

Supporting information for

Highly stable acid-induced emission-enhancing Cd-MOFs: Synthesis, characterization, and detection of glutamic acid in water and iron ions in acid

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1. Instruments and characterizations

The Fourier-transform infrared (FT-IR) spectrum (4000-400 cm^{-1}) was recorded with KBr pellets on the Nicolet 170SX spectrometer. X-ray single-crystal diffractometer with Mo- $K\alpha$ radiation was performed. Elemental analysis (C, H, and N) was performed in a model 2400 Perkin-Elmer analyzer (EDX). Thermogravimetric (TG) analyses were performed on a NETZSCH TG 209F3 thermogravimetric analyzer with a ramp rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ from 30 to 700 $^{\circ}\text{C}$ under nitrogen conditions. The powder X-ray diffraction (PXRD) was collected on a Rigaku Ultima IV with a scan speed of 2 $^{\circ}\cdot\text{min}^{-1}$ from 5 to 50 $^{\circ}$. Luminescent spectra were collected on a Hitachi FL-7000 spectrophotometer. X-ray photoelectron spectroscopy (XPS) were performed on Thermo ESCALAB XI+. The UV-*vis* absorption spectra for the dye adsorption performance were recorded in application of a Shimadzu UV-2550 UV-*vis* spectrophotometer. The porosities and BET surface areas of the samples were recorded by N_2 adsorption/desorption isotherms (Micromeritics ASAP 2020 surface area and porosity analyzer). The scanning electron microscopy (SEM) were done on JEOL JSM-7600F. Fluorescence lifetime decay curves were measured by Edinburgh FLS980.

2. X-ray crystallography

The single crystals of Cd-MOFs **1–2** were treated and then suitable dimensions acquired crystals under an optical microscope. They were coated with high vacuum grease (Dow Corning Corporation) quickly, and mounted on glass fiber for data collection directly. We gathered X-ray crystallography data of **1–2** at 220/150 K on Bruker APEX-II CCD or Bruker SMART diffractometer, respectively, with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω -2 θ

scan mode. The solution and refinement of the structure of **1–2** used ShelXT and ShelXL (Sheldrick, 2015) by direct methods.^[1] There were non-hydrogen atoms being defined by the Fourier synthesis method. Thermal and positional parameters were refined by the full matrix least-squares method (on F^2) to convergence.^[2] Hydrogen atoms were placed at the calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. Their structures were studied through the Addsym subroutine of PLATON to assure that no additional symmetry could be applied to the models.^[3] The PLATON/SQUEEZE was employed to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities.^[4-8]

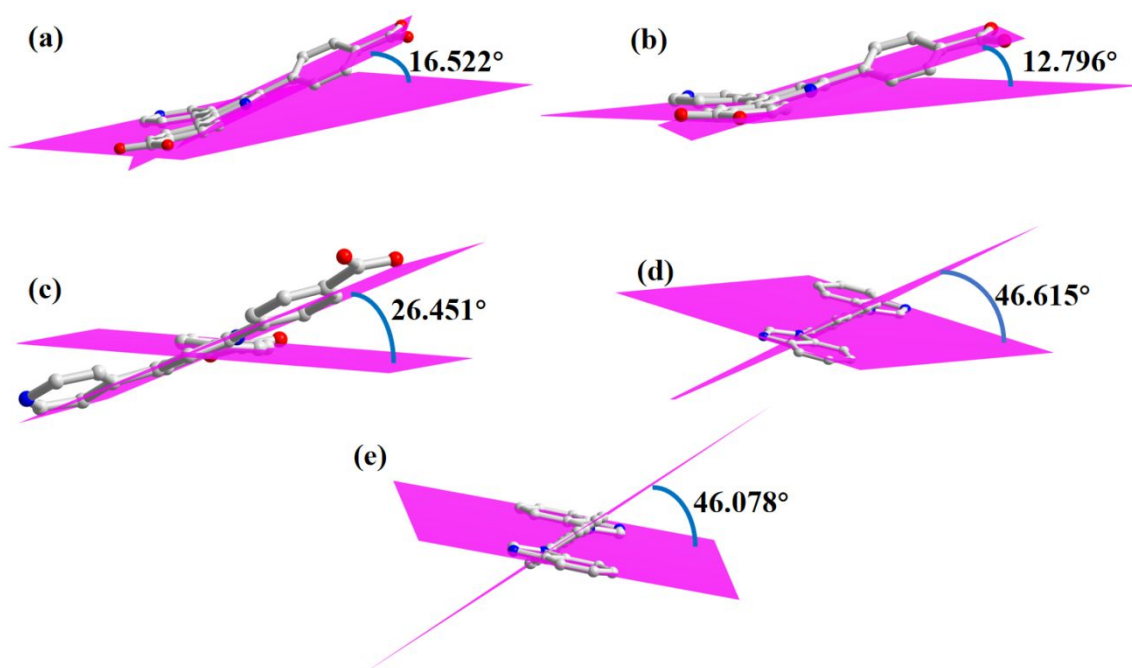


Figure S1. Dihedral angle of (a) pyridine and pyridine, (b-c) pyridine and benzene rings in bpydb ligand;(d-e) Dihedral angle of imidazoles and benzene ring in bbibp in Cd-MOF **1**.

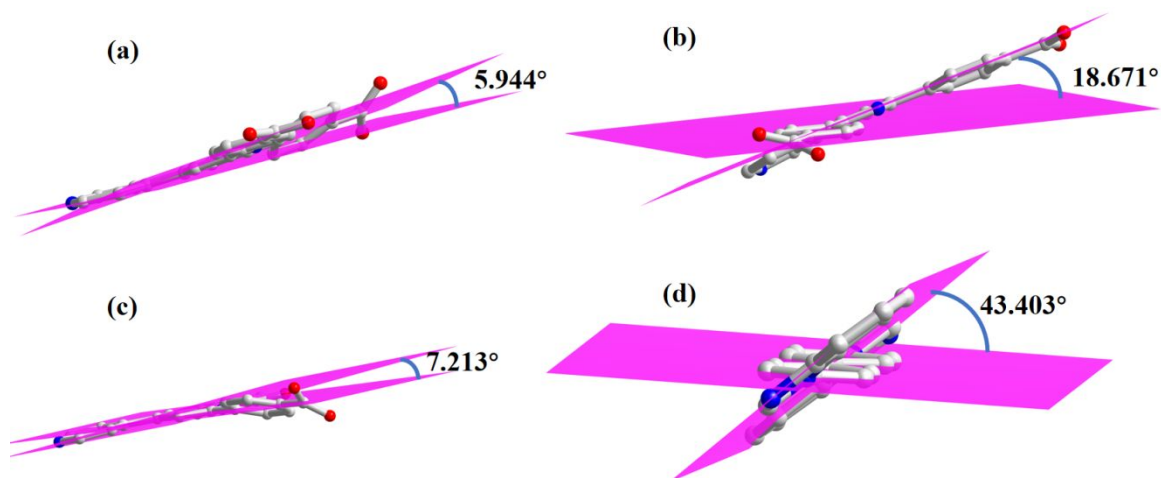


Figure S2. Dihedral angle of (a) pyridine and pyridine, (b-c) pyridine and benzene rings in bpydb ligand;(d) Dihedral angle of imidazoles and benzene ring in bbibp in Cd-MOF **2**.

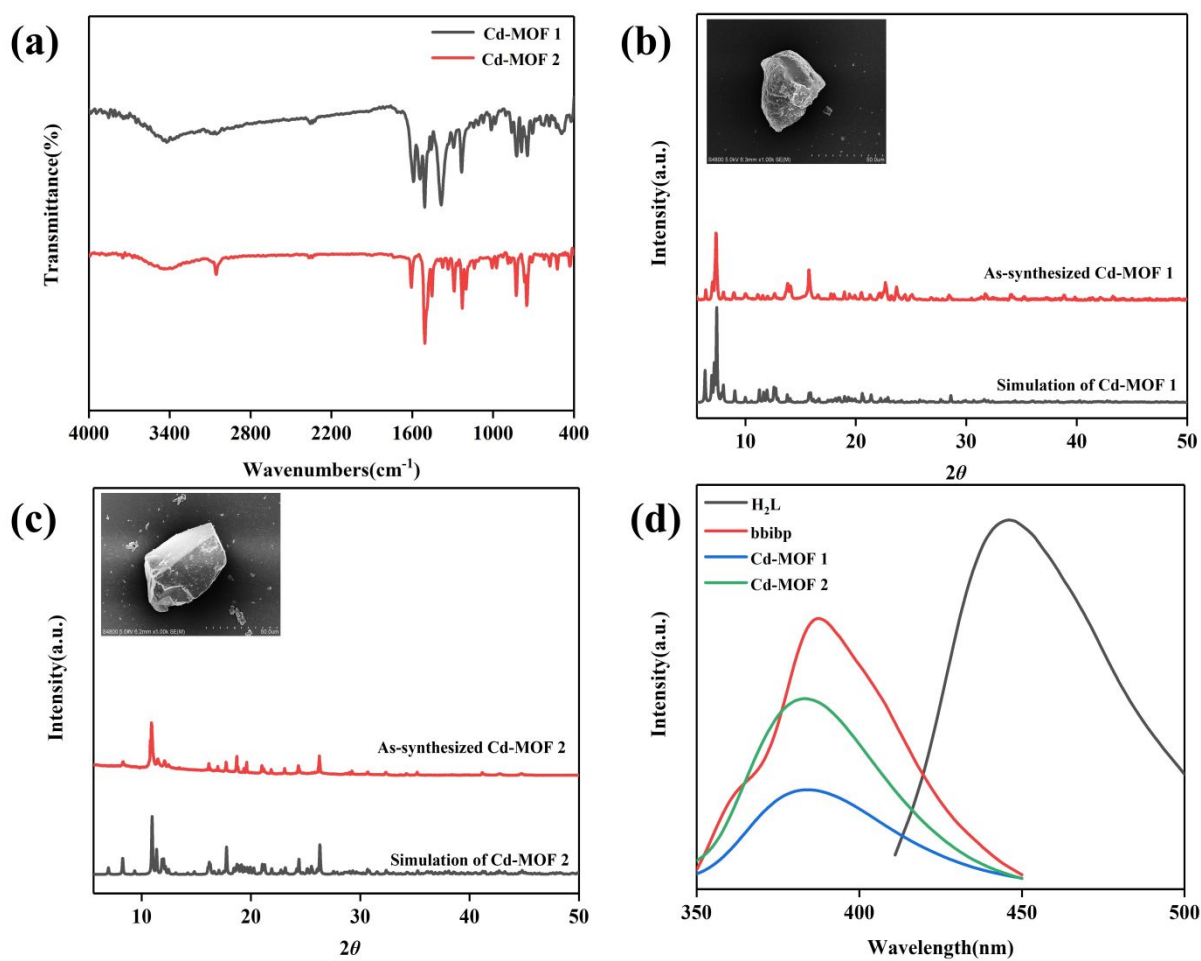


Figure S3. (a) The FT-IR spectra of Cd-MOFs 1–2; (b-c) The PXRD patterns of 1–2 (insert: SEM); (d) The solid-state fluorescence spectra of solid samples of 1–2 and ligands.

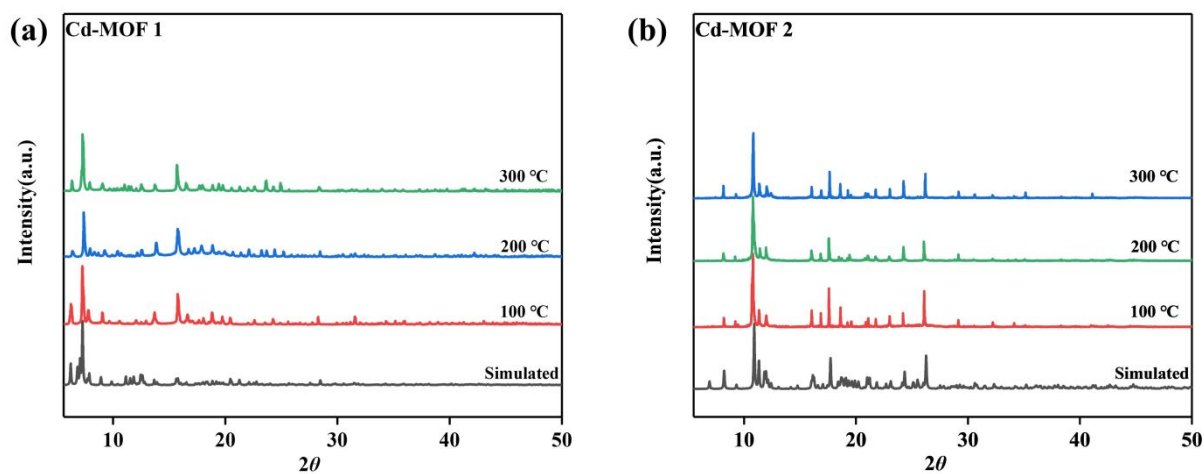


Figure S4. (a)-(b) The PXRD patterns of 1–2 under different temperatures treatment for one hour.

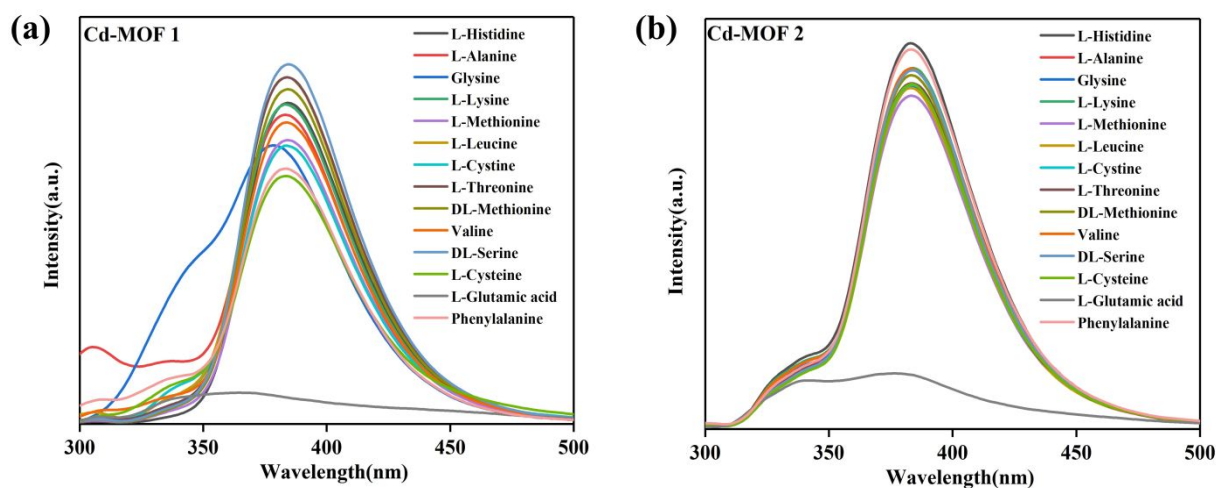


Figure S5. The fluorescent intensity of Cd-MOFs 1–2 for different amino acids.

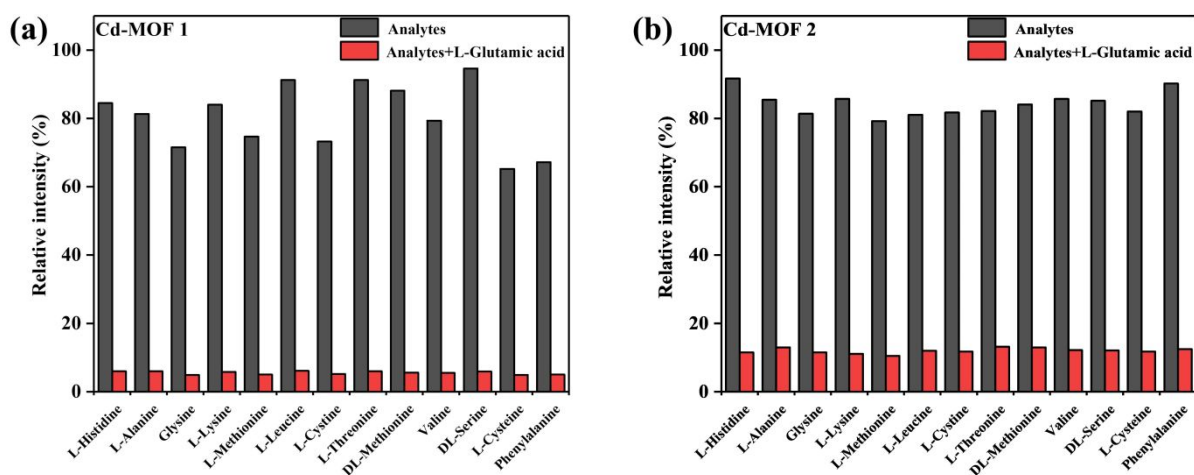


Figure S6. The relative luminescence intensities of Cd-MOFs 1–2 by different amino acids and selective detection of L-Glutamic acid in water.

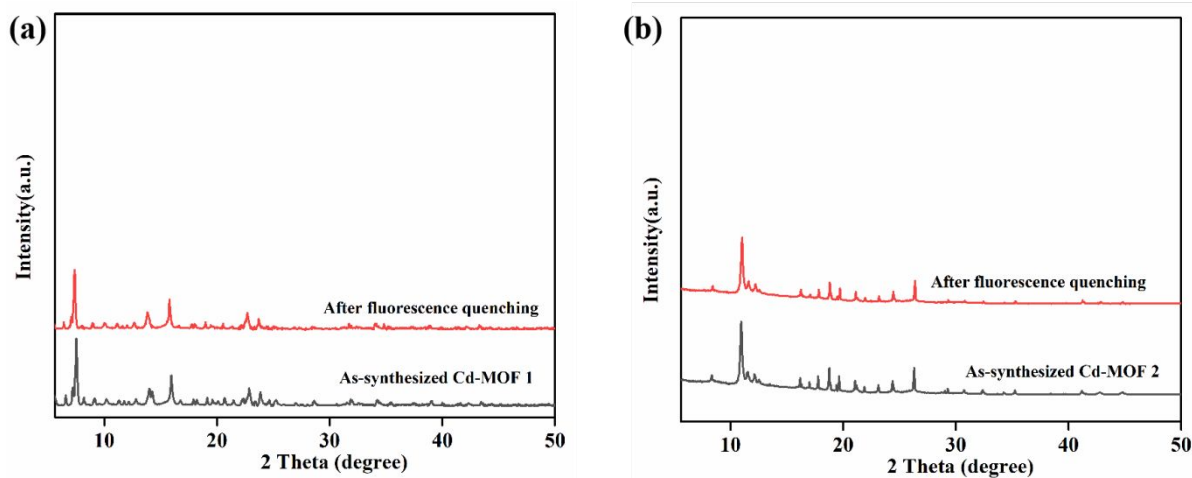


Figure S7. (a)-(b) The PXRD of Cd-MOFs 1–2 before and after fluorescence quenching.

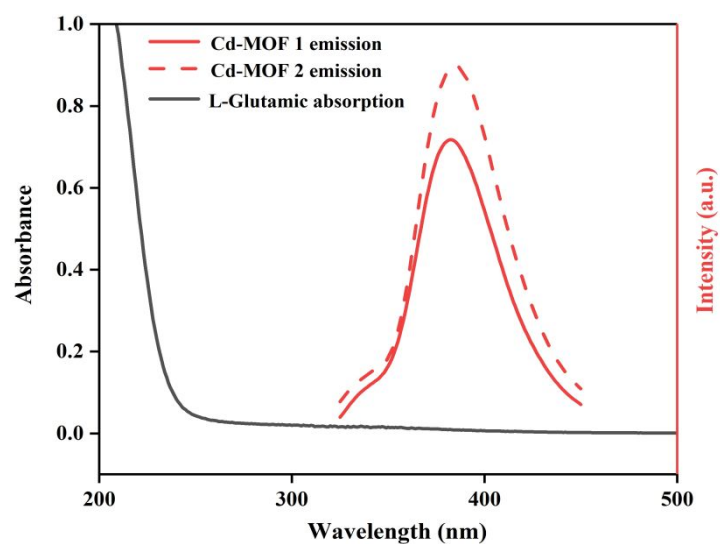


Figure S8. UV-vis spectrum of glutamate solution and luminescence spectrum of Cd-MOFs 1–2.

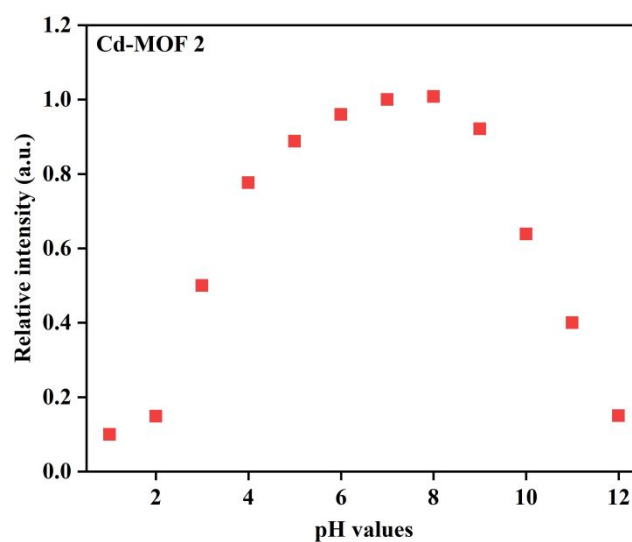


Figure S9. The scatter plot of the relationship between fluorescent intensity of Cd-MOF 2 and pH values.

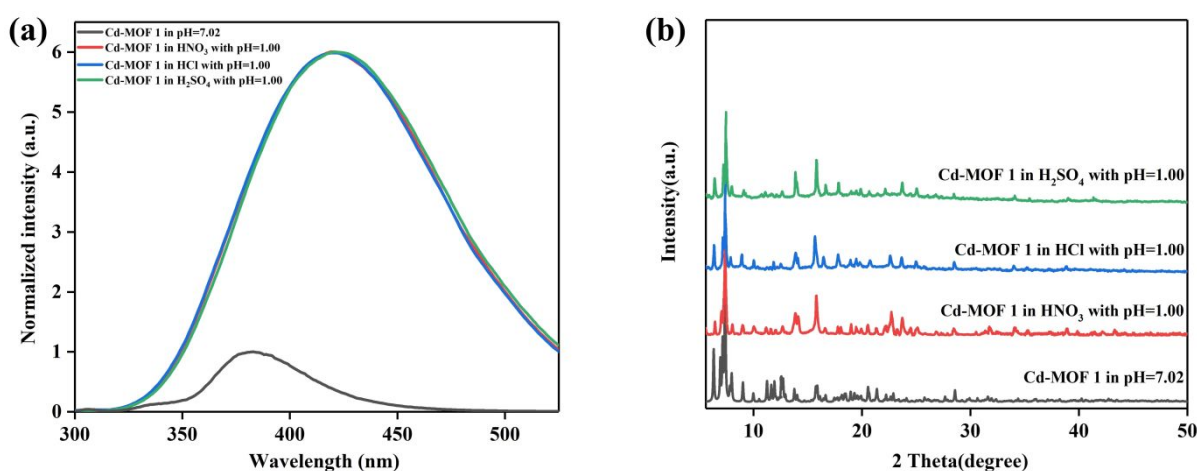


Figure S10. (a) The fluorescent intensity of **1** for different acids; (b) The PXRD patterns of **1** for different acids.

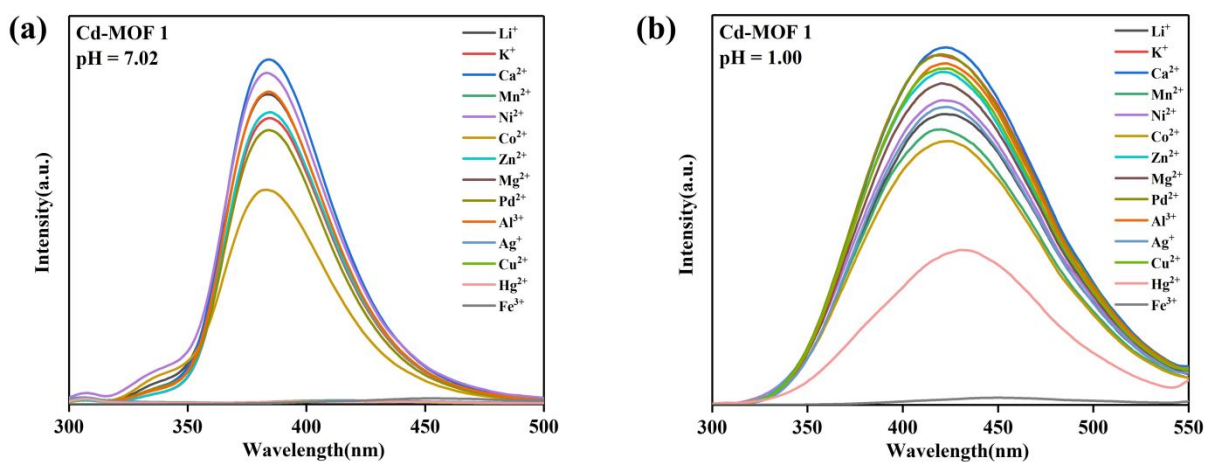


Figure S11. The fluorescent intensity of **1** for different metal ions in pH=1.00 and 7.02.

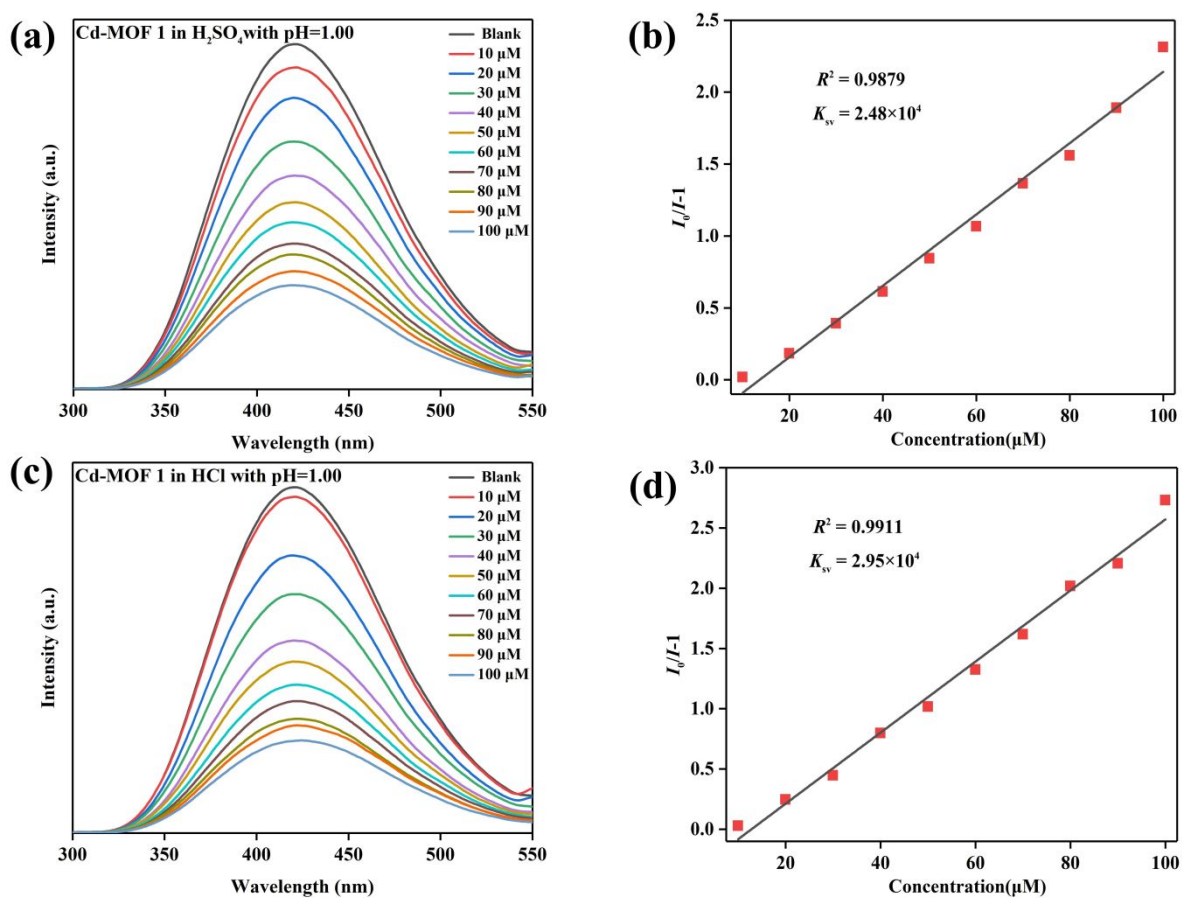


Figure S12. The fluorescent titration curves of **1** after the addition of different amounts of Fe³⁺ in (a) H₂SO₄; (c) HCl; Linear responses of **1** to Fe³⁺ in (b) H₂SO₄; (d) HCl.

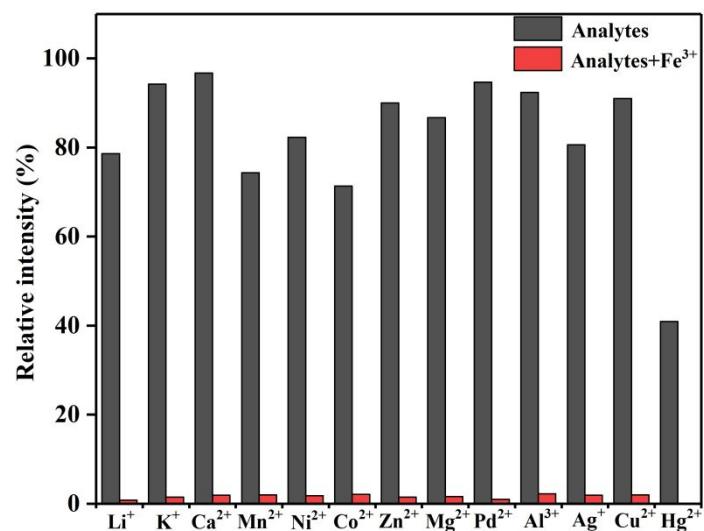


Figure S13. The relative luminescence intensities of **1** by different metal ions and selective detection of Fe³⁺ in pH=1.00.

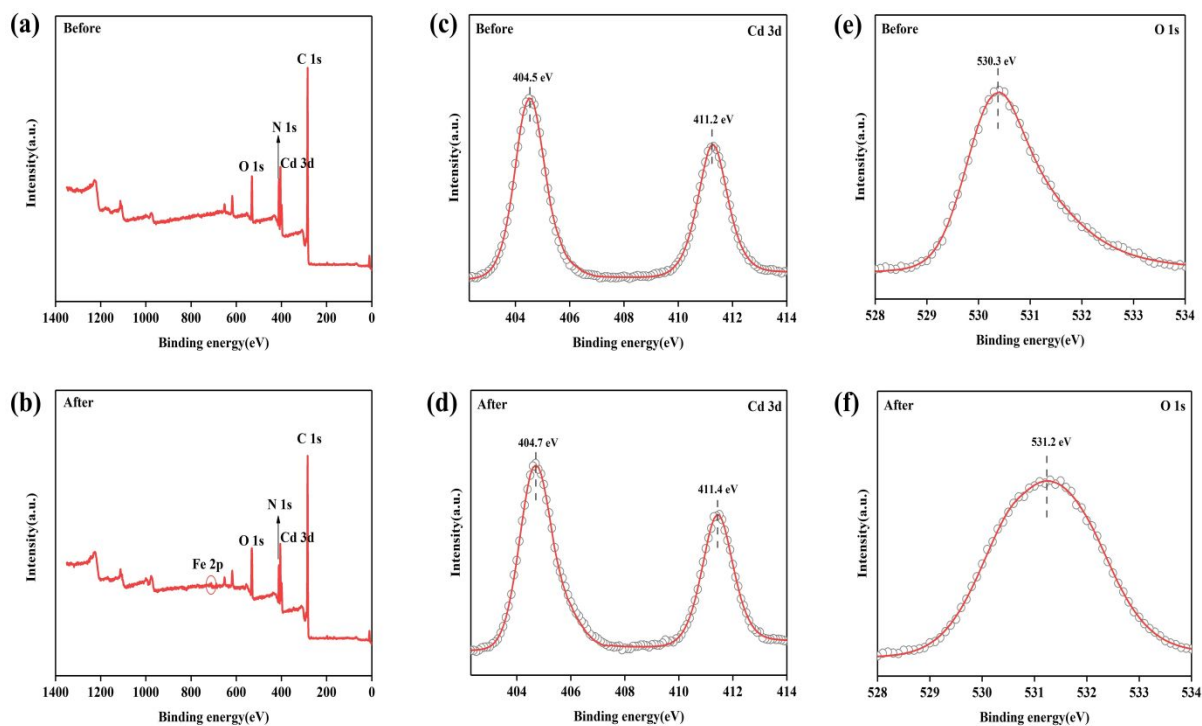


Figure S14. (a-b) XPS of **1** before and after soaked in pH=1.00 solutions of Fe³⁺; (c-d) Cd 3d XPS; (e-f) O 1s XPS before and after being soaked in pH=1.00 solutions of Fe³⁺.

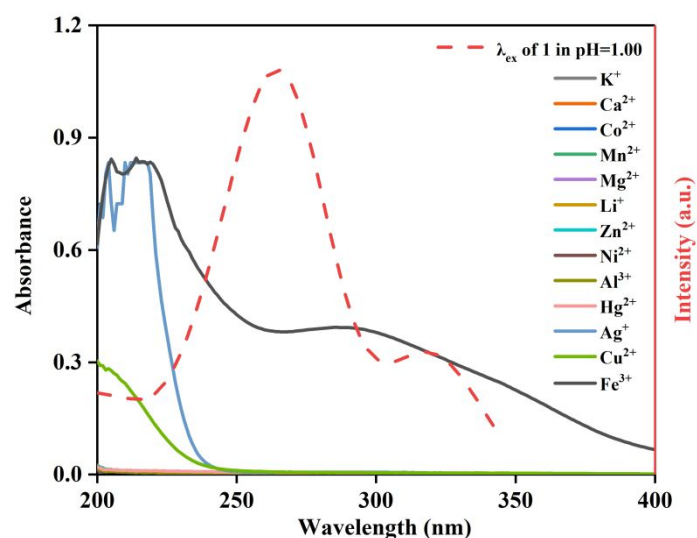


Figure S15. UV-*vis* spectra of cations in aqueous solutions and excitation spectra of Cd-MOF **1** in pH=1.00.

Table S1 Selected bond lengths (Å) and angles (°) for Cd-MOFs **1–2**.

Cd-MOF 1			
Cd1—O1	2.311 (2)	Cd1—N3	2.382 (3)
Cd1—O2	2.603 (3)	Cd1—N2	2.418 (3)
Cd1—O4 ⁱ	2.340 (3)	Cd1—N6 ⁱⁱ	2.321 (3)
Cd1—O3 ⁱ	2.581 (3)		
O1—Cd1—O2	53.24 (8)	O1—Cd1—N3	93.69 (9)
O1—Cd1—O4 ⁱ	83.86 (10)	O1—Cd1—N2	83.19 (10)
O1—Cd1—O3 ⁱ	136.99 (9)	O1—Cd1—N6 ⁱⁱ	139.31 (10)
N3—Cd1—O2	98.95 (10)	N3—Cd1—N2	171.32 (10)
N3—Cd1—O3 ⁱ	87.92 (10)	O4 ⁱ —Cd1—O3 ⁱ	53.12 (9)
N2—Cd1—O2	85.70 (10)	N6 ⁱⁱ —Cd1—O2	86.09 (9)
N2—Cd1—O3 ⁱ	88.87 (11)	N6 ⁱⁱ —Cd1—N3	91.17 (10)
O4 ⁱ —Cd1—O2	136.25 (9)	N6 ⁱⁱ —Cd1—N2	96.48 (10)
O4 ⁱ —Cd1—N3	91.20 (10)	N6 ⁱⁱ —Cd1—O4 ⁱ	136.44 (11)
O4 ⁱ —Cd1—N2	80.44 (10)	N6 ⁱⁱ —Cd1—O3 ⁱ	83.51 (10)
O3 ⁱ —Cd1—O2	167.65 (9)		
Symmetry codes: (i) $x+1, y+1, z+1$; (ii) $x+1, y+1, z$.			
Cd-MOF 2			
Cd1—O3 ⁱ	2.268 (4)	Cd1—N4 ⁱⁱ	2.273 (4)
Cd1—O2 ⁱ	2.424 (4)	Cd1—N2	2.271 (4)

Cd1—O4	2.194 (4)		
O3 ⁱ —Cd1—O2 ⁱ	55.78 (14)	O4—Cd1—O2 ⁱ	137.16 (16)
O3 ⁱ —Cd1—N4 ⁱⁱ	139.57 (17)	O4—Cd1—N4 ⁱⁱ	111.75 (17)
O3 ⁱ —Cd1—N2	100.52 (15)	O4—Cd1—N2	111.00 (17)
O3 ⁱ —Cd1—C24 ⁱ	27.82 (15)	O4—Cd1—C24 ⁱ	116.94 (17)
O2 ⁱ —Cd1—C24 ⁱ	28.05 (15)	N4 ⁱⁱ —Cd1—O2 ⁱ	85.73 (15)

Symmetry codes: (i) $x-1, y, z-1$; (ii) $x, y+1, z-1$.

Table S2 Summary of crystal data and structure refinement parameters of **1** and **1** in pH=1.00

	1	1 in pH=1.00
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	14.5402 (14)	14.4208 (6)
<i>b</i> (Å)	15.0699 (13)	15.0139 (6)
<i>c</i> (Å)	15.3074 (15)	15.2588 (6)
α (°)	96.787 (3)	96.806 (1)
β (°)	105.180 (3)	105.303 (1)
γ (°)	116.708 (3)	116.548 (1)
<i>V</i> (Å ³)	2781.4 (5)	2741.45 (19)
<i>Z</i>	2	1
<i>D</i> _{calcd} (Mg m ⁻³)	1.067	1.444
μ (mm ⁻¹)	0.43	0.46
<i>F</i> (000)	908	1226
<i>T</i> (K)	170	170
<i>R</i> _{int}	0.080	0.078
Final <i>R</i> indices	<i>R</i> ₁ = 0.0510	<i>R</i> ₁ = 0.0665
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.1199	<i>wR</i> ₂ = 0.1473
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0880 <i>wR</i> ₂ = 0.1033	<i>R</i> ₁ = 0.1117 <i>wR</i> ₂ = 0.1825
Gof	1.022	1.071

Table S3 Selected bond lengths (Å) and angles (°) for **1** and **1** in pH=1.00.

1		1 in pH=1.00	
Cd1—O1	2.311 (2)	Cd1—O1	2.303 (4)
Cd1—O2	2.603 (3)	Cd1—O2	2.588 (4)
Cd1—O4 ⁱ	2.340 (3)	Cd1—O4 ⁱ	2.335 (4)
Cd1—O3 ⁱ	2.581 (3)	Cd1—O5 ⁱ	2.559 (5)
Cd1—N3	2.382 (3)	Cd1—N3	2.364 (4)

Cd1—N2	2.418 (3)	Cd1—N5	2.406 (5)
Cd1—N6 ⁱⁱ	2.321 (3)	Cd1—N2 ⁱⁱ	2.313 (4)
O1—Cd1—O2	53.24 (8)	O1—Cd1—O2	53.20 (13)
O1—Cd1—O4 ⁱ	83.86 (10)	O1—Cd1—O4 ⁱ	83.63 (15)
O1—Cd1—O3 ⁱ	136.99 (9)	O1—Cd1—O5 ⁱ	136.86 (14)
N3—Cd1—O2	98.95 (10)	N3—Cd1—O2	99.48 (14)
N3—Cd1—O3 ⁱ	87.92 (10)	N3—Cd1—O5 ⁱ	87.38 (15)
N2—Cd1—O2	85.70 (10)	N5—Cd1—O2	85.58 (16)
N2—Cd1—O3 ⁱ	88.87 (11)	N5—Cd1—O5 ⁱ	88.97 (17)
O4 ⁱ —Cd1—O2	136.25 (9)	O4 ⁱ —Cd1—O2	135.92 (14)
O4 ⁱ —Cd1—N3	91.20 (10)	O4 ⁱ —Cd1—N3	91.17 (14)
O4 ⁱ —Cd1—N2	80.44 (10)	O4 ⁱ —Cd1—N5	80.19 (16)
O3 ⁱ —Cd1—O2	167.65 (9)	O5 ⁱ —Cd1—O2	167.80 (14)
O1—Cd1—N3	93.69 (9)	O1—Cd1—N3	94.11 (15)
O1—Cd1—N2	83.19 (10)	O1—Cd1—N5	83.06 (16)
O1—Cd1—N6 ⁱⁱ	139.31 (10)	O1—Cd1—N2 ⁱⁱ	139.22 (14)
N3—Cd1—N2	171.32 (10)	N3—Cd1—N5	171.15 (15)
O4 ⁱ —Cd1—O3 ⁱ	53.12 (9)	O4 ⁱ —Cd1—O5 ⁱ	53.23 (14)
N6 ⁱⁱ —Cd1—O2	86.09 (9)	N2 ⁱⁱ —Cd1—O2	86.06 (14)
N6 ⁱⁱ —Cd1—N3	91.17 (10)	N2 ⁱⁱ —Cd1—N3	90.95 (15)
N6 ⁱⁱ —Cd1—N2	96.48 (10)	N2 ⁱⁱ —Cd1—N5	96.67 (16)
N6 ⁱⁱ —Cd1—O4 ⁱ	136.44 (11)	N2 ⁱⁱ —Cd1—O4 ⁱ	136.74 (16)
N6 ⁱⁱ —Cd1—O3 ⁱ	83.51 (10)	N2 ⁱⁱ —Cd1—O5 ⁱ	83.74 (15)

Symmetry codes: (i) x+1, y+1, z+1; (ii) x+1, y+1, z.

Table S4 Average fluorescence lifetime of double exponential fit.

	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	R ²	τ _{avg} (ns)
1 in pH=1.00	3102.37	1.20 65.9%	262.14	7.36	0.9935	3.30
1 in pH=7.02	2211.85	1.17 37.5%	992.05	4.34	0.9976	3.15
1 in 1 mM Fe ³⁺	3375.55	1.42 81%	113.01	9.57	0.9850	2.92

$$\tau_{\text{avg}} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$$

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