

## Electronic Supporting Information for

### **A luminescent terbium MOF containing uncoordinated carboxyl groups exhibits highly selective sensing for Fe<sup>3+</sup> ions**

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Fig S5 The UV-vis absorption spectrum of the 0.01M different metal ion aqueous solutions.

## 1. Materials and methods:

All reagents and solvents were used as received from commercial supplies without further purification.

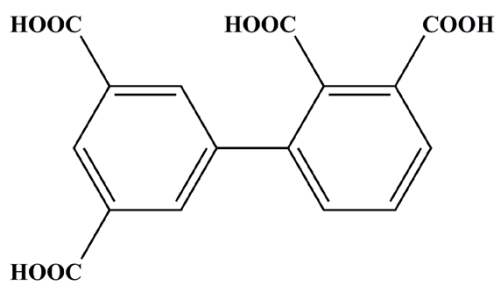
Fourier transform infrared (FTIR) spectra (KBr disk) were measured with a TENSOR 27 FI-IR spectrophotometer. Elemental analyses for C and H were obtained from a Perkin-Elmer 2400 elemental analyzer. The TG curves were recorded on a STA409PC Thermal analyzer were performed under the  $N_2$  atmosphere and at a heating rate of  $10^\circ C/min$  over the temperature range of  $20 \sim 1100^\circ C$ . Powder X-ray diffraction pattern (PXRD) was carried out on a EMPYREAN PANALYTICAL apparatus.

The luminescence spectra for the powdered solid samples were obtained at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. PMT Voltage = 700V, the excitation slit and the emission slit were 1 nm. The luminescence sensing properties of TbMOF-COOH in aqueous solution

were examined under the same conditions except that excitation slit and the emission slit were 5 nm.

The solid-excitation and emission spectra of TbMOF-COOH were investigated at room temperature. To explore the luminescence sensing properties of TbMOF-COOH in aqueous solution, the testing emulsions were prepared by dispersing the grinding TbMOF-COOH into aqueous solution containing various metal ions under ultrasonication for 30 min and stirring for 6h.

## 2. Structure of H<sub>4</sub>btca



[1,1'-biphenyl]-2,3,3',5'-tetracarboxylic acid(H<sub>4</sub>btca)

## 3. Preparation of TbMOF-COOH:

A mixture of Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.5 mmol), H<sub>4</sub>btca (0.5 mmol) and distilled water (16 ml) was sealed in a Teflon-lined stainless vessel (25ml). The vessel was heated to 140°C in 4 h and kept for 96 h under autogenous pressure. Then the reaction system was cooled to room temperature at a rate of 3°C/h. Flaxen block-like crystals were collected by filtration, washed with water, and then dried in the air.

[Tb(Hbtca)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O (TbMOF-COOH) Yield: 75 % (based on Tb<sup>3+</sup>).  
Elemental analysis calculated (%) for C<sub>16</sub>H<sub>13</sub>O<sub>11</sub>Tb (540.18): C, 35.57; H,

2.42, Found: C, 35.55; H, 2.43. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3566(w), 3378(w), 1703(m), 1618(s), 1533(m), 1449(s), 1389(s), 1243(w), 778(s), 735 (s).

#### **4. X-ray Crystallography:**

Structure determination was performed on a Agilent Xcalibur E X-ray single crystal diffractometer equipped with graphite-monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293K. Empirical absorption corrections were applied using the SADABS program.<sup>1</sup> The structure of TbMOF-COOH was solved by direct methods and refined anisotropically by full-matrix least squares techniques on  $F^2$  values, using the SHELX-97 program.<sup>2</sup> Hydrogen atoms were added on appropriate positions in theory and refined with isotropic thermal parameters riding on those parent atoms. The corresponding crystallographic and refinement data for TbMOF-COOH are listed in Table S1. Selected bond lengths and angles are listed in Table S2. CCDC-1005400 corresponds to TbMOF-COOH, containing the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### **References**

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

2 G. M. Sheldrick, SHELXTL. Bruker Analytical X-ray Instruments Inc.  
version 5.1. Madison, WI, 1998.

Table S1. Crystal data and structure refinement parameters for TbMOF-COOH.

Compound	TbMOF-COOH
Empirical formula	C <sub>16</sub> H <sub>13</sub> O <sub>11</sub> Tb
Formula weight	540.18
Temperature (K)	293(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	8.8300(9)
<i>b</i> / Å	10.2225(11)
<i>c</i> / Å	10.2870(12)
$\alpha$ /(°)	66.855(11)
$\beta$ /(°)	74.036(10)
$\gamma$ /(°)	75.820(9)
<i>Z</i>	2
Density(calculated)	2.212
<i>F</i> (000)	524
Crystal size/mm <sup>3</sup>	0.03 x 0.02 x 0.01
Range for data collection/(°)	2.50 –25.02
Limiting indices	-9 ≤ <i>h</i> ≤ 10, -12 ≤ <i>k</i> ≤ 11, -12 ≤ <i>l</i> ≤ 12
Reflections collected / unique	5078 / 2856 [R(int) = 0.0712]
Data / restraints / parameters	2856 / 720 / 253
Goodness-of-fit on F <sup>2</sup>	1.018
Volume / Å <sup>3</sup>	810.99(15)
Final R indices [ <i>I</i> >2σ( <i>I</i> )]	R <sub>1</sub> = 0.0527, wR <sub>2</sub> = 0.0788
R indices (all data)	R <sub>1</sub> = 0.0743, wR <sub>2</sub> = 0.0951

Table S2. Selected bond distances (Å) and angles (°) for TbMOF-COOH.

Bond length (Å)			
Tb(1)–O(3)A	2.287(5)	Tb(1)–O(7)B	2.345(6)
Tb(1)–O(8)C	2.343(6)	Tb(1)–O(4)D	2.393(5)
Tb(1)–O(2)	2.435(5)	Tb(1)–O(9w)	2.446(5)
Tb(1)–O(1)	2.467(6)	Tb(1)–O(10w)	2.503(6)
Bond angle(°)			
O(3)A–Tb(1)–O(7)B	76.9(2)	O(3)A–Tb(1)–O(8)C	79.6(2)
O(7)B–Tb(1)–O(8)C	130.0(2)	O(3)A–Tb(1)–O(4)D	124.6(2)
O(7)B–Tb(1)–O(4)D	75.6(2)	O(8)C–Tb(1)–O(4)D	82.9(2)
O(3)A–Tb(1)–O(2)	86.9(2)	O(7)B–Tb(1)–O(2)	79.7(2)
O(8)C–Tb(1)–O(2)	141.9(2)	O(4)D–Tb(1)–O(2)	132.7(2)
O(3)A–Tb(1)–O(9w)	143.4(2)	O(7)B–Tb(1)–O(9w)	139.3(2)
O(8)C–Tb(1)–O(9w)	71.3(2)	O(4)D–Tb(1)–O(9w)	73.7(2)
O(2)–Tb(1)–O(9w)	102.6(2)	O(3)A–Tb(1)–O(1)	135.2(2)
O(7)B–Tb(1)–O(1)	76.4(2)	O(8)C–Tb(1)–O(1)	144.1(2)
O(4)D–Tb(1)–O(1)	81.7(2)	O(2)–Tb(1)–O(1)	53.4(2)
O(9w)–Tb(1)–O(1)	73.4(2)	O(3)A–Tb(1)–O(10w)	77.3(2)
O(7)B–Tb(1)–O(10w)	140.8(2)	O(8)C–Tb(1)–O(10w)	72.5(2)
O(4)D–Tb(1)–O(10w)	143.7(2)	O(9w)–Tb(1)–O(10w)	73.3(2)
O(2)–Tb(1)–O(10w)	69.8(2)	O(1)–Tb(1)–O(10w)	102.9(2)

A:  $-x+2, -y+1, -z$ ; B:  $-x+1, -y+1, -z+1$ ; C:  $x+1, y+1, z-1$ ; D:  $x, y+1, z$ .

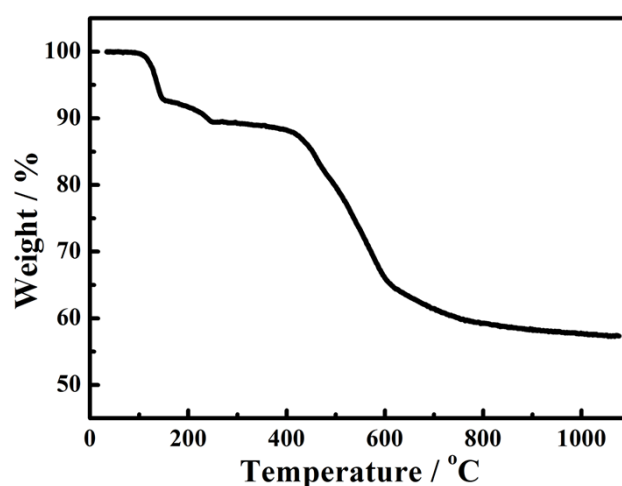
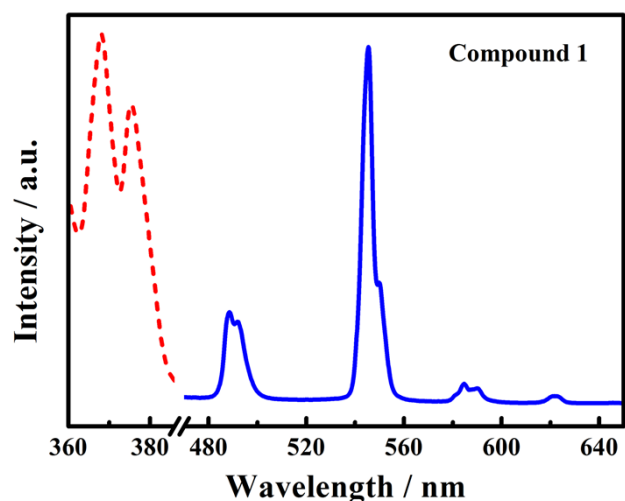
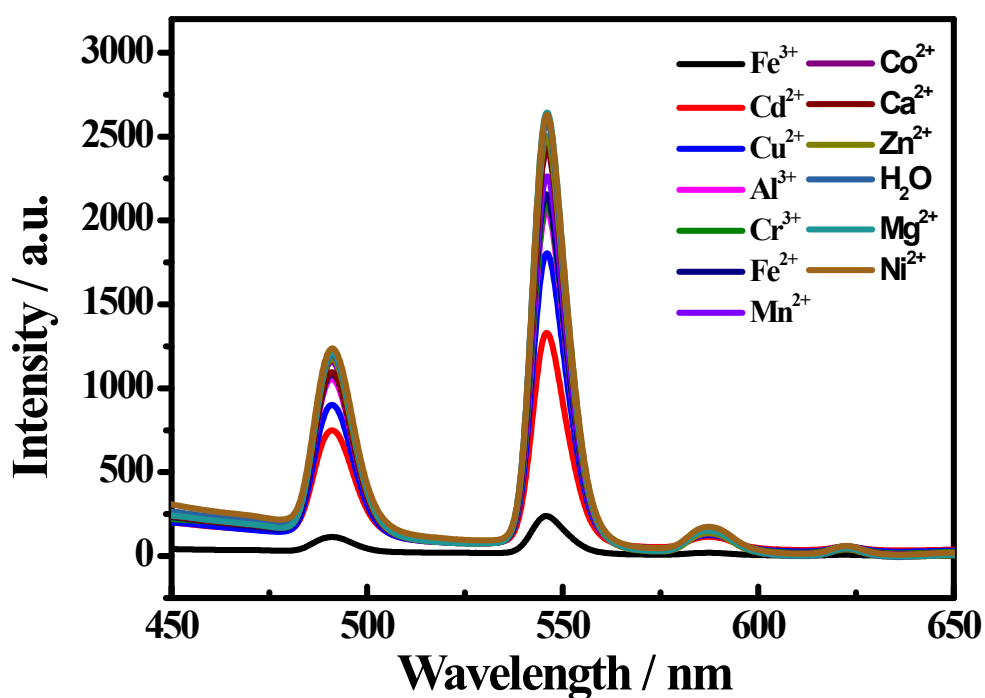


Fig. S1 Thermogravimetric analyses of TbMOF-COOH.



**Fig. S2** Solid-state excitation (dashed) and emission spectra (solid) of TbMOF-COOH.



**Fig. S3** The luminescence intensities of TbMOF-COOH immersed in the individual aqueous solution of  $M^{z+}$  ions ( $M^{z+} = Ni^{2+}, Cu^{2+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{2+}, Mn^{2+}$  and  $Fe^{3+}$ , 0.01 M).

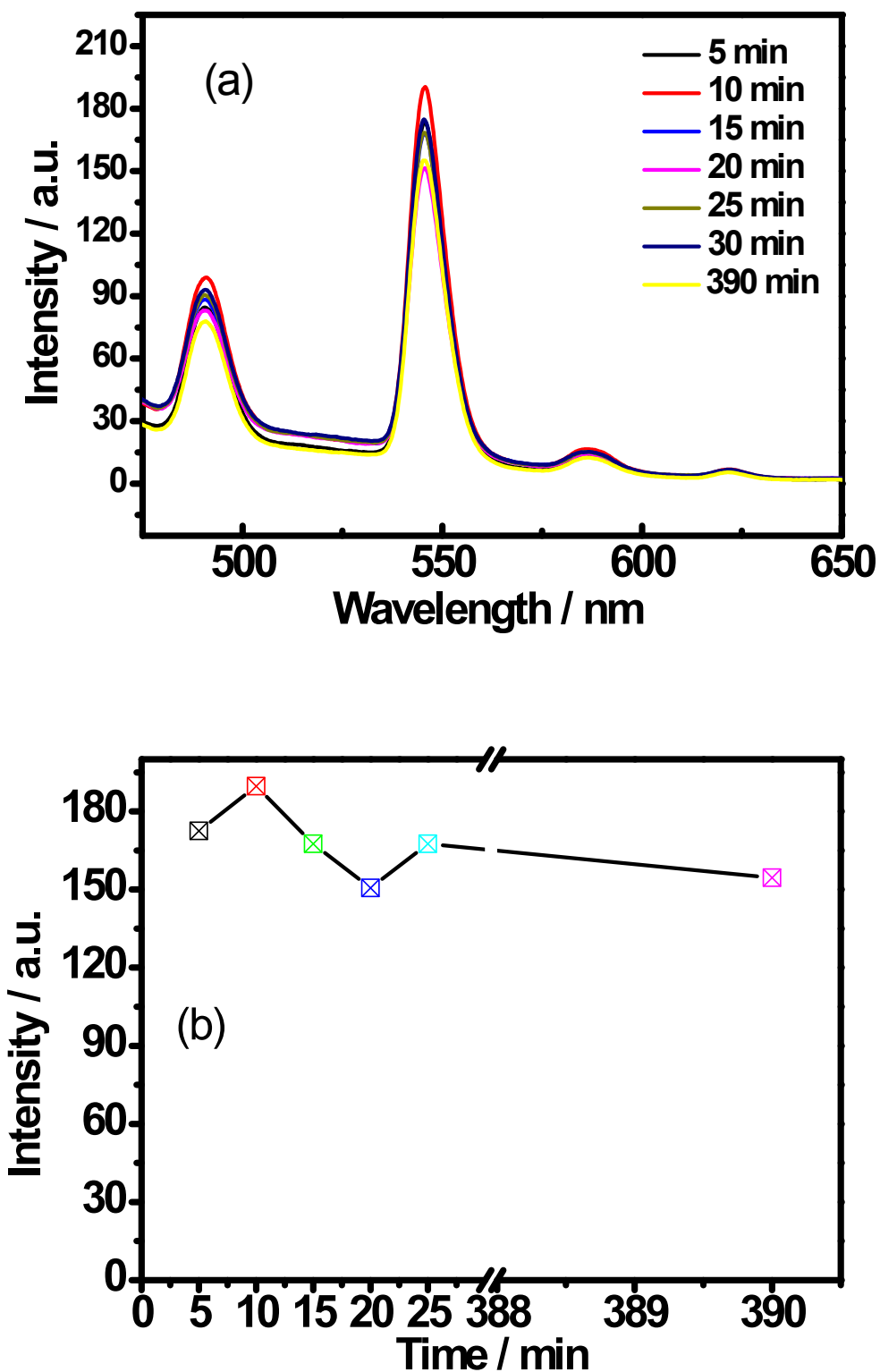
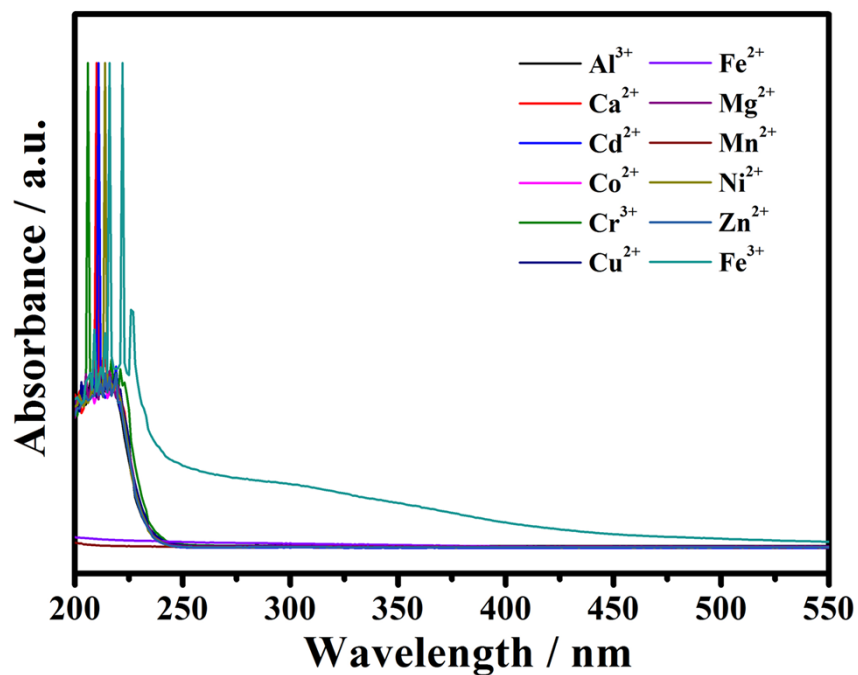


Fig. S4 (a) Variation of luminescence intensity of TMOF-COOH solid powder immersed in 0.01M Fe<sup>3+</sup> aqueous solution. (b) The corresponding



luminescence intensities of the  ${}^5D_4 \rightarrow {}^7F_5$  transition.



**Fig. S5** The UV-vis absorption spectrum of the 0.01M different  $M^{z+}$  ( $M^{z+} = Ni^{2+}, Cu^{2+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{2+}$  and  $Fe^{3+}$ ) aqueous solution.