Supporting Information

A stable, pillar-layer metal−organic framework containing uncoordinated carboxyl groups for separation of transition metal ions

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Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analyses were performed on a Perkin−Elmer Thermal Analysis Pyris Diamond heated from room temperature to 1000 ºC under a N_2 atmosphere at a rate of 10 ºC min^{-1}. The experimental powder X-ray diffraction data (PXRD) were collected on a Bruker D8-FOCUS diffractometer equipped with Cu Kα1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) at a scan speed of 8° min^{-1} and the in situ variable temperature PXRD were collected on PW1700 X-ray diffractometer. The simulated PXRD patterns were calculated by using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. ICP was measured by ICAP 6000 Series (Thermo Fisher Scientific).

Synthesis of Compound 1

$Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), 1,2,4-Triazole (1 mmol), benzene-1,2,4,5-tetracarboxylic acid (0.5 mmol), and DMF (5 mL) was sealed in a 15 mL Teflon-lined stainless-steel autoclave under autogenous pressure and heated at constant 102 °C for 3 days and then was cooled to room temperature slowly. The resulting colorless crystals were collected with a yield of 61% (based on $Zn(NO_3)_2 \cdot 6H_2O$). Elemental analysis for $C_{10}H_{11}N_4O_5Zn$ (**1**) (332.60) (%): calcd. C 36.11, H 3.33, N 16.84; found C 36.18, H 3.27, N 16.81.

Crystal data for **1**: $C_{10}H_{11}N_4O_5Zn$, $M_r = 332.60$, Monoclinic, space group $P2_1/c$, $a = 13.7620(8)$ A, $b = 9.563(5)$ A, $c = 9.883(5)$ A, alpha = 90º, beta = 101.074(5)º, gamma = 90º, $V = 1276.4(9)$Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.731$ g cm^{-3}, final $R_1 = 0.0357$ and w$R_2 = 0.0935$ ($R_{\text{int}} = 0.0330$) for 2536 independent reflections [$I > 2\sigma(I)$]. CCDC 962917.

X-ray crystallography

The X-ray intensity data for the two compounds was collected on a Bruker SMART APEX-II CCD diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) operating at 1.575 kW (45 kV, 35 mA) at room temperature. Data integration and reduction were processed with SAINT software.[1] Multiscan absorption corrections were applied with the SADABS program.[2] All structures were solved by direct methods and refined employing full-matrix least squares techniques based on F^2 using the SHELXTL-97 crystallographic software package.[3] All non-hydrogen atoms were refined with anisotropic temperature parameters.

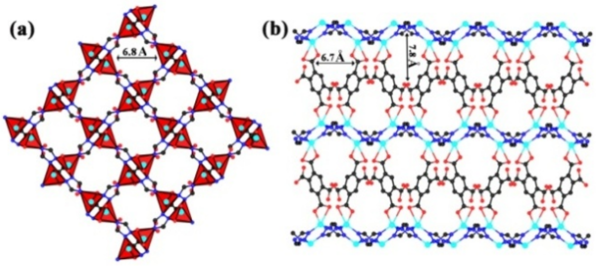


Fig. S1 The quadrangle shape (a) and pear-like shape (b) channels in **1**.

The stability of the compound 1

Compound **1** (0.03 g) was immersed in 10 mL methanol, ethanol, DMA, dichloromethane, THF, acetonitrile, hexane, and dimethyl sulfoxide for 12 h and the PXRD were determined and given as Fig. S3. Compound **1** (0.03 g) was immersed in boiling methanol, ethanol, DMA, dichloromethane, THF, acetonitrile, hexane, and dimethyl sulfoxide for 12 h and the PXRD were determined and given as Fig. S4.

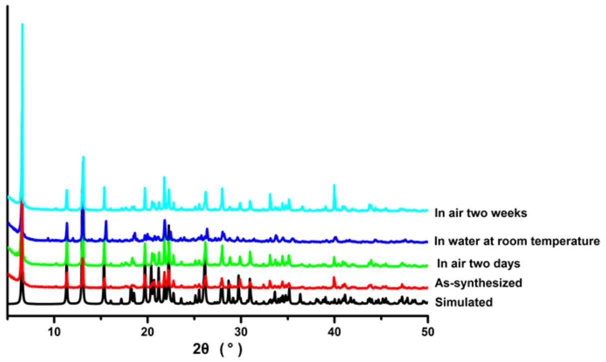


Fig. S2 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples soaked in water for 4 h and exposed in air for two weeks.

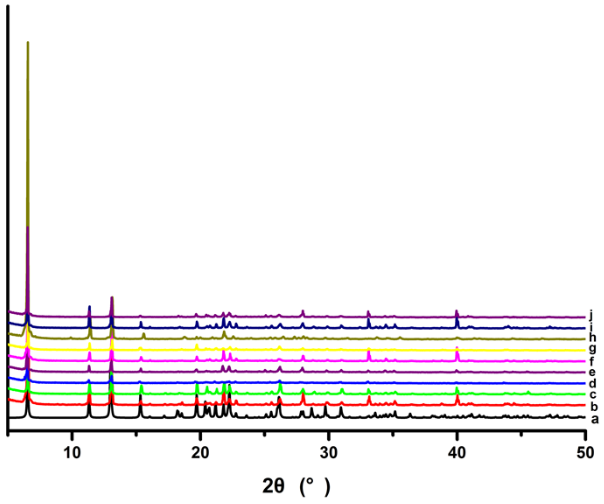


Fig. S3 Powder X-ray diffraction patterns of a) simulated from the X-ray single structure of **1**, b) as-synthesized **1**, and **1** samples soaked in c) methanol, d) ethanol, e) DMA, f) dichloromethane, g) THF, h) acetonitrile, i) hexane, and j) dimethyl sulfoxide solution for 12 h.

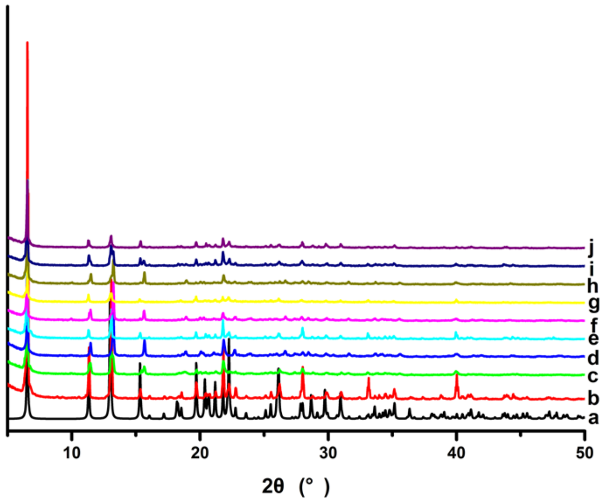


Fig. S4 Powder X-ray diffraction patterns of a) simulated from the X-ray single structure of **1**, b) as-synthesized **1**, and **1** samples soaked in boiling c) methanol, d) ethanol, e) DMA, f) dichloromethane, g) THF, h) acetonitrile, i) hexane, and j) dimethyl sulfoxide solution for 12 h.

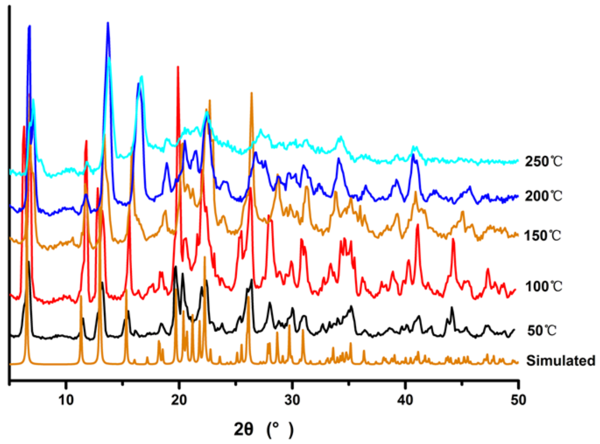


Fig. S5 *In situ* variable temperature Powder X-ray diffraction (VTPXRD) data of compound **1** comparison with the simulated one.

Single metal ion adsorption in compound 1

Compound **1** **(**0.03 g) was immersed in 10 mL, 0.1 mol/L $M(NO_3)_2 \cdot nH_2O$ (M = Cu^{2+}, Co^{2+}, Ni^{2+}, or Cd^{2+}) DMF solution for 5.5 hours. The crystals were filtrated and washed with DMF and CH_3OH twice. It dissolved in concentrated HNO_3 at 180 °C for 1 day. Then the solution was clarified by filtration and analysed by ICP to determinate the ratio of metal ions.

Compound **1** (0.03 g) was immersed in 10 mL, 0.1 mol/L $M(NO_3)_2 \cdot nH_2O$ ($M = Cu^{2+}$, Co^{2+}, Ni^{2+}, or Cd^{2+}) methanol solution for 5.5 hours. The crystals were filtrated and washed with CH_3OH twice. It dissolved in concentrated HNO_3 at 180 °C for 1 day. Then the solution was clarified by filtration and analysed by ICP to determinate the ratio of metal ions.

Compound **1** (0.03 g) was immersed in 10 mL, 0.01 mol/L $M(NO_3)_2 \cdot nH_2O$ ($M = Cu^{2+}$, Co^{2+}, Ni^{2+}, or Cd^{2+}) aqueous solution for 10 min. The crystals were filtrated and washed with CH_3OH twice. It dissolved in concentrated HNO_3 at 180 °C for 1 day. Then the solution was clarified by filtration and analysed by ICP to determinate the ratio of metal ions.

Competition metal ion adsorption in compound 1

Compound **1** (0.03 g) was immersed in 10 mL metal ion DMF solvent with the same concentration (0.1 mol/L) of $Cu(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ for 5.5 hours. The crystals were filtrated and washed with DMF and CH_2Cl_2 twice. It dissolved in concentrated HNO_3 at 180 °C for 1 day. Then the solution was filtrated and analysed by ICP to determine the metal ion concentration.

Compound **1** (0.03 g) was immersed in 10 mL metal ion methanol solvent with the same concentration (0.1 mol/L) of $Cu(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ for 5.5 hours. The crystals were filtrated and washed with CH_3OH twice. It dissolved in concentrated HNO_3 at 180 °C for 1 day. Then the solution was filtrated and analysed by ICP to determine the metal ion concentration.

Compound **1** (0.03 g) was immersed in 10 mL metal ion aqueous solvent with the same concentration (0.01 mol/L) of $Cu(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ for 10 min. The crystals were filtrated and washed with CH_3OH twice. It dissolved in concentrated HNO_3 at 180 °C for 1 day. Then the solution was filtrated and analysed by ICP to determine the metal ion concentration.

Table S1 ICP results for single metal ion adsorption in compound **1**

Solution	Metal ions (M)	M/Zn Mass ratio (experimental)	M/Zn Mol ratio
DMF	Cu	455.1/166400	0.0028142
0.1mol/L	Co	45.88/211200	0.0002409
5.5h	Ni	59.63/210600	0.0003154
	Cd	113.4/205800	0.0003148
	Cu/Co/Ni	118.2/11.49/23.45/206600	0.0005/0.00006/0.00012
MeOH	Cu	1768/204100	0.0089
0.1mol/L	Co	55.51/199500	0.0003087
5.5h	Ni	132.2/215600	0.0006831
	Cd	469.3/235100	0.00116
	Cu/Co/Ni	3322/16.57/70.46/214800	0.0519/0.0000855/0.0003654
H_2O	Cu	54860/157900	0.35
0.01mol/L	Co	3299/187700	0.0195
10min	Ni	8374/223100	0.0418
	Cd	463.7/205600	0.0013
	Cu/Co/Ni	29370/631.0/2861/179200	0.1686/0.0039/0.0178

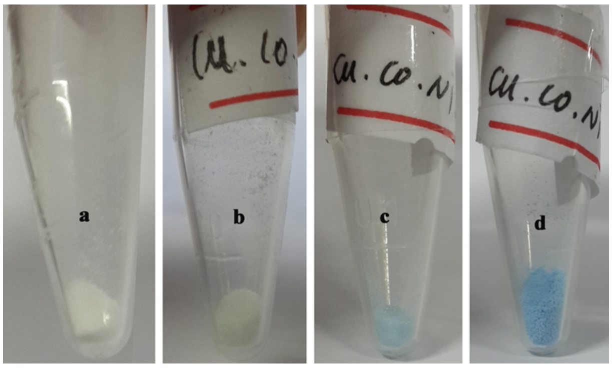


Fig. S6 Photographs of crystals of compound **1** (a); soaked in DMF solution containing $M(NO_3)_2$ (0.1 mol/L, $M^{2+} = Cu^{2+}$, Co^{2+} and Ni^{2+}) for 5.5 h (b); soaked in methanol solution containing $M(NO_3)_2$ (0.1 mol/L, $M^{2+} = Cu^{2+}$, Co^{2+} and Ni^{2+}) for 5.5 h (c); soaked in aqueous solution containing $M(NO_3)_2$ (0.01 mol/L, $M^{2+} = Cu^{2+}$, Co^{2+} and Ni^{2+}) for 10 min (d).

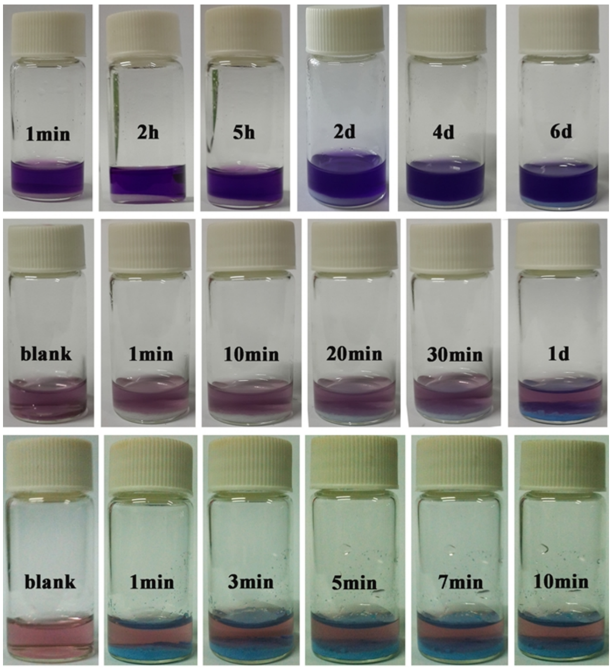


Fig. S7 Metal ion selective adsorption in compound **1**, Top, DMF as solvent; middle, methanol as solvent; bottom, water as solvent.

MOF-based separation column

This separation column (60 mm × 4 mm) was obtained by filling the crystals of compound **1** into a glass tube, and a little of asbestos was placed at the bottom of this glass tube to prevent the crystals flowing out.

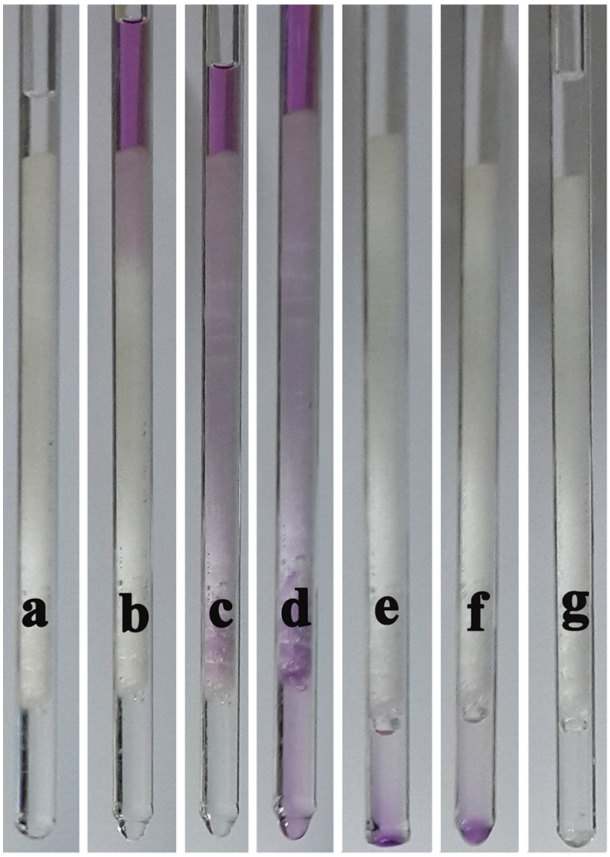


Fig. S8 Separation process of Cu^{2+} and Co^{2+} ions by the MOF-based chromatographic column (DMF as solvent). a) blank; b) 1 min; c) 10 min; d) 20 min; e) 28 min; f) 30 min; g) 36 min.

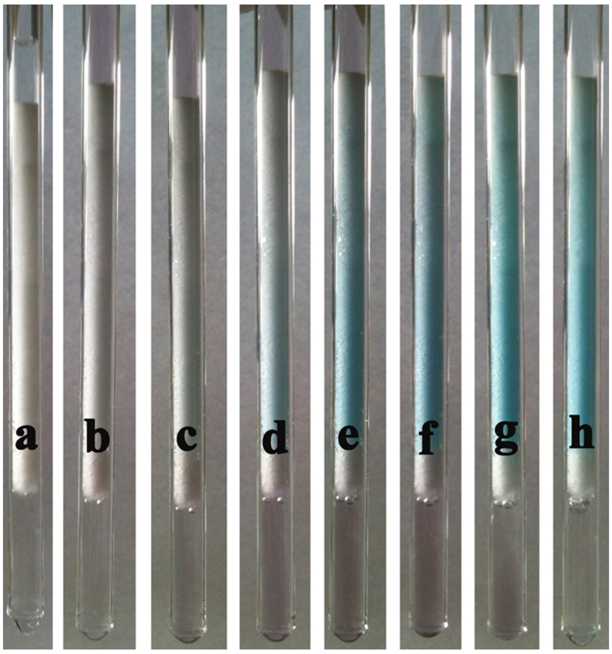


Fig. S9 Separation process of Cu^{2+} and Co^{2+} ions by the MOF-based chromatographic column (methanol as solvent). a) blank; b) 1 min; c) 2 min; d) 10 min; e) 17 min; f) 25 min; g) 30 min; h) 35 min.

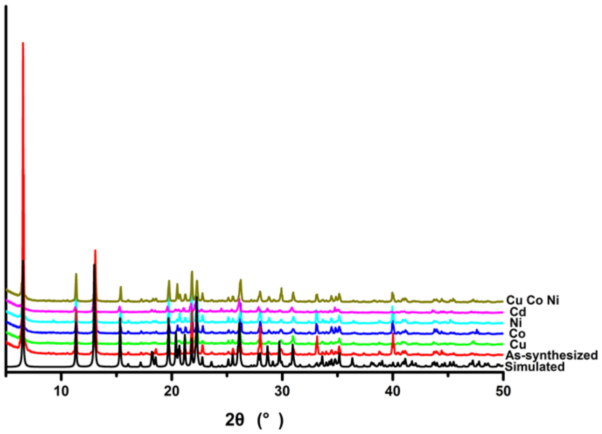


Fig. S10 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples soaked in DMF solution containing $M(NO_3)_2$ (0.1 mol/L, $M^{2+} = Cu^{2+}$, Co^{2+}, Ni^{2+}, Cd^{2+} and $Cu^{2+}/Co^{2+}/Ni^{2+}$) for 5.5 h.

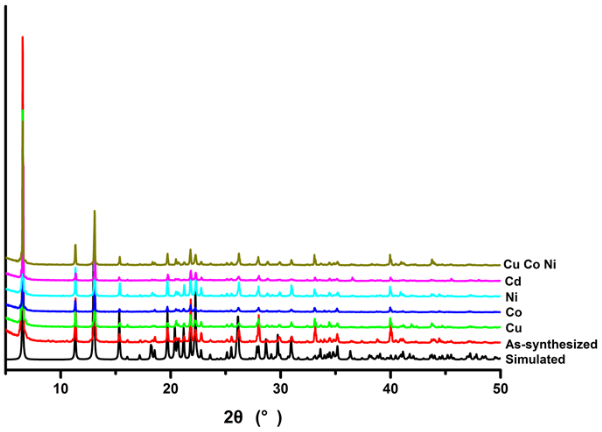


Fig. S11 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples soaked in CH_3OH solution containing $M(NO_3)_2$ (0.1 mol/L, $M^{2+} = Cu^{2+}$, Co^{2+}, Ni^{2+}, Cd^{2+} and $Cu^{2+}/Co^{2+}/Ni^{2+}$) for 5.5 h.

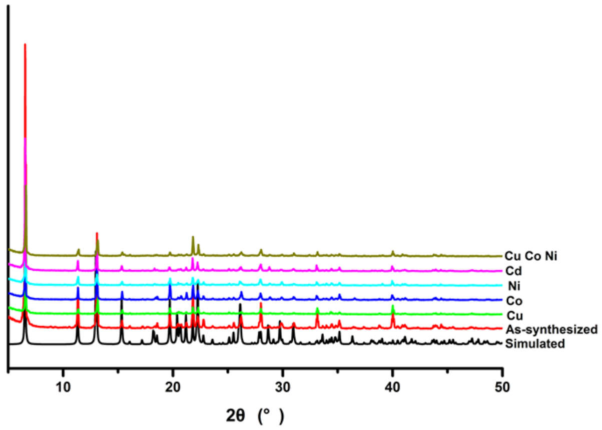


Fig. S12 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples soaked in aqueous solution containing $M(NO_3)_2$ (0.01 mol/L, $M^{2+} = Cu^{2+}$, Co^{2+}, Ni^{2+}, Cd^{2+} and $Cu^{2+}/Co^{2+}/Ni^{2+}$) for 10 min.

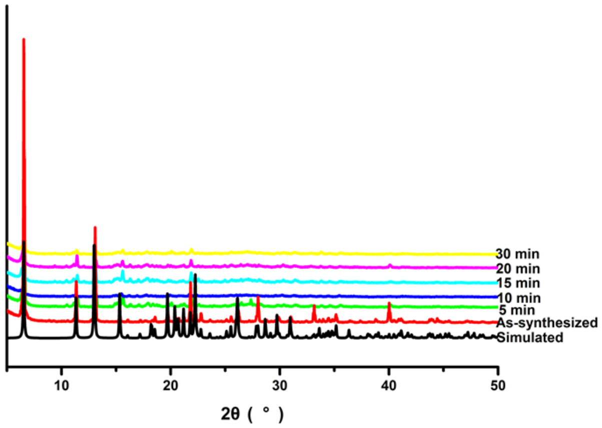


Fig. S13 Powder X-ray diffraction patterns of simulated from the X-ray single structure of **1**, as-synthesized **1**, and **1** samples soaked in aqueous solution containing $Cu(NO_3)_2$ (0.1 mol/L) for 5 min, 10 min, 15 min, 20 min, and 30 min.

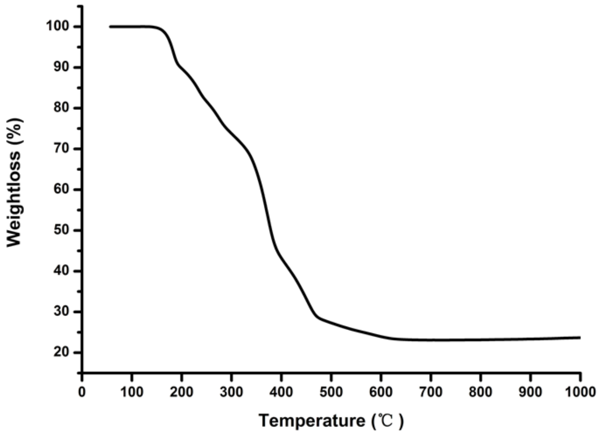


Fig. S14 The TGA curve of compound **1**.

An energy-dispersive X-ray spectra (EDX) was also employed to investigate the sample which immersed in DMF solution containing same concentration Cu^{2+} and Co^{2+} for about one week. As shown in Fig. S15, the signal of the EDX for the sample shows that only Cu^{2+} ions are adsorbed.

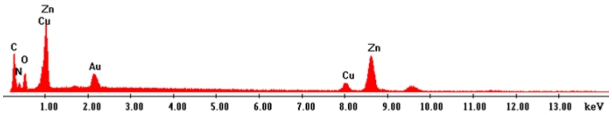


Fig. S15 Energy-dispersive X-ray spectra of Cu- and Co-immersed sample.

We determined the fraction eluted from the column when H_2O as eluting agent. The fraction was analyzed by ICP and the concentration of metal ions at given time was given as Fig. S16. In addition, the ICP result of the total eluting agent reveals that Co/Cu mole ratio is 99.995/0.005 and the fraction eluted from the column is almost pure Co ions.

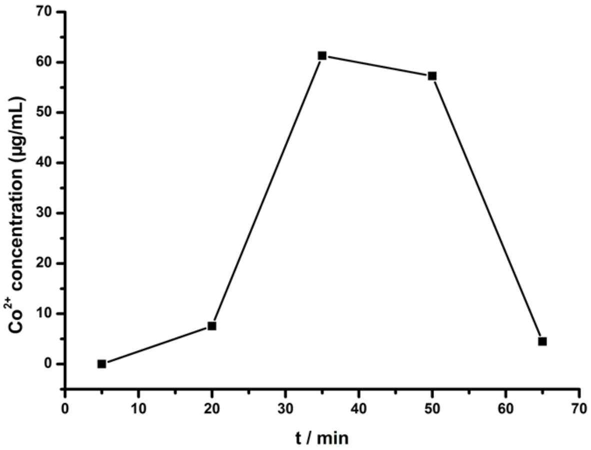


Fig. S16 The Co^{2+} concentration of eluting agent (H_2O) at given time.

Computational details

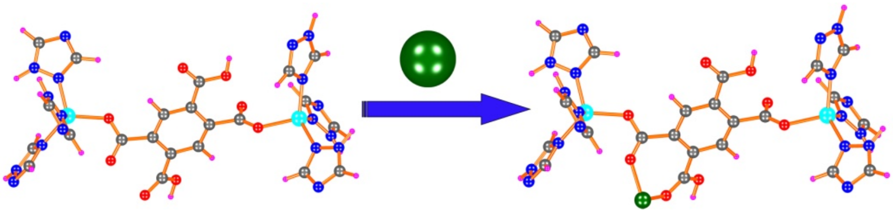


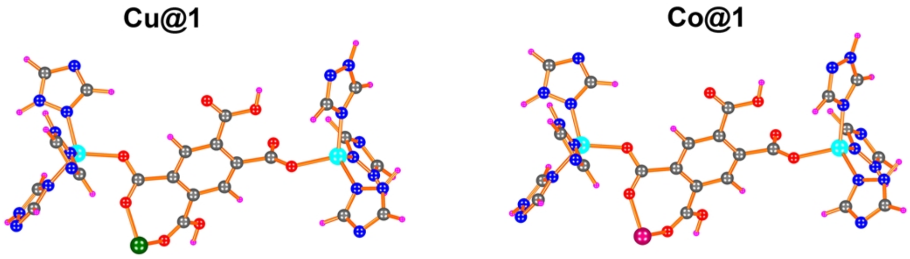
Fig. S17 The optimized model for **1** (left) and the possible adsorption site (right).

An ideal model was truncated for forecasting the stability of the two cases by density functional theory (DFT) calculations. According to previous reports, a hybrid metal exchange-correlation functional named M06 is recommended by Truhlar and co-workers for calculation applications involving organometallic and inorganometallic chemistry.[4-8] All species here were calculated with M06 hybrid functional. The structures were optimized in gas state and the interaction energies were calculated at the presence of within the nonequilibrium polarizable continuum model (PCM)[9-13] approach simulating the solvent effect (methanol). Taking into account the relativistic effect for transition-metal ion, the effective core potential (ECP)[14] double-ζ(DZ) basis set of LanL2DZ is applied to the Co, Cu and Zn atoms and the 6-31G* basis set is used for the nonmetal atoms. Our calculation models consist of a truncated MOF framework and a metal ion, the chemical formulas for the models are labeled as **Cu@1** and **Co@1**, respectively. As the experiments have proved that the framework **1** is stable and rigid, thus full geometry optimizations were carried out firstly on the **1** with M06 functional. In addition, the interaction energy (ΔE) of the metal ion M^{2+} with **1** is calculated as follows:

$$\Delta E = E_{(M@1)} - E_{(1)} - E_{(M^{2+})}$$

The calculated important geometry parameters are labeled at the corresponding position in Fig. S18. DFT calculations exhibit that Cu^{2+} ions are chelated between in O···O ($R_{Cu\text{-}O}$ = 2.01/1.98 Å). In addition, the O···Co···O chelated coordination model are also optimized at the same level. Comparing with the interaction energy (ΔE) of the Cu^{2+} and Co^{2+} ions, the results indicate that interactions between Cu^{2+} ions and **1** are stronger, (-129.77 vs. -66.34 kal/mol), which is well agreement with the experimental results.

All of the calculations were performed with the Gaussian 09 program package.[15]



Cu-O 1.98/2.01 Å

Co-O 1.97/1.99 Å

Fig. S18 The geometrical results of optimized models.

Table S2 The energy (au) of **Cu@1**, **Co@1**, individual MOF fragment and metal ions M^{2+} calculated at M06/6-31G* (LanL2DZ for metal atoms).

	Cu@1	**Co@1**
$E_{(total)}$	-2764.083327	-2712.992116
$E_{(MOF\ fragment)}$	-2568.257044	-2568.256374
$E_{(M^{2+})}$	-195.6333135	-144.6370922

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