Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information (ESI)

A Cd-MOF fluorescence sensor with dual functional sites for efficient detection of metal ions in multifarious water environments

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S1. Experimental section

S1.1 Materials and methods

The ligand Htpc was synthesized by a modified literature method.[S1-S3] Other chemicals were obtained commercially and used as received. Powder X-ray diffraction (PXRD) were performed on a D/MAX-rA (Rigaku) diffractometer with Cu *K*α radiation (λ = 1.542 Å) with a scan rate of 4 ◦/min at 36 kV and 20 mA. X-ray photoelectron spectrums (XPS) were performed on ESCALAB Xi+. Thermogravimetric (TG) analyses were performed on TGA550 instrument at a heating rate of 20 ℃/min from 50 ℃ to 800 ℃ under nitrogen atmosphere. FT-IR spectra were conducted with a NICOLET iS50 FT-IR spectrometer. UV-Vis measurements were carried out by a UV- 3600 Plus spectrophotometer. Luminescence lifetimes were carried out on a FLS1000 spectrophotometer analyzer of Edinburgh instruments. Fluorescence sensing properties were performed on the Hitachi F-7000 fluorescence spectrophotometer.

S1.2 Syntheses of LCU-109

A mixture of $CdCl_2 \cdot 4H_2O$ (220.1 mg, 1.2 mmol), Pyrazine dicyanide (65 mg, 1.0 mmol), NaN_3 (65 mg, 1.0 mmol), $NaHCO_3$ (2.5 mg, 0.003mmol) and H_3btc (35.7 mg, 0.17 mmol) with 15 mL of water was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated to 140 ℃. The autoclave was kept at 140 ℃ for 3 days and then cooled to room at a cooling rate of 4 ℃/h. Yellow block crystals of **LCU-109** were obtained, washed with water, and dried in air. Yield: 29 % based on Cd. Elemental analysis (%) for **LCU-109**, $C_{15}H_{11}Cd_2N_7O_9$ (M = 658.11): Calcd.: C, 27.36; H, 1.68;

N, 14.90; Found: C, 37.48; H, 1.61; N, 14.85. The FT-IR spectra see **Fig. S1** in **ESI**.

S1.3 X-ray crystallography

Single crystal X-ray diffraction measurement was carried out on a Rigaku SCX-mini diffractometer and determined at 298(2) K with Mo-*K*α radiation (λ = 0.71073 Å). The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the SHELXL-97 crystallographic software packages. Cd atoms in **LCU-109** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of organic ligands were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. The hydrogen atoms of coordinated H_2O and free H_2O were added by successive difference Fourier syntheses. During the refinement of the compound, the command "omit -1 50.04" was used to omit some disagreeable reflections. Further details of crystal data and structure refinement for **LCU-109** were summarized as follows in **Table S1**. Selected bond lengths of **LCU-109** were given in **Table S2**. Full crystallographic data for **LCU-109** have been deposited with the **CCDC (No.: 2095374)**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement parameters for **LCU-109**.

MOF		LCU-109	
Formula	$C_{15}H_{11}Cd_2N_7O_9$	γ [°]	80.6270(10)
F_w	658.11	V (Å3)	940.00(15)
λ/Å	0.71073	Z	2
T/K	298(2)	D_c/Mg/m^3	2.325
Crystal system	Triclinic	F(000)	636
Space group	P-1	Reflections collected/unique	4623/3258
a [Å]	8.3887(7)	R_{int}	0.0724
b [Å]	10.3405(9)	Data/Restraints/Parameters	3258/3/298
c [Å]	11.1345(11)	R_1/wR_2 [I>2σ(I)][a]	0.0930/0.2815
α[°]	80.6520(10)	R_1/wR_2 [(all data)][b]	0.1012/0.3073
β[°]	89.883(2)	GOF on F^2	0.957

[a]$R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$; [b]$wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Table S2 The selected bond lengths [Å] and angles [º] of **LCU-109**.

N(5)-Cd(2)#1	2.499(10)	Cd(1)-O(6)#4	2.229(9)
O(3)-Cd(2)#2	2.286(8)	Cd(1)-O(4)#2	2.277(9)
O(4)-Cd(1)#2	2.277(9)	Cd(1)-O(2)	2.280(8)
O(6)-Cd(1)#3	2.229(9)	Cd(1)-O(1W)	2.290(9)
N(4)-Cd(2)#1	2.433(8)	Cd(1)-N(2)	2.331(9)
Cd(1)-O(5)#4	2.605(11)	Cd(2)-O(1)	2.342(9)
Cd(2)-O(3)#2	2.286(8)	Cd(2)-N(3)	2.398(10)
Cd(2)-O(2W)	2.295(10)	Cd(2)-N(4)#1	2.434(8)
O(5)-Cd(1)#3	2.605(10)	Cd(2)-N(5)#1	2.499(10)

O(6)#4-Cd(1)-O(4)#2	99.3(4)	O(4)#2-Cd(1)-N(2)	83.4(3)
O(6)#4-Cd(1)-O(2)	141.8(3)	O(2)-Cd(1)-N(2)	113.1(3)
O(4)#2-Cd(1)-O(2)	86.3(3)	O(1W)-Cd(1)-N(2)	91.2(3)
O(6)#4-Cd(1)-O(1W)	91.8(4)	O(6)#4-Cd(1)-O(5)#4	53.0(3)
O(4)#2-Cd(1)-O(1W)	168.6(3)	O(4)#2-Cd(1)-O(5)#4	102.7(3)
O(2)-Cd(1)-O(1W)	86.7(4)	O(2)-Cd(1)-O(5)#4	88.8(3)
O(6)#4-Cd(1)-N(2)	105.1(4)	O(1W)-Cd(1)-O(5)#4	86.1(3)
O(3)#2-Cd(2)-O(2W)	88.7(4)	N(2)-Cd(1)-O(5)#4	157.7(3)
O(3)#2-Cd(2)-O(1)	84.0(3)	N(3)-Cd(2)-N(4)#1	88.4(3)
O(2W)-Cd(2)-O(1)	163.7(3)	O(3)#2-Cd(2)-N(5)#1	75.6(3)
O(3)#2-Cd(2)-N(3)	127.3(3)	O(2W)-Cd(2)-N(5)#1	98.6(4)
O(2W)-Cd(2)-N(3)	93.5(4)	O(1)-Cd(2)-N(5)#1	93.6(3)
O(1)-Cd(2)-N(3)	79.6(3)	N(3)-Cd(2)-N(5)#1	154.5(3)
O(3)#2-Cd(2)-N(4)#1	144.2(3)	N(4)#1-Cd(2)-N(5)#1	69.2(3)
O(2W)-Cd(2)-N(4)#1	90.7(4)	O(1)-Cd(2)-N(4)#1	103.7(3)

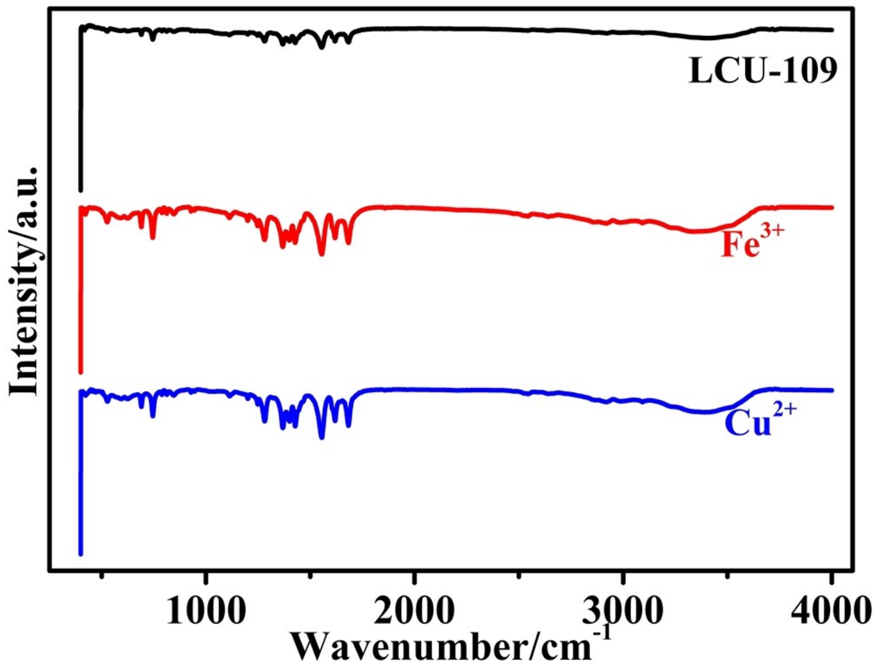


Fig. S1 IR spectrum of **LCU-109** soaked in water solutions containing Fe^{3+} or Cu^{2+} for three days.

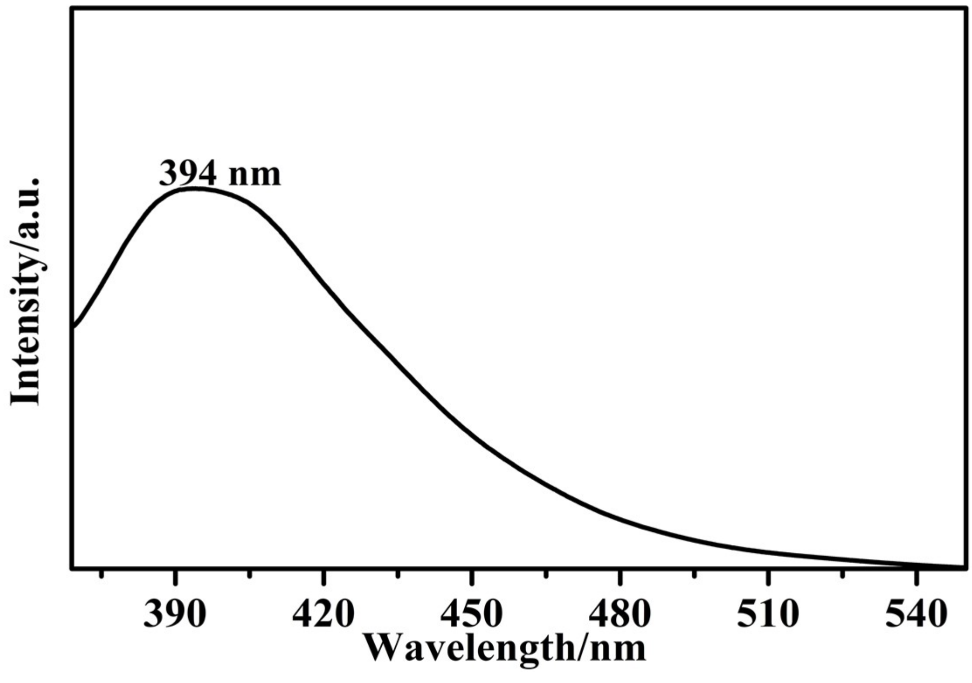


Fig. S2 The emission spectra of H_3btc in the solid state at room temperature (λ_{ex} = 348 nm).

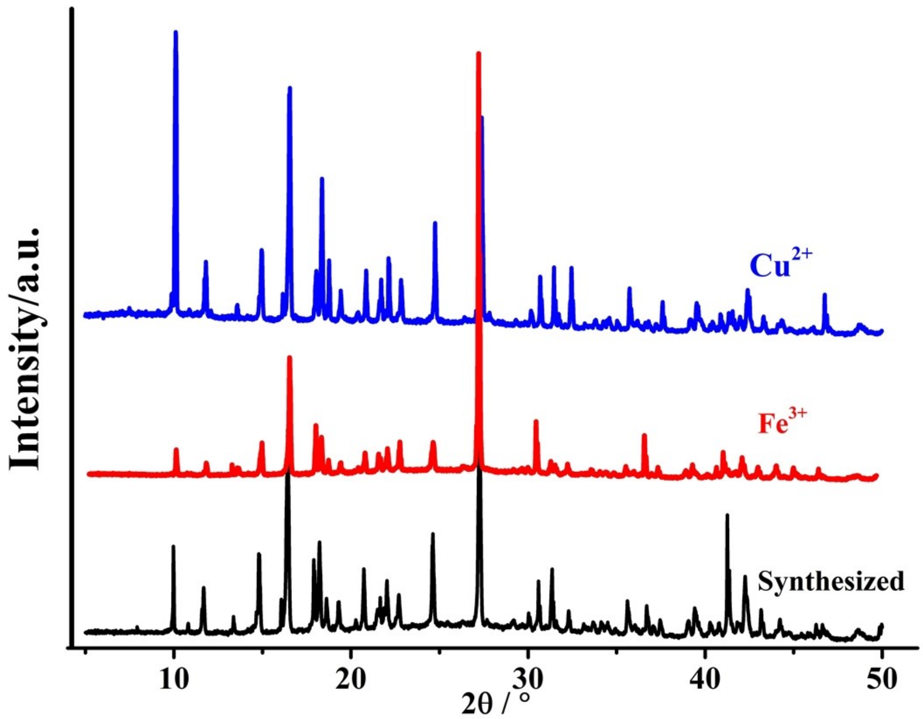


Fig. S3 PXRD of **LCU-109** soaked in water solutions containing Fe^{3+} or Cu^{2+} for three days.

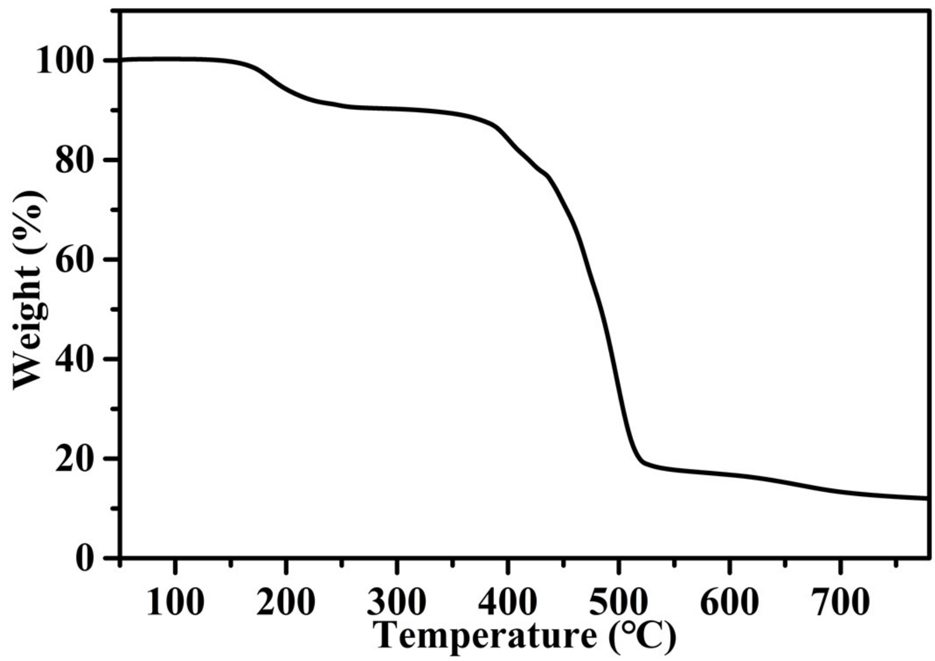


Fig. S4 TGA curve of **LCU-109**.

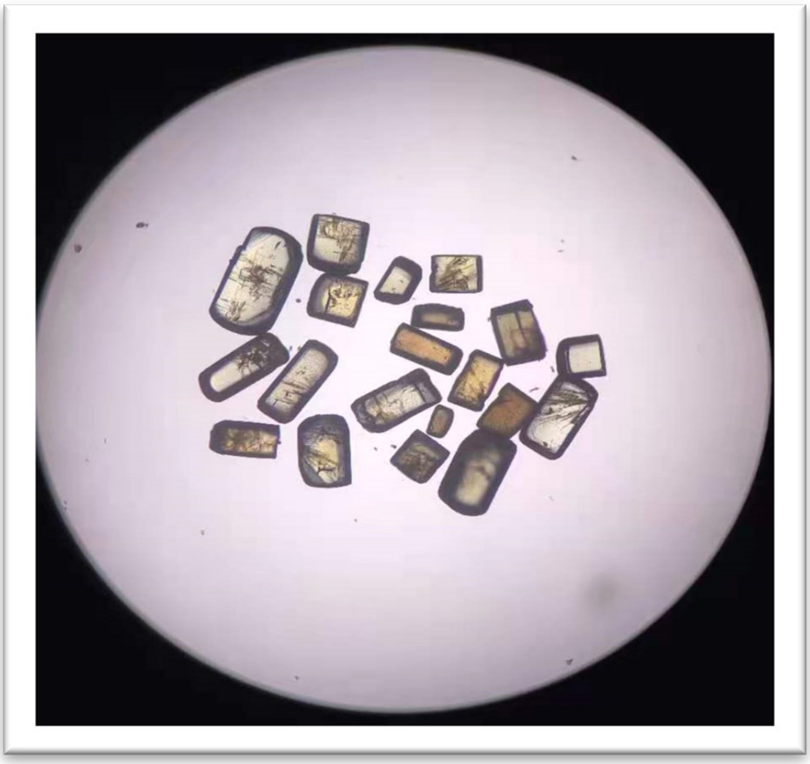


Fig. S5 A picture of **LCU-109** under a microscope.

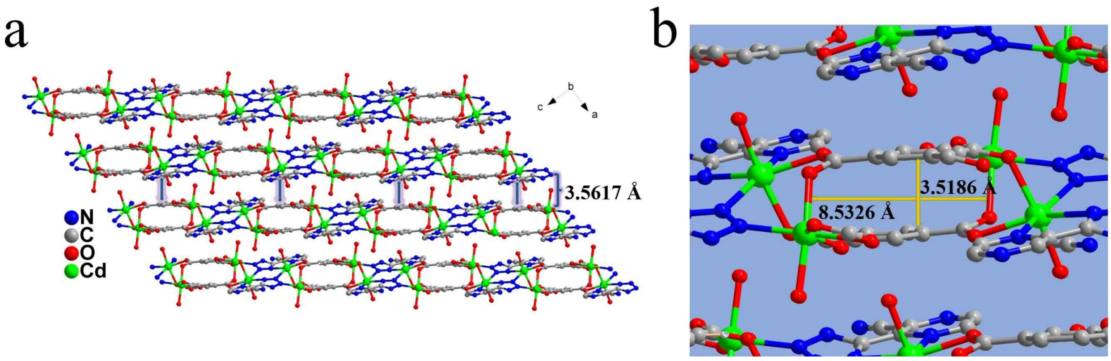


Fig. S6 (a) 3D stacked structure of **LCU-109**. (b) The hole of **LCU-109** along the *b* axis.

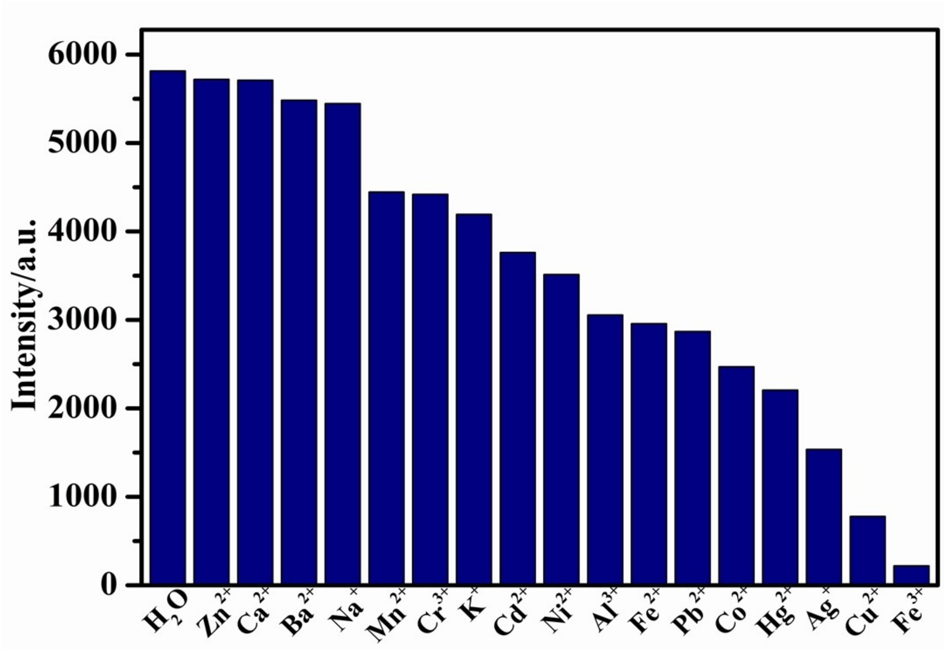


Fig. S7 Luminescence intensities of **LCU-109** in water solutions with different cations (10^{-3} M).

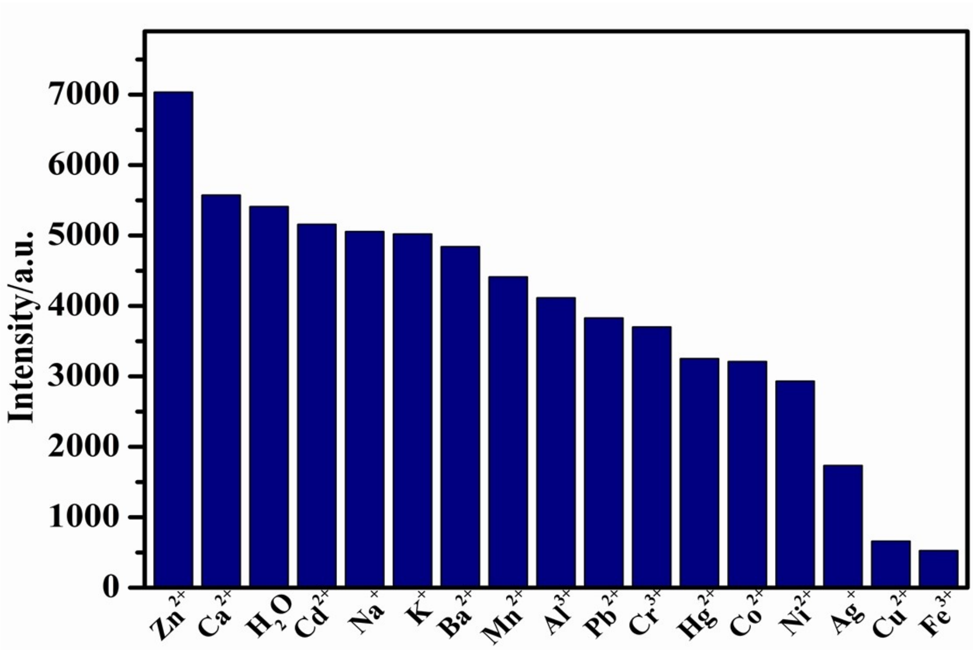


Fig. S8 Luminescence intensities of **LCU-109** in actual water samples with different cations (10^{-3} M).

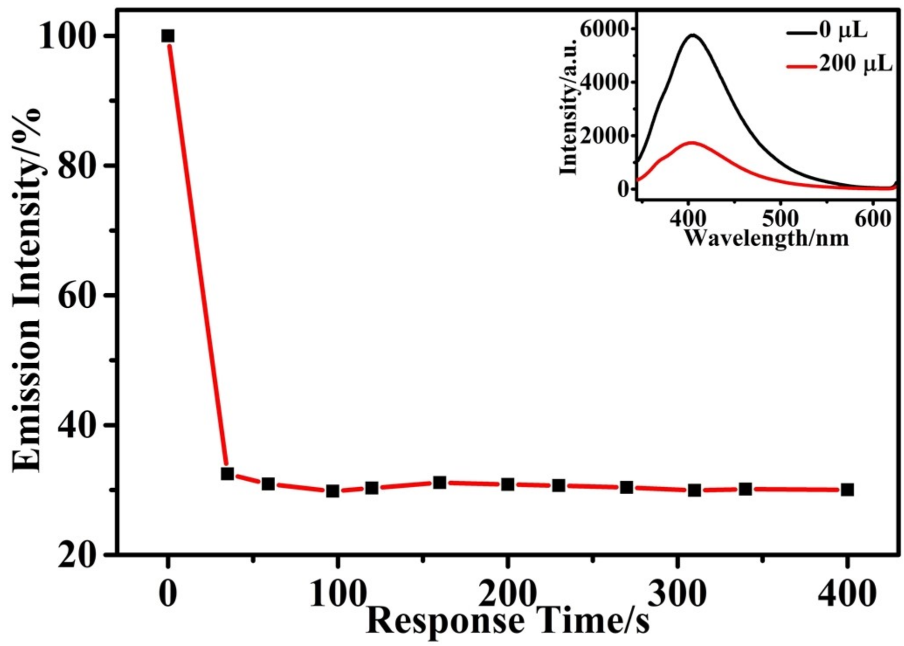


Fig. S9 Time response for Fe^{3+} recognition of **LCU-109**.

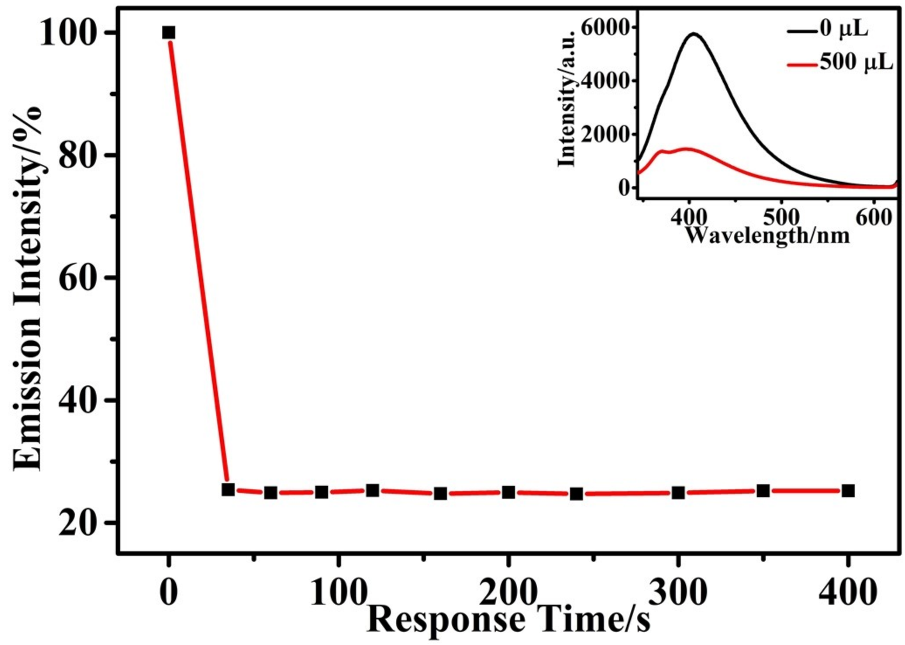


Fig. S10 Time response for Cu^{2+} recognition of **LCU-109**.

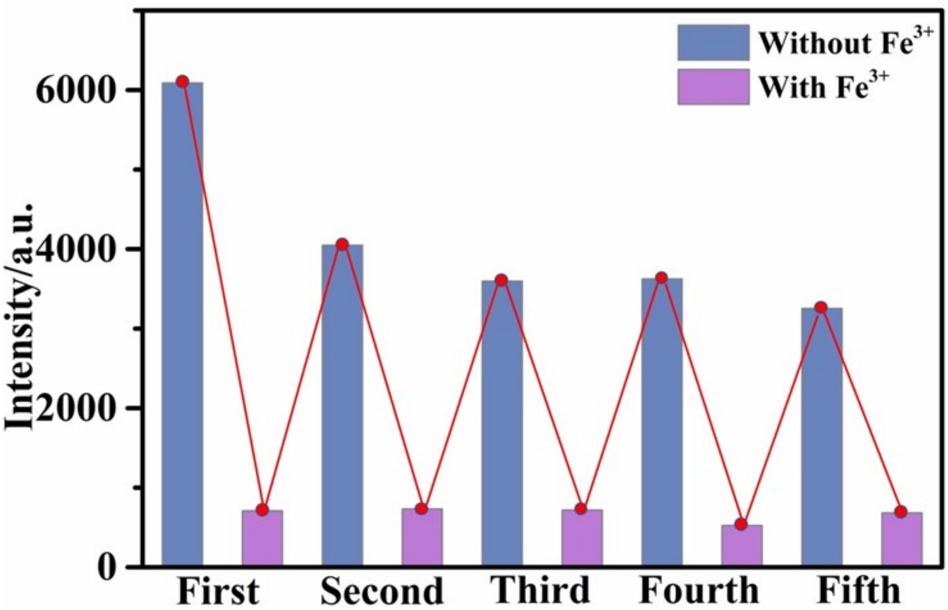


Fig. S11 Recyclability of **LCU-109** after five runs of sensing Fe^{3+} ions.

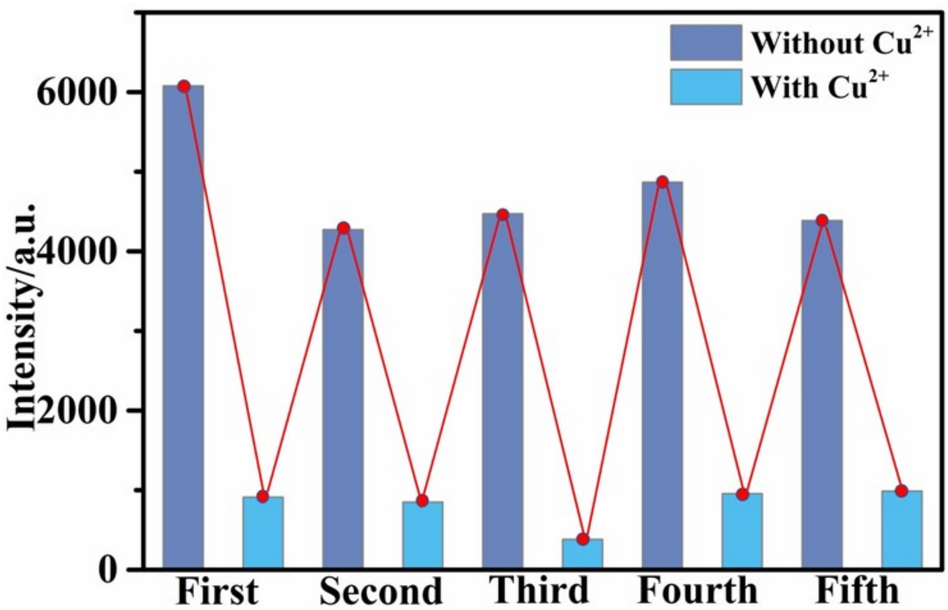


Fig. S12 Recyclability of **LCU-109** after five runs of sensing Cu^{2+} ions.

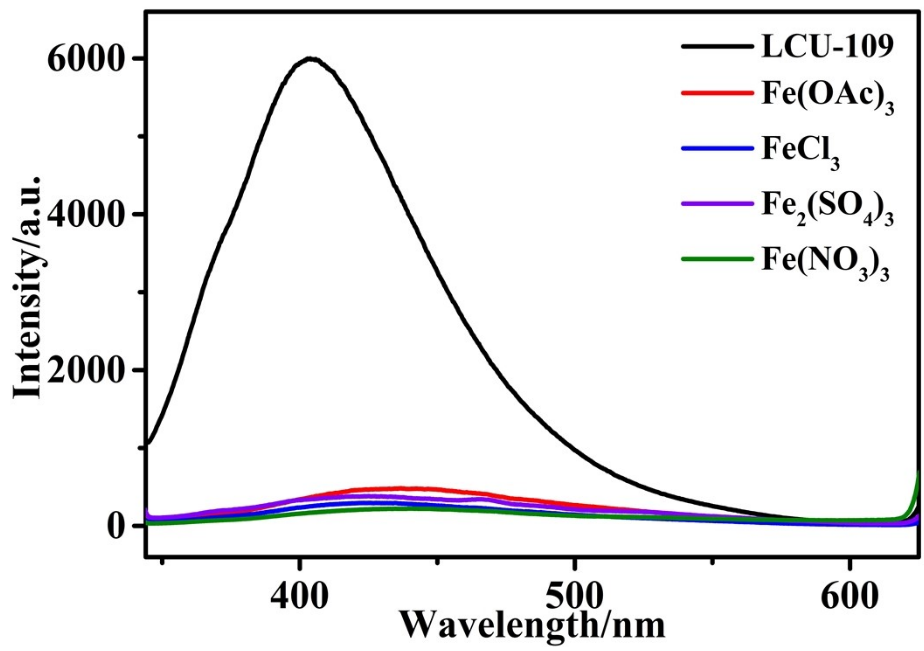


Fig. S13 The emission spectra of **LCU-109** relative to different kinds of ferric salts.

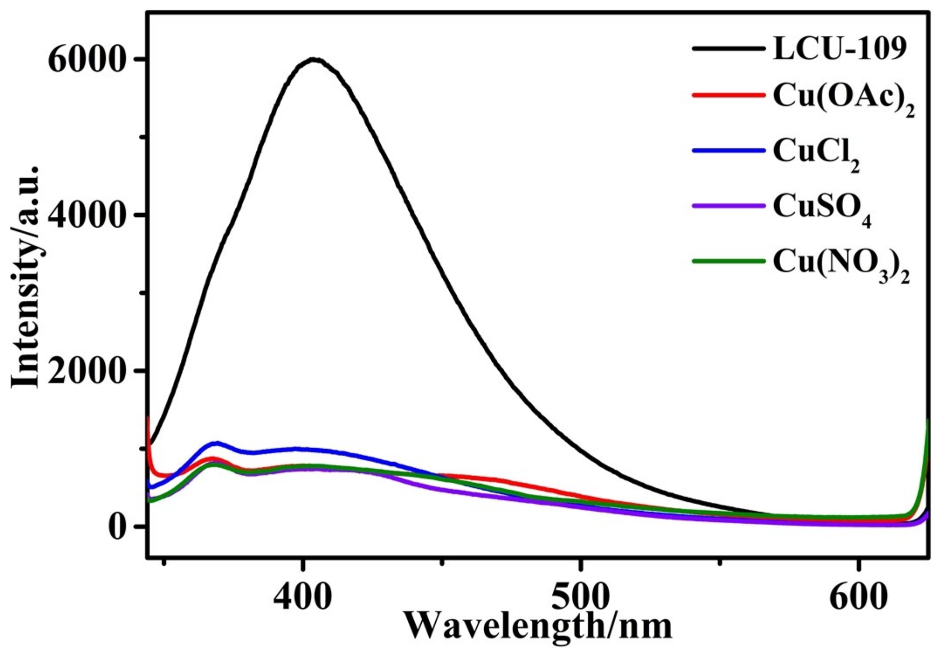


Fig. S14 The emission spectra of **LCU-109** relative to different kinds of copper salts.

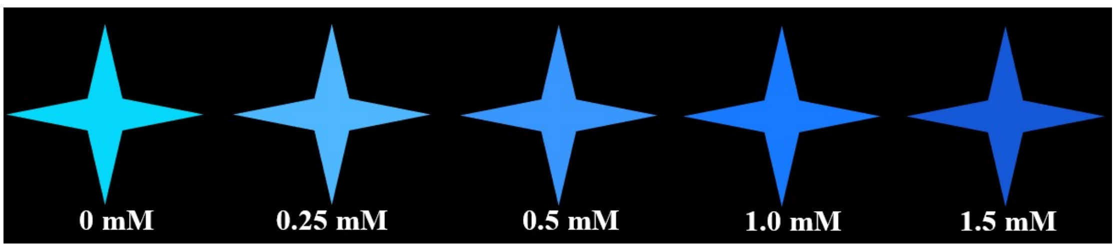


Fig. S15 Luminous test papers of **LCU-109** prepared by soaking in different concentrations of Cu^{2+} aqueous solutions under 365 nm UV lamp.

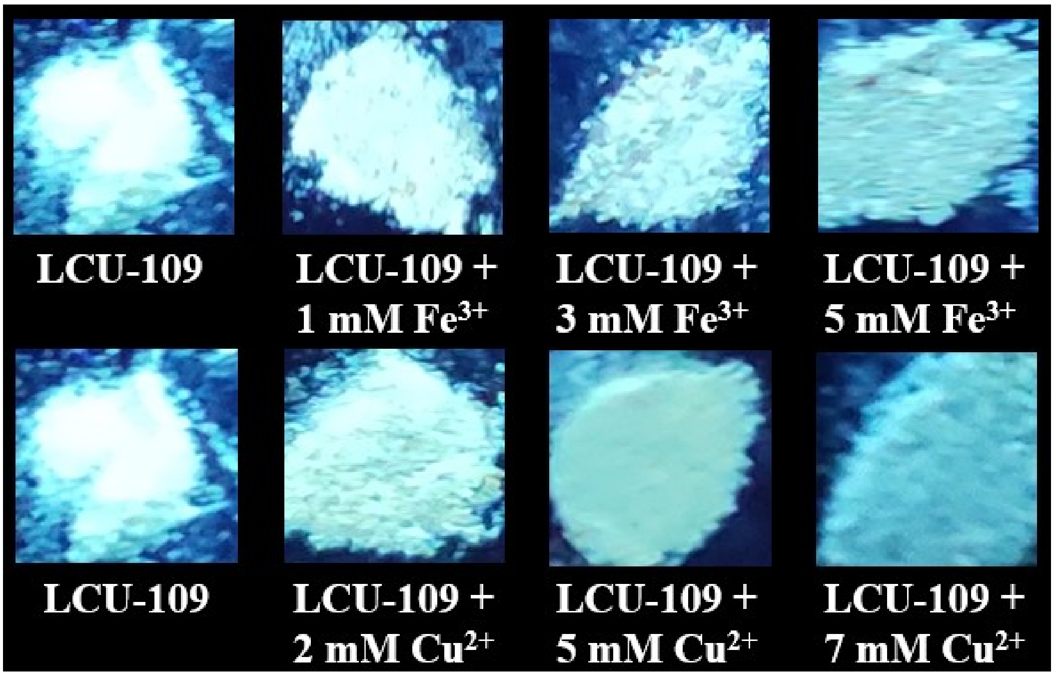
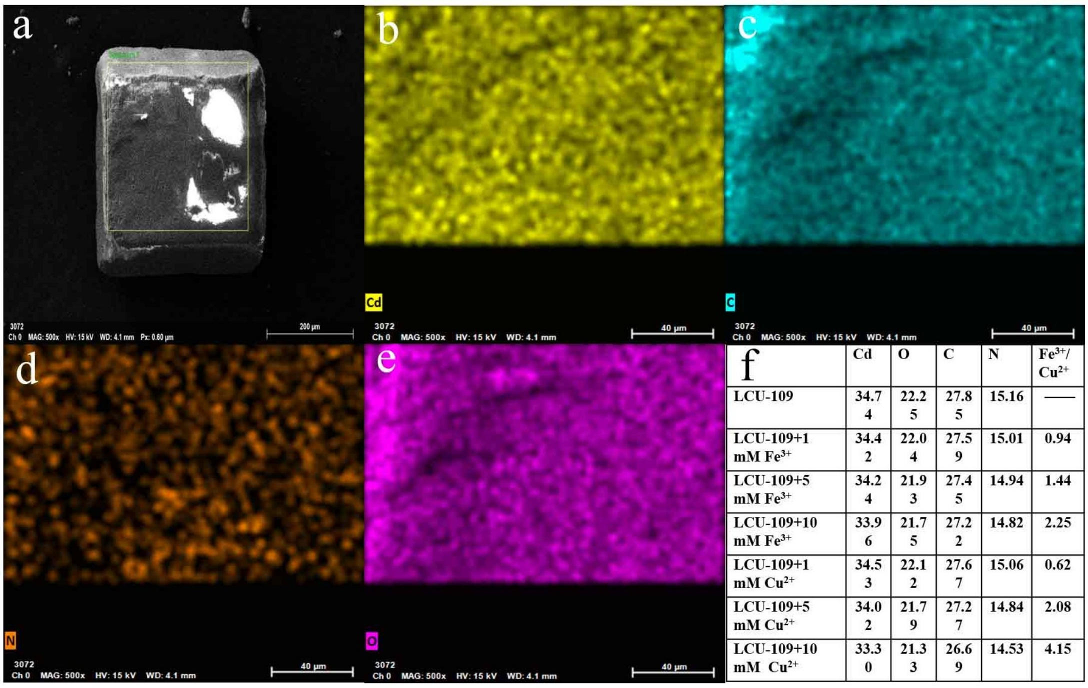


Fig. S16 Photos of **LCU-109** soaked in different concentrations of Fe^{3+} / Cu^{2+} aqueous solution under 365 nm UV lamp.



f	Cd	O	C	N	Fe^{3+}/ Cu^{2+}
LCU-109	34.74	22.25	27.85	15.16	——
LCU-109+1 mM Fe^{3+}	34.42	22.04	27.59	15.01	0.94
LCU-109+5 mM Fe^{3+}	34.24	21.93	27.45	14.94	1.44
LCU-109+10 mM Fe^{3+}	33.96	21.75	27.22	14.82	2.25
LCU-109+1 mM Cu^{2+}	34.53	22.12	27.67	15.06	0.62
LCU-109+5 mM Cu^{2+}	34.02	21.79	27.27	14.84	2.08
LCU-109+10 mM Cu^{2+}	33.30	21.33	26.69	14.53	4.15

Fig. S17 (a) SEM images of **LCU-109**. (b)-(e) EDS mapping images of selected regions: Cd, C, N, and O. (f) The element ratio of **LCU-109** untreated and treated with different concentrations of Fe^{3+} or Cu^{2+} aqueous solution.

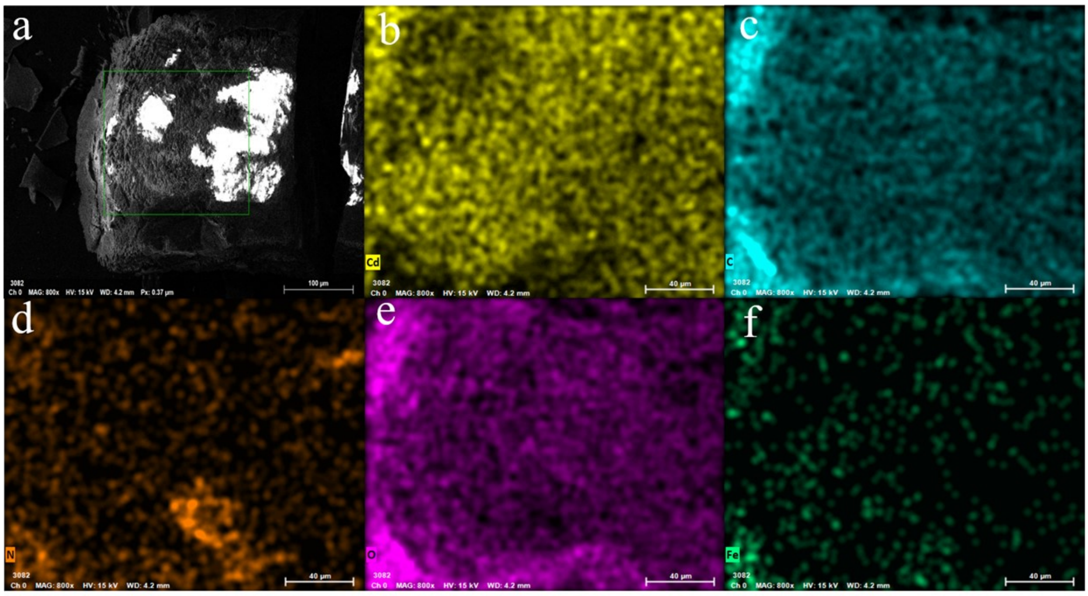


Fig. S18 (a) SEM images of **LCU-109** treated with 1 mM Fe^{3+} aqueous solution. (b)-(f) EDS mapping images of selected regions: Cd, C, N, O and Fe.

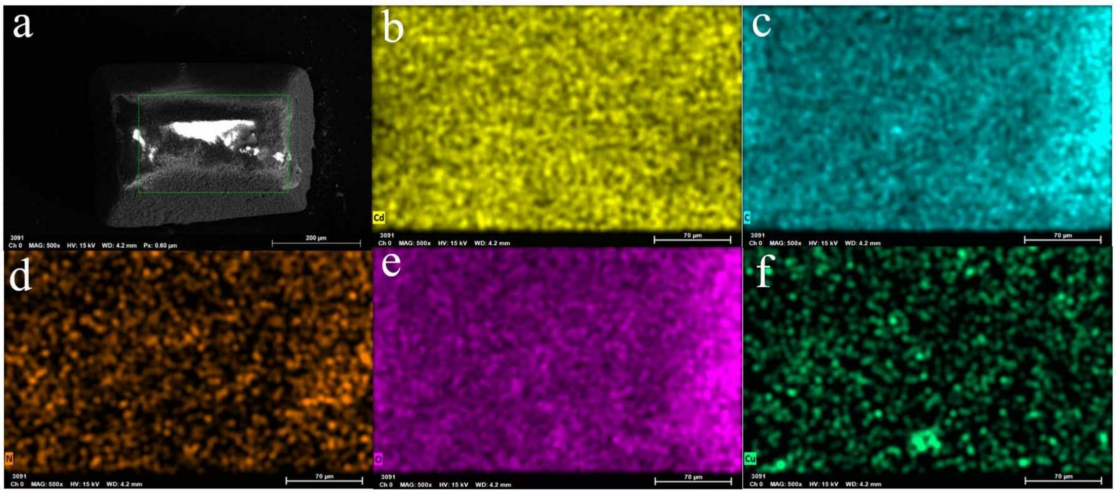


Fig. S19 (a) SEM images of **LCU-109** treated with 5 mM Fe^{3+} aqueous solution. (b)-(f) EDS mapping images of selected regions: Cd, C, N, O and Fe.

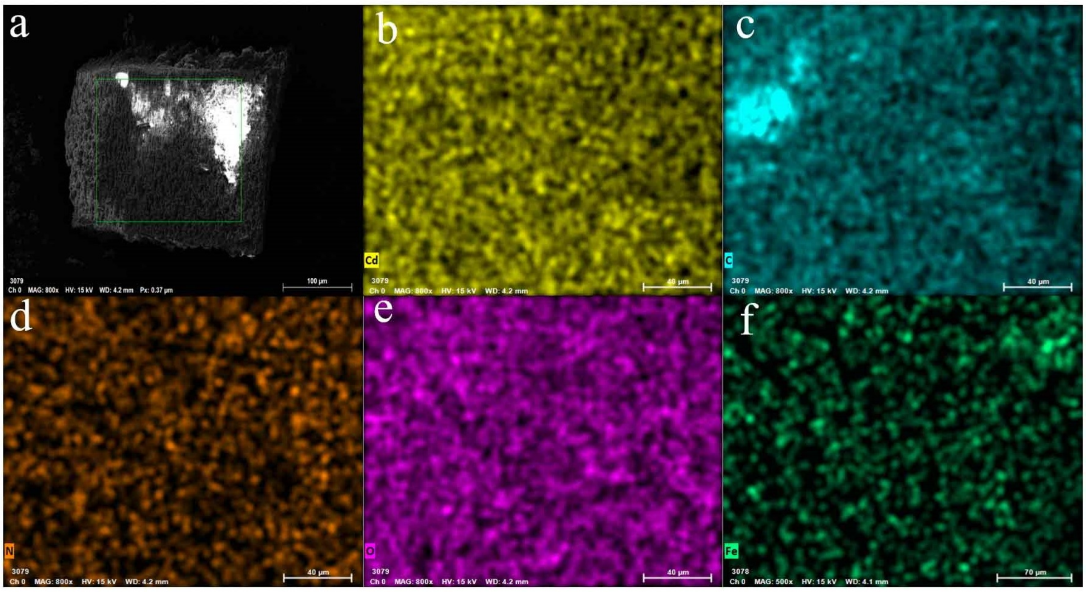


Fig. S20 (a) SEM images of **LCU-109** treated with 10 mM Fe^{3+} aqueous solution. (b)-(f) EDS mapping images of selected regions: Cd, C, N, O and Fe.

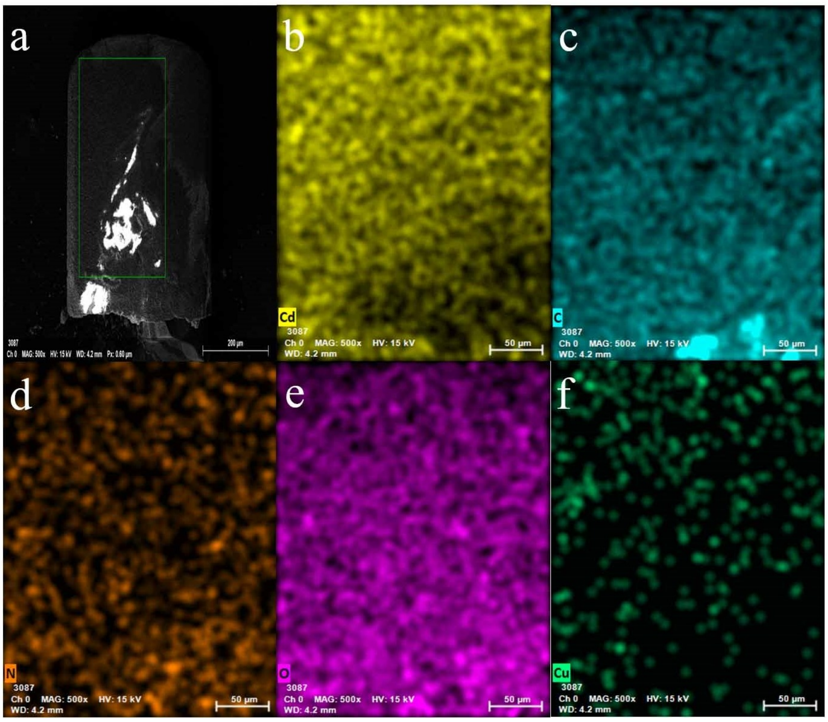


Fig. S21 (a) SEM images of **LCU-109** treated with 1 mM Cu^{2+} aqueous solution. (b)-(f) EDS mapping images of selected regions: Cd, C, N, O and Cu.

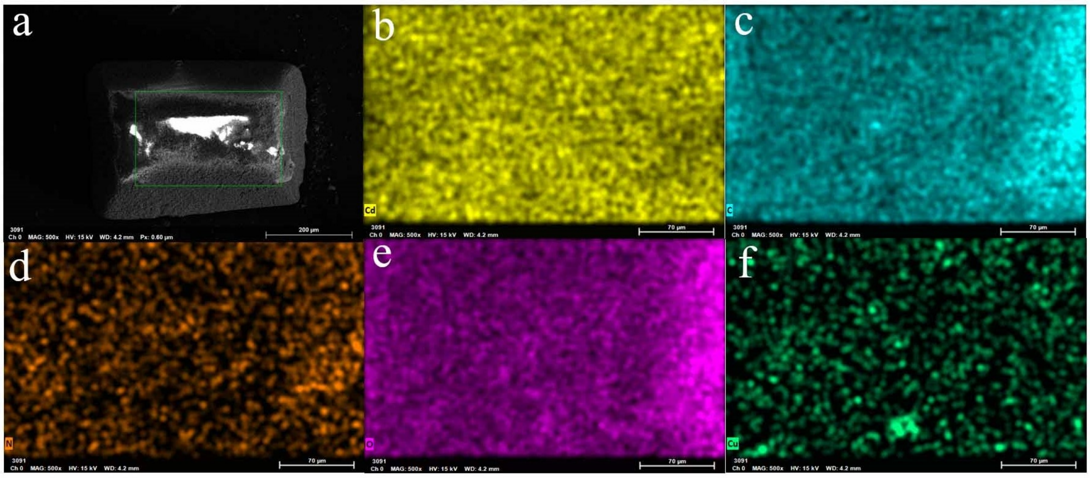


Fig. S22 (a) SEM images of **LCU-109** treated with 5 mM Cu^{2+} aqueous solution. (b)-(f) EDS mapping images of selected regions: Cd, C, N, O and Cu.

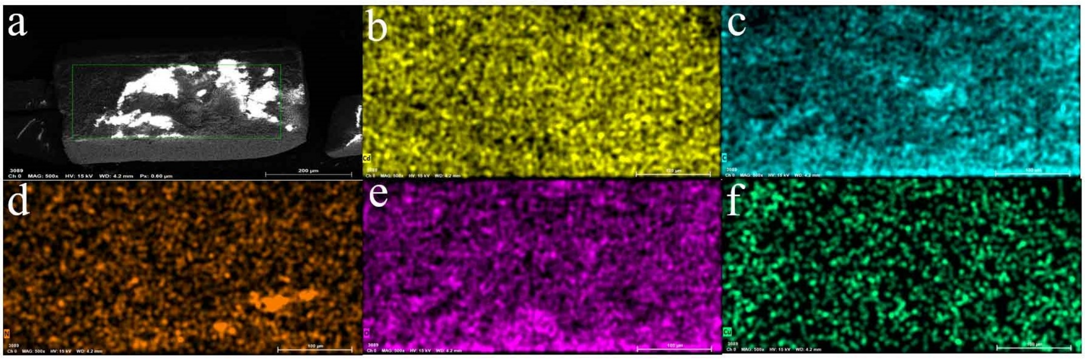


Fig. S23 (a) SEM images of **LCU-109** treated with 10 mM Cu^{2+} aqueous solution. (b)-(f) EDS mapping images of selected regions: Cd, C, N, O and Cu.

Table S3. The K_{sv} values and LODs comparison for sensing Fe^{3+}.

Fe^{3+}				
MOFs/Guidelines	K_{SV}/M^{-1}	LODs/ppm	Medium used	Refs.
LCU-109	5.71×10^4	0.0043	H_2O	This work
$[Zn_2(tpeb)(bpdc)_2]$	1.326×10^4	0.0494	H_2O	S4
$[Zn_2Na_2(TPHC)(4,4'\text{-}Bipy)(DMF)]\cdot 8H_2O$	5.77×10^4	0.358	DMF	S5
MIL-53(Al)	----	0.0504	H_2O	S6
$[Cd_2(L)(BPDC)_2]\cdot DMF\cdot 9H_2O$	1.08×10^4	0.297	DMF	S7
ZnMOF-74	1.35×10^7	0.300	H_2O	S8

$[Mg_2(APDA)_2(H_2O)_3]\cdot 5DMA\cdot 5H_2O$	2.06×10^4	0.152	DMF	S9
$[Cd(bipa)]_n$	1.9×10^4	0.076	H_2O	S10
ZSTU-1	2.69×10^6	0.0036	H_2O	S11
$[Zn_{1.5}(dttz)(Hdpa)]_n$	1.79×10^4	1.45	DMF	S12
$[Cd(Hcbic)]_n$	1.8×10^5	1.74	H_2O	S13
$[Zn_5(hfipbb)_4(trz)_2(H_2O)_2]$	4.1×10^5	10.08	H_2O	S14
$[Zn_2(TPOM)(NDC)_2]\cdot 3.5H_2O$	1.9×10^4	0.112	H_2O	S15
$Cd_3(Hdcapdc)_2$	1.04×10^4	5.798	H_2O	S16
r-PDANPs	----	0.0084	H_2O	S17
L	1.44×10^3	0.550	DMSO/ H_2O	S18
PMDA-TAPB	1.087×10^4	0.0202	DMF	S19
TT-COF	5.63×10^3	0.0469	EtOH	S20

Table S4. The K_{sv} values and LODs comparison for sensing Cu^{2+}.

Cu^{2+}				
MOFs/Guidelines	K_{SV}/M^{-1}	LODs/ppm	Medium used	Refs.
LCU-109	2.81×10^4	0.0028	H_2O	This work
$[Zn_2(L)_2(2,2'\text{-bipy})_2]$	2.82×10^3	1.04	DMF	S21
$[Zn(L)(4,4'\text{-bipy})]$	2.41×10^3	2.57	DMF	S21
NH_2-MIL-125(Ti)	3.2×10^4	0.0403	H_2O	S22
$[Cd(L)(atpa)]_n$	8.89×10^3	0.0768	H_2O	S23
MIL-53-L	6.15×10^3	----	H_2O	S24

$\{[Nd_2(NH_2\text{-}BDC)_3(DMF)_4]\}_n$	----	1.397	DMF	S25
$[Eu(pdc)_{1.5}(dmf)]\cdot(DMF)_{0.5}(H_2O)_{0.5}$	89.4	----	DMF	S26
Cd-MOF-74	1.806×10^3	5	H_2O	S27
$Zr_6O_4(OH)_4(TCPP\text{-}H_2)_3$	4.5×10^5	0.0043	H_2O	S28
NH_2-MIL-101(Al)@ZIF-8	----	0.0109	H_2O	S29
Eu(bcpba)	5.7×10^4	31.87	DMF	S30
L	3.32×10^4	0.674	DMSO/ H_2O	S18
Alkyne-modified AuNPs	----	0.369	H_2O	S31
CorMeO-COF	4.68×10^4	0.0718	THF	S32
Silica nanoparticles	----	0.0254	HEPES	S33

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