer using Cu K α radiation. TGA were performed on a Labsys NETZSCH TG 209 Setaram apparatus with a heating rate of 10 °C / min in nitrogen atmosphere. UV-vis spectroscopic studies were collected on a Jasco V-570 spectrophotometer. IR was recorded in the range 400–4000 cm⁻¹ on a Bruker TENOR 27 spectrophotometer using KBr pellets. The luminescent properties were measured on a Varian Cary Eclipse in suspensions at room temperature.

2. Synthesis of **1** and **2**

Synthesis of {[Zn₃Tb₂(TTHA)₂(H₂O)₆]• 10H₂O}_n (**1**) A mixture of Tb(NO₃)₃•6H₂O (0.1 mmol, 0.0435 g), Zn(NO₃)₂•6H₂O (0.5 mmol, 0.1490 g), H₆TTHA (0.15 mmol, 0.0711 g), and H₂O (10 mL) was added in a 25 mL Teflon-lined stainless steel reactor and heated at 150 C for 72 h, and then, slowly cooled to room temperature. Needle-like single crystals suitable for X-ray data collection were obtained by filtration, washed with distilled water, and air-dried. Yield: 55% based on Tb. Elemental analysis found (calcd) for Zn₃Tb₂C₃₀N₁₂O₄₀H₅₆: C, 20.55 (20.72); H, 3.20 (3.25); N, 9.53 (9.67).

Synthesis of {[Co₃Tb₂(TTHA)₂(H₂O)₆]• 10H₂O}_n (**2**) Synthesis of **2** was similar to that of **1** using Co(NO₃)₂•6H₂O (0.5 mmol, 0.1455 g) instead of Zn(NO₃)₂•6H₂O. Yield: 48% based on Tb. Elemental analysis found (calcd) for Co₃Tb₂C₃₀N₁₂O₄₀H₅₆: C, 20.75 (20.96); H, 3.34 (3.28); N, 9.67 (9.78).

3. X-ray Crystallography

Diffraction intensity data for single crystals of **1** and **2** were collected on a Agilent Technologies SuperNova Single Crystal Diffractometer at 293 K equipped with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms of organic ligand were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature

factors. The selected crystal parameters, data collection, and refinements are summarized in Table S1. Further details on the crystal structure investigations can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, on quoting the depository numbers: CCDC 1017363 and 1017364.

4. Thermogravimetric analysis

Thermogravimetric (TGA) curves of **1** and **2** were performed in the temperature range of 30–800 °C. The trends of weight loss are similar due to the isostructural nature. Obvious weight losses in the temperature range 25–101 °C and 25–102 °C are attributed to the loss of ten free water molecules per formula for **1** (calcd 10.35%, found 9.98%) and **2** (calcd 10.47%, found 10.31%), respectively. The following weight losses of 6.45% (calcd 6.21%) from 101 to 195 °C for **1** and 6.26% (calcd 6.28%) from 102 to 197 °C for **2** correspond to the loss of six coordinated water molecules, as confirmed by the single crystal X-ray diffraction analysis. From then on, both of them almost have no loss until 400 °C, and then they begin to decompose.

5. Luminescent measurements

The luminescent properties of HMOF **1** were investigated in both the solid state and suspensions at room temperature, and HMOF **2** were investigated in the solid state. The suspensions of **1** \supset solvent were prepared by introducing each sample (3.0 mg) as a powder into different solvents (each 2.0 mL) and then vigorously agitated using ultrasound. For the experiments of sensing ethylbenzene, different amounts of ethylbenzene were added into a standard suspension of **1** \supset methanol, while the concentration of the **1** was kept constant.

References:

- 1 (a) P. De. Hoog, P. Gamez, W. L. Driessen and J. Reedijk, *J. Tetrahedron Lett.*, 2002, **43**, 6783; (b) Q. L. Zhu, T. L. Sheng, R. B. Fu, S. M. Hu, J. S. Chen, S. C. Xiang, C. J. Shen and X. T. Wu, *Cryst. Growth Des.*, 2009, **9**, 5128.
- 2 (a) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112; (b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

Table S1. Crystal Data and Structural Refinement Parameters for **1** and **2**

	1	2
formula	Zn ₃ Tb ₂ C ₃₀ N ₁₂ O ₄₀ H ₅₆	Co ₃ Tb ₂ C ₃₀ N ₁₂ O ₄₀ H ₅₆
fw	1738.90	1719.47
λ / Å	0.71073	0.71073
crystal system	monocline	monocline
space group	<i>C2/m</i>	<i>C2/m</i>
a (Å)	17.3863(12) Å	17.3855(15) Å
b (Å)	17.9923(11) Å	17.8778(17) Å
c (Å)	10.7535(7) Å	10.7117(8) Å
α (deg)	90.00	90.00
β (deg)	125.455(5) °	125.437(6) °
γ (deg)	90.00°	90.00°
V / Å ³	2740.1(3)	2712.6(4)
Z	2	2
ρ_{calc} / mg mm ⁻³	2.005	2.002
μ / mm ⁻¹	3.953	3.583
reflns collected / unique	5939 / 2498	5463 / 2466
R(int)	0.0294	0.0650
2 θ range / deg	5.76 – 50.00	5.76 – 50.00
F(000)	1616	1598
GOF on F ²	1.046	1.086
R1 / wR2[I > 2 σ (I)]	0.0252 / 0.0670	0.0526 / 0.1295
R1 / wR2 (all data)	0.0274 / 0.0684	0.0708 / 0.1559
largest diff. peak / hole / e Å ⁻³	1.045 / -1.103	1.428 / -1.996

Table S2 Selected bond lengths (Å) and angles (°) for **1** and **2**.

1					
Tb(1)-O(0AA)	2.299(3)	O(0AA)-Tb(1)-O(3)#1	150.31(9)	O#2-Zn(2)-O(4)	91.89(11)
Tb(1)-O(0AA)#1	2.299(3)	O(0AA)#1-Tb(1)-O(3)#1	118.13(9)	O(4)#2-Zn(2)-O(4)	180
Tb(1)-O(2)#1	2.447(3)	O(2)#1-Tb(1)-O(3)#1	125.99(9)	O-Zn(2)-O(5)#2	93.04(12)
Tb(1)-O(2)	2.447(3)	O(2)-Tb(1)-O(3)#1	78.56(9)	O#2-Zn(2)-O(5)#2	86.96(12)
Tb(1)-O(3)#1	2.488(3)	O(0AA)-Tb(1)-O(3)	118.13(9)	O(4)#2-Zn(2)-O(5)#2	89.83(12)
Tb(1)-O(3)	2.488(3)	O(0AA)#1-Tb(1)-O(3)	150.31(10)	O(4)-Zn(2)-O(5)#2	90.17(12)

Tb(1)-O(1)#1	2.537(3)	O(2)#1-Tb(1)-O(3)	78.56(9)	O-Zn(2)-O(5)	86.96(12)
Tb(1)-O(1)	2.537(3)	O(2)-Tb(1)-O(3)	125.99(9)	O#2-Zn(2)-O(5)	93.04(12)
Zn(2)-O	2.035(3)	O(3)#1-Tb(1)-O(3)	62.70(11)	O(4)#2-Zn(2)-O(5)	90.17(12)
Zn(2)-O#2	2.035(3)	O(0AA)-Tb(1)-O(1)#1	129.61(9)	O(4)-Zn(2)-O(5)	89.83(12)
Zn(2)-O(4)#2	2.132(3)	O(0AA)#1-Tb(1)-O(1)#1	78.56(10)	O(5)#2-Zn(2)-O(5)	180
Zn(2)-O(4)	2.132(3)	O(2)#1-Tb(1)-O(1)#1	52.11(9)	O(6)-Zn(3)-O(6)#3	179.999(1)
Zn(2)-O(5)#2	2.134(3)	O(2)-Tb(1)-O(1)#1	137.89(9)	O(6)-Zn(3)-O(3)#3	92.43(11)
Zn(2)-O(5)	2.134(3)	O(3)#1-Tb(1)-O(1)#1	79.93(9)	O(6)#3-Zn(3)-O(3)#3	87.57(11)
Zn(3)-O(6)	2.063(4)	O(3)-Tb(1)-O(1)#1	72.35(9)	O(6)-Zn(3)-O(3)#1	92.43(11)
Zn(3)-O(6)#3	2.063(4)	O(0AA)-Tb(1)-O(1)	78.57(10)	O(6)#3-Zn(3)-O(3)#1	87.57(11)
Zn(3)-O(3)#3	2.087(2)	O(0AA)#1-Tb(1)-O(1)	129.61(9)	O(3)#3-Zn(3)-O(3)#1	103.35(14)
Zn(3)-O(3)#1	2.087(2)	O(2)#1-Tb(1)-O(1)	137.89(9)	O(6)-Zn(3)-O(3)#4	87.57(11)
Zn(3)-O(3)#4	2.087(2)	O(2)-Tb(1)-O(1)	52.11(9)	O(6)#3-Zn(3)-O(3)#4	92.43(11)
Zn(3)-O(3)	2.087(2)	O(3)#1-Tb(1)-O(1)	72.34(9)	O(3)#3-Zn(3)-O(3)#4	76.66(14)
O(0AA)-Tb(1)-O(0AA)#1	76.63(14)	O(3)-Tb(1)-O(1)	79.93(9)	O(3)#1-Zn(3)-O(3)#4	180
O(0AA)-Tb(1)-O(2)#1	80.38(10)	O(1)#1-Tb(1)-O(1)	147.48(13)	O(6)-Zn(3)-O(3)	87.57(11)
O(0AA)#1-Tb(1)-O(2)#1	79.02(10)	O-Zn(2)-O#2	180.00(17)	O(6)#3-Zn(3)-O(3)	92.43(11)
O(0AA)-Tb(1)-O(2)	79.02(10)	O-Zn(2)-O(4)#2	91.89(11)	O(3)#3-Zn(3)-O(3)	180.00(14)
O(0AA)#1-Tb(1)-O(2)	80.37(10)	O#2-Zn(2)-O(4)#2	88.11(11)	O(3)#1-Zn(3)-O(3)	76.65(14)
O(2)#1-Tb(1)-O(2)	153.65(14)	O-Zn(2)-O(4)	88.11(10)	O(3)#4-Zn(3)-O(3)	103.34(14)
Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1 #2 -x+1/2,-y+1/2,-z+1 #3 -x+1,-y+1,-z+1 #4 x,-y+1,z #5 -x+1/2,-y+1/2,-z					

2					
Tb(1)-O(6)#1	2.287(6)	O(6)#1-Tb(1)-O#1	118.7(2)	O(2)-Co(2)-O(20)#2	93.1(3)
Tb(1)-O(6)	2.287(6)	O(6)-Tb(1)-O#1	150.7(2)	O(20)-Co(2)-O(20)#2	179.998(1)
Tb(1)-O(1)	2.439(6)	O(1)-Tb(1)-O#1	77.5(2)	O(2)#2-Co(2)-O(3)#2	92.2(2)
Tb(1)-O(1)#1	2.439(6)	O(1)#1-Tb(1)-O#1	126.2(2)	O(2)-Co(2)-O(3)#2	87.8(2)
Tb(1)-O#1	2.454(6)	O(6)#1-Tb(1)-O	150.7(2)	O(20)-Co(2)-O(3)#2	90.1(2)
Tb(1)-O	2.454(6)	O(6)-Tb(1)-O	118.7(2)	O(20)#2-Co(2)-O(3)#2	89.9(2)
Tb(1)-O(5)#1	2.543(6)	O(1)-Tb(1)-O	126.2(2)	O(2)#2-Co(2)-O(3)	87.8(2)
Tb(1)-O(5)	2.543(6)	O(1)#1-Tb(1)-O	77.5(2)	O(2)-Co(2)-O(3)	92.2(2)
Co(2)-O(2)#2	2.044(7)	O#1-Tb(1)-O	63.4(3)	O(20)-Co(2)-O(3)	89.9(2)
Co(2)-O(2)	2.044(7)	O(6)#1-Tb(1)-O(5)#1	78.8(2)	O(20)#2-Co(2)-O(3)	90.1(2)
Co(2)-O(20)	2.096(6)	O(6)-Tb(1)-O(5)#1	128.4(2)	O(3)#2-Co(2)-O(3)	179.999(1)
Co(2)-O(20)#2	2.096(6)	O(1)-Tb(1)-O(5)#1	137.3(2)	O(4)#3-Co(3)-O(4)	179.998(1)
Co(2)-O(3)#2	2.125(6)	O(1)#1-Tb(1)-O(5)#1	51.9(2)	O(4)#3-Co(3)-O#1	91.2(2)
Co(2)-O(3)	2.125(6)	O#1-Tb(1)-O(5)#1	80.9(2)	O(4)-Co(3)-O#1	88.8(2)
Co(3)-O(4)#3	2.034(8)	O-Tb(1)-O(5)#1	72.6(2)	O(4)#3-Co(3)-O#3	91.2(2)
Co(3)-O(4)	2.034(8)	O(6)#1-Tb(1)-O(5)	128.4(2)	O(4)-Co(3)-O#3	88.8(2)
Co(3)-O#1	2.090(6)	O(6)-Tb(1)-O(5)	78.8(2)	O#1-Co(3)-O#3	103.9(3)
Co(3)-O#3	2.090(6)	O(1)-Tb(1)-O(5)	51.9(2)	O(4)#3-Co(3)-O	88.8(2)
Co(3)-O	2.090(6)	O(1)#1-Tb(1)-O(5)	137.3(2)	O(4)-Co(3)-O	91.2(2)
Co(3)-O#4	2.090(6)	O#1-Tb(1)-O(5)	72.6(2)	O#1-Co(3)-O	76.1(3)

O(6)#1-Tb(1)-O(6)	74.7(3)	O-Tb(1)-O(5)	80.9(2)	O#3-Co(3)-O	180
O(6)#1-Tb(1)-O(1)	80.0(2)	O(5)#1-Tb(1)-O(5)	148.9(3)	O(4)#3-Co(3)-O#4	88.8(2)
O(6)-Tb(1)-O(1)	79.8(2)	O(2)#2-Co(2)-O(2)	179.998(1)	O(4)-Co(3)-O#4	91.2(2)
O(6)#1-Tb(1)-O(1)#1	79.8(2)	O(2)#2-Co(2)-O(20)	93.1(3)	O#1-Co(3)-O#4	179.999(1)
O(6)-Tb(1)-O(1)#1	80.0(2)	O(2)-Co(2)-O(20)	86.9(3)	O#3-Co(3)-O#4	76.1(3)
O(1)-Tb(1)-O(1)#1	154.5(3)	O(2)#2-Co(2)-O(20)#2	86.9(3)	O-Co(3)-O#4	103.8(3)
Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z #2 -x+1/2,-y+1/2,-z #3 -x+1,-y+1,-z #4 x,-y+1,z #5 -x+1,-y+1,-z+1					

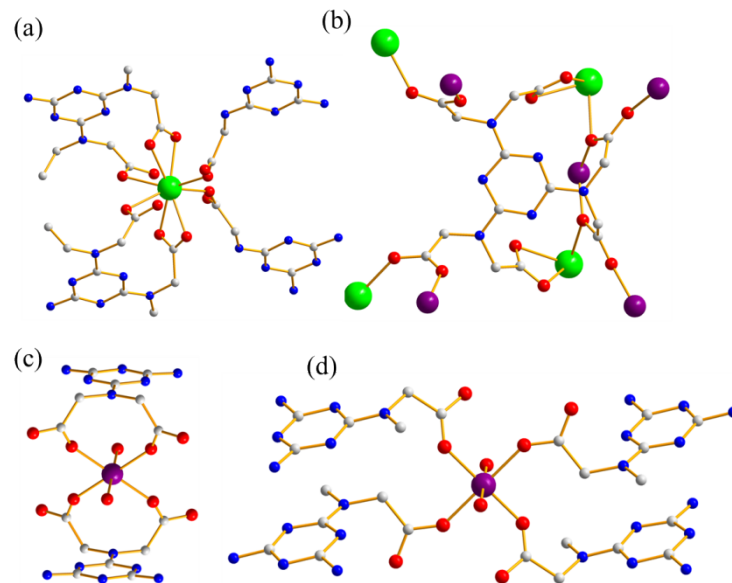


Fig. S1 Crystal structure of **1**: (a) the coordination environment of Tb^{3+} ion, (b) the coordination modes of TTHA^{6-} , including chelating/bridging tridentate, *syn-syn* bridging and chelating bidentate coordination modes, (c) the coordination environment of Zn1, (d) the coordination environment of Zn2. Tb: green, Zn: purple, O: red, N: blue, and C: grey (H atoms were omitted for clarity).

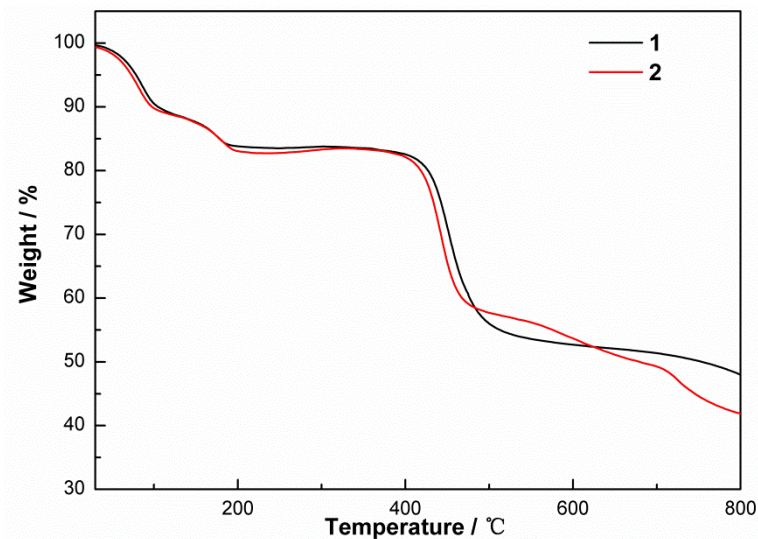
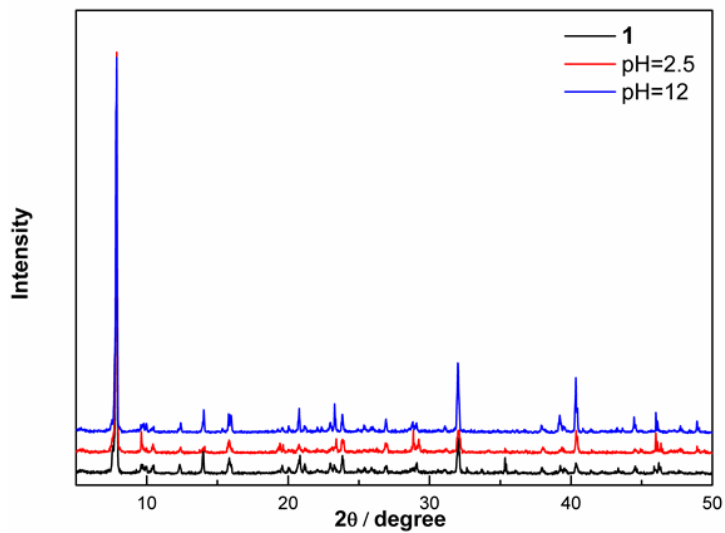
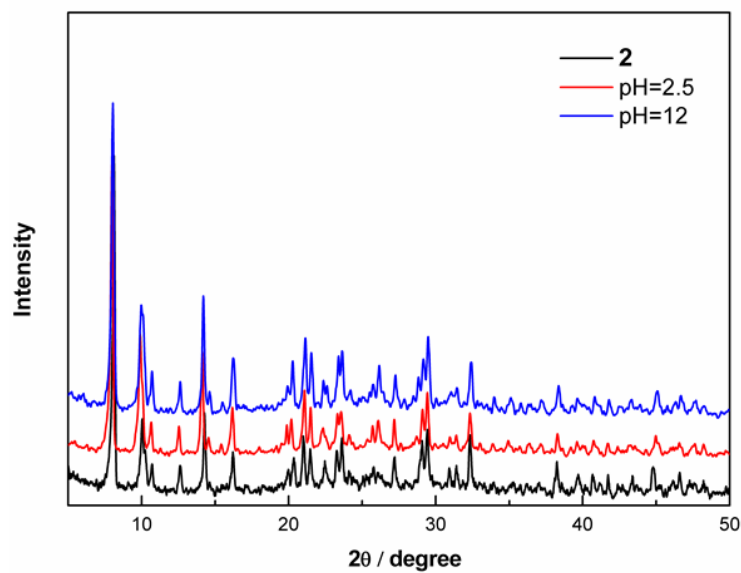


Fig. S2 Thermogravimetric (TGA) curves of **1** and **2**.



(a)



(b)

Fig. S3 PXRD patterns of **1** and **2** after immersing in the solution of pH = 2.5 and pH = 12 for one week.

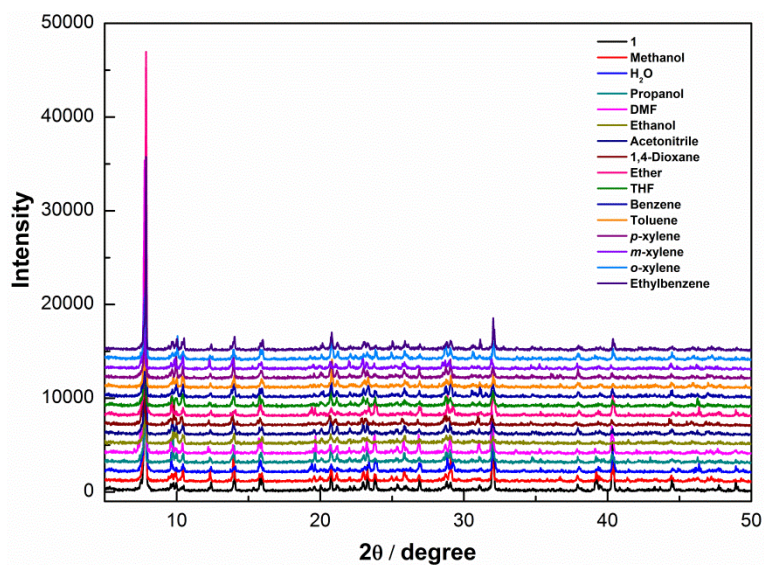


Fig. S4 PXRD patterns of **1** after immersing in different solvents for one week.

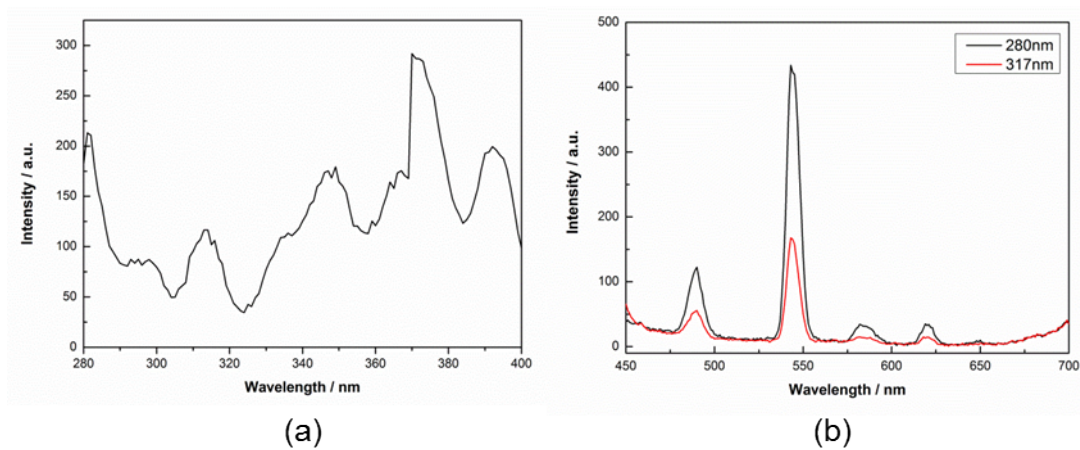


Fig. S5 The solid-state excitation spectrum (a) and comparison of the emission spectra with the excitation wavelength of 280 nm and 317 nm (b) of **1** at room temperature.

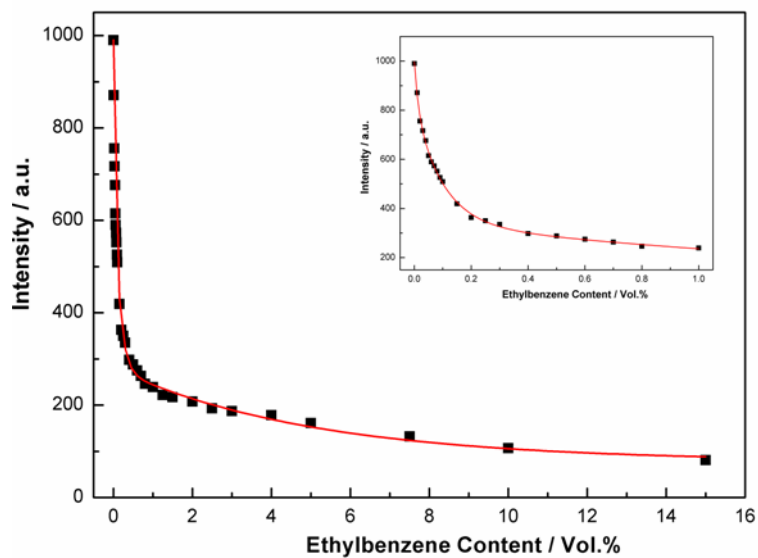


Fig. S6 The ${}^5D_4 \rightarrow {}^7F_5$ transition intensity of **1** in methanol suspension as a function of ethylbenzene contents between 0.01% and 15%. The inset shows ${}^5D_4 \rightarrow {}^7F_5$ transition intensity of **1** in methanol suspension as a function of ethylbenzene contents between 0.1% and 1%.

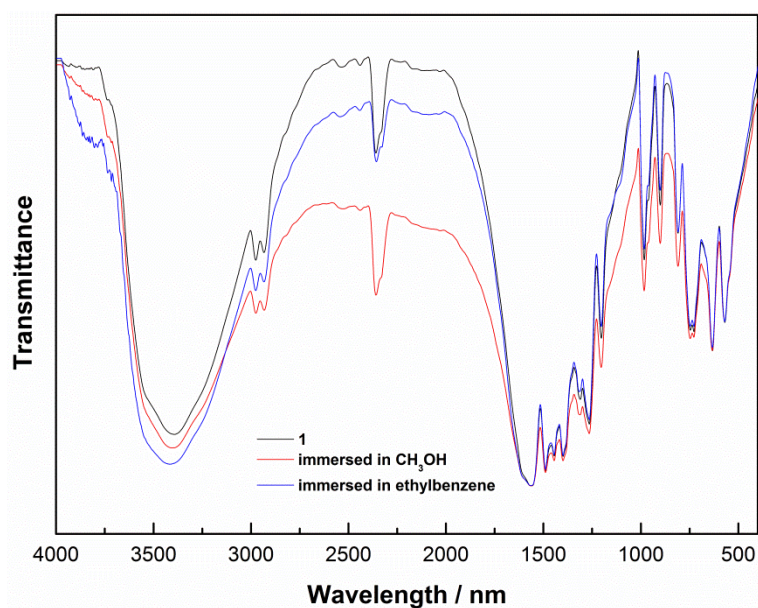


Fig. S7 FT-IR spectra for HMOF **1**, HMOF **1** immersed in CH_3OH and in ethylbenzene for half an hour.

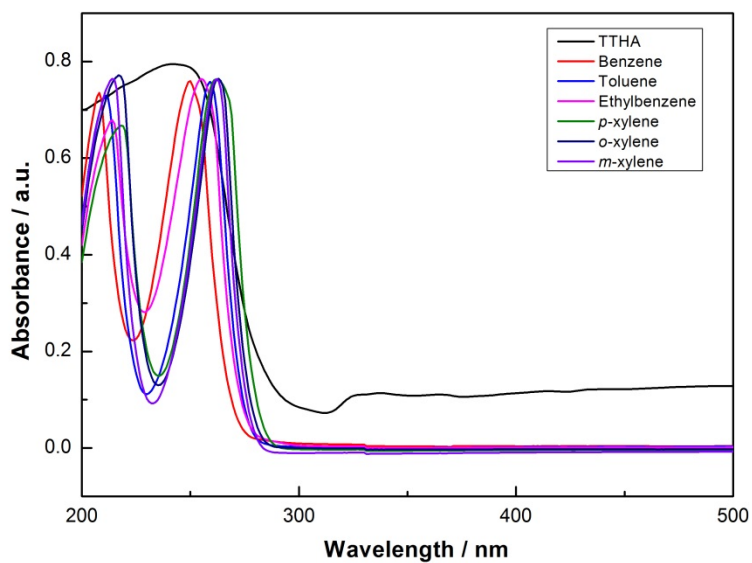


Fig. S8 The UV-vis absorption spectra for H₆TTHA, benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene and *o*-xylene.

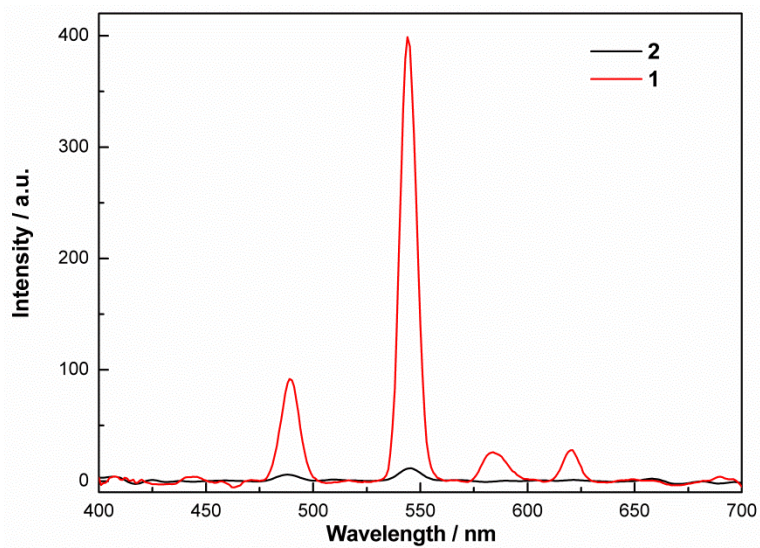


Fig. S9 The contrast of solid-state emission spectra between **2** and **1** at room temperature when excited at 280 nm.