Supporting Information for the Manuscript

A Microporous Luminescent Metal-Organic Framework for Highly Selective and Sensitive Sensing of Cu^{2+} in Aqueous Solution

By Yunqing Xiao, Yuanjing Cui, Qian Zheng, Shengchang Xiang, Guodong Qian* and Banglin Chen*

Thermal gravimetric analyses (TGA) data were collected on a TA SDT Q600 instrument under N_2 atmosphere. Sample was heated at 10 °C/min. Powder X-ray diffraction were measured by RIGAKU D/MAX 2550/PC X-ray diffractometer with copper Kα line. The sample powder was loaded to a glass holder and leveled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 4° and 60°. The scan step-width and rate were set to 0.01° and 0.01°/s, respectively.

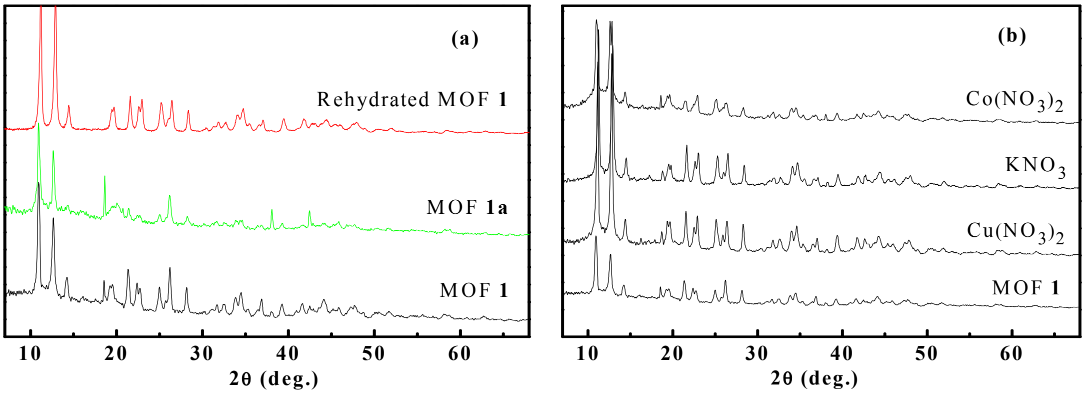


Figure S1 Powder XRD patterns of (a) black, ay-synthesized MOF **1**; green, dehydrated MOF **1a** (120 °C heated); Red, rehydrated MOF **1** in water. (b) MOF **1a** immersed in $Co(NO_3)_2$, $Cu(NO_3)_2$ and KNO_3 aqueous solutions, and then dried at 60 °C under vacuum.

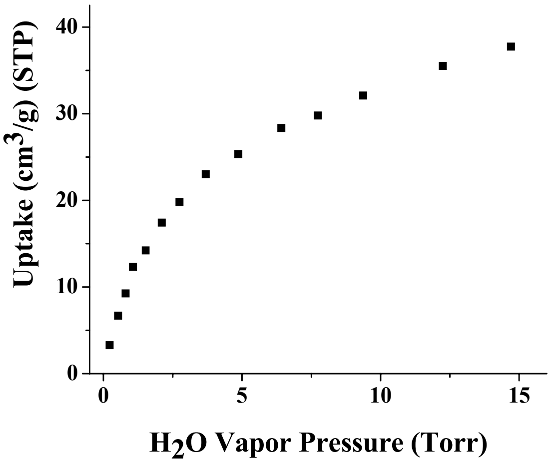


Figure S2 Water vapor adsorption isotherm of MOF **1a** at room temperature.

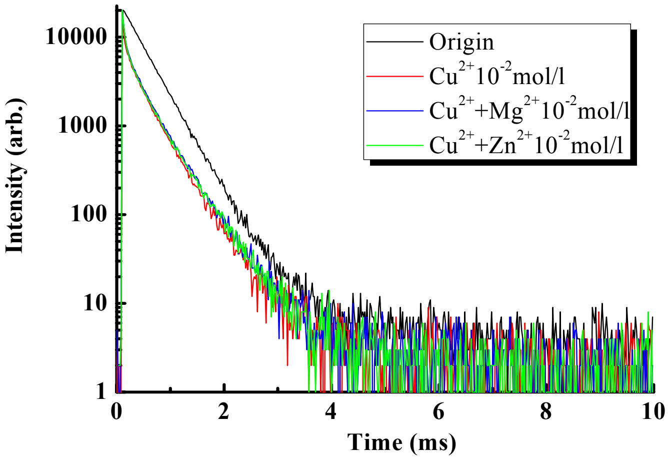


Figure S3 Comparison of the fluorescence lifetime studies of Eu^{3+} in original MOF **1b** and Cu^{2+}, Mg^{2+} or Zn^{2+}-incorporated **1b** activated in 10^{-2} $Cu(NO_3)_2$ aqueous solution.

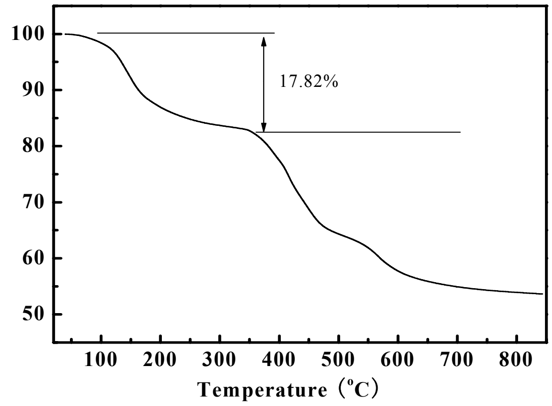


Figure S4 TG curve of MOF **1**.

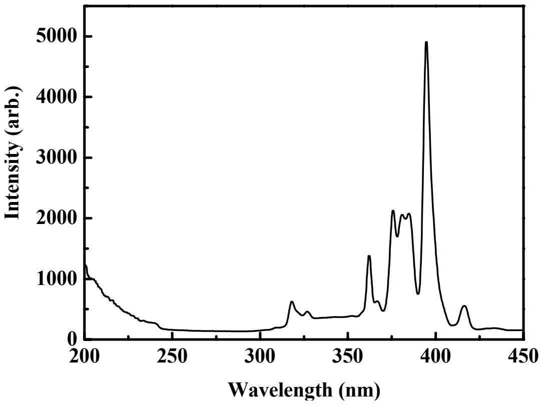


Figure S5 Excitation spectrum of MOF **1** (monitored at 617 nm).

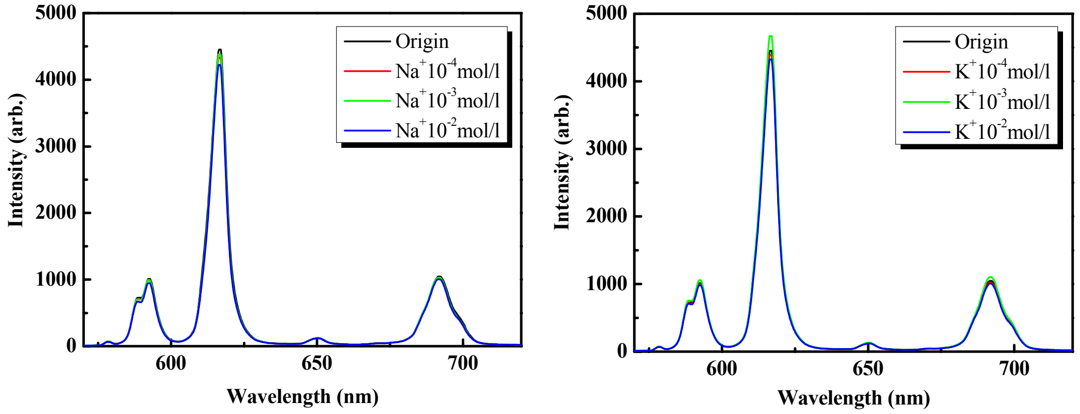
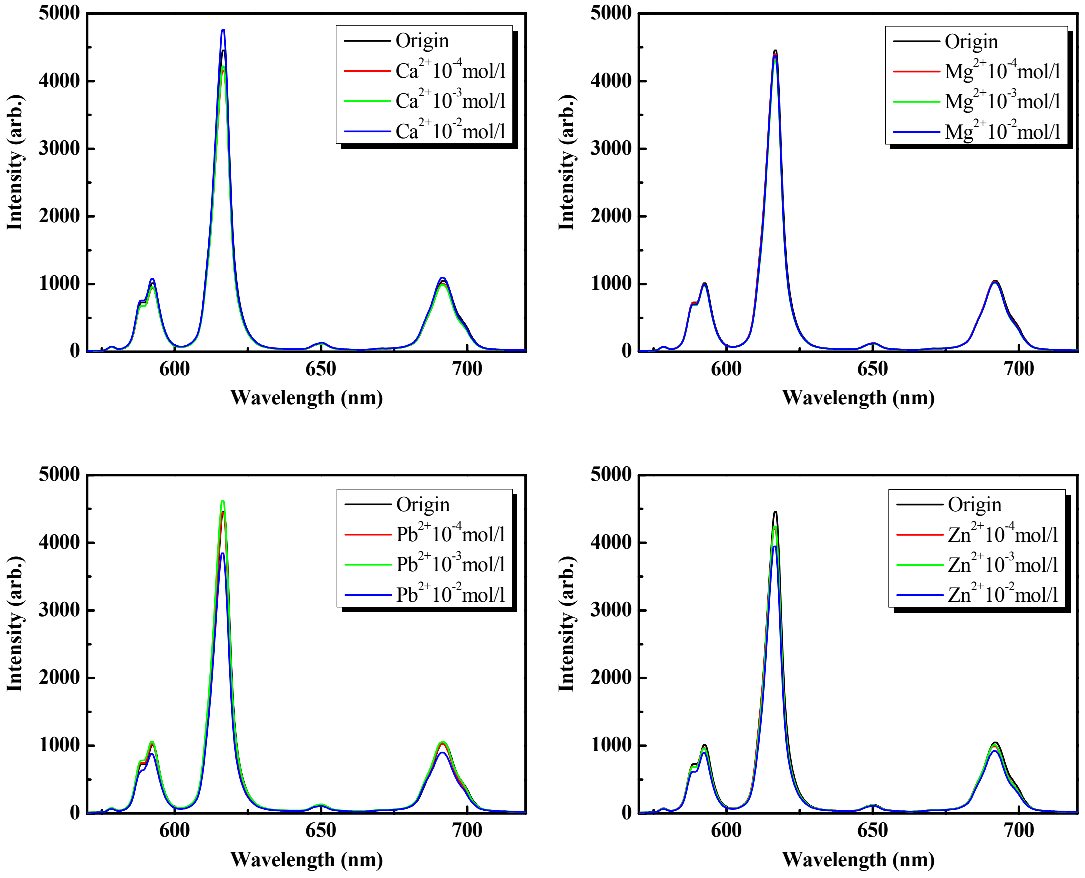


Figure S6 Emission spectra of MOF **1b** after immersed in Na^+ and K^+ aqueous solutions, excited at 394 nm.



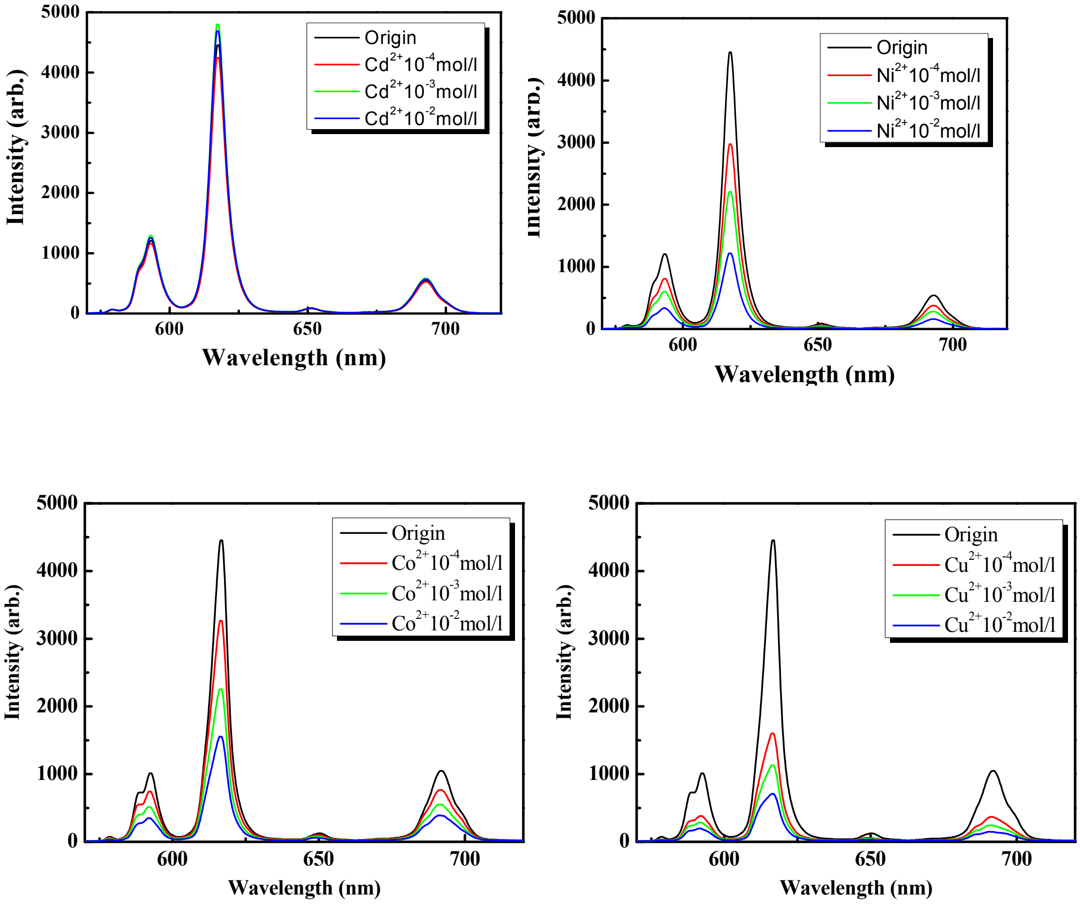


Figure S7 Emission spectra of MOF **1b** after immersed in Ca^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+} aqueous solutions, excited at 394 nm.

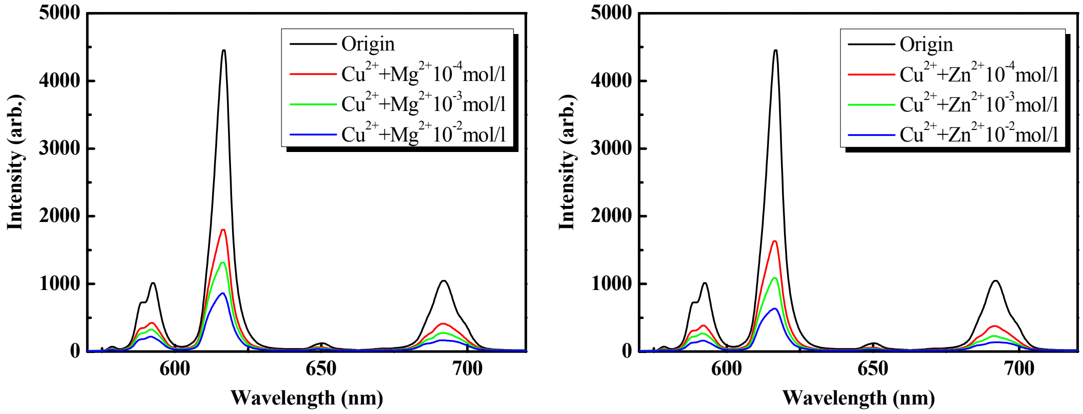


Figure S8 Emission spectra of MOF **1b** after immersed in mixture of (Cu^{2+}+Mg^{2+}), and (Cu^{2+}+Zn^{2+}) aqueous solutions (excited at 394 nm).

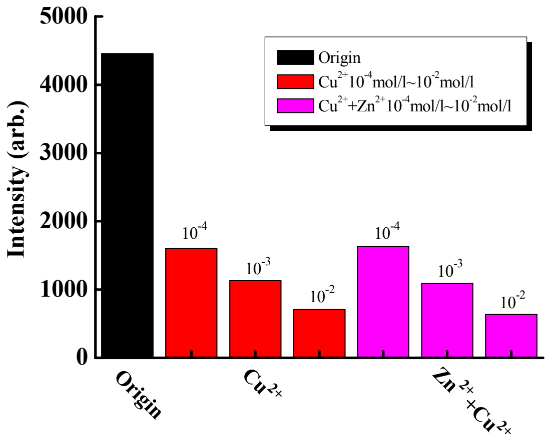


Figure S9 The luminescence intensity of $^5D_0 \rightarrow {}^7F_2$ transition of MOF **1b** at 616 nm upon the addition of Cu^{2+} and (Cu^{2+} + Zn^{2+}) ions (excited at 394 nm).

Table S1. Quenching effect coefficients (Ksv) of different metal ions on the luminescence intensity of metal-ion-incorporated MOF **1b**.

Metal Ion	$K_{sv}(M^{-1})$
$Na^+(NO_3^-)$	~0
$K^+(NO_3^-)$	~0
$Mg^{2+}(NO_3^-)_2$	~0
$Ca^{2+}(NO_3^-)_2$	~0
$Cd^{2+}(NO_3^-)_2$	~0
$Zn^{2+}(NO_3^-)_2$	12.9
$Pb^{2+}(NO_3^-)_2$	15.9
$Cu^{2+}(NO_3^-)_2$	528.7
$Co^{2+}(NO_3^-)_2$	186.6
$Ni^{2+}(NO_3^-)_2$	266.0

Table S2. Observed Cu^{2+} ion amount in MOF **1b** by atomic absorption spectroscopy.

MOF **1b**	Added Cu^{2+} ion amount in aqueous solution	Observed Cu^{2+} ion amount in MOF **1b**
1.00×10^{-4} M Cu^{2+}	2.41×10^{-3} mg	3.56×10^{-4} mg
1.00×10^{-2} M Cu^{2+}	2.41×10^{-1} mg	3.20×10^{-3} mg

(MOF **1b** were dissolved in 4 ml nitric acid for the atomic absorption spectroscopy study with HITACHI 180-50, burner head height: 7.5, slit width: 1.3 nm, acetylene flow: 1.3 kg/m^2, air flow: 1.6 kg/m^2, wavelength: 324.8 nm.)

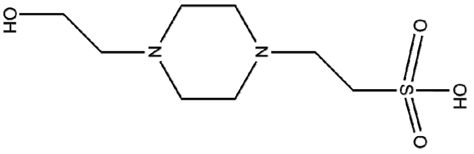
Table S3. Observed Eu^{3+} ion amount in the filtrate solution of MOF **1a** before and after the addition of different concentration of $Cu(NO_3)_2$ determined by ICP-AES **(**Inductively Coupled Plasma-Atomic Emission Spectroscopy).

Concentration of $Cu(NO_3)_2$ added to MOF **1a**	Observed Eu^{3+} ion amount in the filtrate solution	Eu^{3+} leaching percentage (%) (total of 39.8 mg Eu^{3+} in 100 mg original MOF **1**)
0	1.20×10^{-2} mg	0.03
1.00×10^{-4} M Cu^{2+}	5.70×10^{-2} mg	0.14
1.00×10^{-3} M Cu^{2+}	9.00×10^{-2} mg	0.23
1.00×10^{-2} M Cu^{2+}	3.98×10^{-1} mg	1.00

(Each 100 mg MOF **1** was activated and immersed in 0 M, 1.00×10^{-4} M , 1.00×10^{-3} M and 1.00×10^{-2} M $Cu(NO_3)_2$ aqueous solution, respectively. The filtrate solution was examined by ICP-AES to determine the Eu^{3+} amount. ICP-AES were carried out by IRIS INTREPID II XSP of Thermo Electron Corporation).

Studies in the simulated physiological conditions

We use HEPES (2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid) which was purchased from Alfa Aesar without further purification as biological solution raw material according to Christopher Chang Group's work [1-5]. HEPES (Figure 1) is a zwitterionic organic chemical buffering agent which is widely used in cell culture, largely because it is better at maintaining physiological pH despite changes in carbon dioxide concentration (produced by cellular respiration) when compared to bicarbonate buffers, which are also commonly used in cell culture. The solution (20mM HEPES aqueous solution, buffer pH 7) was prepared by introducing 476 mg HEPES into 100 ml water. The metal ion incorporated MOF **1c** were prepared by introducing 20 mg of MOF 1a (heated at 120 °C under vacuum) into 2.00 ml Cu^{2+}@HEPES solutions which was prepared by adding $Cu(NO_3)_2$ into buffered solution, collected by filtration and dried under vacuum for 24 h at 60 °C.



HEPES structure

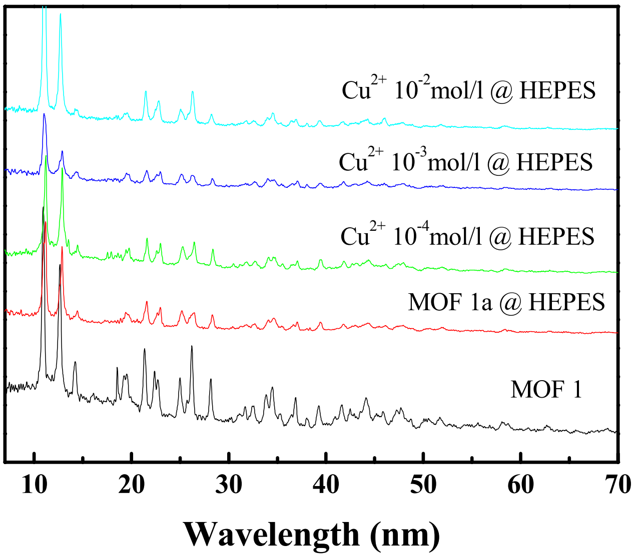


Figure S11 Powder XRD patterns of ay-synthesized MOF **1** (black), dehydrated MOF **1a** in 20mM HEPES aqueous solution (red), and dehydrated MOF **1a** in 20mM HEPES aqueous solution containing different amount of Cu $(NO_3)_2$ (green, 10^{-4} M; blue, 10^{-3} M; cyan, 10^{-2} M) after collected and dried at 60°C under vacuum.

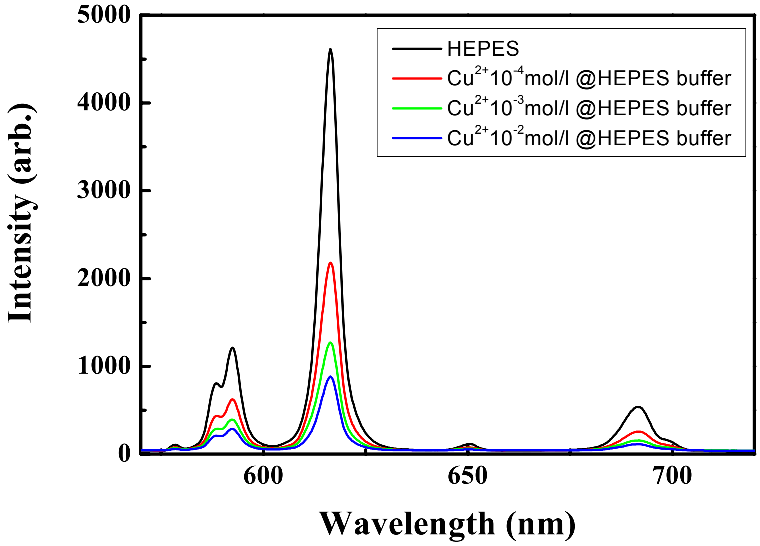


Figure S12 Emission spectra of MOF **1c** after immersed in Cu^{2+}@HEPES aqueous buffer solutions, excited at 394 nm.

References:

[1] S. Yoon, E. W. Miller, Q. He, P. H. Do, C. J. Chang. *Angew. Chem. Int. Ed.* **2007**, 46, 6658.

[2] E. W. Miller, Q. He, C. J. Chang. *Nature Protocols* **2008**, 3, 777.

[3] E. L. Que, D. W. Domaille, C. J. Chang. *Chem. Rev.* **2008**, 108, 1517.

[4] D. W. Domaille, E. L. Que, C. J. Chang. *Nat. Chem. Biol.* **2008**, 4, 168.

[5] Q. He, E. W. Miller, A. P. Wong, C. J. Chang. *J. Am. Chem. Soc.* **2006**, 128, 9316.