Electronic Supplementary Information (ESI)

Exceptionally water stable heterometallic gyroidal MOFs: Tuning porosity and hydrophobicity by doping metal ions

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Section S1. General Procedure

Starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Powder X-ray diffraction patterns (PXRD) of the samples were measured on a Bruker D8 Advance diffractometer (Cu Kα, λ = 1.5418 Å) at room temperature. Thermal analysis (TGA) was carried out in a nitrogen stream using a Seiko Extar 6000 TG/DTA equipment with heating rate of 5 °C·min^{-1}. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) measurements were conducted on a Shimadzu ICPE-9000. Low-pressure (up to 1 bar) gas adsorption isotherms (N_2 and CO_2) were measured on a Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. The water adsorption isotherms were measured on an Intelligent Gravimetric Sorption Analyzer (IGA100B).

Section S2. Syntheses of metal doped STU-1s

S2A. Ligand synthesis.

The ligand 1,2-bis((5H-imidazol-4-yl)methylene)hydrazine (BIm) was prepared by the reported method.[S1] A methanol solution (10.0 mL) of hydrazine monohydrate (1.001 g, 10.0 mmol) was added to a methanol solution (25.0 mL) of 4-formylimidazole (3.832 g, 20.0 mmol). The mixture was stirred overnight at 50 °C. A light-yellow precipitate was collected by filtration (3.275 g, yield, 87.0 %). The solubility of BIm in DMSO, DMF, ethanol, and methanol is very poor. The NMR characterization is not performed on the BIm. IR (KBr disk): 3133w, 3064w, 2995w, 2962w, 2902w, 2774m, 2667m, 2594m, 1637s, 1543w, 1512m, 1445s, 1311w, 1278m, 1254w, 1218w, 1170w, 1118w, 1092m, 993s, 908w, 923w, 908w, 874m, 859m, 819m, 786m, 777m, 692w, 627s.

S2B. Syntheses of metal doped STU-1s.

Synthesis of $Cu_{0.10}$-STU-1.

Method 1 (Direct heating): The mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (803.17 mg, 2.70 mmol), $Cu(NO_3)_2$ (72.48 mg, 0.30 mmol) and BIm (564.60 mg，3.0 mmol) were dissolved into DMF/ethanol mixed solvent (200 mL, 4:1, v/v) , which were sealed in a flask and

heated at 100 °C for 3 days. The mixture was cooled to room temperature, and the resulting powder was collected by filtration and washed with DMF (3×20 mL) and methanol (3×20 mL) and then dried under vacuum to afford the product as a light green crystalline powder (Yield: 637.4 mg).

Method 2 (Solvothermal): $Zn(NO_3)_2 \cdot 6H_2O$ (10.71 mg，0.036 mmol), $Cu(NO_3)_2$ (0.9664 mg，0.004 mmol) and BIm (7.45 mg，0.04 mmol) were dissolved into a mixture solvent (1.6 mL DMF and 0.4 mL EtOH). The solution was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 72 hours, and then cooled to room temperature at a rate of 5 °C/h. Light green polyhedral crystals were collected and washed with DMF (3×2 mL) and methanol (3×2 mL) (Yield: 5.1 mg).

Method 3 (Microwave): A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (72.29 mg, 0.243 mmol), $Cu(NO_3)_2$ (6.52 mg, 0.027 mmol), and BIm (50.00 mg, 0.27 mmol) and trimethylamine (1.5 mL) were dissolved in 15 mL of DMF. The solution was then sealed with a Pyrex sample vial and heated at 200 W for a reaction time of 10 minutes. The obtained light green crystalline powder was filtered and washed with DMF (3 × 5 mL) (Yield: 56.5 mg).

Method 4 (Diffusion): The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (141.89 mg, 0.477 mmol), $Cu(NO_3)_2$ (13.04 mg, 0.053 mmol), and BIm (100 mg, 0.53 mmol) were dissolved into DMF (25 mL) under stirring with a magnetic bar. The mixture solution was separated into 5 small vials. Then the small vials were placed into a large bottle with an atmosphere of triethylamine (1 mL) in hexane (25 mL), and were allowed to sit at room temperature for 3 days. The obtained light green crystalline powder was filtered and washed with DMF (3×5 mL) and methanol (3×5mL) to afford the product (Yield: 103.2 mg).

Method 5 (Mechanical synthesis): A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (141.89 mg, 0.477 mmol), $Cu(NO_3)_2$ (13.04 mg, 0.053 mmol), and BIm (100 mg, 0.53 mmol) were grinded for 1 hour until it turned to be green. 3×2 mL triethylamine was dropwise added with grinding until it was dried. The light green crystalline powder was washed with

DMF (3×10 mL) and methanol (3×10 mL) to afford the product (Yield: 36.4 mg).

Syntheses of $Cu_{0.01}$-STU-1

The mixture of $Zn(NO_3)_2·6H_2O$ (883.49 mg, 2.97 mmol), $Cu(NO_3)_2$ (7.25 mg, 0.03 mmol) and BIm (564.60 mg，3 mmol) were dissolved into DMF/ethanol mixed solvent (200 mL, 4:1, v/v) , sealed in a flask and heated at 100 °C for 3 days. The mixture was cooled to room temperature. The resulting powder was collected by filtration and washed with DMF (3×20 mL) and methanol (3×20 mL) and then dried under vacuum to afford the yellow-green crystalline powder product (Yield: 509.2 mg).

Syntheses of $Cu_{0.05}$-STU-1

The mixture of $Zn(NO_3)_2·6H_2O$ (847.79 mg, 2.85 mmol), $Cu(NO_3)_2$ (36.24 mg, 0.15 mmol) and BIm (564.60 mg，3 mmol) were dissolved into DMF/ethanol mixed solvent (200 mL, 4:1, v/v) , sealed in a flask and heated at 100 ° C for 3 days. After the mixture was cooled to room temperature, the resulting precipitate was collected by filtration and washed with DMF (3×20 mL) and methanol (3×20 mL) and then dried under vacuum to afford a yellow-green crystalline powder product (Yield: 424.8 mg).

Syntheses of $Cu_{0.167}$-STU-1

The mixture of $Zn(NO_3)_2·6H_2O$ (743.38 mg, 2.50 mmol), $Cu(NO_3)_2$ (121.04 mg, 0.50 mmol) and BIm (564.60 mg，3 mmol) were dissolved into a DMF/ethanol mixed solvent (200 mL, 4:1, v/v) , sealed in a flask and heated at 100 °C for 3 days. After the mixture was cooled to room temperature, the resulting precipitate was collected by filtration and washed with DMF (3 ×20 mL) and methanol (3×20 mL) and then dried under vacuum to afford the light green crystalline powder product (Yield: 657.1 mg).

Syntheses of $Cd_{0.6}$-STU-1

The mixture of $Zn(NO_3)_2·6H_2O$ (356.96 mg, 1.20 mmol), $Cd(NO_3)_2·4H_2O$ (554.40 mg, 1.80 mmol) and BIm (564.60 mg，3 mmol) were dissolved into DMF/ethanol mixed solvent (200 mL, 4:1, v/v) , sealed in a flask and heated at 100 °C for 3 days. After the mixture was cooled to room temperature, the resulting precipitate was collected by

filtration and washed with DMF (3×20 mL) and methanol (3×20 mL) and then dried under vacuum to afford a yellow crystalline powder product (Yield: 318.4 mg).

Syntheses of $Fe_{0.10}$-STU-1

The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (803.17 mg, 2.70 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (121.21 mg, 0.30 mmol) and BIm (564.60 mg，3 mmol) were dissolved into DMF/ethanol mixed solvent (200 mL, 4:1, v/v) , sealed in a flask and heated at 100 °C for 3 days. After the mixture was cooled to room temperature, the resulting powder was collected by filtration and washed with DMF (3×20 mL) and methanol (3×20 mL) and then dried under vacuum to afford the brown crystalline powder (Yield: 202.5 mg).

Section S3. Characterization of $Cu_{0.10}$-STU-1

S3A. Crystallographic studies

Single crystal structures of $Cu_{0.10}$-STU-1S was measured by X-ray diffraction. Data collection were performed on an Agilent Technologies Gemini A System (Cu Kα, λ = 1.54178 Å) at 293K. The data were processed using CrysAlis$^{Pro.1}$. The structures were solved by direct methods and refined by full-matrix least-squares refinements based on F^2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were conducted using SHELXL-97 programs. [S2] The treatment for the guest molecules in the giant cavities involves the use of the SQUEEZE program of PLATON. [S3] A summary of crystal data and structure refinement parameters is listed in Table S1.

Table S1 Summary of Crystal Data and Structure Refinement Parameters for $Cu_{0.10}$-STU-1S

Parameter	$Cu_{0.10}$-STU-1S
Chemical formula	$C_{384}H_{288}Cu_{4.8}N_{288}Zn_{43.2}$
Formula weight	12066.00
Crystal system	Cubic
Space group	$Ia\bar{3}d$
a (Å)	34.4885(2)
b (Å)	34.4885(2)
c (Å)	34.4885(2)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
V (Å^3)	41022.6(4)
Z	2
D_{calcd}(g cm^{-3})	0.977
μ (mm^{-1})	1.865
Reflections collected	18071
Unique reflections	3440
R_{int}	0.0655
Goodness-of-fit on F^2	0.928
R_1[a] [I > 2σ(I)]	0.0602
wR_2[b] [I > 2σ(I)]	0.1592
R_1[a] [all refl.]	0.1111
wR_2[b] [all refl.]	0.1865

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

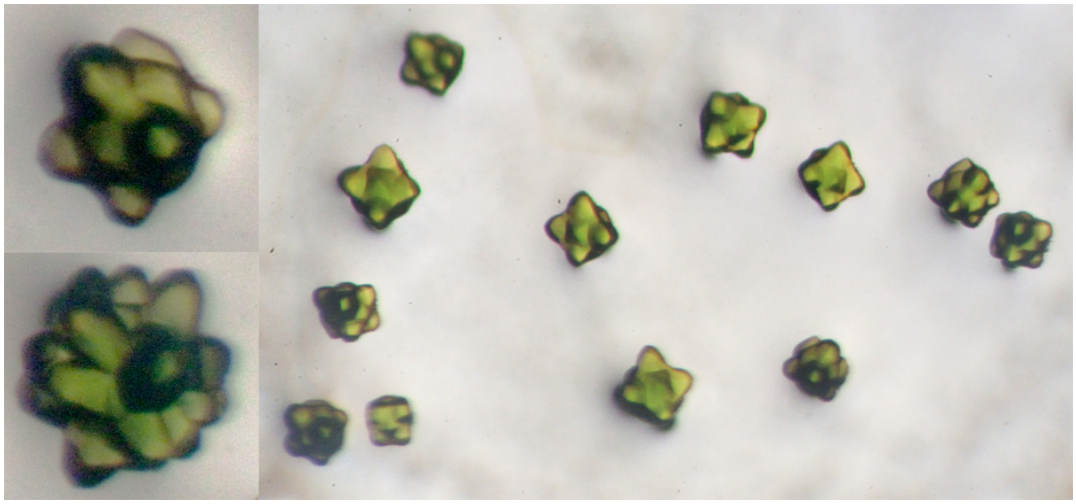

Fig. S1 Photograph of $Cu_{0.10}$-STU-1S crystals.

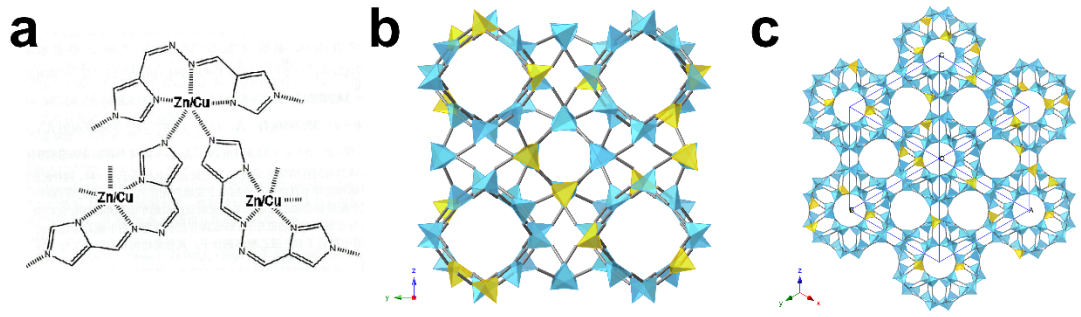

Fig. S2 The coordination mode of BIm and Zn^{2+}/Cu^{2+} ions (a), and the overview of the 3D topologic framework of $Cu_{0.10}$-STU-1s: view along the *a*-axis (b) and 111 direction (c). Color code: Zn = Blue, Cu = Yellow, Ligand = Gray. The yellow tetrahedrons are randomly chosen to highlight the doping framework.

S3B. Characterizations of ICP-AES, EDS, and TGA

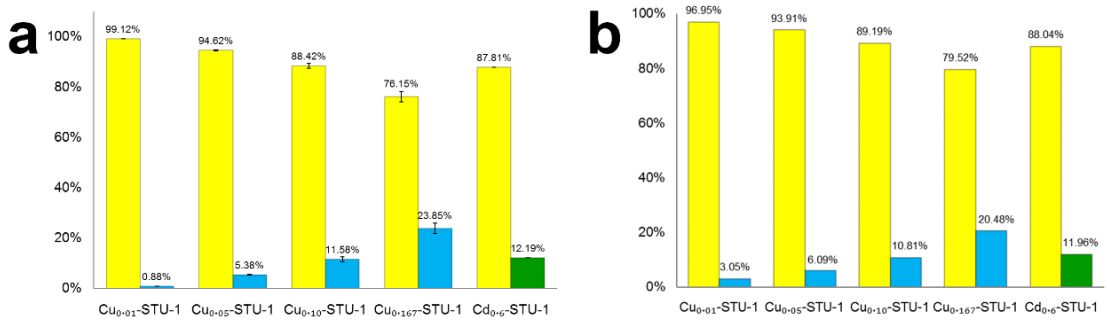

Fig. S3 The illustration of ratio of metals (%) versus metals, which were measured by (a) ICP-AES and (b) EDS. Column colors: Zn = Yellow, Cu = Blue, Cd = Green.

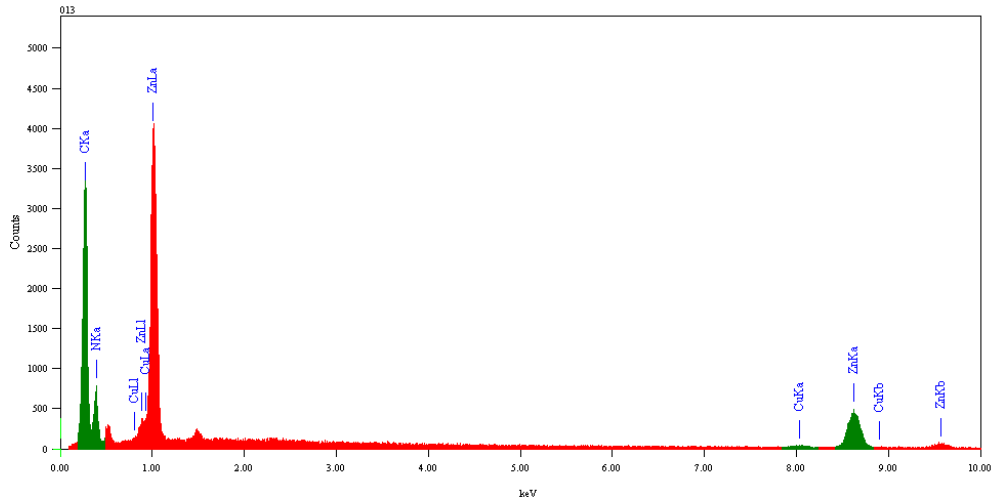

Fig. S4 X-ray Energy Dispersive Spectroscopy (EDS) of $Cu_{0.01}$-STU-1.

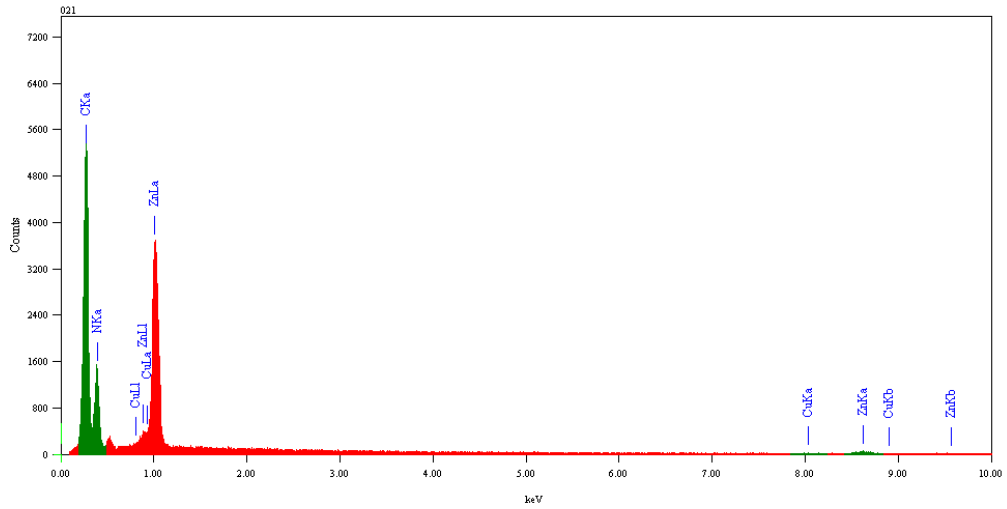

Fig. S5 X-ray Energy Dispersive Spectroscopy (EDS) of $Cu_{0.05}$-STU-1.

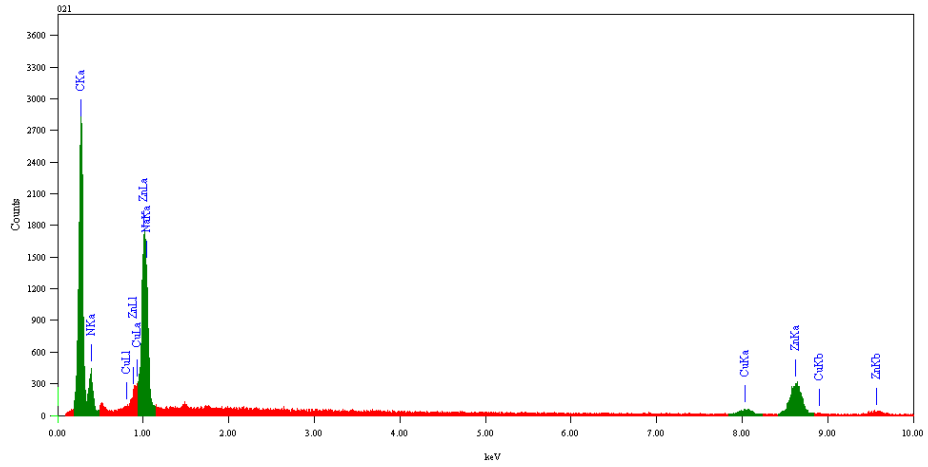

Fig. S6 X-ray Energy Dispersive Spectroscopy (EDS) of $Cu_{0.10}$-STU-1.

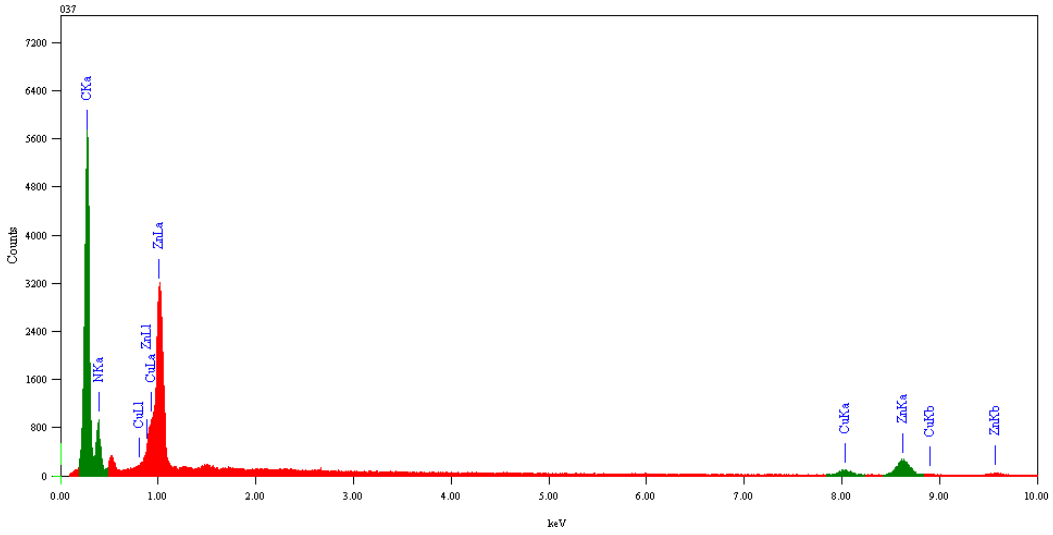

Fig. S7 X-ray Energy Dispersive Spectroscopy (EDS) of $Cu_{0.167}$-STU-1.

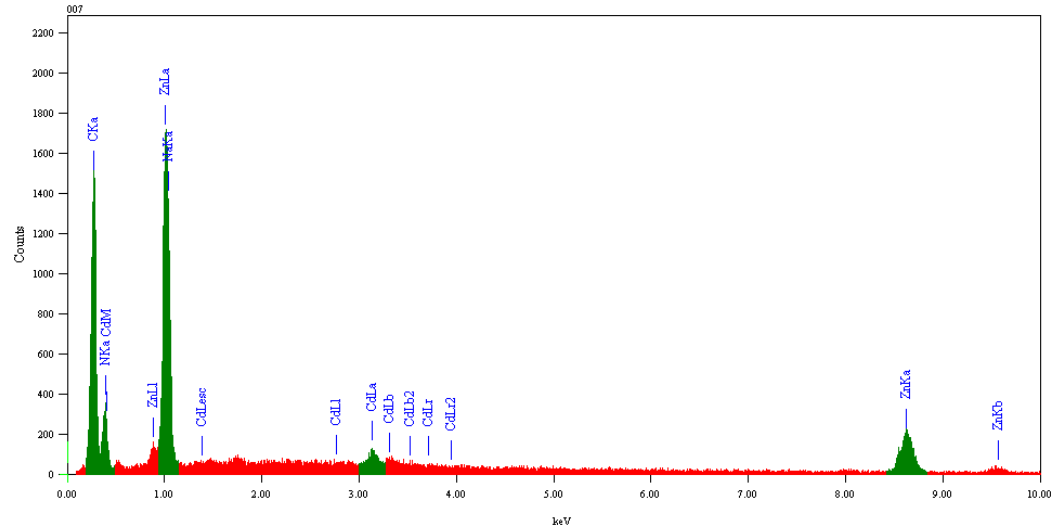

Fig. S8 X-ray Energy Dispersive Spectroscopy (EDS) of $Cd_{0.6}$-STU-1.

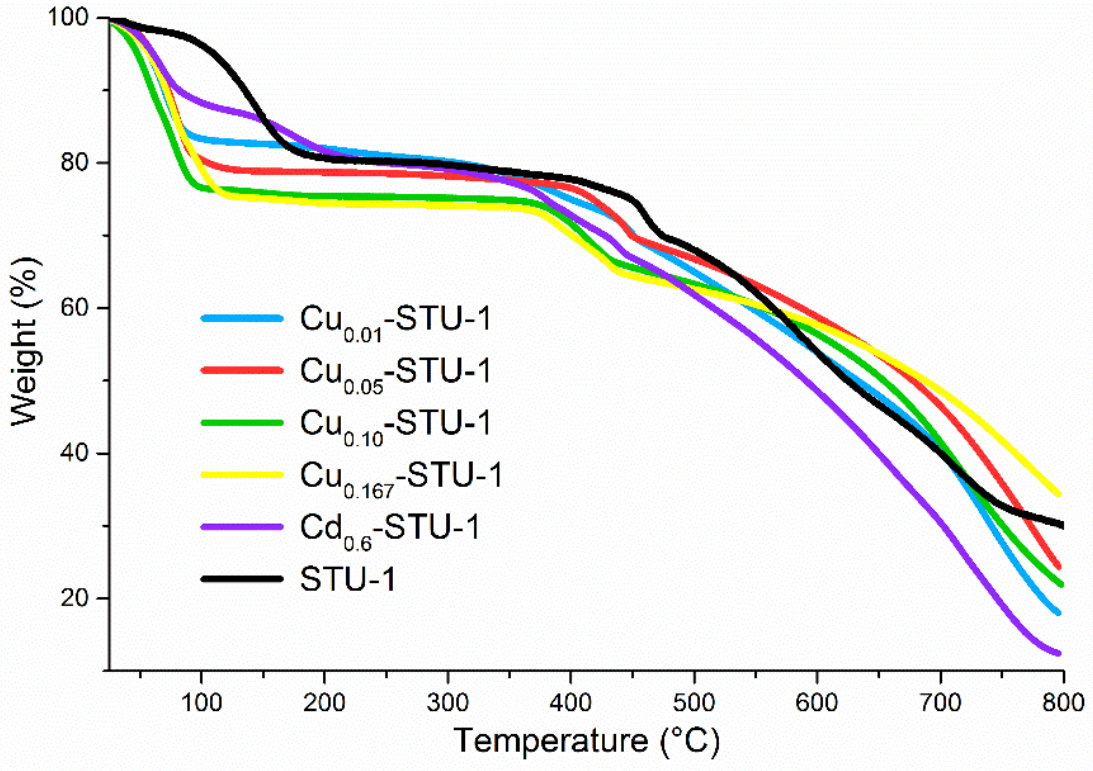

Fig. S9 The TGA plot of metal doped STU-1s.

Section S4. Chemical Stabilities of metal doped STU-1s and STU-1

S4A. Water stability of STU-1

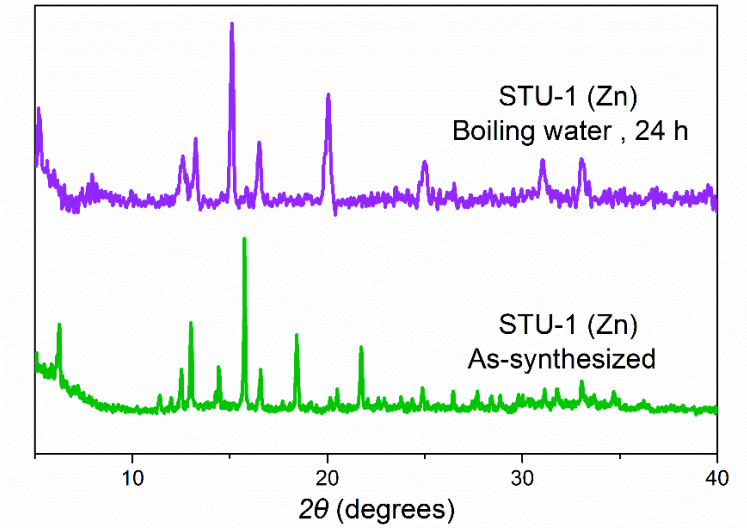

Fig. S10 PXRD patterns of as-synthesized STU-1 samples and that soaked in boiling water for 24 h.

S4B. Chemical stability of metal doped STU-1s

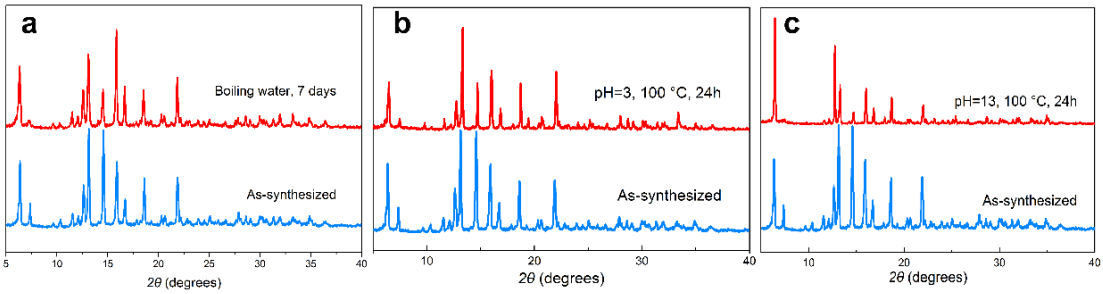

Fig. S11 PXRD patterns for $Cu_{0.01}$-STU-1 measured for chemical stability tests: (a) as-synthesized sample and that soaked in boiling water 7 days, (b) as-synthesized sample and that soaked in an aqueous HCl solution (pH = 3.0) at 100 °C for up to 24 h, and (c) as-synthesized sample and that soaked in an aqueous NaOH solution (pH = 13.0) at 100 °C for up to 24 h.

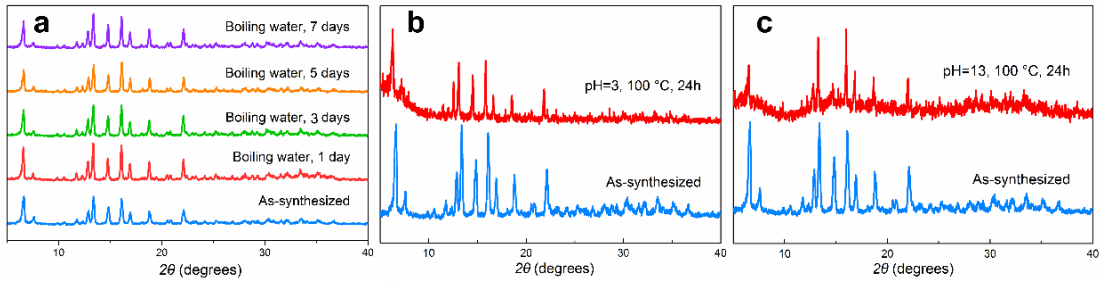

Fig. S12 PXRD patterns for $Cu_{0.05}$-STU-1 measured for chemical stability tests: (a) as-synthesized sample and that soaked in boiling water for 1, 3, 5 and 7 days, respectively. (b) as-synthesized sample and that soaked in an aqueous HCl solution (pH = 3.0) at 100 °C for up to 24h, and (c) as-synthesized sample and that soaked in an aqueous NaOH solution (pH = 13.0) at 100 °C for up to 24h.

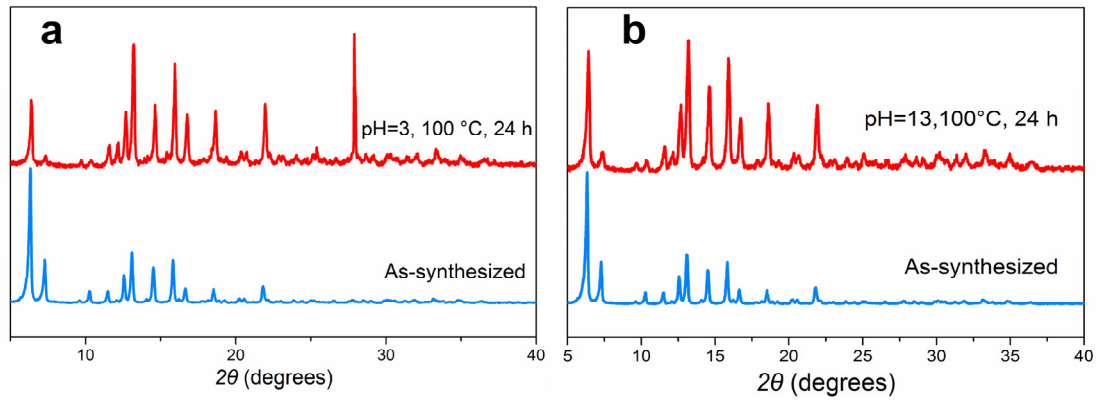

Fig. S13 PXRD patterns for $Cu_{0.10}$-STU-1 measured for chemical stability tests: (a) as-synthesized sample and that soaked in an aqueous HCl solution (pH = 3.0) at 100 °C for up to 24 h, and (b) as-synthesized sample and that soaked in an aqueous NaOH solution (pH = 13.0) at 100 °C for up to 24 h.

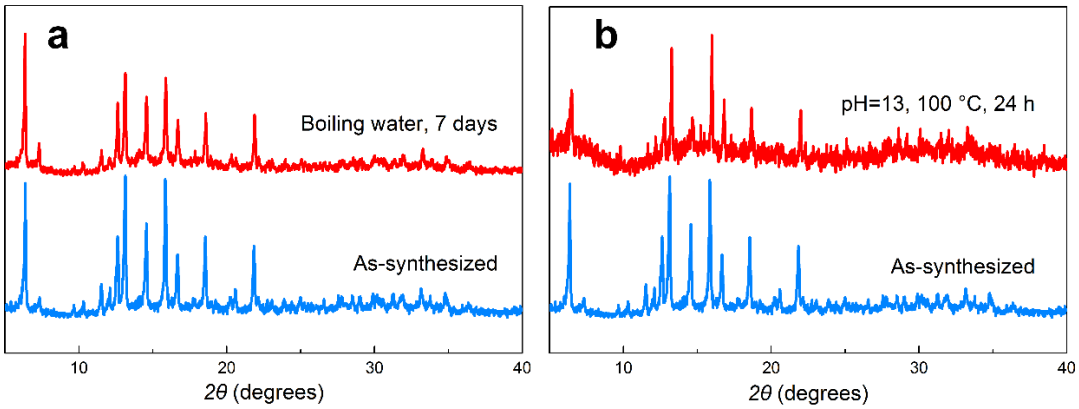

Fig. S14 PXRD patterns for $Cd_{0.6}$-STU-1 measured for chemical stability tests: (a) as-synthesized sample and that soaked in boiling water 7 days. (b) as-synthesized sample and that soaked in an aqueous NaOH solution (pH = 13.0) at 100 °C for up to 24 h.

Section S5. Gas sorption studies

S5A. Gas-Sorption Measurements.

Gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. Prior to the measurement, the samples were exchanged with methanol (3×10 mL) over a three-day period at room temperature, and then dried under dynamic vacuum (<10^{-3} torr) at room temperature overnight. Then, the samples were heated and evacuated by using the "outgas" function of the surface area analyzer for 10 hours at 120°C. Finally, the treated samples of metal doped STU-1s were used for N_2 sorption measurement at 77 K with liquid nitrogen, and CO_2 sorption measurement at 273.15 K (ice-water bath).

S5B. Gas adsorption isotherms of the boiling water treated samples

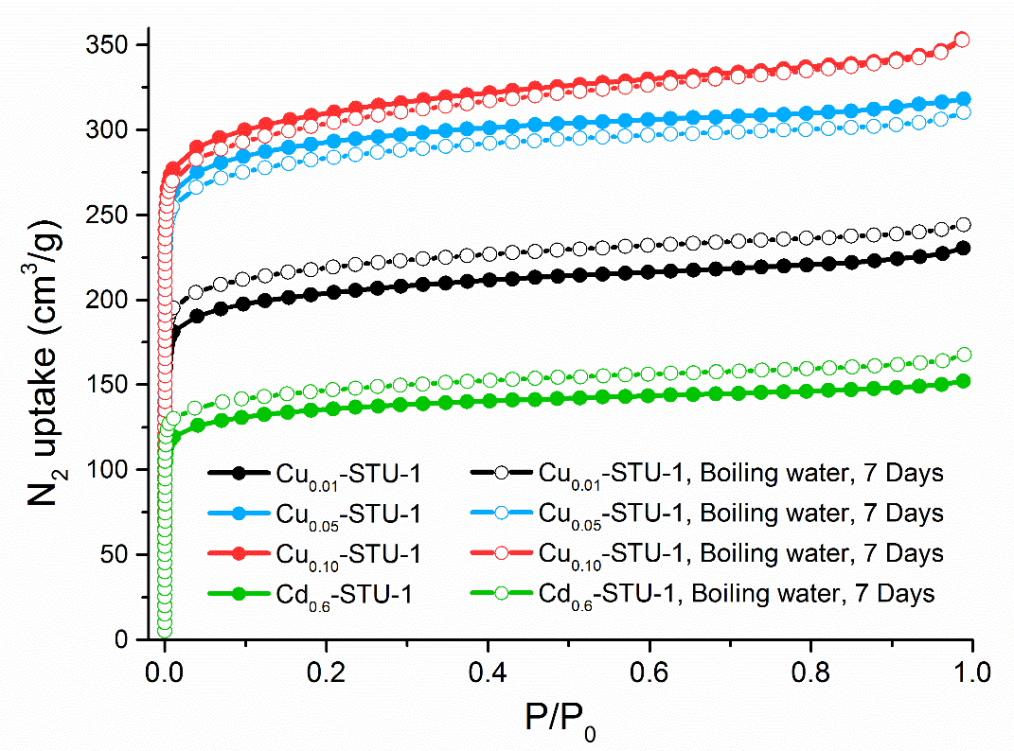

Fig. S15 Experimental N_2 adsorption isotherms for metal doped STU-1s and that soaked in boiling water for 7 days at 77 K.

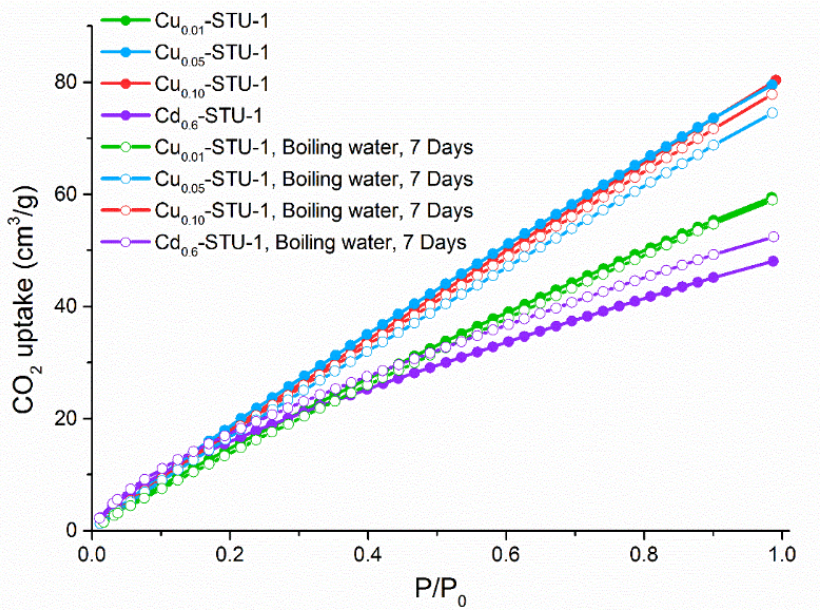

Fig. S16 Experimental CO_2 adsorption isotherms for as synthesized sample of metal doped STU-1s and that soaked in boiling water for 7 days at 273 K.

Section S6. Scanning electron microscopy studies

S6A. Experimental detail

Scanning electron microscopy (SEM) analyses were carried out on a JSM-6360LA microscope (JEOL) at an accelerating voltage of 10.0 kV. The SEM specimens were prepared by placing a xerogel on a conductive carbon adhesive, followed by gold coating in a sputter coater (Desk-II; Den-ton Vacuum).

S6B. Scanning Electron Microscopy Imaging (SEM)

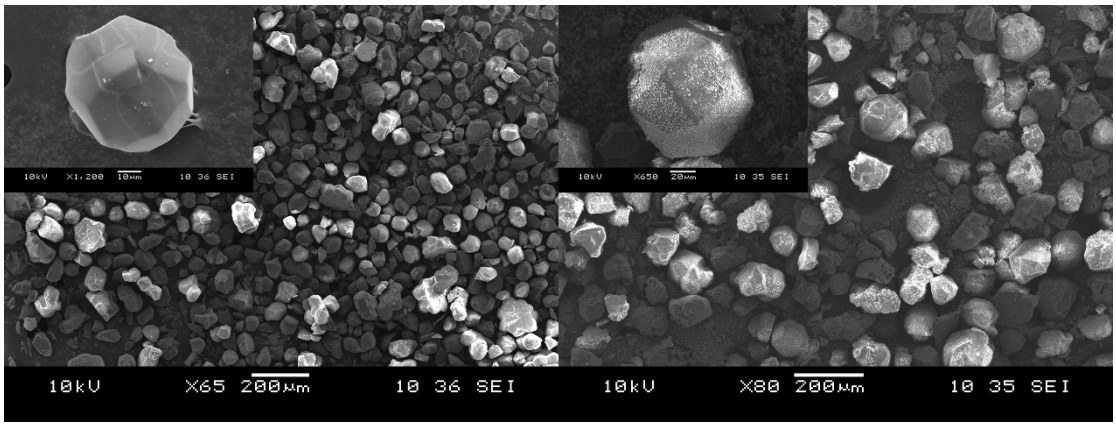

Fig. S17 SEM image of $Cu_{0.01}$-STU-1 (left: as-synthesized samples, right: sample soaked in boiling water for up to 7 days).

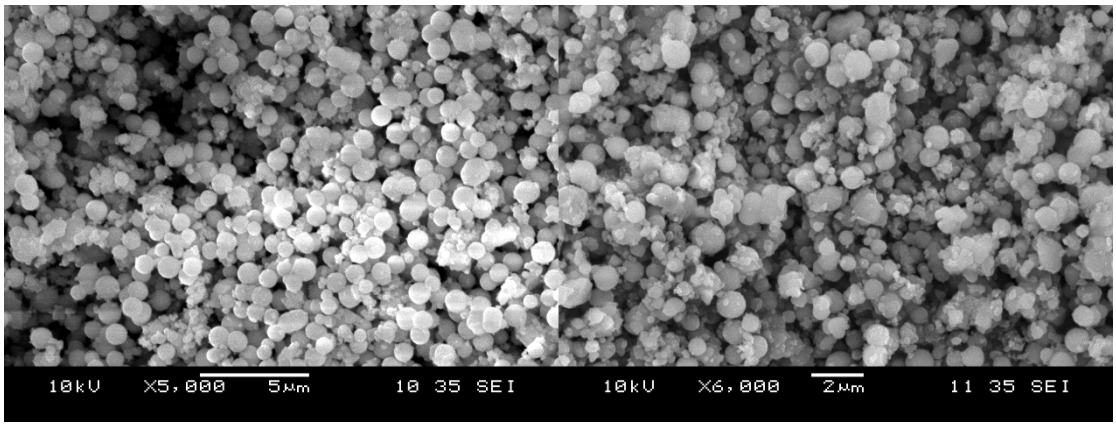

Fig. S18 SEM image of $Cu_{0.05}$-STU-1 (left: as-synthesized samples, right: sample soaked in boiling water for up to 7 days).

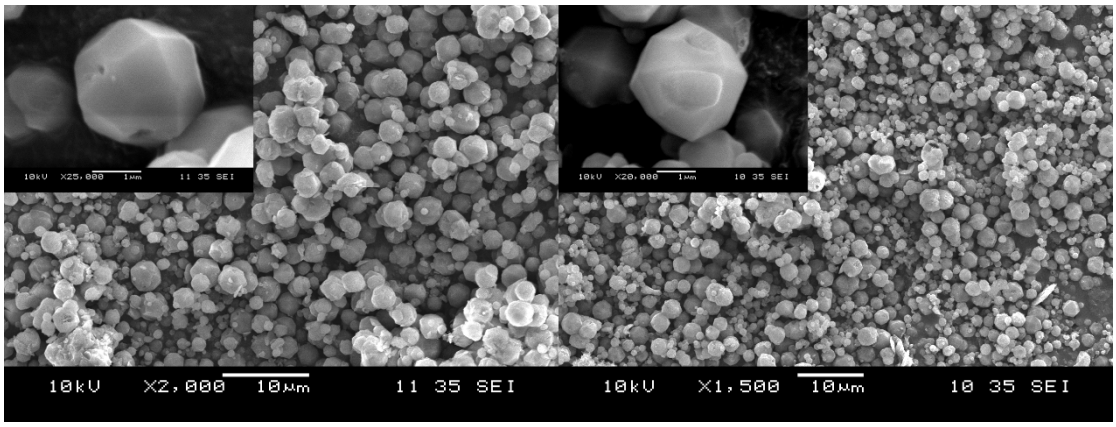

Fig. S19 SEM image of $Cu_{0.167}$-STU-1 (left: as-synthesized samples, right: samples in boiling water for up to 7 days.

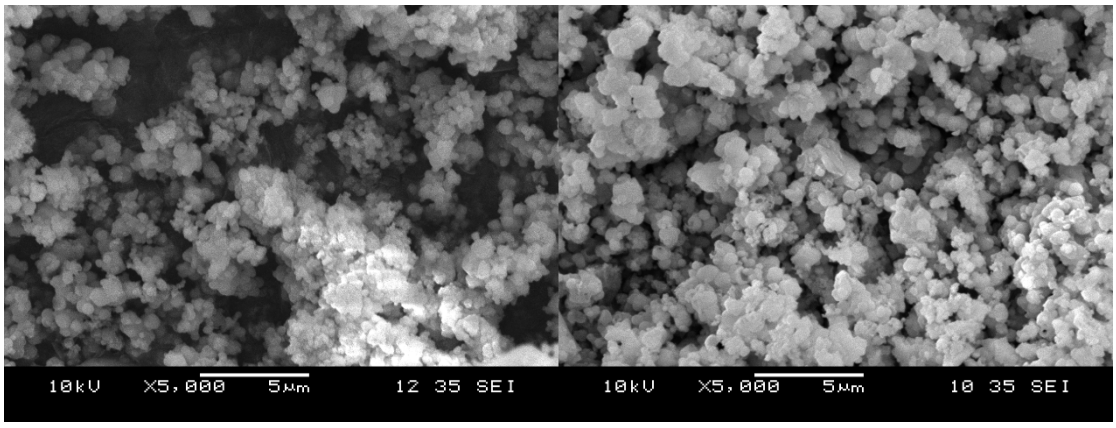

Fig. S20 SEM image of $Cd_{0.6}$-STU-1 (left: as-synthesized samples, right: sample soaked in boiling water for up to 7 days).

Section S7. Water stability of other MOFs

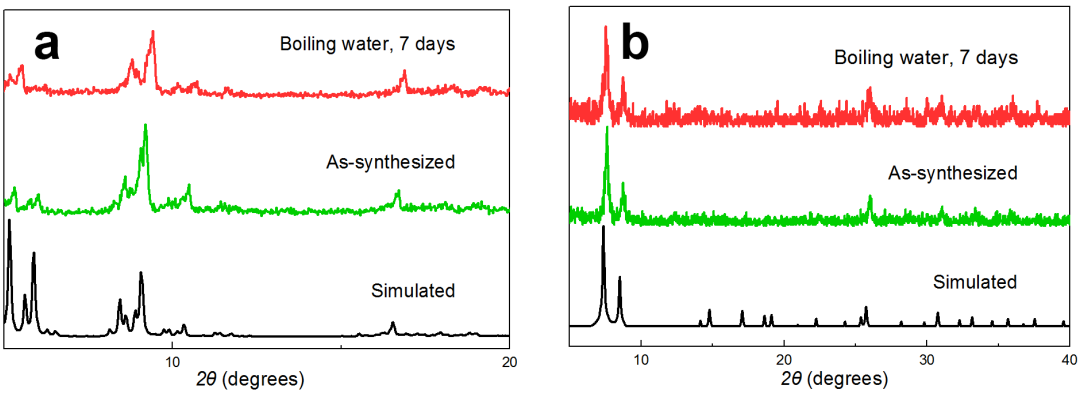

Fig. S21 PXRD patterns monitoring the hydro-stability of (a) MIL-101 and (b) UiO-66.

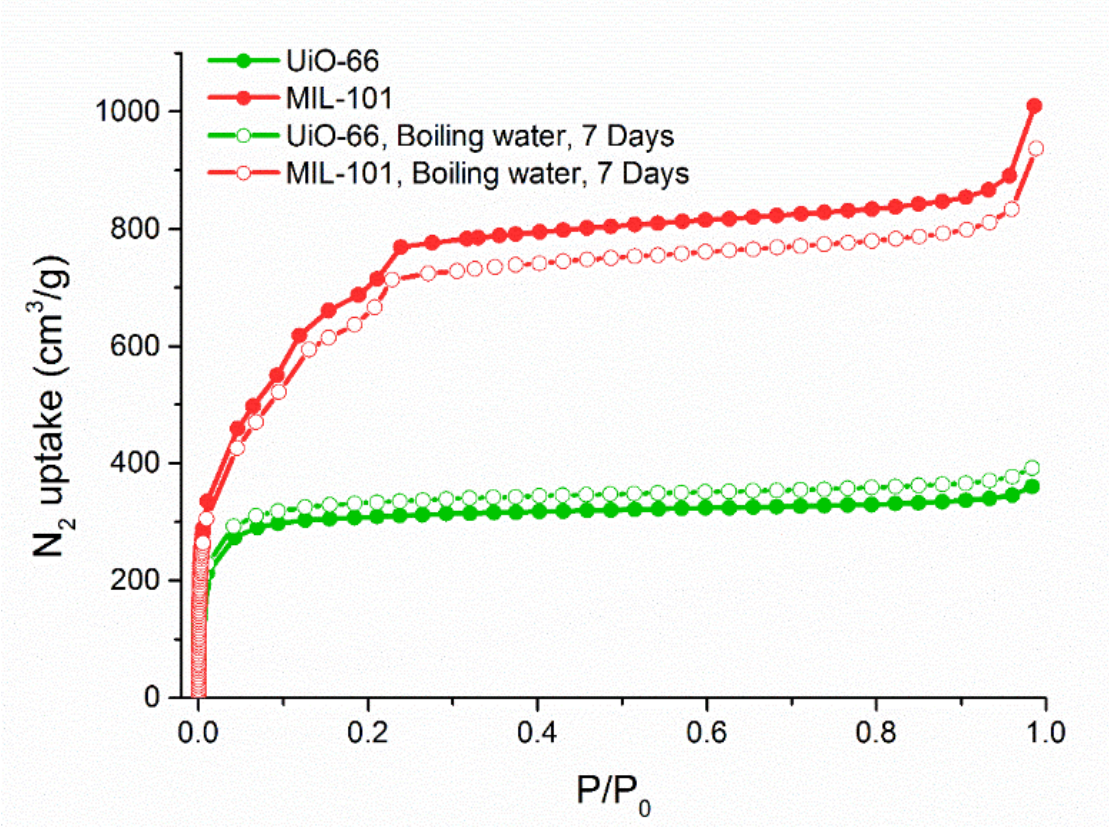

Fig. S22 Experimental N_2 adsorption isotherms for MIL-101and UiO-66 and that soaked in boiling water for 7 days at 77 K.

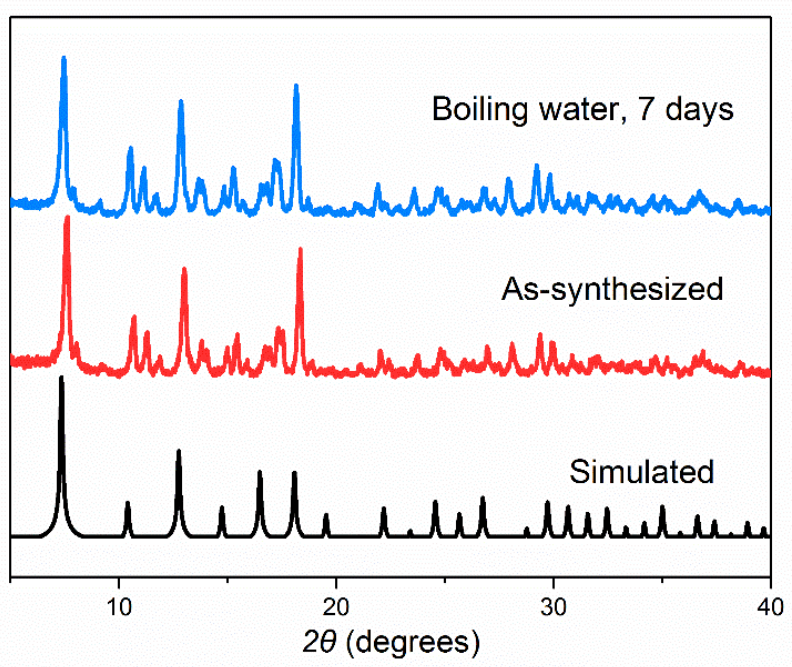

Fig. S23 PXRD patterns ZIF-8: calculated, as-synthesized sample, and that soaked in boiling water for 7 days at 77 K.

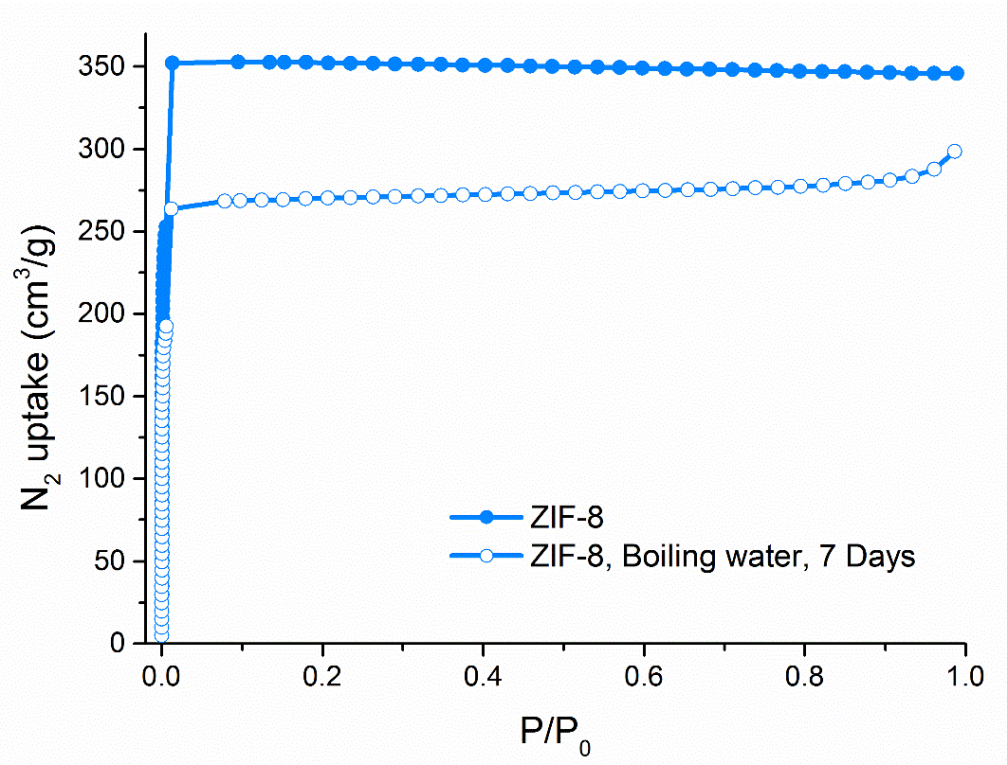

Fig. S24 Experimental N_2 adsorption isotherms for ZIF-8: as synthesized sample and that soaked in boiling water for 7 days at 77 K.

Section S8. Water stability of STU-3 and types of water sorption isotherms

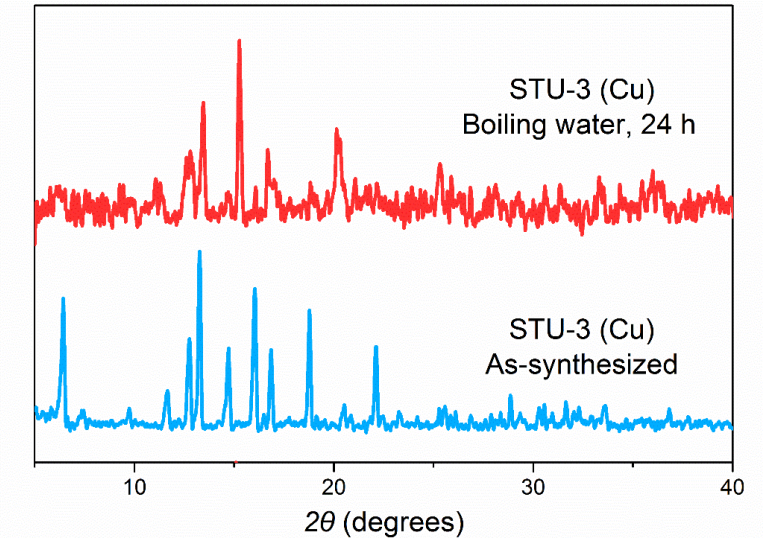

Fig. S25 PXRD patterns of as-synthesized STU-3 sample and that soaked in boiling water for 24 h.

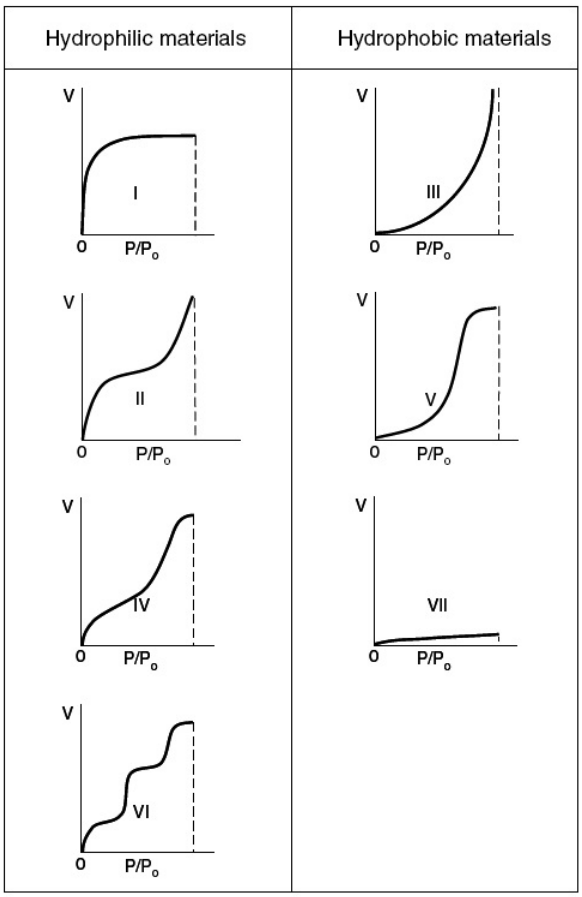

Fig. S26 Seven types of water sorption isotherms according to IUPAC.[S4]

Section S9. Characterization of Fe^{2+} doped STU-1

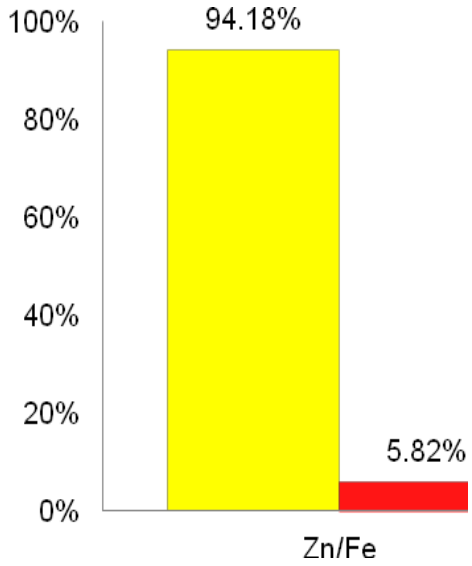

Fig. S27 Metal ratio of $Fe_{0.10}$-STU-1 measured by ICP-AES. Column colors: Zn = Yellow, Fe = Red.

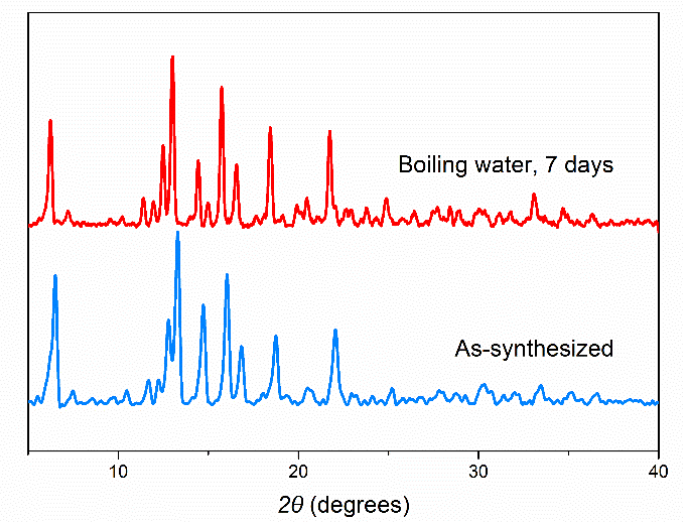

Fig. S28 PXRD patterns of $Fe_{0.10}$-STU-1: as-synthesized sample and that soaked in boiling water for 24 h.

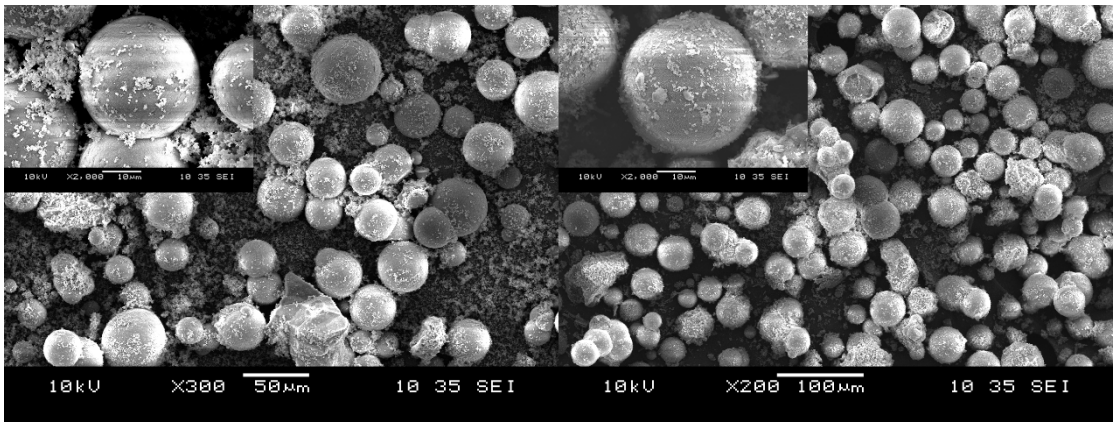

Fig. S29 SEM image of $Fe_{0.10}$-STU-1 (left: as-synthesized samples, right: sample was soaked in boiling water for up to 7 days).

References

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