# Supporting Information

## A difunctional metal organic framework with Lewis basic sites

# demonstrating turn-off sensing of Cu<sup>2+</sup> and sensitization of Ln<sup>3+</sup>

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### Materials and Instrumentation:

All chemicals were obtained commercially and used without additional purification. Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD II area-detector diffractometer with graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at room temperature. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer and the metal conents were determined with a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 4000-400 cm<sup>-1</sup> on Mattson Alpha-Centauri spectrometer using KBr pellets. Thermal gravimetric (TG) analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N<sub>2</sub> with a heating rate of 10 °C/min. Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAX-3 instrument with Cu  $K\alpha$  radiation in the angular range 2 $\theta = 3^{\circ}$ -50° at 293 K. Gas adsorption measurement was measured with Quantachrome Autosorb-iQ. The emission spectra were recorded using the F-4500 FL spectrophotometer.

## Synthesis of [Zn(BPTC)0.5(Tz)]·DMF·CH<sub>3</sub>OH (1):

A mixture of biphenyl-3,3',5,5'-tetracarboxylate (H<sub>4</sub>BPTC, 17mg, 0.05 mmol), tetrazolate (Tz, 35mg, 0.5 mmol) and Zn(Ac)<sub>2</sub>·2H<sub>2</sub>**O** (30 mg, 0.15 mmol) were dissolved in 3 mL N,N-dimethylformamide (DMF) and 3 mL methanol(MeOH) and stirred for 10 minutes. Then the mixture was transferred into and sealed in a Teflon reactor (18 mL) and heated at 100 °C for 72 h. Colorless block crystals of the product were formed and collected by filtration and washed with DMF several times after the mixture was cooled to room temperature. Yield: 30 mg (~48.8% based on H4BPTC). Elemental analysis for C<sub>13</sub>H<sub>15</sub>N<sub>5</sub>O<sub>6</sub>Zn (%): calcd. H: 3.75, C: 38.77, N: 17.39%. found: H: 3.81, C: 38.69, N: 17.46%.

## X-ray Crystallography:

Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD II area-detector diffractometer with graphite-monochromated Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography. Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through the full-matrix least-squares method on F2 using SHELXS-97. The total interstitial solvent molecule contents were determined by TGA.

Crystal data of 1: Monoclinic, Fw = 4128.19 g/mol, space group P21/c, Z = 4, a = 12.345 (5) Å, b = 9.502 (5) Å, c = 18.610 (5) Å,  $\beta = 99.448$  (5) deg, V = 2153.4 (15) Å<sup>3</sup>, T = 293 (2) K, 11092 reflections measured, 3870 independent reflections ( $R_{int} = 0.0339$ ). The final  $R_1$  values were 0.0806 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.2790 ( $I > 2\sigma(I)$ ). The goodness of fit on  $F^2$  was 1.098.

#### Gas adsorption experiment

The  $N_2$  and  $CO_2$  sorption measurements were performed on an automatic volumetric adsorption equipment (Quantachrome Autosorb-iQ). Before gas adsorption measurements, the synthesized sample was immersed in dichloromethane for 24 h,

and the extract was decanted. Fresh dichloromethane was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the dichloromethane solvates. After the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum at 373 K overnight to obtain desolvated sample (donated as 1a). Before the measurement, 1a was dried again by using the 'outgas' function of the surface area analyzer for 12 h at 373 K.

#### **Experiment of sensing metal ions**

For the experiments of sensing metal ions, powder of **1a** (3 mg) was immersed in methanol solutions containing MCl<sub>x</sub> (10<sup>-1</sup> M;  $M = K^+$ , NH<sub>4</sub><sup>+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> Ba<sup>2+</sup> Co<sup>2+</sup>,Cu<sup>2+</sup>) as well as the same way used for the sensing in mixed metal ions (the concentration of  $10^{-2}$  M for Cu<sup>2+</sup> ion and  $10^{-1}$  M for other metal ions). Before photoluminescence measurements, the suspensions were oscillated for 30 min using ultrasonic waves to ensure uniform dispersion. For the titration experiments of Cu<sup>2+</sup> ion, **1a** powder (3 mg) was immersed in methanol solutions contain other metal ions with the dropped addition of different concentrations of Cu<sup>2+</sup> in methanol.

### Encapsulation of lanthanide(III) ions in 1a:

Desolvated compound **1** (50 mg) was soaked in the methanol solutions of the chloride salts of  $Eu^{3+}$ ,  $Tb^{3+}$ ,  $Sm^{3+}$  and  $Dy^{3+}$  (2 mL, 0.4 mmol). After soaking for 2 days, the crystals were washed with methanol several times to remove residual lanthanide(III) cations on the surface.



Fig. S1 The asymmetric unit in compound 1.



Fig. S2 The 1D rhomboid channel viewed along 110 direction.



Fig. S3 The triangle channels in compound 1 viewed along c axis.



Fig. S4 The *bbf* topology of compound 1.



Fig. S5 Powder X-ray diffraction patterns of simulated from the X-ray single structure

of **1**, as-synthesized **1** and desolvated **1a**.



Fig. S6 The IR spectroscopy of compound 1 and H<sub>4</sub>BPTC.



Fig. S7 The TG curve of compound 1



Fig. S8 The TG curve of desolvated compound 1 (1a).



Fig. S9 Colour change of compound 1a before and after sorption of  $Cu^{2+}$  ions.

Metal ions (M)	M/Zn Mass ratio (experimental)	M/Zn Mol ratio (calculation)
Cu	4.30/21.43	0.2
Со	0.29/21.72	0.014
Ba	0.23/23.73	0.0046
Ni	0.21/23.61	0.0098
Mn	0.18/22.32	0.009
Cd	0.10/23.62	0.002
K	0.17/22.63	0.0125

Table S1. ICP results for single metal ion adsorption in compound 1a



**Fig, S10** Stern-Volmer plot constructed for quenching of the emission of **1a** by Cu<sup>2+</sup>. Here the plot has been constructed for [Q] = 0,  $10^{-7}$ ,  $10^{-6}$ ,  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ .

	Ln <sup>3+</sup> content(%	Zn <sup>2+</sup> content (%)	The Ln <sup>3+</sup> /Zn <sup>2+</sup> Mol ratio	
Sm <sup>3+</sup> @1a	4.17	25.72	0.0702	
Dy <sup>3+</sup> @ <b>1a</b>	4.36	23.84	0.0728	
Eu <sup>3+</sup> @ <b>1a</b>	4.26	24.77	0.0735	
Tb <sup>3+</sup> @ <b>1a</b>	4.28	24.63	0.0712	

**Table S2**. ICP results for  $Ln^{3+}$  and  $Zn^{2+}$  in  $Ln^{3+}@1a$ 



Fig. S11 PXRD patterns of 1 and  $Ln^{3+}@1a$ .



**Fig. S12** Emission spectra of **1a**, Sm<sup>3+</sup>@**1a**, Dy<sup>3+</sup>@**1a**, Eu<sup>3+</sup>@**1a** and Tb<sup>3+</sup>@**1a** in the solid state at room temperature.