

Supporting Information for

**Post-Synthetic Modification of Tb-based Metal–Organic Framework for  
Highly Selective and Sensitive Detection of Metal Ions in Aqueous  
Solution**

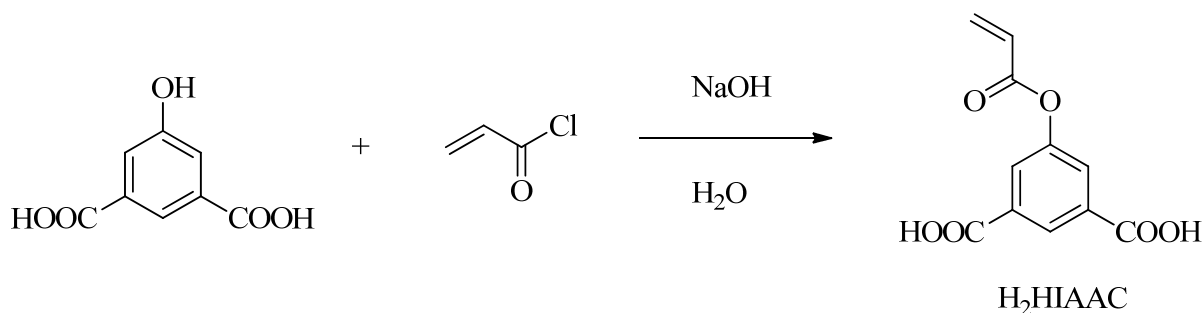
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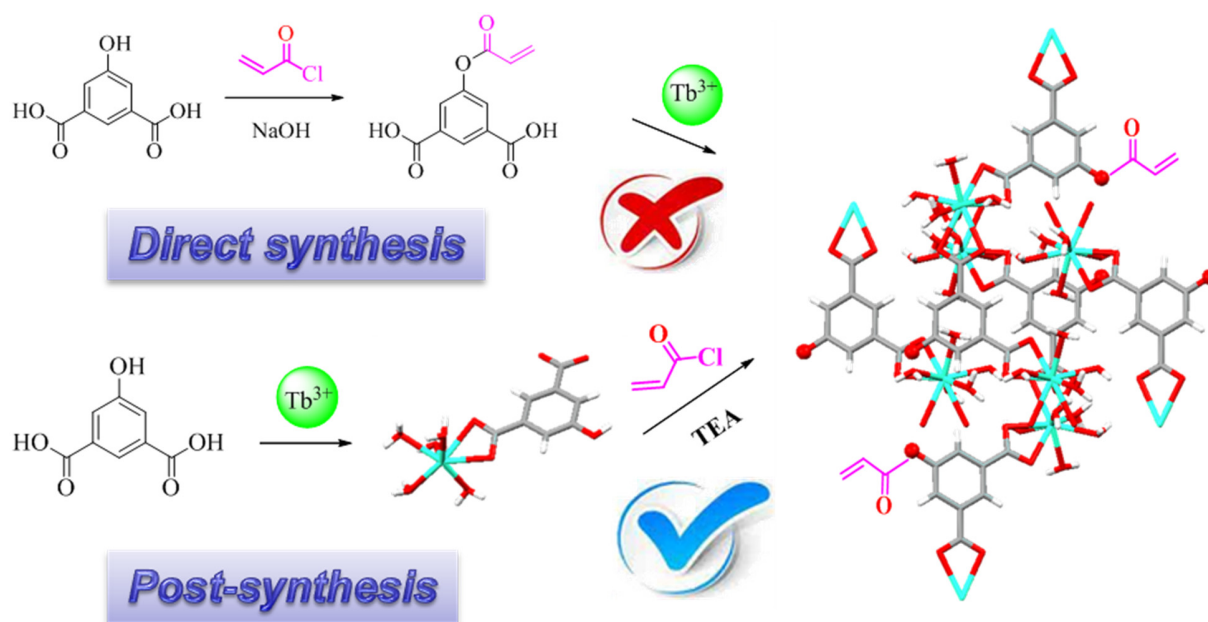
## 1. Materials and Methods.

**Reagents and chemicals:** All reagents and solvents were of AR grade and used without further purification unless otherwise noted. 5-Hydroxyisophthalic acid was provided from Beijing Innochem Science & Technology Co.,Ltd. Metal nitrate salts were provided from Shanghai Fourth Chemical Reagent Company (China). Stock solution ( $2 \times 10^{-2}$  M) of the aqueous nitrate salts of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  were prepared for further experiments.

**Instruments and spectroscopic measurements:**  $^1\text{H}$  NMR spectra were measured on a Bruker-400 spectrometer with  $\text{Me}_4\text{Si}$  as an internal standard. X-ray powder diffraction (XRD) patterns of the Tb-HIA and Tb-HIAAC were recorded on a Rigaku D/max-2400 X-ray powder diffractometer (Japan) using  $\text{Cu-K}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation. Elemental analyses (C, H, O) were performed on an Elementar Vario EL analyzer. The metal content were measured by Inductively Coupled Plasma Spectrometer (Perkin Elmer). FT-IR spectra were recorded as KBr pellets on JASCO FT/IR-430. Fluorescence spectra of the solution were obtained using the F-4600 spectrometer (Hitachi). Both excitation and emission slit widths were 2.5 nm. Fluorescence measurements were carried out in a 1 cm quartzcuvette with stirring the suspension of Tb-HIAAC.



**Synthesis of H<sub>2</sub>HIAAC:** 5-Hydroxyisophthalic acid (1.82 g, 0.010 mol) was neutralized with an equivalent NaOH solution, and then the mixture was placed into a flask. Acryloyl chloride (1.09 g, 0.012 mol) was added dropwise within 2 h at 0 °C and stirred at room temperature for an additional 12 h. Finally, the mixture was adjusted to acid with dilute hydrochloric acid and subsequently washed with water and hot water. After drying, H<sub>2</sub>HIAAC was obtained. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.39 (s, 1H), 7.92 (s, 2H), 6.6 (d, *J* = 8.0 Hz, 1H), 6.41 (q, *J* = 8.0 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H).



**Synthesis of Tb-HIA1:** 5-(acryloyloxy)isophthalic acid (H<sub>2</sub>HIAAC, 0.03 mmol, 7.1 mg), Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.045 mmol, 20 mg), NaOH (0.06 mmol, 2.4 mg), H<sub>2</sub>O (3 mL) were placed in a 10 mL glass vial, which was sealed and heated to 110 °C for 72 h, and then cooled to room temperature. The colorless crystals formed were collected and air-dried (60% based on H<sub>2</sub>HIAAC).

**Synthesis of Tb-HIA:** 5-hydroxyisophthalic acid (H<sub>2</sub>HIA, 0.03 mmol, 5.5 mg), Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.045 mmol, 20 mg), NaOH (0.06 mmol, 2.4 mg), H<sub>2</sub>O (2 mL) were placed in a 10 mL glass

vial, which was sealed and heated to 110 °C for 72 h, and then cooled to room temperature. The colorless crystals formed were collected and air-dried (94% based on H<sub>2</sub>HIA). Anal calc. for C<sub>8</sub>H<sub>14</sub>NO<sub>13</sub>Tb: C 19.56, H 2.87, O 42.35%; Found: C 19.57, H 2.90, O 42.33%.

**Post-Synthesis of Tb-HIA:** To a solution of Tb-HIA (54 mg) in dry dichloromethane (5 mL) was dropwise added acryloyl chloride (0.5 mL) and Et<sub>3</sub>N (0.2 mL). The resulting mixture was stirred at room temperature and stirred overnight. After the reaction, the colorless product of Tb-HIAAC was obtained. The products were collected by filtration, washed with dichloromethane, and dried in air.

## 2. X-ray Crystallography (Single-crystal diffraction) and Characterizations.

### 2.1 Crystal data of Tb–HIA:

$C_8H_{14}NO_{13}Tb$ ,  $M_r = 491.12$ , Monoclinic, space group  $C2/c$ ,  $a = 19.6573(14)$ ,  $b = 10.5231(7)$ ,  $c = 17.6988(12)$  Å,  $\alpha = 90.00$ ,  $\beta = 107.4200(10)$ ,  $\gamma = 90.00$ ,  $V = 3493.2(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.868$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 4.109$  mm<sup>-1</sup>,  $T = 173(2)$  K. 9997 unique reflections [ $R_{\text{int}} = 0.0.97$ ]. Final  $R_I$ [with  $I > 2\sigma(I)$ ] = 0.0446,  $wR_2(\text{all data}) = 0.1427$ , GOOF = 1.028. CCDC number: 1856599.

### 2.2 Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo- $K\alpha$  ( $\lambda = 0.71073$  Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods with SHELXTL version 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. Hydrogen atoms of the carboxylate moieties were found from the difference Fourier maps and refined with the isotropic parameters fixed as 1.5 times of those oxygen atoms they attached and with the O–H distance fixed at 0.85 Å.

### 2.3 Table S1. Selective bond distance (Å) and angle (°) in Tb–HIA.

Tb(1)–O(5W)	2.380(5)	Tb(1)–O(4W)	2.388(4)
Tb(1)–O(3W)	2.394(5)	Tb(1)–O(1W)	2.402(6)
Tb(1)–O(3)	2.441(5)	Tb(1)–O(2W)	2.444(4)

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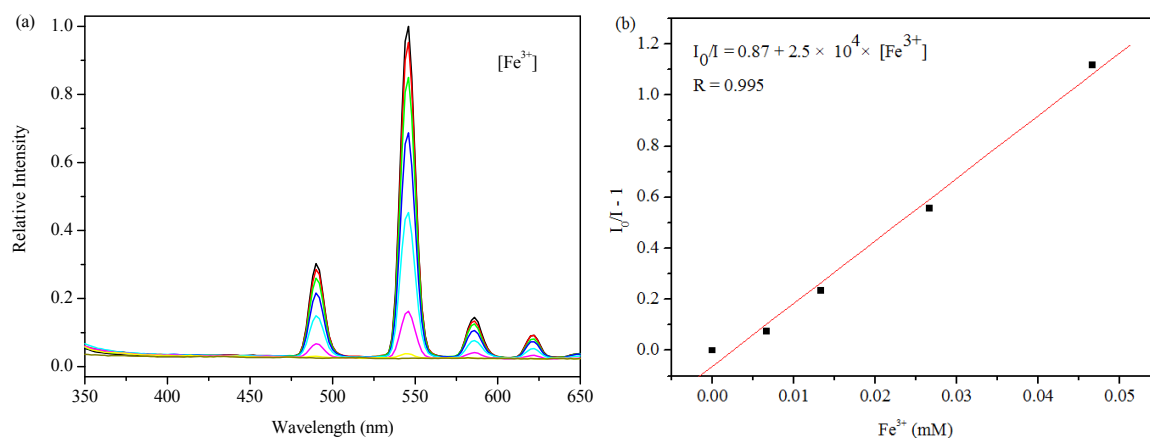
Tb(1)–O(2A)	2.470(4)	Tb(1)–O(1A)	2.491(5)
Tb(1)–O(4)	2.505(4)		
O(5W)–Tb(1)–O(4W)	138.80(16)	O(5W)–Tb(1)–O(3W)	72.84(17)
O(4W)–Tb(1)–O(3W)	76.74(16)	O(5W)–Tb(1)–O(1W)	145.02(19)
O(4W)–Tb(1)–O(1W)	75.25(19)	O(3W)–Tb(1)–O(1W)	136.66(18)
O(5W)–Tb(1)–O(3)	71.48(18)	O(4W)–Tb(1)–O(3)	141.25(17)
O(3W)–Tb(1)–O(3)	141.70(17)	O(1W)–Tb(1)–O(3)	74.4(2)
O(5W)–Tb(1)–O(2W)	70.54(17)	O(4W)–Tb(1)–O(2W)	73.71(17)
O(3W)–Tb(1)–O(2W)	71.00(16)	O(1W)–Tb(1)–O(2W)	129.5(2)
O(3)–Tb(1)–O(2W)	108.94(17)	O(1)–Tb(1)–O(4)	144.11(18)
O(5W)–Tb(1)–O(2A)	76.06(16)	O(4W)–Tb(1)–O(2A)	127.74(15)
O(3W)–Tb(1)–O(2A)	82.24(15)	O(1W)–Tb(1)–O(2A)	87.5(2)
O(3)–Tb(1)–O(2A)	74.13(14)	O(2W)–Tb(1)–O(2A)	142.89(16)
O(5W)–Tb(1)–O(1A)	118.18(18)	O(4W)–Tb(1)–O(1A)	75.65(15)
O(3W)–Tb(1)–O(1A)	71.00(17)	O(1W)–Tb(1)–O(1A)	70.4(2)
O(3)–Tb(1)–O(1A)	115.26(16)	O(2W)–Tb(1)–O(1A)	135.42(17)
O(2)–Tb(1)–O(1A)	52.11(15)	O(5W)–Tb(1)–O(4)	91.28(17)
O(4W)–Tb(1)–O(4)	96.04(15)	O(3W)–Tb(1)–O(4)	141.97(15)
O(1W)–Tb(1)–O(4)	73.7(2)	O(3)–Tb(1)–O(4)	52.35(14)
O(2W)–Tb(1)–O(4)	71.14(16)	O(2)–Tb(1)–O(4)	126.07(14)

Symmetry code A:  $x, -y, -0.5+z..$

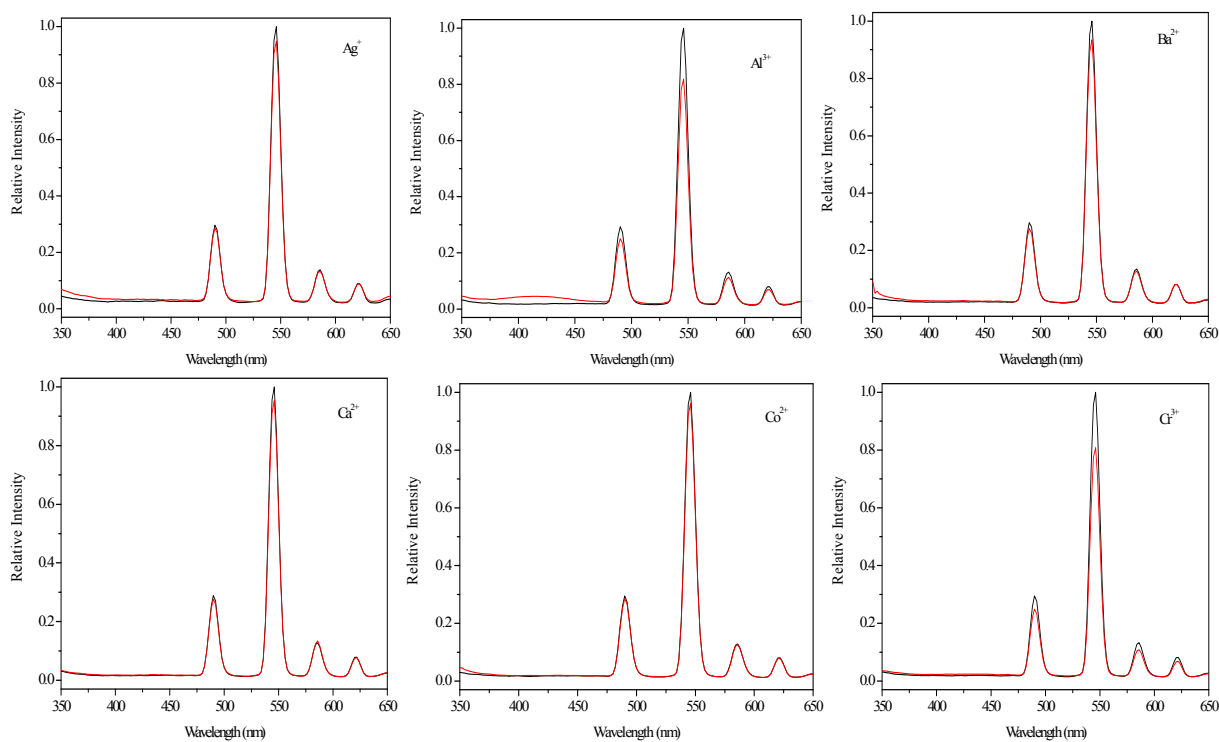
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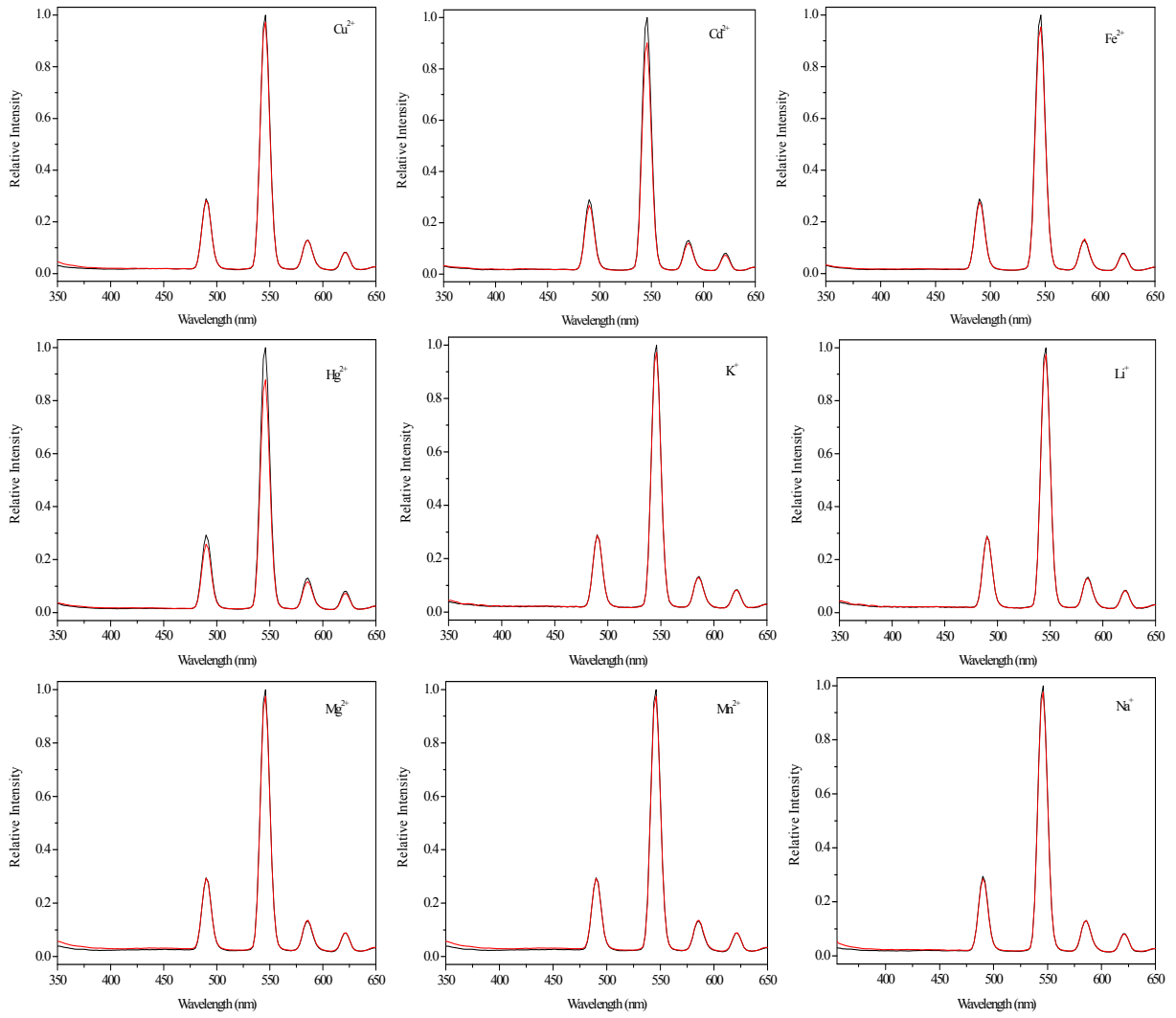
### 3. Recognition properties for metal ions based on Tb–HIAAC.

**3.1 Figure S1.** (a) The fluorescence spectra of Tb–HIAAC in water solution upon the addition of 0.20 mM of  $\text{Fe}^{3+}$ . (b) The Stern–Volmer plot of Tb–HIAAC quenched by  $\text{Fe}^{3+}$  aqueous solution.

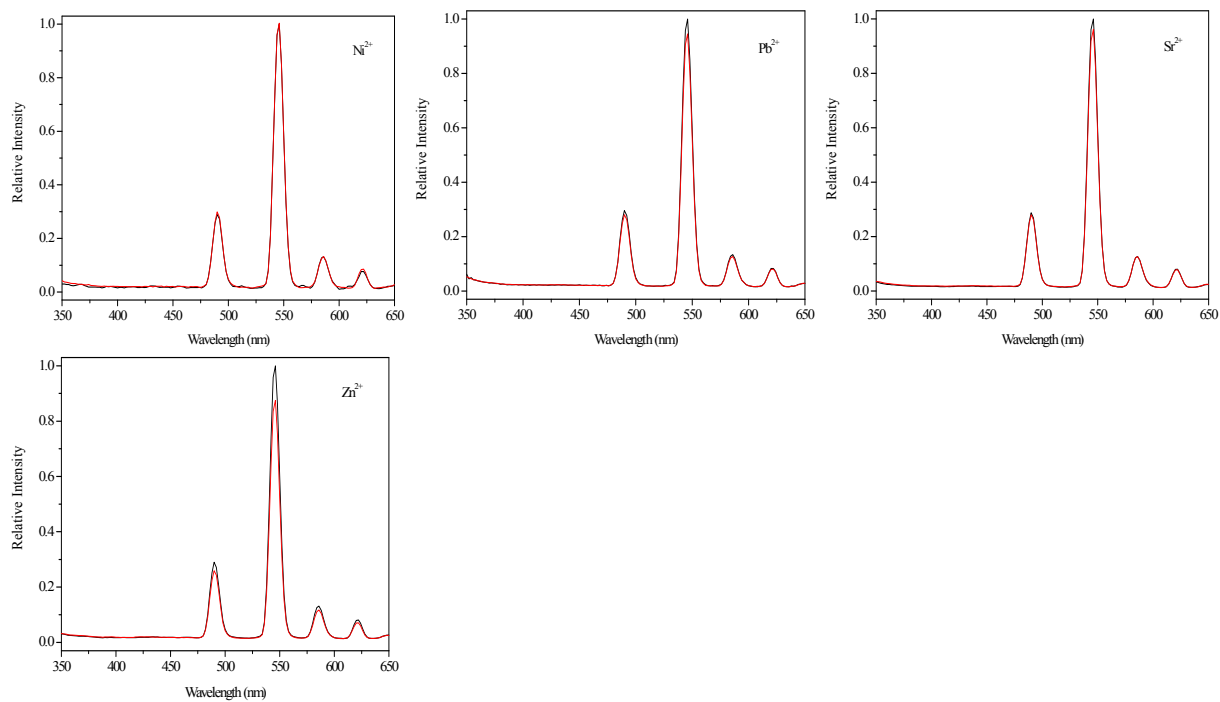


**3.2 Figure S2.** The fluorescence spectra of Tb–HIAAC in water solution upon the addition of 0.20 mM of various metal ions.

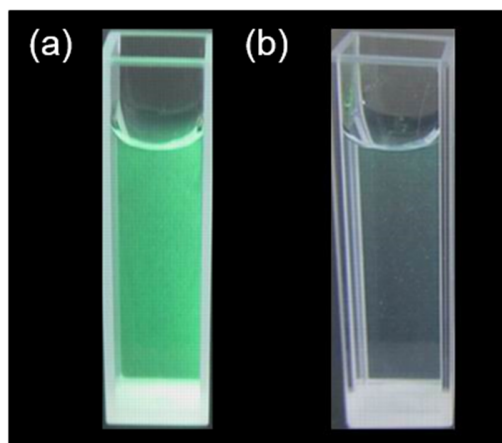








**3.3 Figure S3.** The luminescence change before (a) and after the addition of  $\text{Fe}^{3+}$  (0.20 mM, b) on MOF Tb-HIAAC under 254 nm UV radiation.



**3.4 Table S2** Comparison of the detective sensitivity in various MOFs for Fe<sup>3+</sup>.

No.	References	MOF	Detection limit
1	<i>Dalton Trans.</i> , 2018, 47, 16190	FJU-13a-Eu FJU-13a-Tb	1.41 μM 1.01 μM
2	<i>New J. Chem.</i> , 2016, 40, 8600	[Eu(bpda) <sub>1.5</sub> H <sub>2</sub> O] <sub>n</sub>	0.9 μM
3	<i>ACS Appl. Mater. Interfaces</i> , 2017, 9, 10286	BUT-14	3.8 μM
4	<i>Cryst. Growth Des.</i> , 2016, 16, 5429	BUT-15 {[Eu <sub>2</sub> K <sub>2</sub> (dcppa) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]·5H <sub>2</sub> O} <sub>n</sub>	0.8 μM 1.0 μM
5	<i>J. Mater. Chem. A</i> , 2014, 2, 13691	Eu <sup>3+</sup> @MIL-53-COOH (Al)	0.5 μM
6	<i>Chem. Eur. J</i> , 2016, 22, 18769	Eu <sub>4</sub> L <sub>3</sub>	10 μM
7	<i>Dalton Trans</i> , 2018, 47, 9466	{[Cd <sub>3</sub> (HL) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]·3H <sub>2</sub> O·2CH <sub>3</sub> CN} <sub>n</sub>	90.6 μM
8	<i>Dalton Trans</i> , 2018, 47, 11806	PCN-604	6.2 μM
9	<i>ACS Appl. Mater. Interfaces</i> , 2018, 10, 23976	Tb-MOF	1.0 μM
10	<i>J. Mater. Chem. C</i> , 2017, 5, 2015	534-MOF-Tb	0.13 mM
11	<i>CrystEngComm</i> , 2017, 19, 2570	[Cd(μ <sub>6</sub> -cpta) <sub>2</sub> (py) <sub>2</sub> ] <sub>n</sub>	0.21 mM
12	This work	Tb-HIAAC	70 nM
13	This work	Tb-HIA	n.d.

#### 4. Recognition properties for metal ions based on Tb–HIA.

4.1 **Figure S4.** The fluorescence spectra of Tb–HIA in water solution upon the addition of 0.20 mM of various metal ions.

