

## Supporting Information

Rhodamine B functionalized luminescent metal-organic frameworks for ratiometric fluorescence sensing of hydroquinone

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## Experimental Section

### Chemical and Materials

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), rhodamine B (RhB), glucose (Glu), citric acid (CA), cysteine (Cys), proline (Pro), and methylene chloride were obtained from Aladdin Reagent Company (Shanghai, China). 2-Amino-1,4-benzene dicarboxylic acid ( $\text{NH}_2\text{-BDC}$ ), hydroquinone (HQ), catechol (CC), resorcinol (RC), phloroglucinol (Phg), pyrogallol (Pyg), and tert-butyl hydroquinone (TBHQ) were gained from Sigma-Aldrich Company (St. Louis, MO, USA). Other metal ions and inorganic anions were purchased from Beijing Chemical Works (Beijing, China) or Energy Chemical Corporation (Anhui, China). Ethanol, methanol, and N,N-dimethylformamide (DMF) were obtained from Tiantai Fine Chemicals Company (Tianjin, China). Relevant inorganic compounds and solvents were used without any further purification. All aqueous solutions were prepared with ultrapure water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ).

### Characterization

XPS data were collected with an X-ray photoelectron spectrometer (Thermo Electron, USA). Powder X-ray diffraction (PXRD) patterns were recorded in the range of  $2\theta = 5\text{-}40^\circ$  using a D/Max-IIIIC instrument (Rigaku, Japan) with  $\text{Cu K}\alpha$  radiation. Scanning electron microscopic (SEM) images were acquired on a SU8020 ESEM microscope (Hitachi, Japan). Fourier-transform infrared (FT-IR) spectra were obtained using a Thermo Nicolet 670 FT-IR instrument (Thermo Nicolet Corporation, USA) with the recorded range of  $4000\text{-}450 \text{ cm}^{-1}$ . Brunauer-Emmett-Teller (BET) surface area measurements were performed with an ASAP 2420 gas adsorption instrument (Micromeritics, Atlanta, USA). Thermogravimetric analysis (TGA) was taken with STA 6000 simultaneous thermal analyzer (PerkinElmer, USA). Fluorescence emission spectra of different samples were obtained on an FL5301 fluorescence

spectrophotometer (Shimadzu, Japan). An OHAUS ST3200 digital pH meter (OHAUS, China) was used for pH measurements. Fluorescence lifetime was measured with an FLS920 fluorescence spectrophotometer (Edinburgh Instruments, England). Ultraviolet-visible (UV-vis) absorption spectra were collected using a UV-2450 spectrophotometer (Shimadzu, Japan). All the luminescence color images were taken under 365 nm UV light.

### **Optimization of solvents**

The RhB@IRMOF-3 powder was added into aqueous solutions containing ethanol with different concentrations (0%, 25%, 50%, 75%, and 100%). The suspensions were sonicated for 30 min, and then the fluorescence spectra were measured.

### **Optimization of RhB@IRMOF-3 concentrations**

1, 2, 4, 6, 8, and 10 mg RhB@IRMOF-3 was immersed in 4 mL mixture of ethanol and water (1:1, v/v), respectively. The suspensions were sonicated for 30 min, and then the fluorescence spectra were measured.

### **pH and Fluorescence Stabilities of RhB@IRMOF-3**

The chemical stability of RhB@IRMOF-3 under various pH surroundings was investigated as follows. 4 mg RhB@IRMOF-3 was immersed in 4 mL mixture of ethanol and water (1:1, v/v) with pH values of 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12, respectively. The solutions were sonicated for 30 min, and then the fluorescence spectra were measured.<sup>1</sup>

The inter-day fluorescence stability of RhB@IRMOF-3 was investigated as follows. 4 mg RhB@IRMOF-3 was immersed in 4 mL mixture of ethanol and water (1:1, v/v) and sonicated for 30 min. The fluorescence spectra were measured after storage for 1 day, 2 days, 3 days, 1 week, and 2 weeks, respectively.<sup>2</sup>

### **Calculation of LOD and RSD**

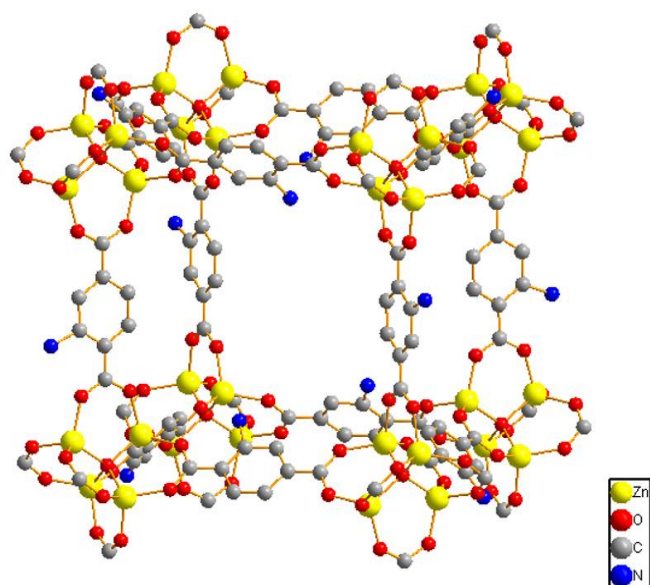
The limit of detection (LOD) was calculated based on IUPAC recommendations (LOD =  $3S/k$ , in which  $S$  is the standard deviation of 10 blank samples, and  $k$  is the slope of the calibration curve).

The relative standard deviation (RSD) was calculated by the following formula:

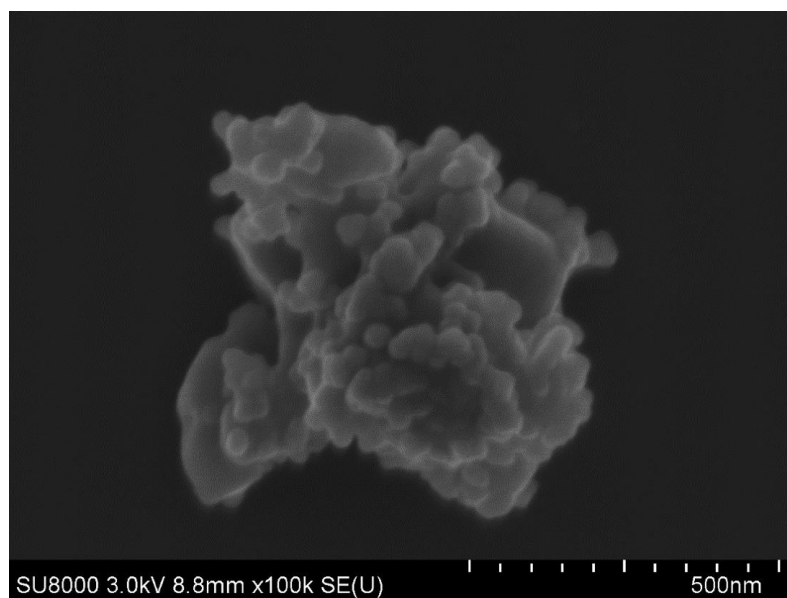
$$\text{RSD} = \frac{\text{SD}}{\text{X}} \times 100\%$$

in which  $SD$  is the standard deviation of the fluorescence intensity of 3 samples at the same concentration, and  $X$  is their arithmetic mean.

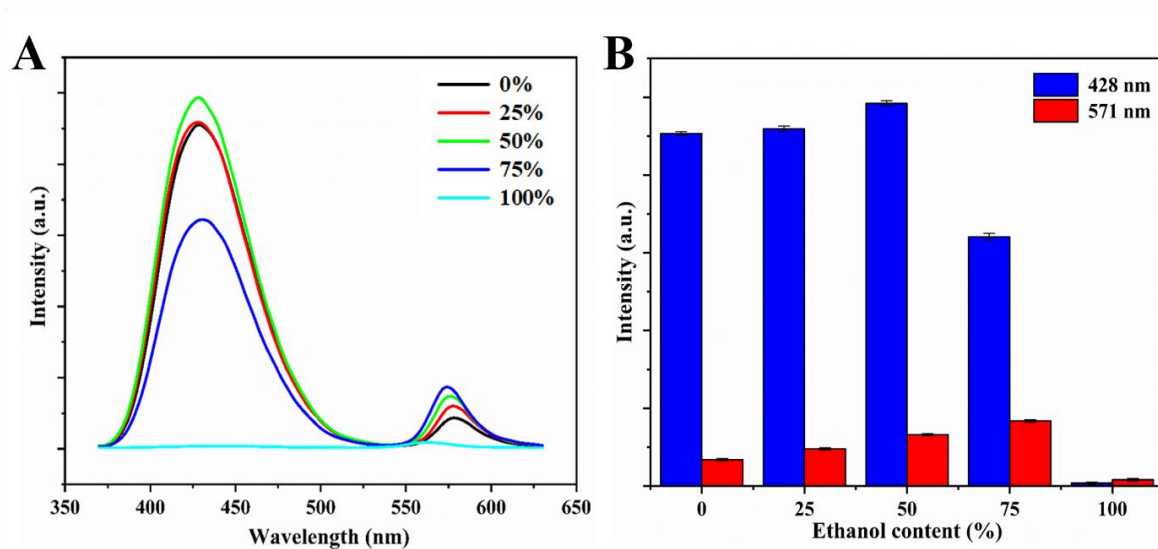
## FIGURES



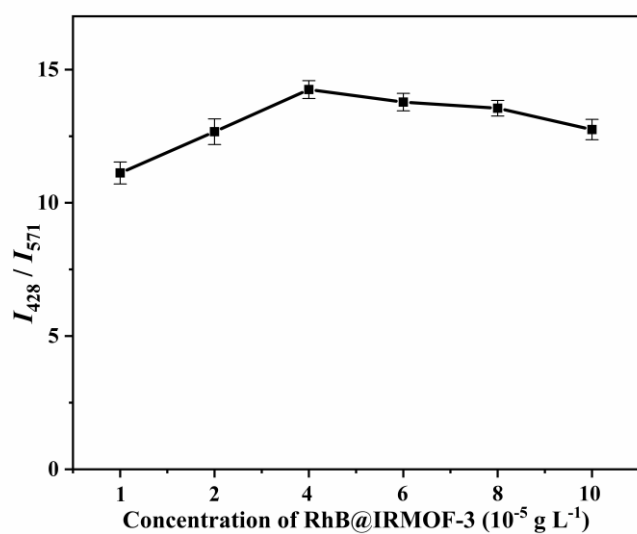
**Fig. S1.** Chemical structure of the cuboidal block of IRMOF-3.



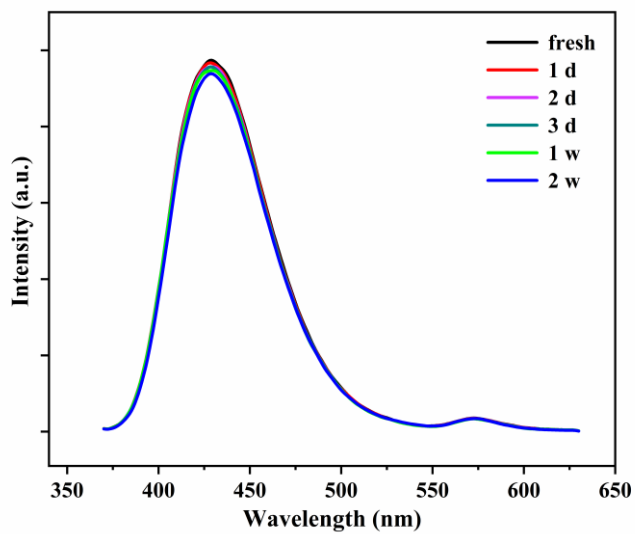
**Fig. S2.** SEM images of RhB@IRMOF-3.



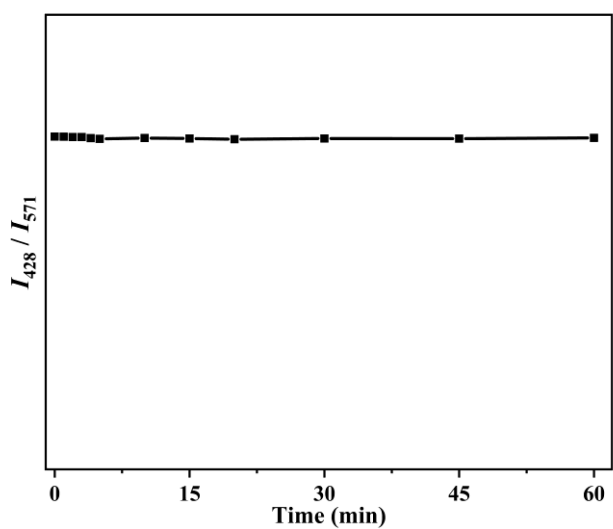
**Fig. S3.** Fluorescence intensity of RhB@IRMOF-3 sensor in aqueous solutions containing ethanol with different concentrations.



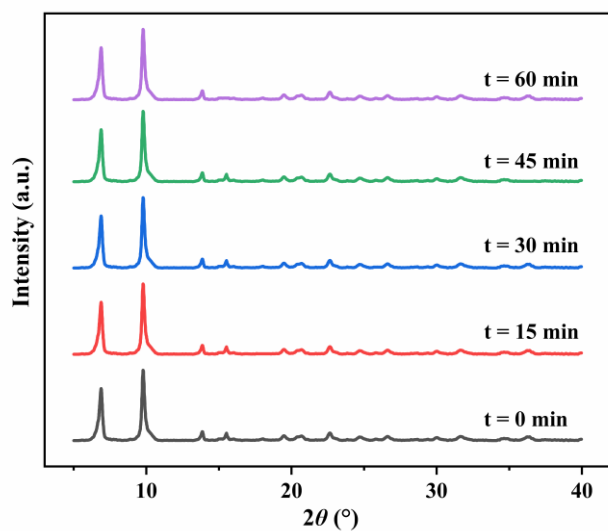
**Fig. S4.** Fluorescence intensity ratio ( $I_{428}/I_{571}$ ) of RhB@IRMOF-3 with different concentrations.



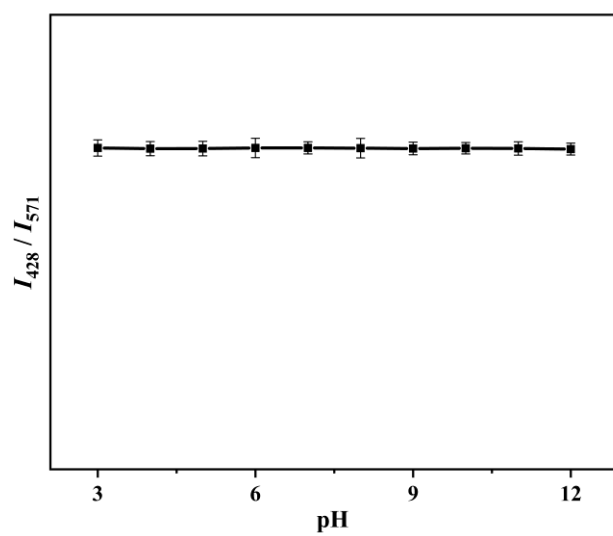
**Fig. S5.** Inter-day stability of RhB@IRMOF-3.



**Fig. S6.** Fluorescence intensity variation of RhB@IRMOF-3 after exposure to UV light illumination for 60 min.

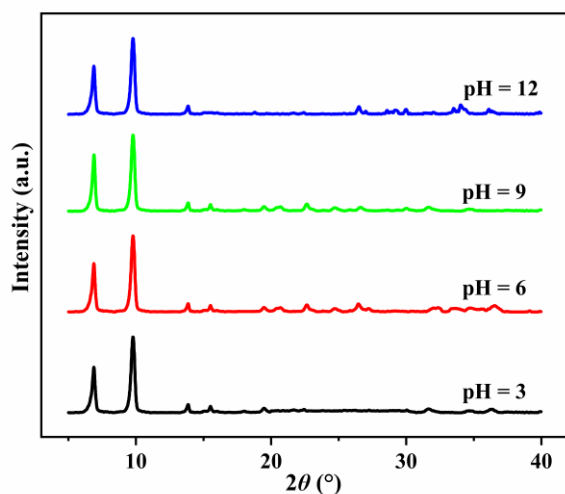


**Fig. S7.** PXRD patterns of RhB@IRMOF-3 irradiated with UV light for different time.

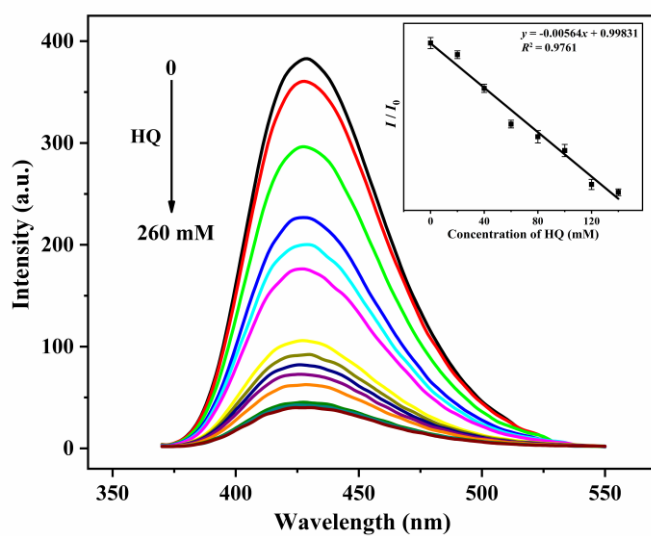


**Fig. S8.** Effect of solution pH on the fluorescence intensity of RhB@IRMOF-3.

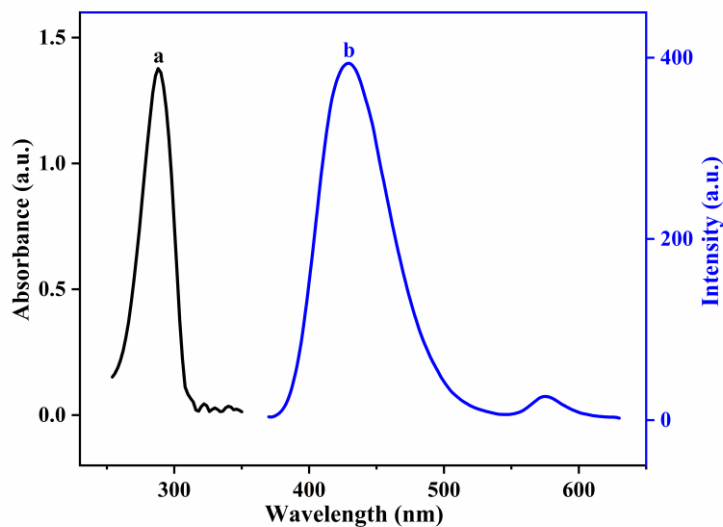




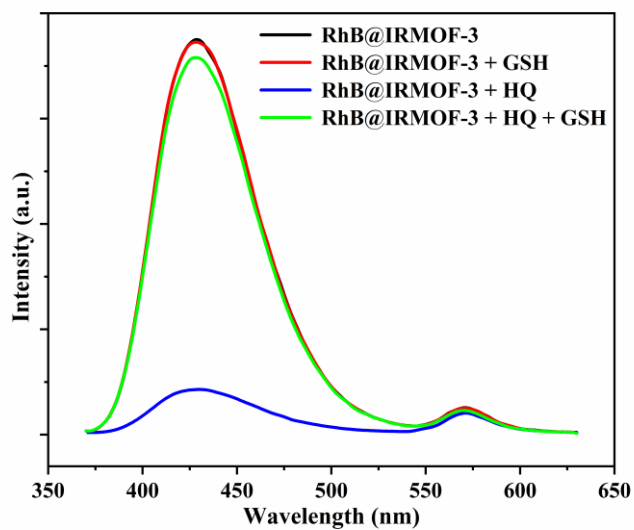
**Fig. S9.** PXRD patterns of RhB@IRMOF-3 under various pH surroundings.



**Fig. S10.** Fluorescence spectra of IRMOF-3 after adding HQ with different concentrations. Inset: Fluorescence intensity ratios ( $I/I_0$ ) of IRMOF-3 after adding HQ with different concentrations.



**Fig. S11.** (a) UV absorption spectrum of HQ and (b) fluorescence emission spectrum of RhB@IRMOF-3.



**Fig. S12.** Fluorescence emission spectra of RhB@IRMOF-3, RhB@IRMOF-3 + GSH, RhB@IRMOF-3 + HQ, and RhB@IRMOF-3 + HQ + GSH.

**TABLE****Table S1.** Comparison of the present method with other reported methods for HQ determination.

Method	Linear range	LOD	Response time	Ref.
Capillary electrophoresis	5–90 $\mu\text{g mL}^{-1}$	1.37 $\mu\text{g mL}^{-1}$	5 min	3
Colorimetry	5–110 $\mu\text{M}$	2.7 $\mu\text{M}$	10 min	4
GC	0.5–200 $\mu\text{g mL}^{-1}$	0.009 $\mu\text{g mL}^{-1}$	5 min	5
HPLC	0.5–100 $\mu\text{g mL}^{-1}$	0.2 $\mu\text{g mL}^{-1}$	10 min	6
Electrochemistry	4–5000 $\mu\text{M}$	0.63 $\mu\text{M}$	30 min	7
Spectrophotometry	0.36–3.96 $\mu\text{g mL}^{-1}$	0.16 $\mu\text{g mL}^{-1}$	6 min	8
ECL	0.55–37 $\mu\text{M}$	0.91 nM	5 min	9
Chemiluminescence	1.8–91 nM	1.2 $\mu\text{M}$	30 min	10
Fluorescence	0.1–50 $\mu\text{M}$	0.1 $\mu\text{M}$	60 min	11
Fluorescence	0.5–11.6 $\mu\text{M}$	0.04 $\mu\text{M}$	35 min	12
Fluorescence	0.1–140 mM	3.26 mM	15 s	This work

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