

## Supporting information

### **A luminescent Dye@MOF as dual-emitting platform for sensing explosives**

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## S1. Materials and measurements

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400  $\text{cm}^{-1}$  on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu  $K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation in the range of 3–60° at a rate of 5°/min. The UV-Vis absorption spectra were examined on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200–800 nm. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. TG was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 °C at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 Edinburgh Fluorescence Spectrometer.

## S2. X-ray crystallography

Single-crystal X-ray diffraction data for **1** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296(2) K. Absorption corrections were applied using multi-scan technique. Their structures were solved by the direct method of SHELXS-97 and refined by full-matrix least-square techniques with the SHELXL-97 program. Because guest molecules in the channels of **1** were highly disordered and could not be modeled properly, the SQUEEZE routine of PLATON was applied to remove their contributions to the scattering. The reported refinements are of the guest-free structures obtained by the SQUEEZE routine, and the results were attached to the CIF file.

The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table S1.

### **S3. Preparation of C<sub>60</sub>N<sub>6.5</sub>O<sub>19</sub>H<sub>60.5</sub>Zn<sub>4</sub> (1)**

A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (60 mg, 0.2 mmol), NTB (18 mg, 0.05 mmol), and NO<sub>2</sub>-bdc (21 mg, 0.1 mmol) was dissolved in 6 mL of DMA (N,N-Dimethylacetamide). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 100 °C for 3 days. Yellow crystals were obtained, which were washed with mother liquid, and dried under ambient conditions. Elemental analysis: Anal. Calcd for C<sub>60</sub>N<sub>6.5</sub>O<sub>19</sub>H<sub>60.5</sub>Zn<sub>4</sub>: C 50.11; H 4.24; N 6.33. Found: C 49.88; H 4.02; N 6.02. IR (KBr, cm<sup>-1</sup>): 441.77 (w), 837.96 (w), 710.14 (w), 593.09 (w), 676.34 (w), 1014.87 (w), 527.02 (w), 2933.27 (m), 1175.12 (m), 782.94 (m), 3434.88 (m), 1505.60 (m), 1270.12 (m), 1557.22 (s), 1313.57 (s), 1398.00 (s), 1595.04 (s).

### **S4. The description of experiment**

#### **Dye adsorption and separation**

Freshly prepared **1** (20 mg) were transferred to aqueous solutions (8 mL) of Basic Red 2/Methyl Orange, Rhodamine B (RB)/Methyl Blue, and Crystal Violet/Solvent Yellow 2 (1/1, 2 × 10<sup>-5</sup> mol L<sup>-1</sup>) in 10 mL sealed glass bottles. UV/Vis spectra and photographs were used to determine the selective adsorption ability of **1** after certain time intervals.

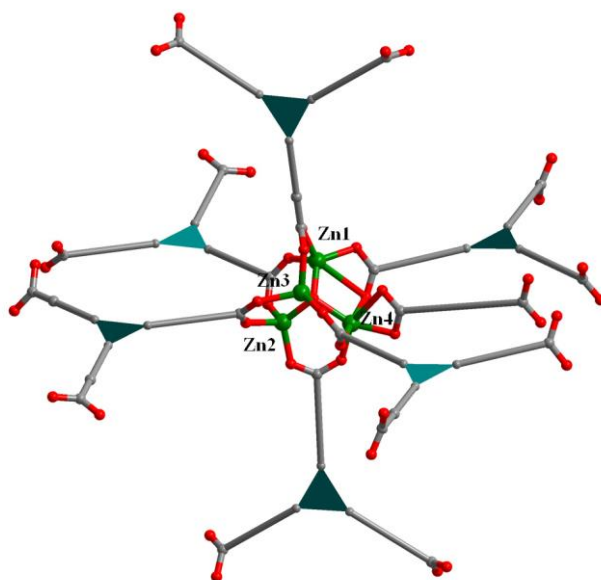
#### **Dye release**

Compound **1** loaded with Basic Red 2, Rhodamine B, and Crystal Violet (10 mg) were transferred to pure DMA and saturated NaCl in DMA solution (4 mL) in 10 mL sealed glass bottles. UV/Vis spectra were used to determine the selective release of **1** after certain time intervals.

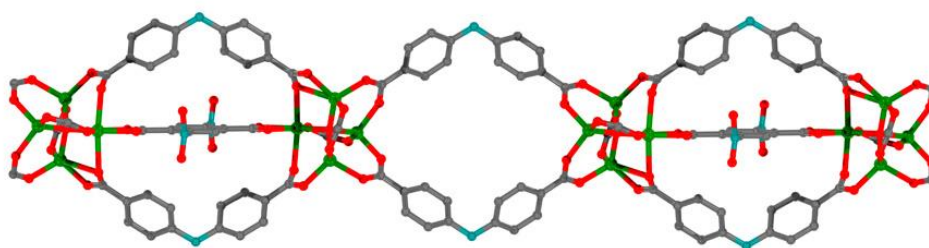
#### **The solvent sensing experiment**

The solvent sensing experiment has been performed as follows: finely ground samples of activated **1a** was immersed in different organic solvents (3 mL), treated by

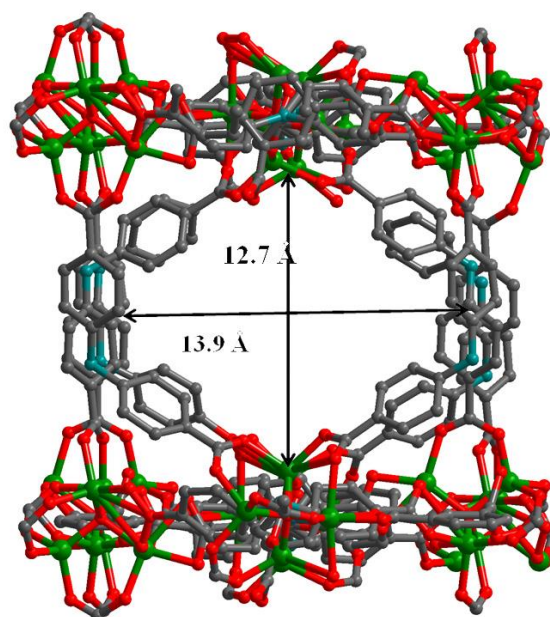
ultrasonication for 30 minutes, and then aged to form stable emulsions before fluorescence was measured.



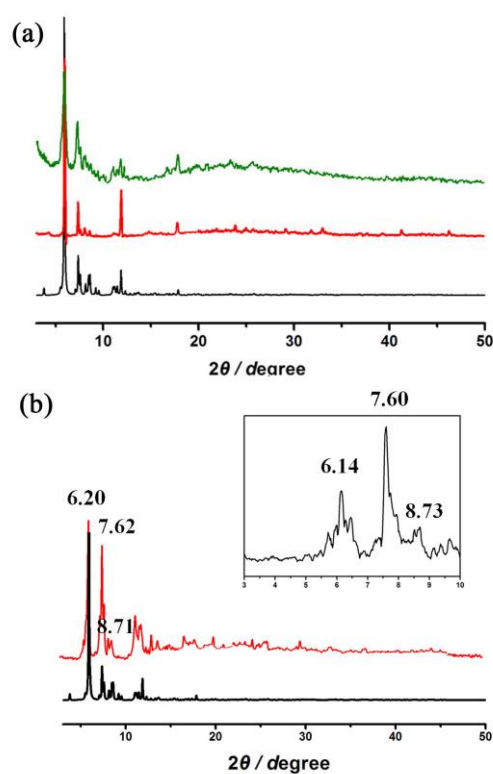
**Fig. S1** The coordination environment of the Zn(II) center.



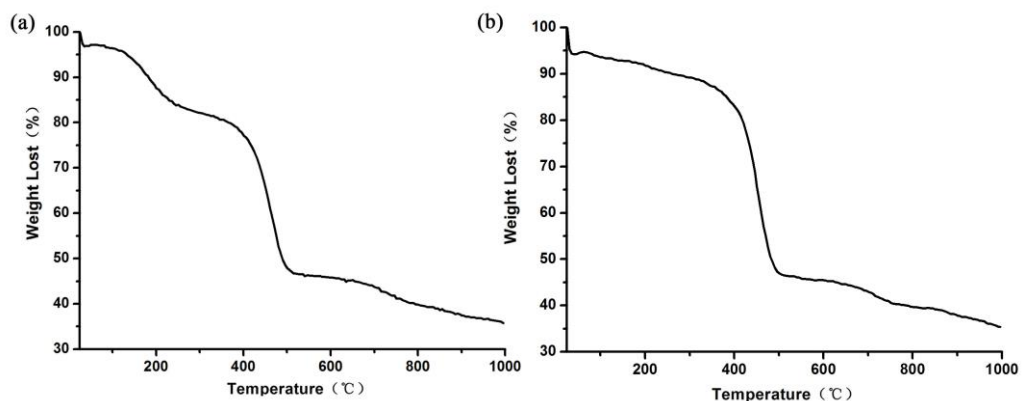
**Fig. S2** Schematic presentation of one-dimensional chains in a "A-A A" form.



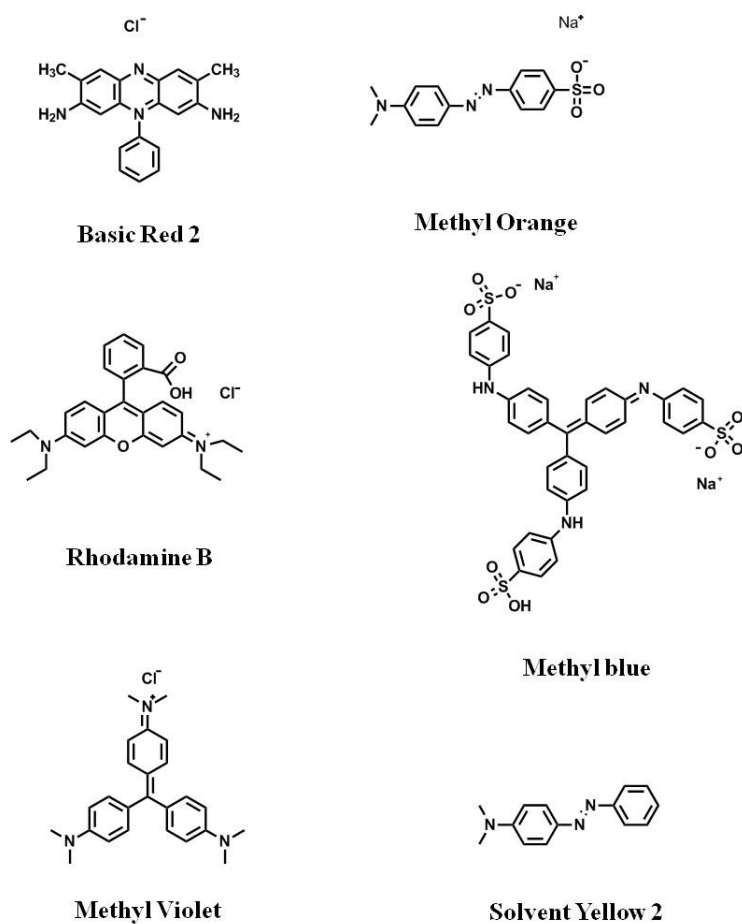
**Fig. S3** 3D presentation of hexagonal channel running along the [101] direction.



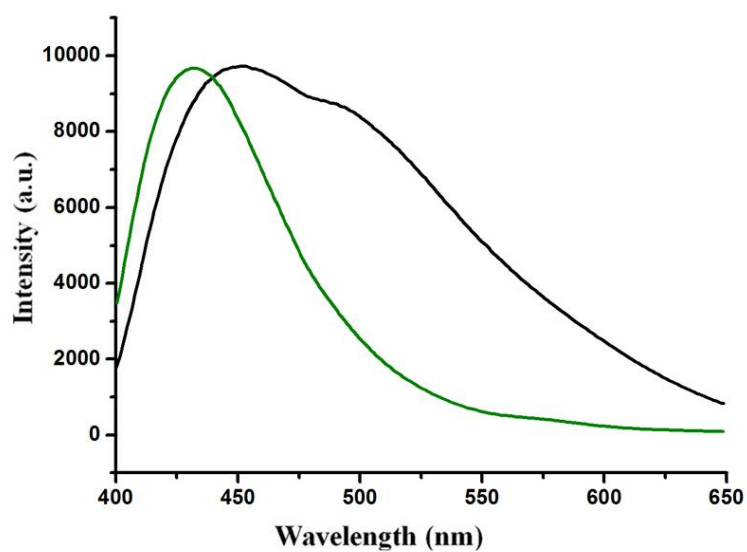
**Fig. S4** (a) X-ray powder diffraction patterns of **1**: simulated (black), as-synthesized (red) and after 5 cycles of exchange-release process (green); (b) X-ray powder diffraction patterns of simulated (black) of **1**, **Rho@1** (red), and the small angle XRD of **Rho@1** (top).



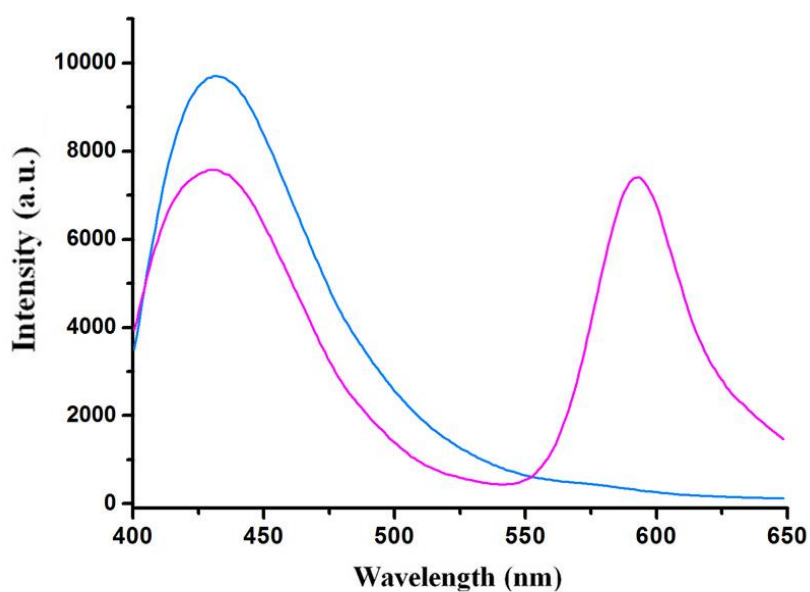
**Fig. S5** TG curve of **1** (a) and **Rho@1** (b).



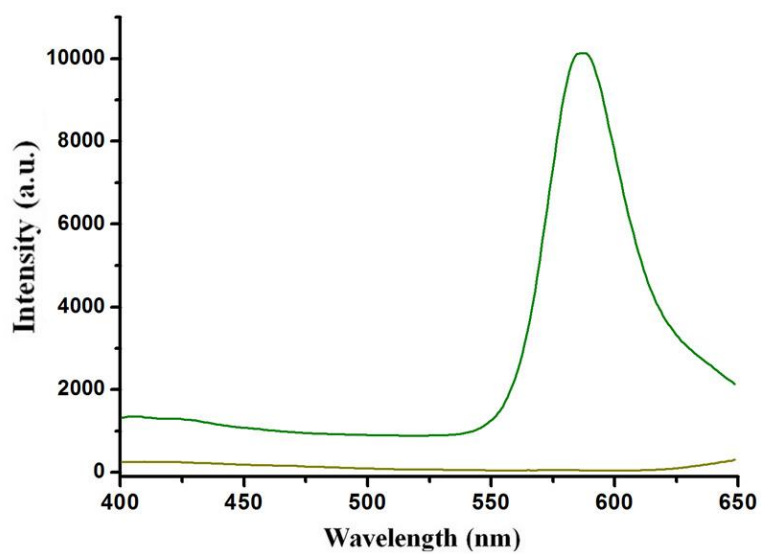
**Fig. S6** The structures of dye molecules that were used in the experiment of dye separation.



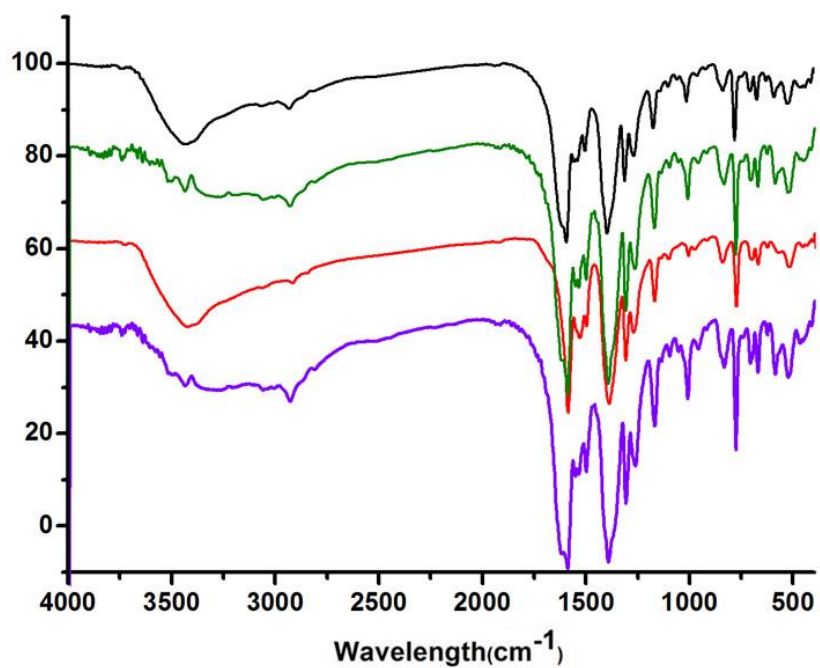
**Fig. S7** The emission spectra of H<sub>3</sub>NTB ligand (black) and **1** (green).



**Fig. S8** The emission spectra of grinded mixture of dye and **1** (blue), **Rho@1** (pink) excited at 350 nm in the solid state at room temperature

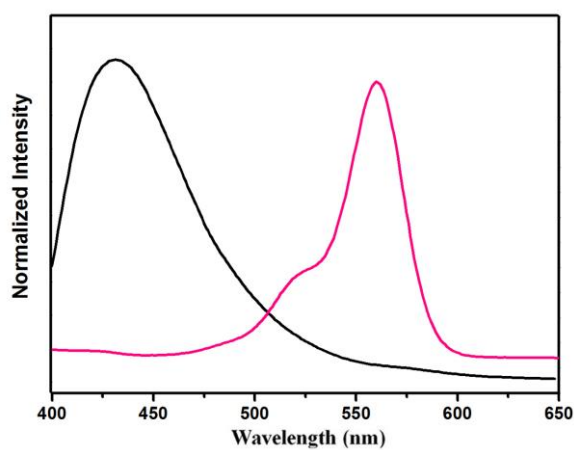


**Fig. S9** The emission spectra of Rhodamine B dye in solid state at room temperature (dark yellow), and in the DMA solution (green).

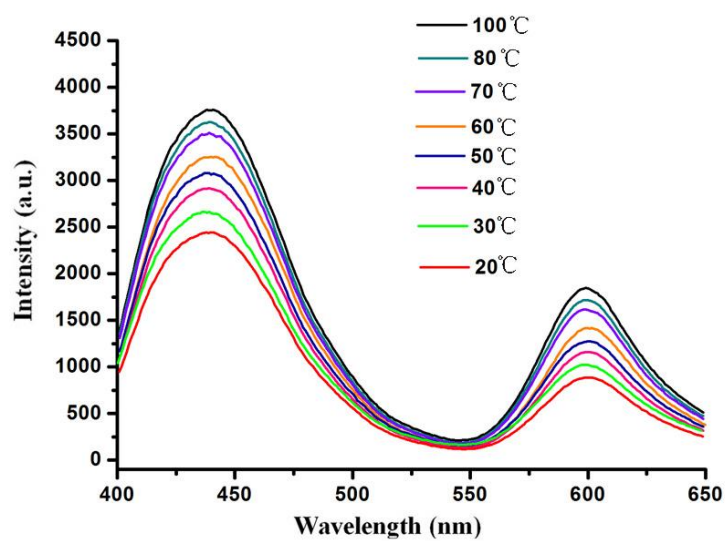


**Fig. S10** FT-IR spectra of as-synthesized **1** (black), Basic Red 2@**1** (green), Rhodamine B@**1** (red) and Methyl Violet@**1** (purple).

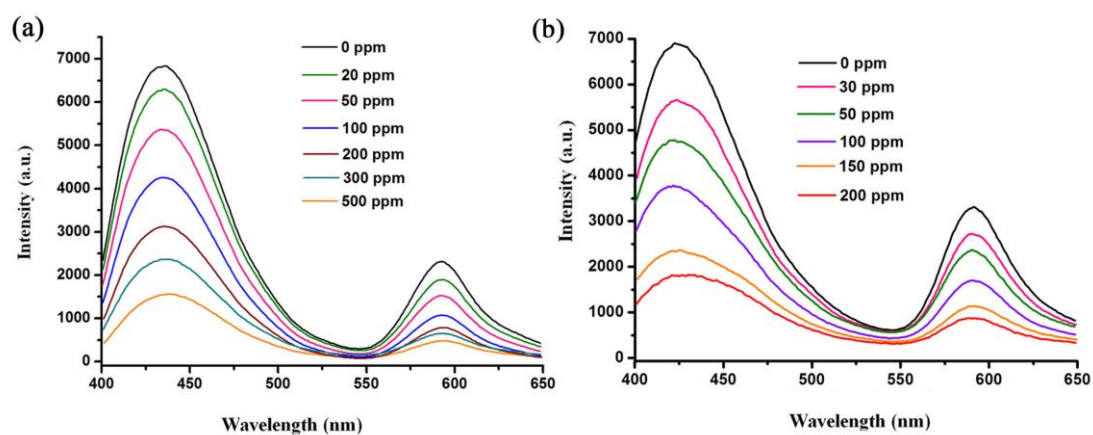




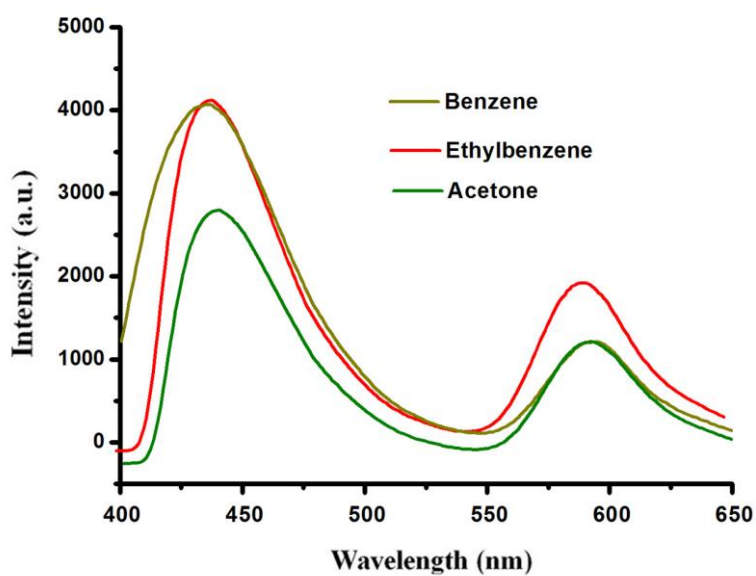
**Fig. S11** The emission spectra of **1** (black) and the UV/Vis spectra of dye Rhodamine B (red).



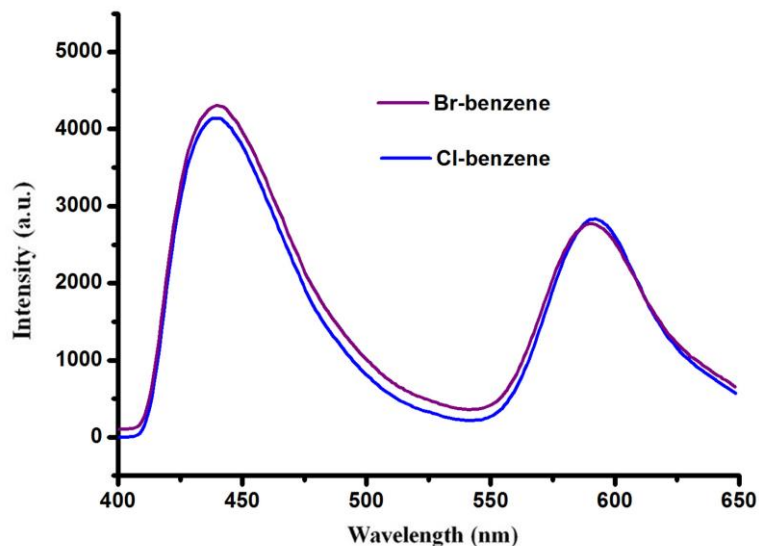
**Fig. S12** Emission spectra of **Rho@1** recorded from 20 to 100 °C, excited at 369 nm.



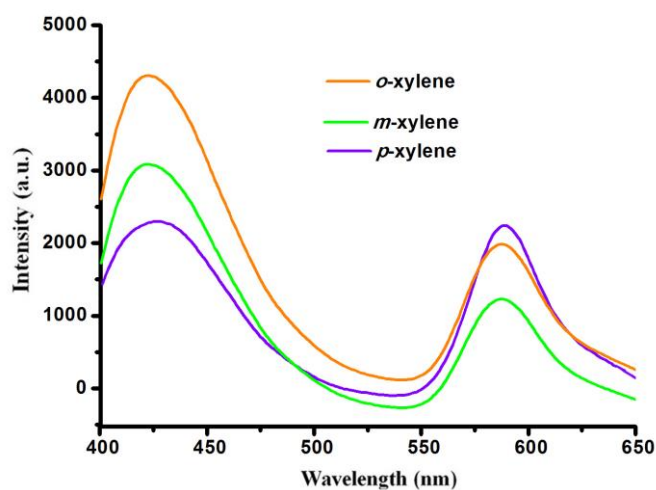
**Fig. S13** Emission spectra of **Rho@1** dispersed in DMA upon incremental addition of NB (a) and TNP (b) (excited at 369 nm).



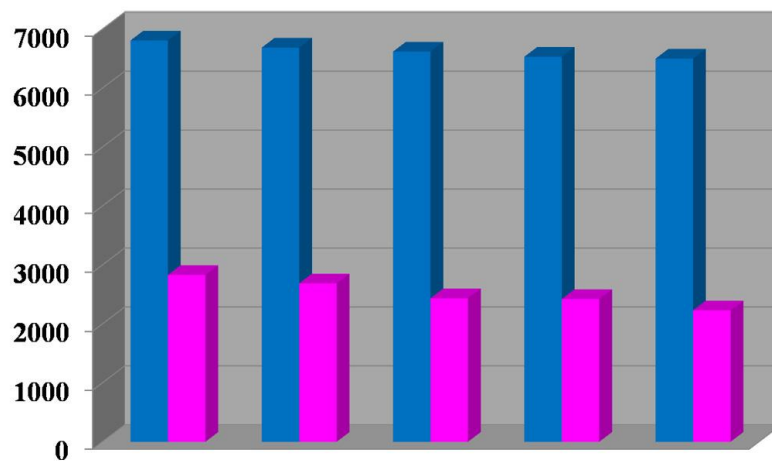
**Fig. S14** The photoluminescence spectra of **Rho@1** after adsorption of benzene, toluene, and ethylbenzene molecules, excited at 369 nm in the solid state at room temperature.



**Fig. S15** The photoluminescence spectra of **Rho@1** after adsorption of Br-benzene, Cl-benzene molecules, excited at 369 nm in the solid state at room temperature.



**Fig. S16** The photoluminescence spectra of **Rho@1** after adsorption of *o*-xylene, *m*-xylene and *p*-xylene molecules, excited at 369 nm in the solid state at room temperature.



**Fig. S17** The quenching and recyclability test of **Rho@1** in probing nitrobenzene molecules for 5 cycles (blue = MOF, pink = Rhodamine B).

**Table S1** Crystal data and structure refinements for compound **1**

Formula	<b>C<sub>60</sub>N<sub>6.5</sub>O<sub>19</sub>H<sub>60.5</sub>Zn<sub>4</sub> (1)</b>
Formula weight	1484.3
Crystal system	monoclinic
Space group	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	24.736(7)
<i>b</i> (Å)	21.702(6)
<i>c</i> (Å)	25.337(7)
<i>α</i> (°)	90.00
<i>β</i> (°)	109.956(5)
<i>γ</i> (°)	90.00
<i>V</i> (Å <sup>3</sup> )	12785(6)
<i>Z</i>	4
<i>D<sub>calcd.</sub></i> [gcm <sup>-3</sup> ]	0.587
<i>F</i> (000)	2266
Reflections collected	72601/22453
<i>R</i> (int)	0.1223
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.013
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ ( <i>I</i> )]	0.0464
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.1306
<sup>a</sup> <i>R</i> <sub>1</sub> = Σ   <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>   /Σ  <i>F</i> <sub>o</sub>  , <sup>b</sup> <i>wR</i> <sub>2</sub> = [Σw(  <i>F</i> <sub>o</sub>   <sup>2</sup> -   <i>F</i> <sub>c</sub>   <sup>2</sup> ) <sup>2</sup> /Σw( <i>F</i> <sub>o</sub> <sup>2</sup> ) <sup>2</sup> ] <sup>1/2</sup>	

**Table S2** The selective dyes in the ion-exchange experiment

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Cationic dyes	Basic Red 2	Rhodamine B	Methyl Violet
	√	√	√
Anionic (neutral) dyes	Methyl Orange	Methyl Blue	Solvent Yellow 2 (neutral)
	×	×	×

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