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Electronic Supplementary Information

Controllable synthesis of isoreticular pillared-layer MOFs based on N-rich triangular prism building units：gas adsorption and luminescent properties

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S1. Materials and measurements

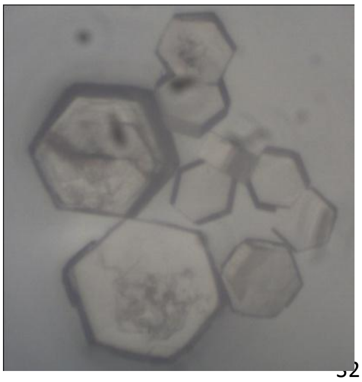
All chemical materials were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were performed on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å) radiation in the range of 3 - 50 ° at 293 K. The fourier transformed infrared spectroscopy (FT-IR) spectra were recorded in the range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 ℃ at a ramp rate of 5 ℃/min under nitrogen gas atmosphere. Elemental analyses (C, H and N) were conducted on a Perkin-Elmer 2400CHN elemental analyzer. The gas sorption measurements were performed on automatic volumetric adsorption equipment (Micromeritics ASAP2050). Before gas adsorption measurements, the samples were immersed in methanol for 24 h, and the extract was decanted. Fresh methanol was subsequently added, and the crystals were stay for an additional 24 h to remove the nonvolatile solvates. The samples were collected by decanting and treated with dichloromethane similarly to remove methanol solvates. After the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum at room temperature overnight to form the activated samples. Before the measurement, the sample was dried again by using the 'outgas' function of the surface area analyzer for 12 h at 90 ℃. The photoluminescence spectra were performed on an F-4600 FL Spectrophotometer equipped with a xenon lamp at room temperature.

S2. MOFs synthesis and characterization

Synthesis of MOF 1

$Zn(NO_3)_2·6H_2O$ (0.06 g, 0.2 mmol), H_2btca (H_2btca = benzotriazole-5-carboxylic acid) (0.0163g, 0.1 mmol) and H_2bdc (1,4-benzenedicarboxylic acid) (0.0166 g, 0.1 mmol) were dissolved in 6 mL DMF (N, N-dimethylformamide), and then 3 drops of HCl (2 M) were added. The final mixture was placed into a Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 100 ℃ for 3 days, and thereafter was slowly cooled to room temperature. Colorless crystals were obtained, which were washed with mother liquid, in about 76 % yield based on H_2btca. IR (KBr, cm^{-1}): 3445.40 (s), 2931.18 (m), 1667.66 (s), 1503.95 (m), 1437.86 (s), 1389.19 (s), 1277.12 (m), 1254.64 (m), 1158.19 (w), 1098.48 (s), 1061.90 (w), 1018.37 (w), 958.39 (w), 828.91 (w), 787.19 (s), 752.00 (m), 708.76 (w), 662.45 (s), 589.78 (m).

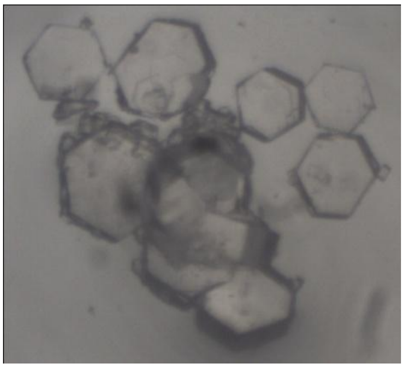
Synthesis of MOF 2



The synthetic procedure is similar with 1 except that H_2bdc was replaced by 2-NH_2-H_2bdc (2-amino-1,4-benzenedicarboxylic acid). $Zn(NO_3)_2·6H_2O$ (0.06 g, 0.2 mmol), H_2btca (0.0163g, 0.1 mmol), and 2-NH_2-H_2bdc (0.0181 g, 0.1 mmol) were dissolved in 6 mL DMF, and then 3 drops of HCl (2 M) were added. The final mixture was placed into a Teflon-lined stainless-steel vessel (15 mL) under autogenous pressure and heated at 100 ℃

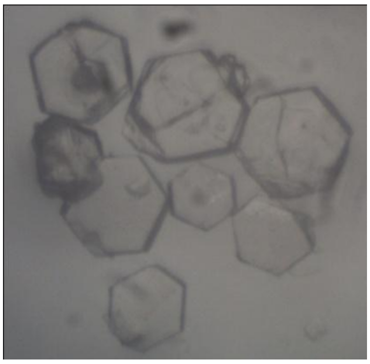
for 3 days, and thereafter was slowly cooled to room temperature. Yellow crystals were obtained, which were washed with mother liquid, in about 73 % yield based on H_2btca. IR (KBr, cm^{-1}): 3447.24 (m), 2930.79 (w), 1668.26 (s), 1569.51 (s), 1495.64 (m), 1437.43 (s), 1388.91 (s), 1255.22 (m), 1158.95 (w), 1098.10 (s), 1061.34 (w), 839.49 (w), 787.00 (m), 708.68 (w), 662.46 (m), 590.62 (w).

Synthesis of MOF 3



The synthetic procedure is similar with 1 substituting 2-Br-H_2bdc (2-bromo-1,4-benzenedicarboxylic acid) for H_2bdc. $Zn(NO_3)_2 \cdot 6H_2O$ (0.06 g, 0.2 mmol), H_2btca (0.0163g, 0.1 mmol), and 2-Br-H_2bdc (0.0245 g, 0.1 mmol) were dissolved in 6 mL DMF, and then 3 drops of HNO_3 (2 M) were added. The final mixture was placed into a Teflon-lined stainless-steel vessel (15 mL) under autogenous pressure and heated at 100 ℃ for 3 days, and thereafter was slowly cooled to room temperature. Colorless crystals were obtained, which were washed with mother liquid, in about 57 % yield based on H_2btca. IR (KBr, cm^{-1}): 3429.57 (s), 2930.25 (m), 1660.13 (s), 1487.98 (s), 1388.05 (s), 1279.29 (s), 1252.97 (m), 1158.72 (w), 1100.24 (m), 1060.84 (w), 1037.54 (w), 958.71 (w), 829.41 (w), 785.78 (s), 761.09 (m), 708.40 (m), 662.64 (m), 590.67 (w).

Synthesis of MOF 4



The synthetic procedure is similar with that of **1** except that H_2bdc was replaced by 1,4-H_2ndc (1,4-naphthalenedicarboxylic acid). $Zn(NO_3)_2 \cdot 6H_2O$ (0.06 g, 0.2 mmol), H_2btca (0.0163g, 0.1 mmol), and 1,4-H_2ndc (0.0216 g, 0.1 mmol) were dissolved in 6 mL DMF, and then 3 drops of HBF_4 (wt% ~ 20%) were added. The final mixture was placed into a Teflon-lined stainless-steel vessel (15 mL) under autogenous pressure and heated at 100 ℃ for 3 days, and thereafter was slowly cooled to room temperature. Colorless crystals were obtained, which were washed with mother liquid, in about 61% yield based on H_2btca. IR (KBr, cm^{-1}): 3837.58 (w), 3748.58 (w), 3445.02 (m), 2929.65 (m), 1669.00 (s), 1561.35 (s), 1504.50 (m), 1390.02 (s), 1255.97 (s), 1096.34 (s), 958.20 (w), 835.67 (w), 789.38 (s), 760.02 (m), 707.84 (w), 661.36 (m), 585.85 (m).

Table S1. Elemental analysis for MOFs **1-4** (Before testing, all the samples were activated to get a relatively accurate result).

MOFs	C (%)		H (%)		N (%)	
	Calcd	Found	Calcd	Found	Calcd	Found
1	40.53	41.03	2.24	2.49	13.51	13.83
2	39.67	39.98	2.33	2.29	15.20	15.99
3	36.38	36.83	1.88	2.07	12.12	12.98
4	44.27	44.98	2.36	2.56	12.60	12.79

S3. Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data for MOFs in this work were recorded by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 293 K. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen positions were fixed at calculated positions and refined isotropically. All the structures were solved by Direct Method and refined by full-matrix least-squares techniques using the SHELXL-2018[1] program within Olex-2[2] software. All the solvent molecules which are highly disordered and not able to be modeled were treated by the SQUEEZE[3] routine in PLATON[4]. Thus, all of electron densities from free solvent molecules have been "squeezed" out.

The detailed crystallographic data and structure refinement parameters for **1** and **2** summarized in Table S2. CCDC for **1**: 1583101.

Table S2. Crystal data and structure refinements for MOF **1** and **2**.

Identification code	**1**	**2**
formula	$C_{103}H_{123}N_{31}O_{35}Zn_8$	$C_{94}H_{105}N_{31}O_{32}Zn_8$
Formula weight	2878.44	2704.37
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3/m$	$P\ 6_3/m$
a (Å)	20.054 (3)	20.034 (5)
b (Å)	20.054 (3)	20.034 (5)
c (Å)	30.430 (5)	30.459 (5)
α (°)	90.00	90.000
β (°)	90.00	90.000
γ (°)	120.00	120.000
V (Å^3)	10598	10587
Z	2	2
$D_{calcd.}$[g cm^{-3}]	0.621	0.631
F(000)	1968	1986.0
Reflections collected	88677 / 6385	60098/6353
R(int)	0.0961	0.2119
Goodness-of-fit on F^2	1.040	0.976
$R_1{}^a$ [I>2σ (I)]	0.0348	0.1030
$wR_2{}^b$	0.0850	0.2483

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = |\Sigma w(|F_o|^2-|F_c|^2)|/\Sigma|w(F_o{}^2)^2|^{1/2}$.

S4. Heat of adsorption calculation for gas uptake

The isosteric heat of adsorption values were calculated using the Clausius-Clapeyron equation:

$$\ln(P1/P2) = \Delta Habs \times (T2 - T1) / R\ T1\ T2$$

Where Pi = pressure for isotherm i

Ti = temperature for isotherm i

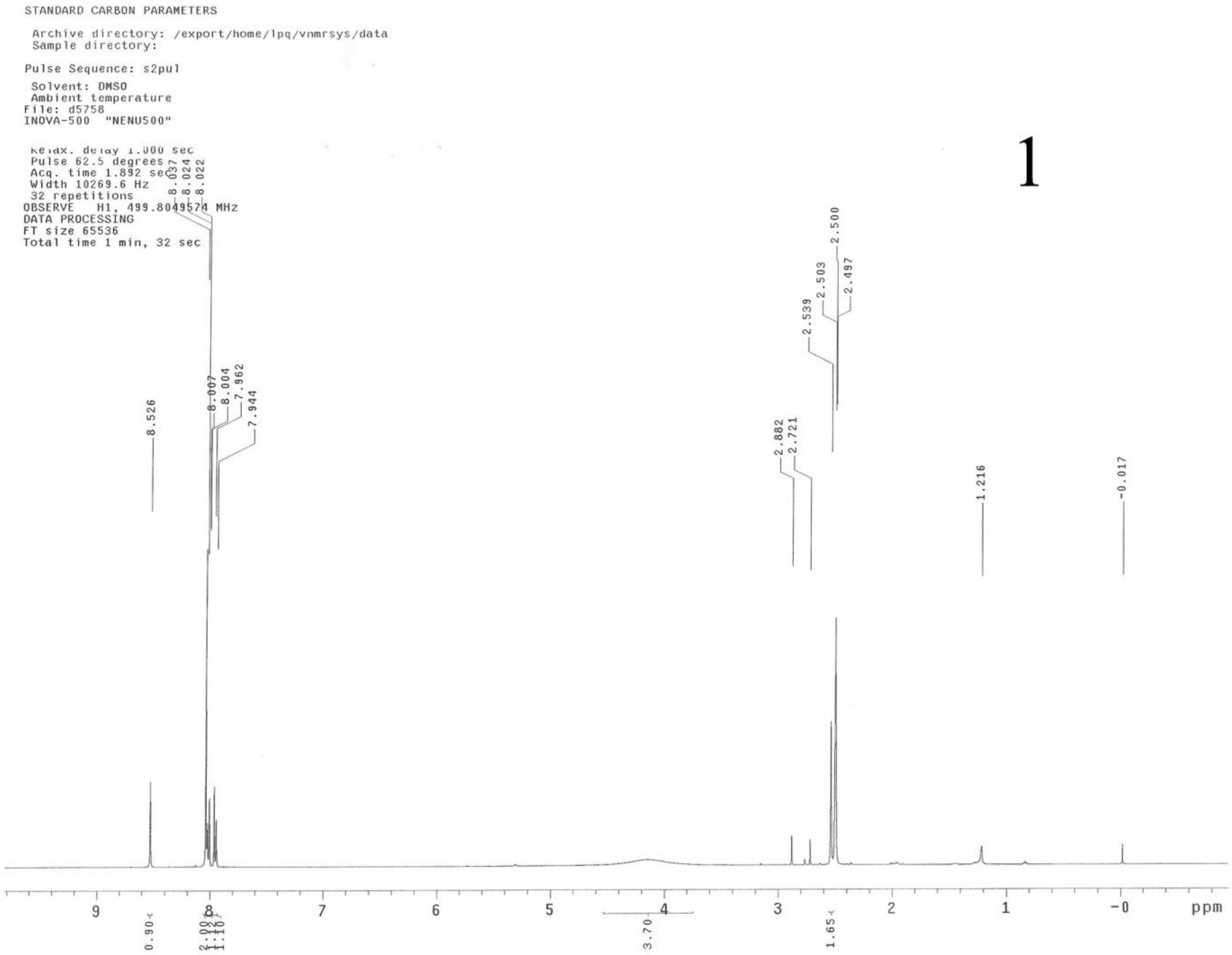
R = 8.314 J / (K*mol)

The equation can be applied to calculate the enthalpy of adsorption of a gas as a function of the quantity of gas adsorbed.

S5. ^{1}H NMR analysis of digested MOF samples

General

For ^{1}H NMR spectroscopy, the mother liquor of the as-synthesized MOF crystals was replaced with fresh dry DMF multiple times. The MOF crystals were then filtered through a sintered glass filter funnel under suction and the surfaces of the crystals were allowed to dry. The crystals were then digested using the following protocol: 25 µL of a 35% DCl solution in D_2O was mixed with 1 mL of DMSO-d_6 to give a DCl/DMSO-d_6 stock solution. Around 5 mg of MOF was digested in 150 µL of this stock solution together with 500 µL of DMSO-d_6. Spectra were acquired immediately following dissolution. Spectra for all MOFs (**1-4**) are presented below.



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 Sample directory:

Pulse Sequence: s2pul

 Solvent: DMSO
 Ambient temperature
File: d5758
INOVA-500  "NENU500"

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 Acq. time 1.892 sec
 Width 10269.6 Hz
 32 repetitions
OBSERVE   H1, 499.8049574 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 32 sec
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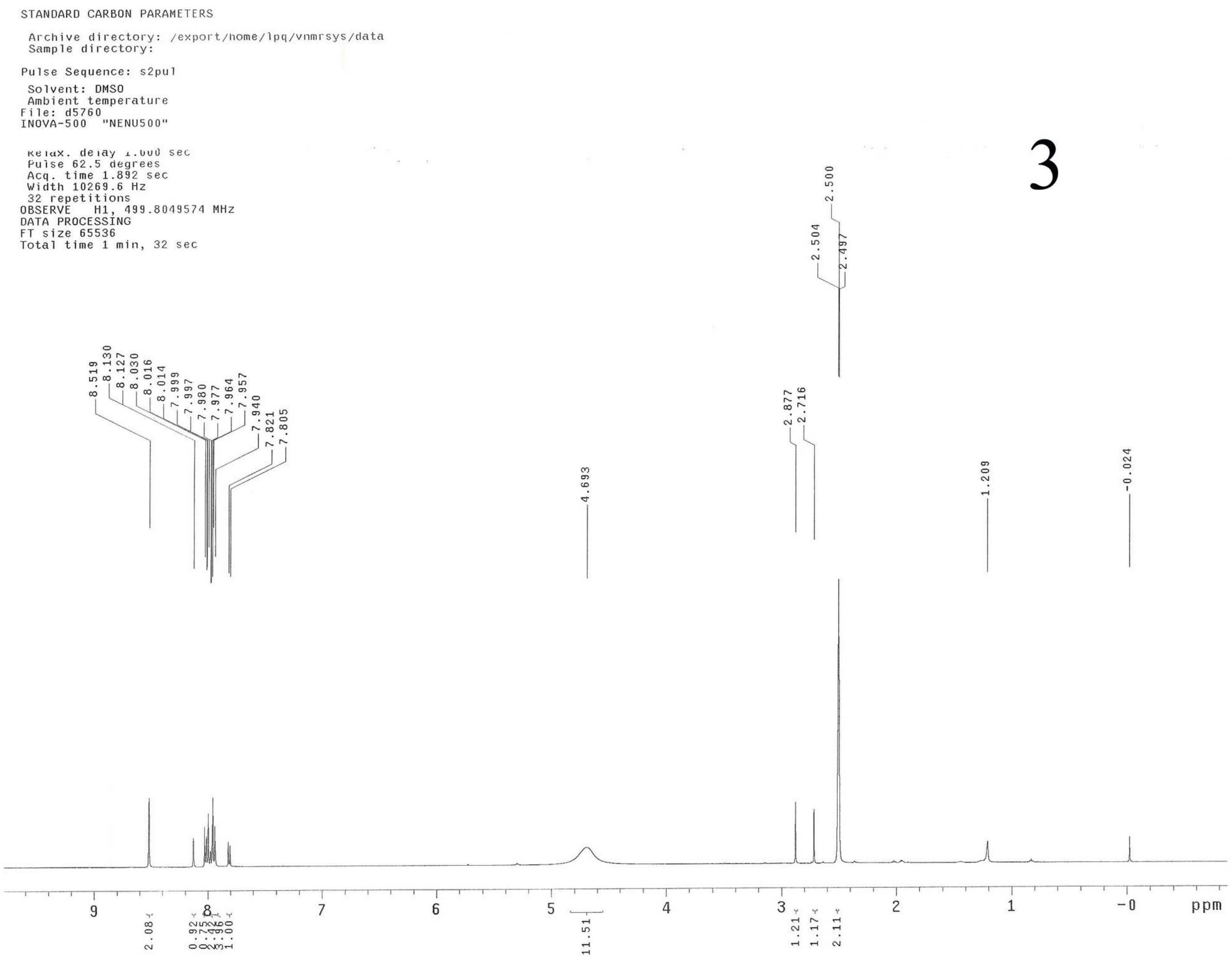
1



3

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 Ambient temperature
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 Acq. time 1.892 sec
 Width 10269.6 Hz
 32 repetitions
OBSERVE   H1, 499.8049574 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 32 sec
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STANDARD CARBON PARAMETERS

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 Sample directory:

Pulse Sequence: s2pul

 Solvent: DMSO
 Ambient temperature
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INOVA-500  "NENU500"

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 Pulse 62.5 degrees
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DATA PROCESSING
FT size 65536
Total time 1 min, 32 sec
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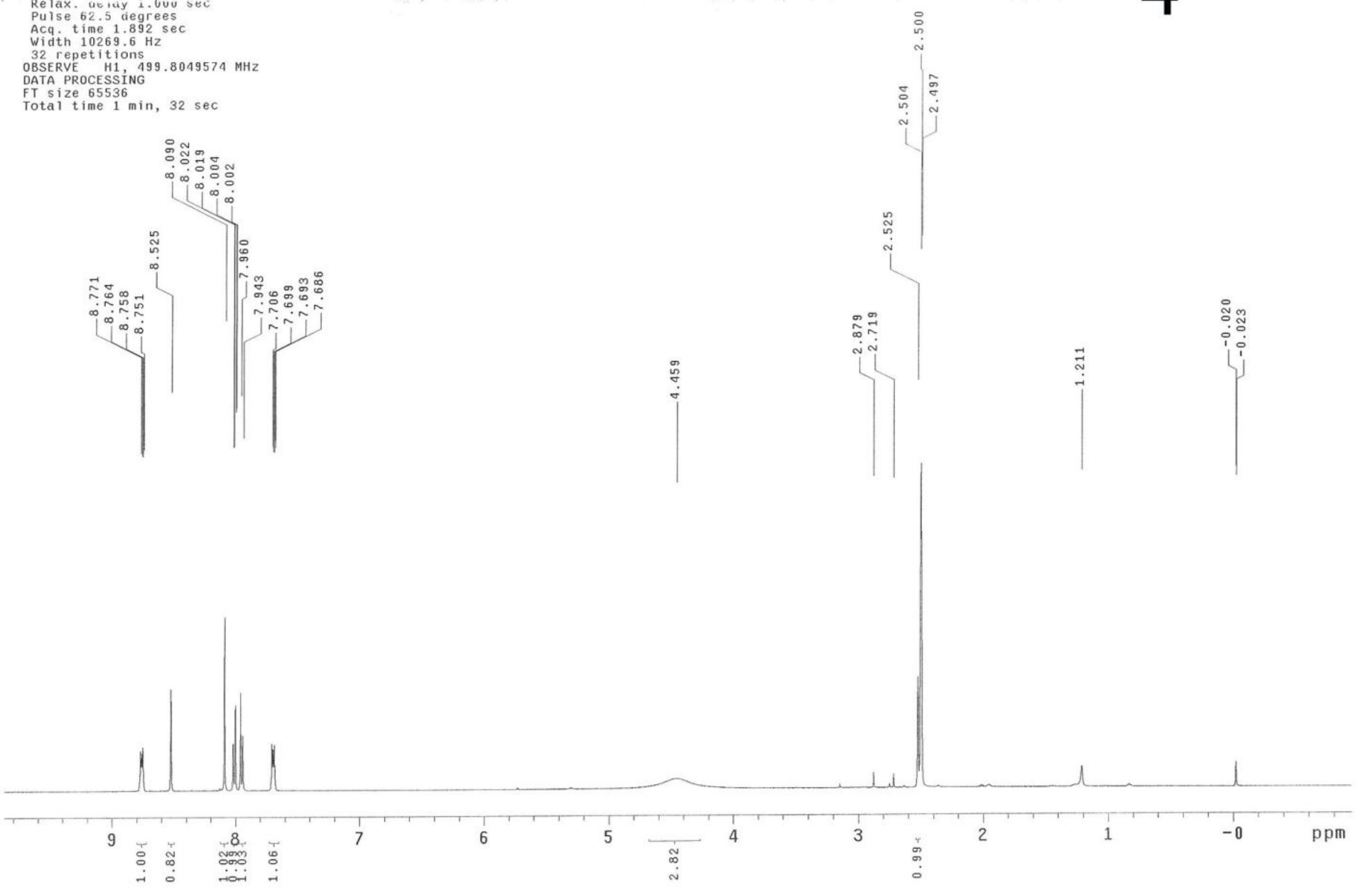
4



S6. MOF 2 sensing small solvent molecules

The solvent sensing experiments have been performed as follows: finely ground samples of **2** (5mg) were immersed in different solvents (3 mL), treated by ultrasonication, and then aged to form stable emulsions before fluorescence were measured.

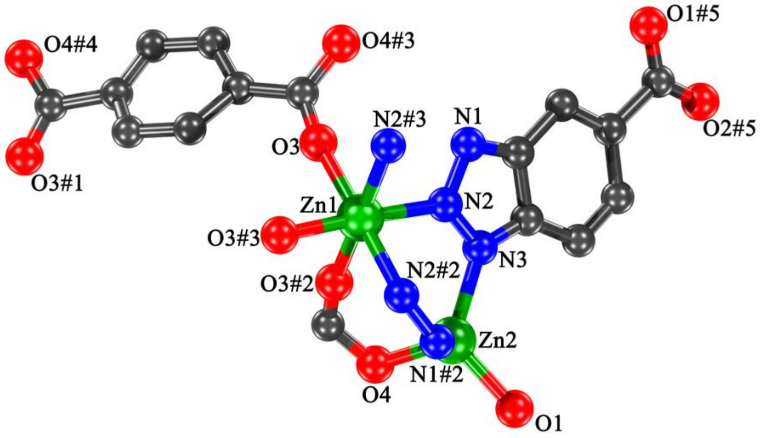


Fig. S1 The coordination modes of Zn^{2+} ions in **1,** symmetry codes: #1 x, y, 1.5-z; #2 1-y, x-y, z; #3 1-x+y, 1-x, z; #4 1-x+y, 1-x, 1.5-z, #5 1+x-y, x, 1-z. All hydrogen atoms have been omitted for clarity. Green = Zn; dark gray = C; red = O; blue = N.

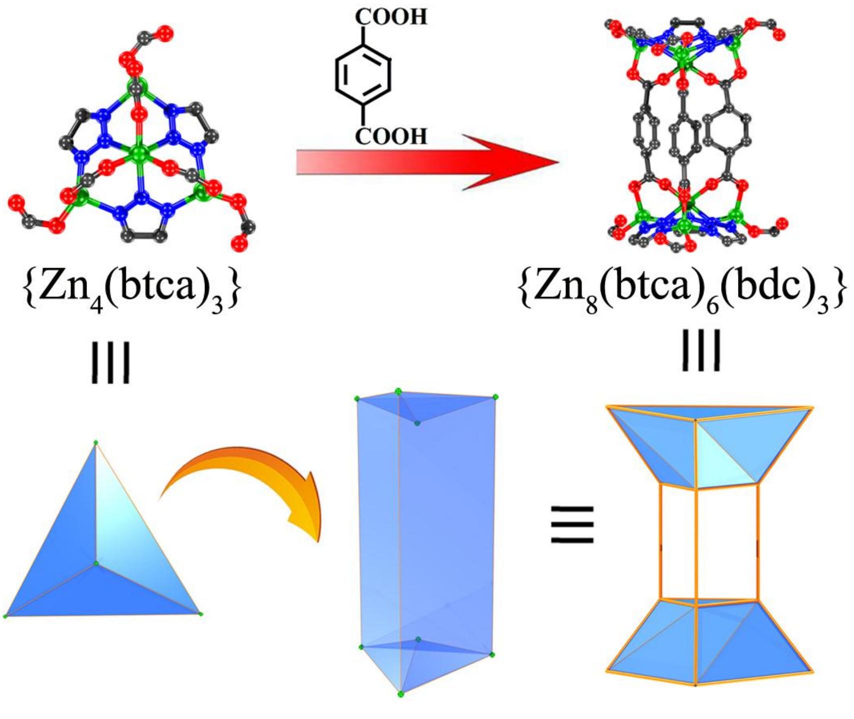


Fig. S2 The double SBU triangular prism building unit {$Zn_8(btca)_6(bdc)_3$} in **1**.

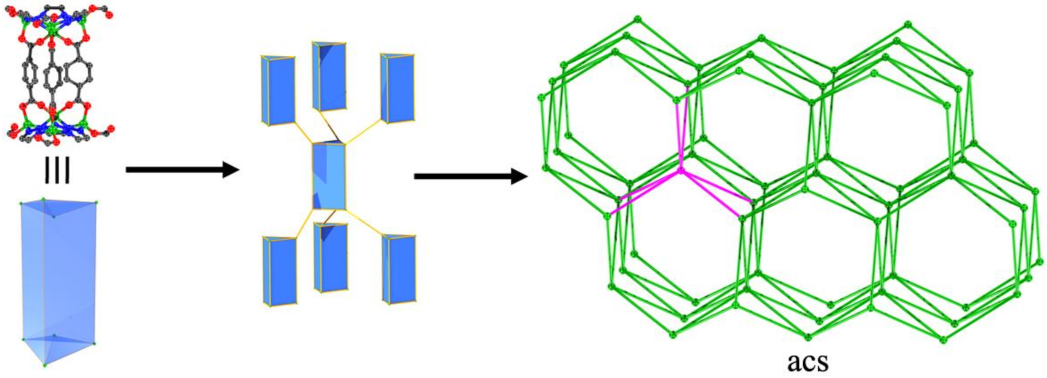


Fig. S3 Deconstruction of **1** into the **acs** net.

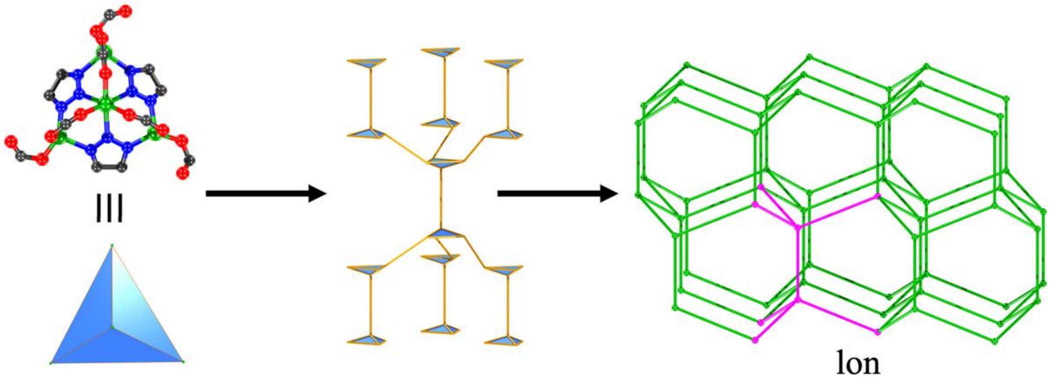


Fig. S4 The 4-connected **lon** topology network in **1**.

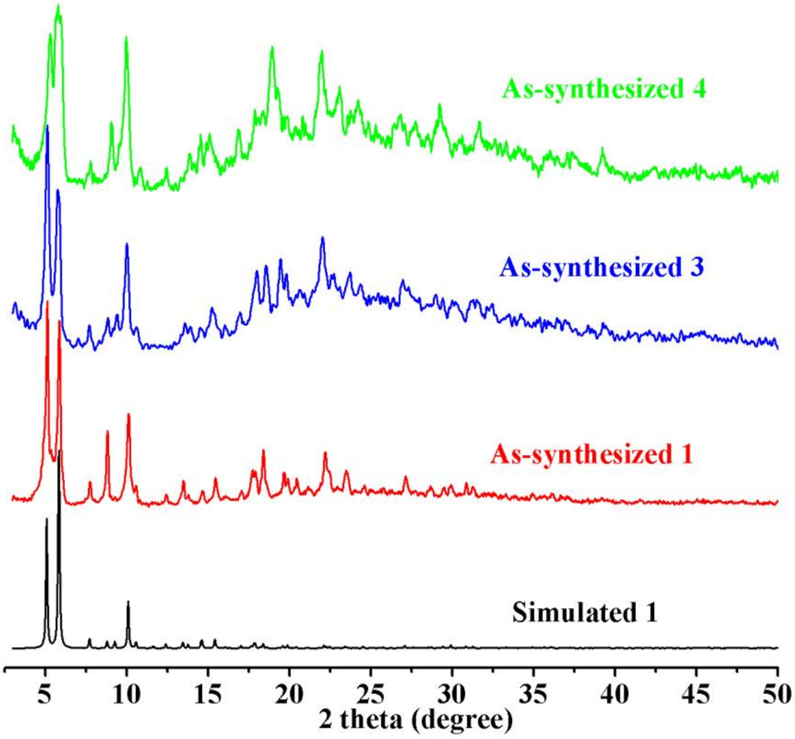


Fig. S5 X-ray powder diffraction patterns of simulated **1** and as-synthesized **1**, **3**, and **4**.

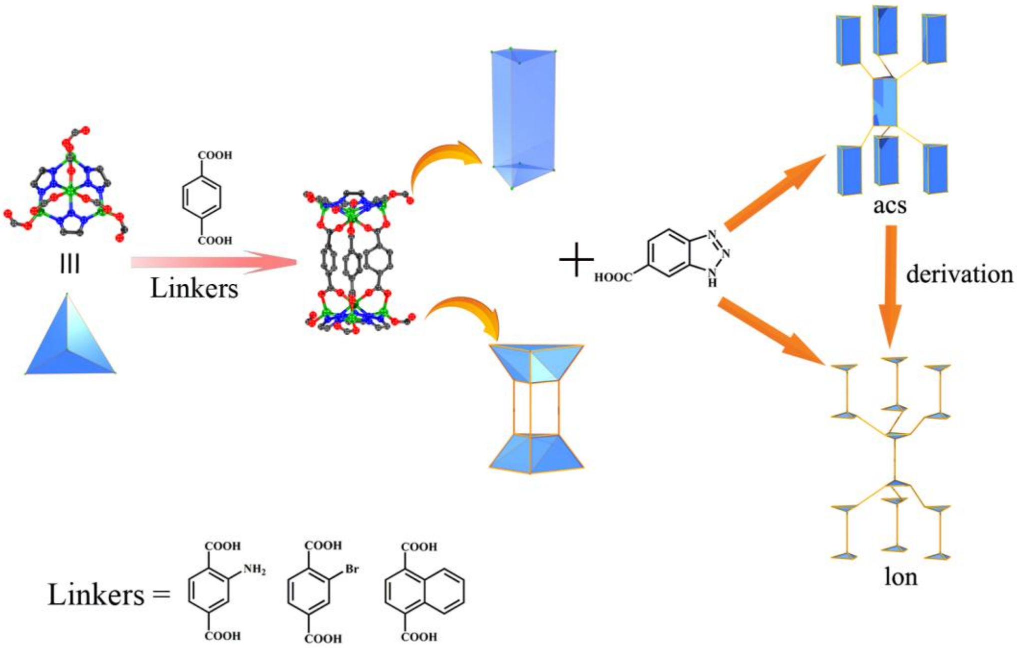


Fig. S6 Scheme of reticular synthesis of a family MOFs based on the triply bound triangular frusta SBUs connected with ditopic organic ligands.

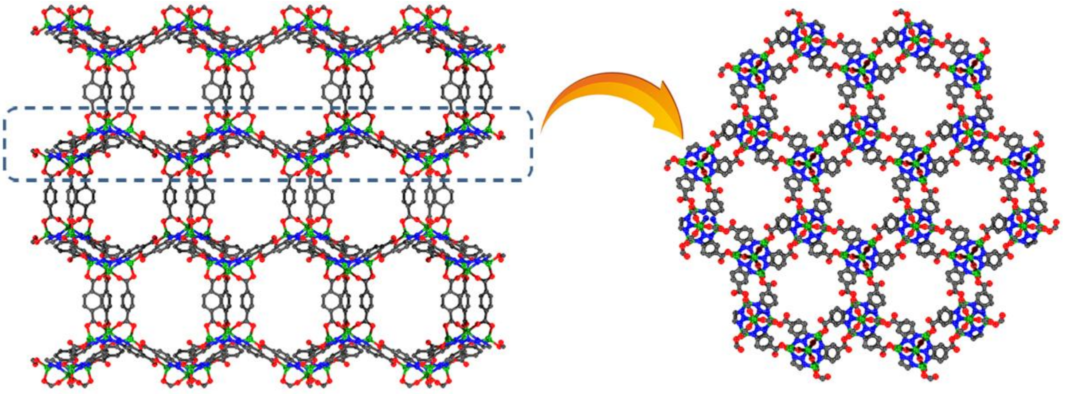


Fig. S7 Ball-and-stick representations of the 3D pillared-layer structure of **1**; the layer is formed by {$Zn_4(btca)_3$} units linked by H_2btca ligands.

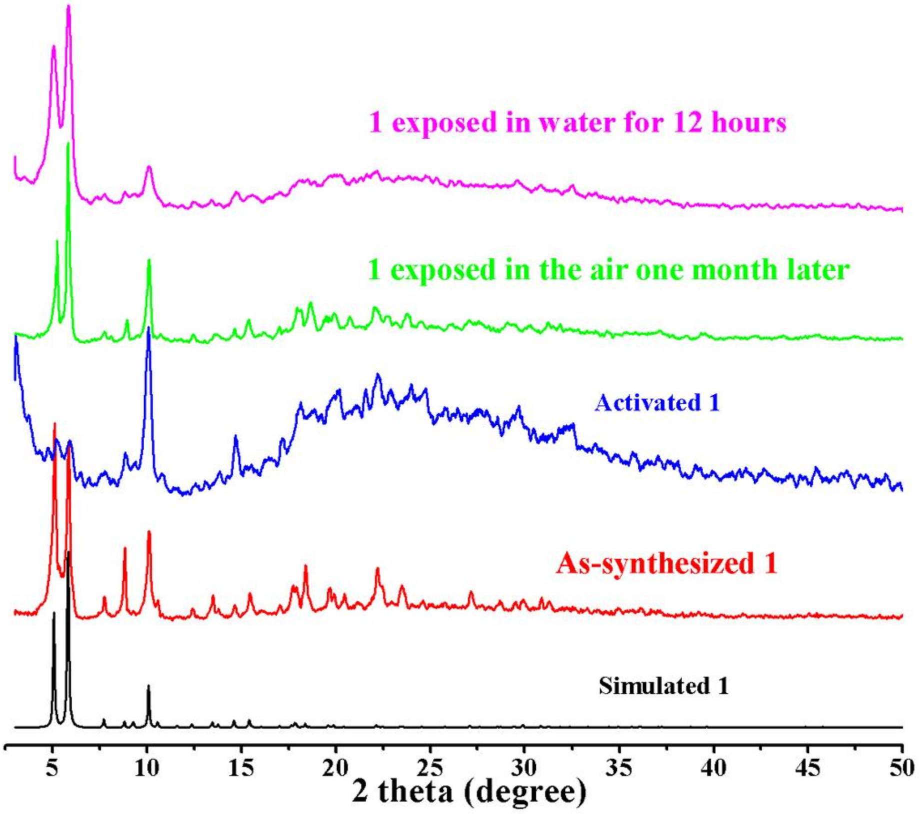


Fig. S8 PXRD patterns of **1**: simulated (black), experimental (red), activated (blue), samples exposed in the air one month later (green), and exposed in water for 12 hours (pink) respectively.

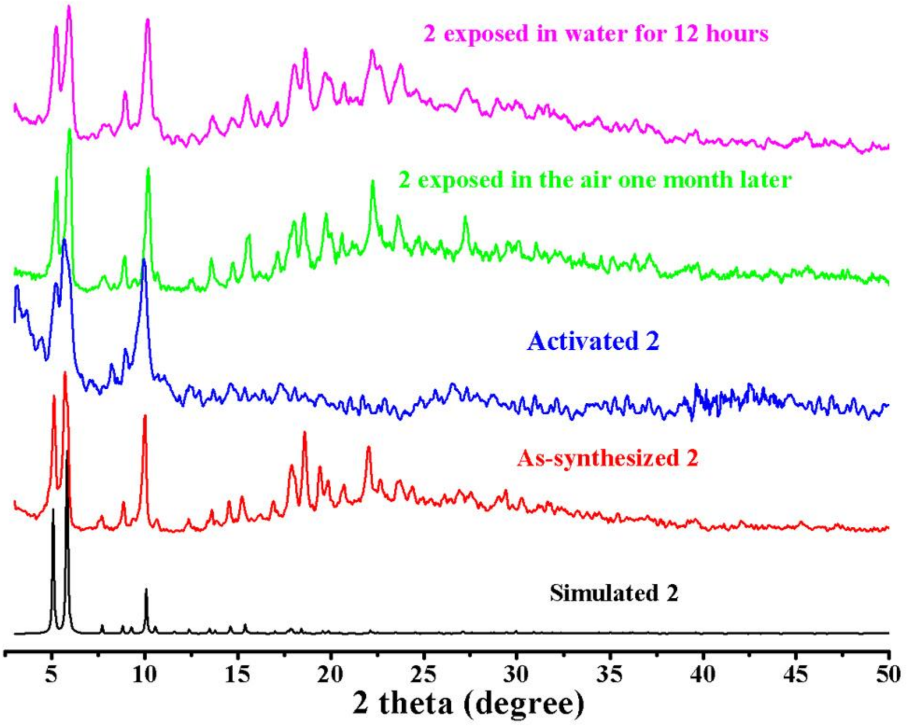


Fig. S9 PXRD patterns of **2**: simulated (black), experimental (red), activated (blue), samples exposed in the air one month later (green), and exposed in water for 12 hours (pink) respectively.

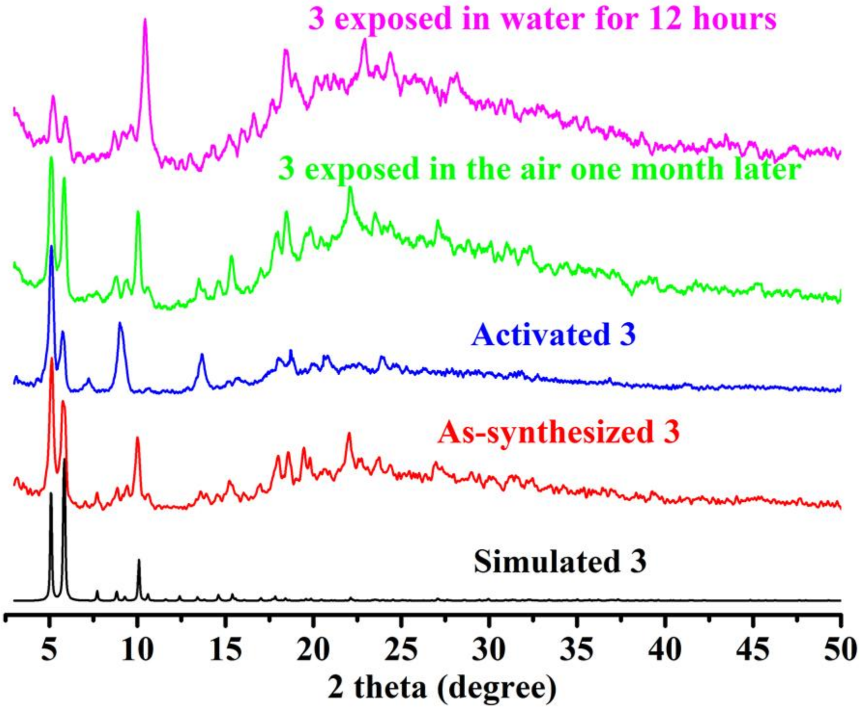


Fig. S10 PXRD patterns of simulated **3** (black), experimental **3** (red), activated **3** (blue), **3** samples exposed in the air one month later (green), and **3** exposed in water for 12 hours (pink) respectively.

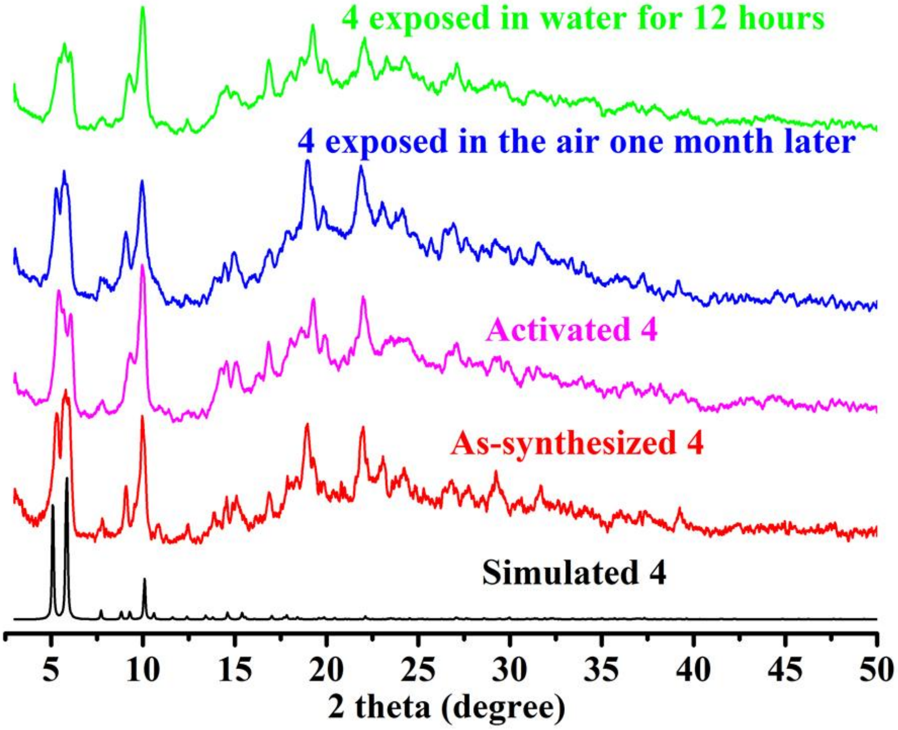


Fig. S11 PXRD patterns of simulated **4** (black), experimental **4** (red), activated **4** (pink), **4** samples exposed in the air one month later (blue), and **4** exposed in water for 12 hours (green) respectively.

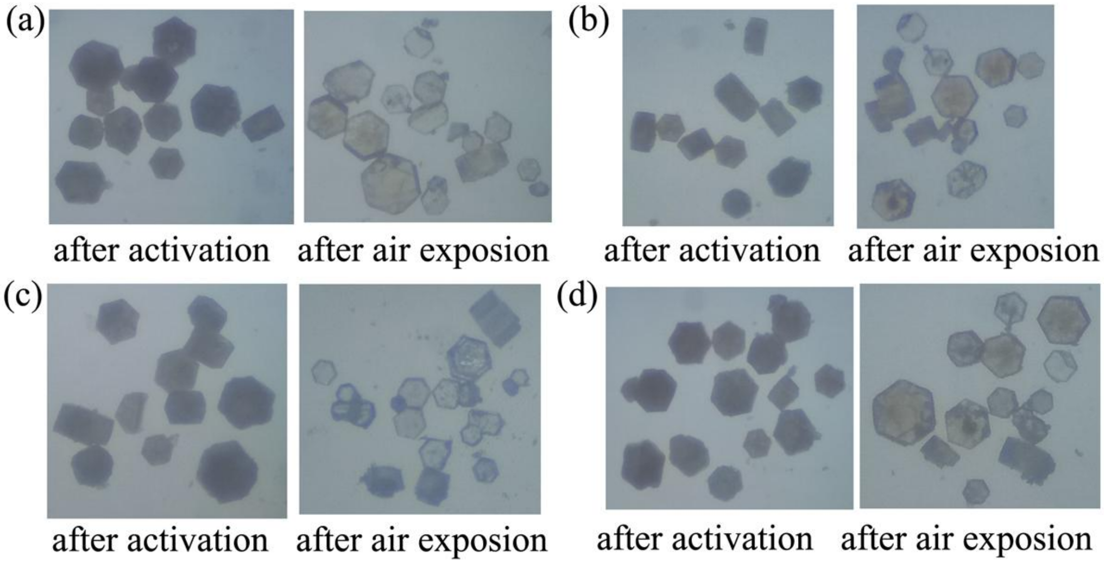


Fig. S12 The microscope pictures of **1** (a), **2** (b), **3** (c), and **4** (d) samples after activation and air exposion.

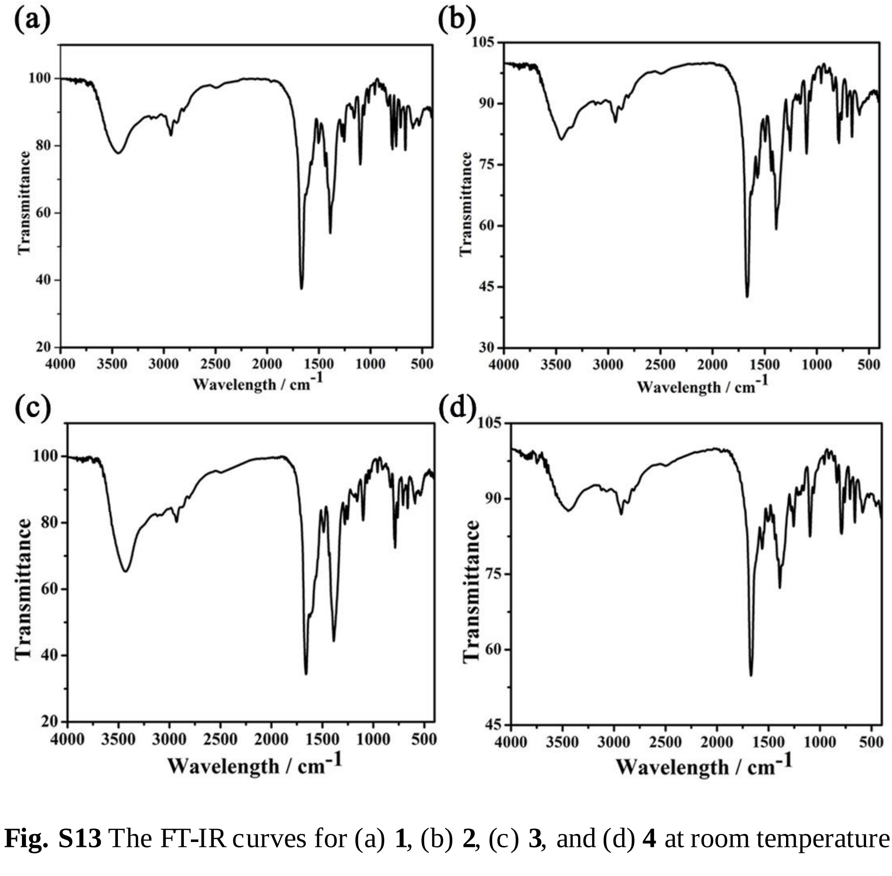


Fig. S13 The FT-IR curves for (a) **1**, (b) **2**, (c) **3**, and (d) **4** at room temperature.

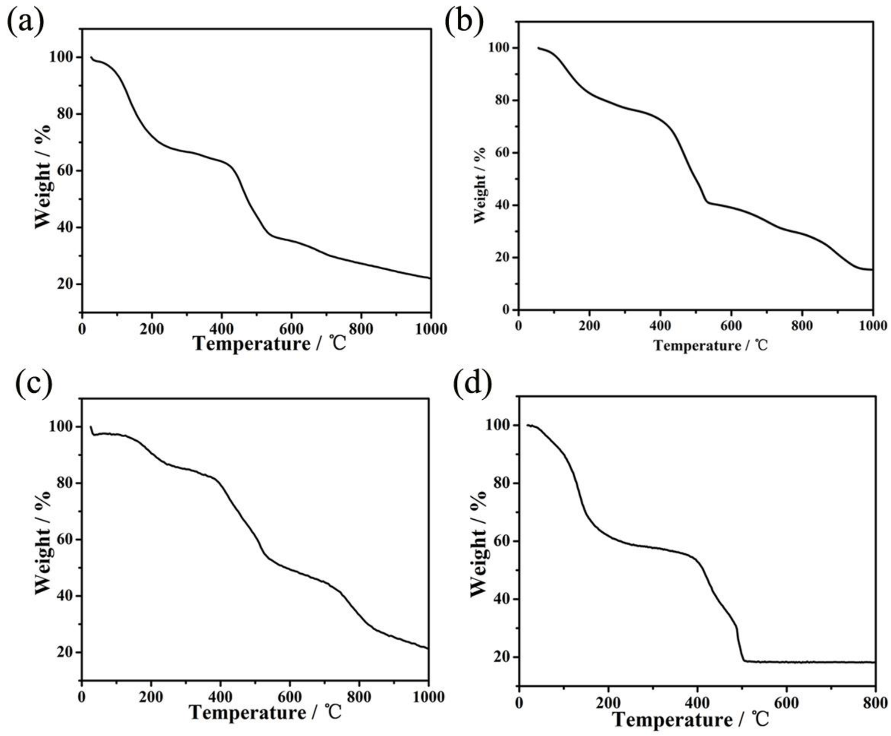
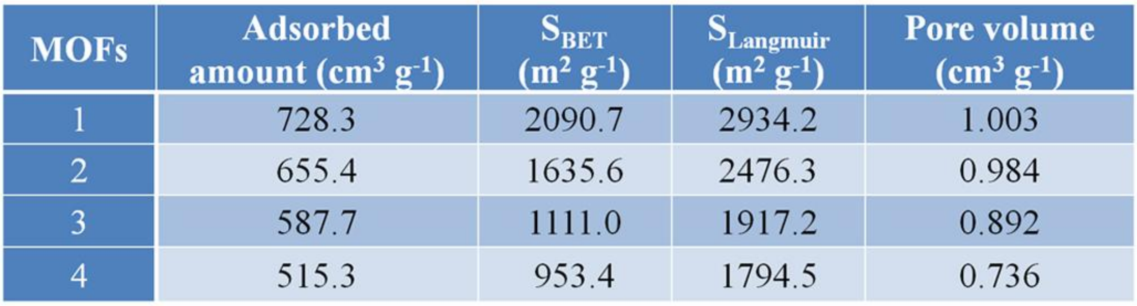


Fig. S14 TGA curves of as-synthesized MOFs (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

Table S3. The summary of N_2 uptake properties of **1-4**.



MOFs	Adsorbed amount ($cm^3\ g^{-1}$)	S_{BET} ($m^2\ g^{-1}$)	$S_{Langmuir}$ ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
1	728.3	2090.7	2934.2	1.003
2	655.4	1635.6	2476.3	0.984
3	587.7	1111.0	1917.2	0.892
4	515.3	953.4	1794.5	0.736

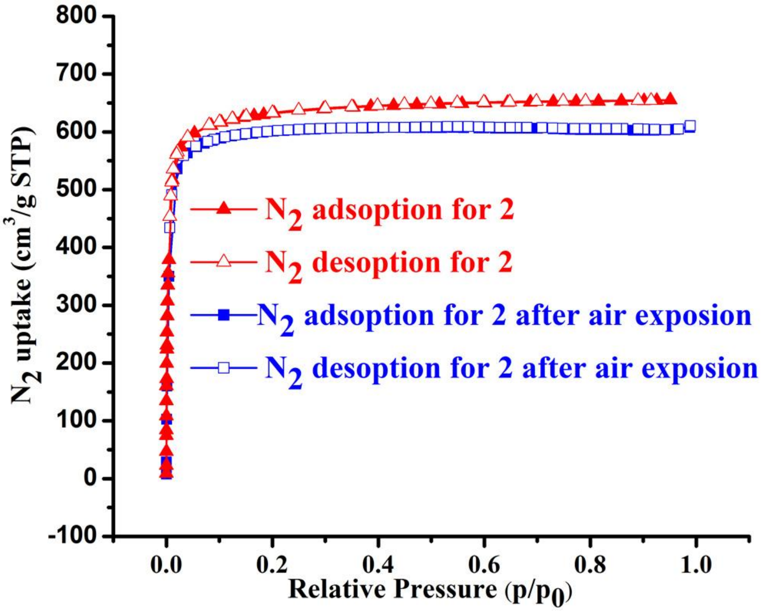


Fig. S15 The N_2 sorption isotherms at 77 K for MOF **2** and **2** after air exposion.

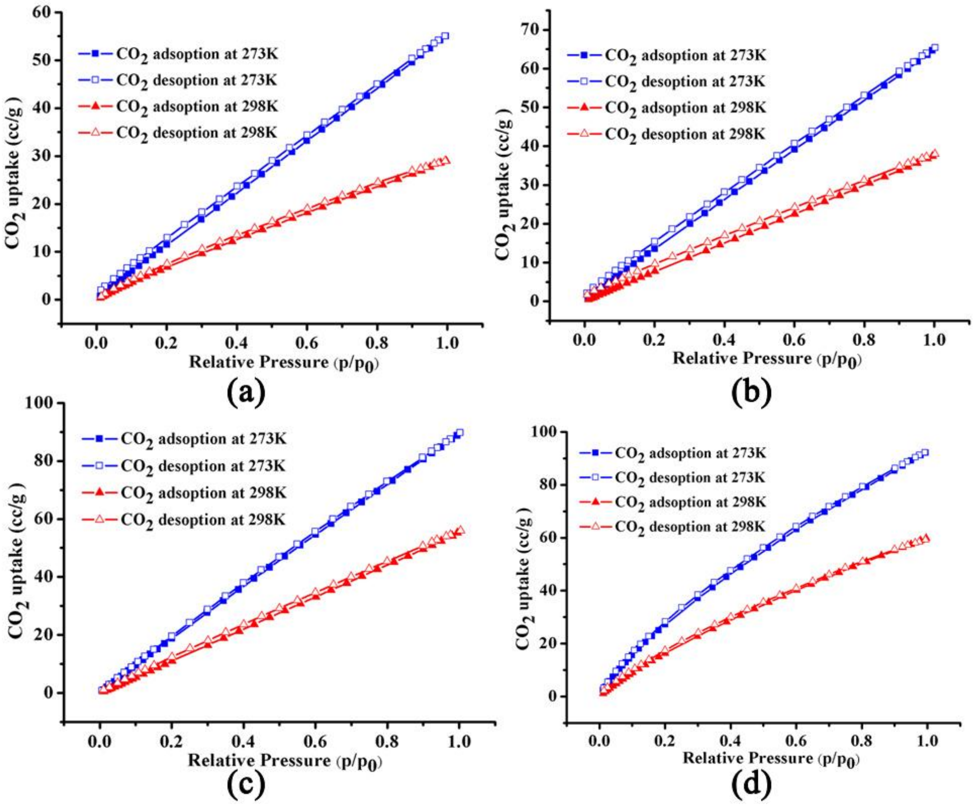


Fig. S16 The CO_2 sorption isotherms for activated (a) **1**, (b) **2**, (c) **3** and (d) **4** at 273 K and 298 K.

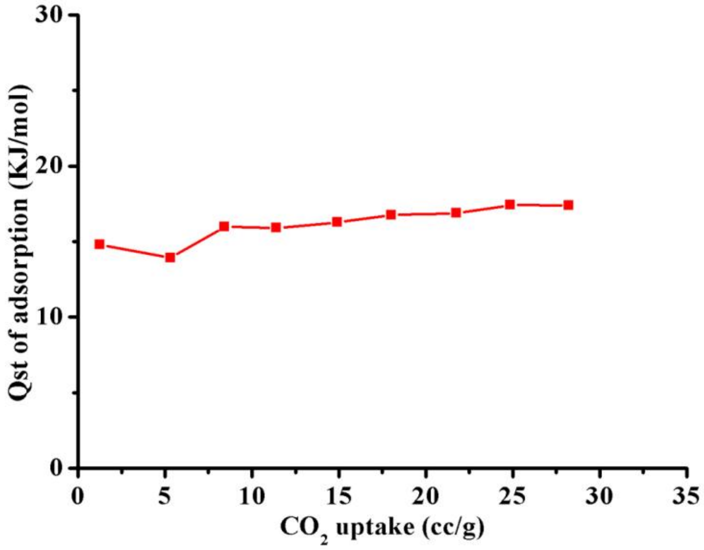


Fig. S17 Isosteric heat of adsorption for CO_2 on **1** (using the isotherms at 273 K and 298 K).

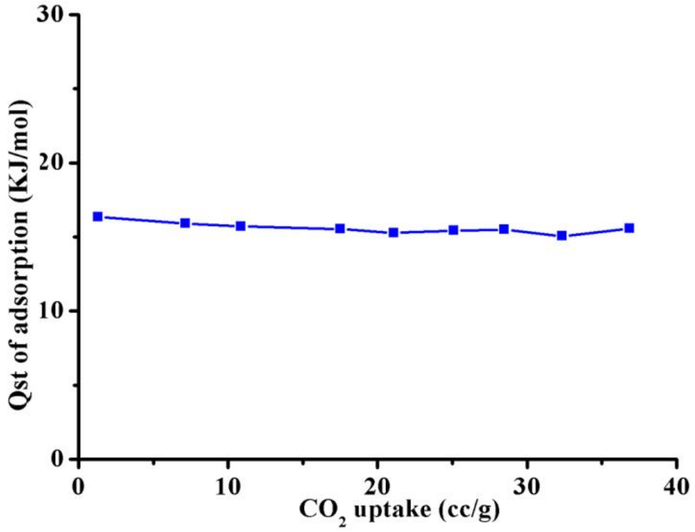


Fig. S18 Isosteric heat of adsorption for CO_2 on **2** (using the isotherms at 273 K and 298 K).

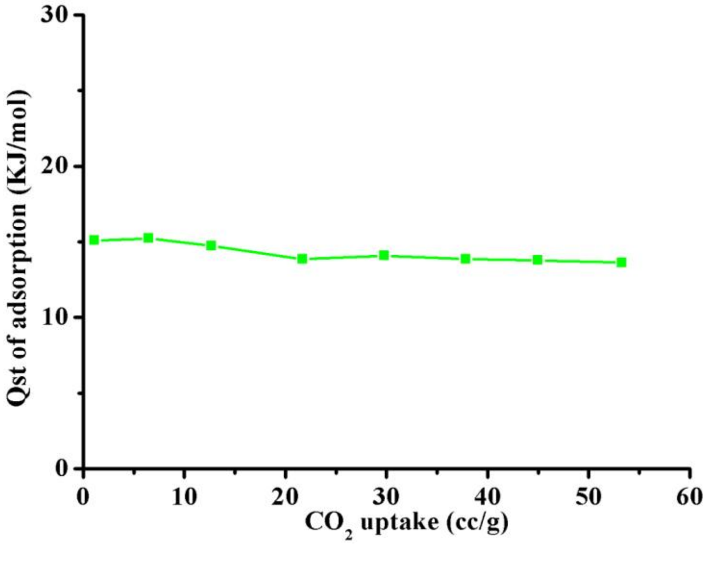


Fig. S19 Isosteric heat of adsorption for CO_2 on **3** (using the isotherms at 273 K and 298 K).

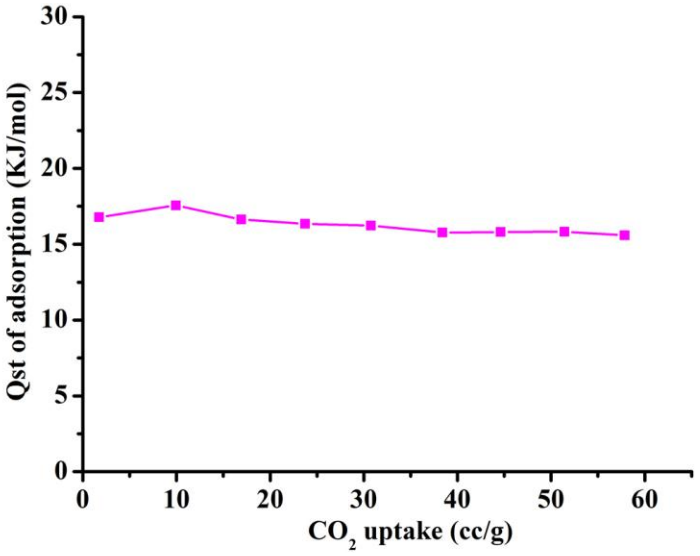


Fig. S20 Isosteric heat of adsorption for CO_2 on **4** (using the isotherms at 273 K and 298 K).

Table S4. The CO_2-uptakes and enthalpy of adsorption for **1-4**.

MOFs	Adsorbed amount (273 K, $cm^3\ g^{-1}$)	Adsorbed amount (298 K, $cm^3\ g^{-1}$)	Qst (KJ mol^{-1})
1	55.06	28.97	14.97
2	65.37	37.99	16.33
3	89.64	55.96	15.09
4	92.09	59.19	16.78

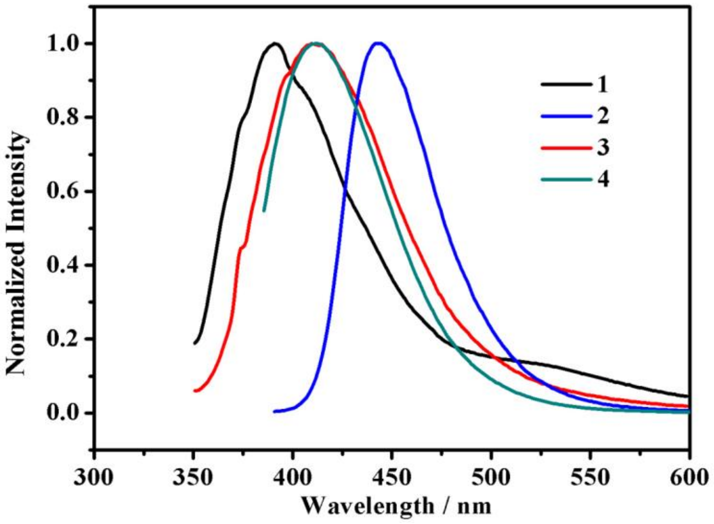


Fig. S21 The emission spectra of MOFs **1-4** (**1, 3** λ_{ex} = 330 nm, **2, 4** λ_{ex} = 365 nm) in the solid state at room temperature.

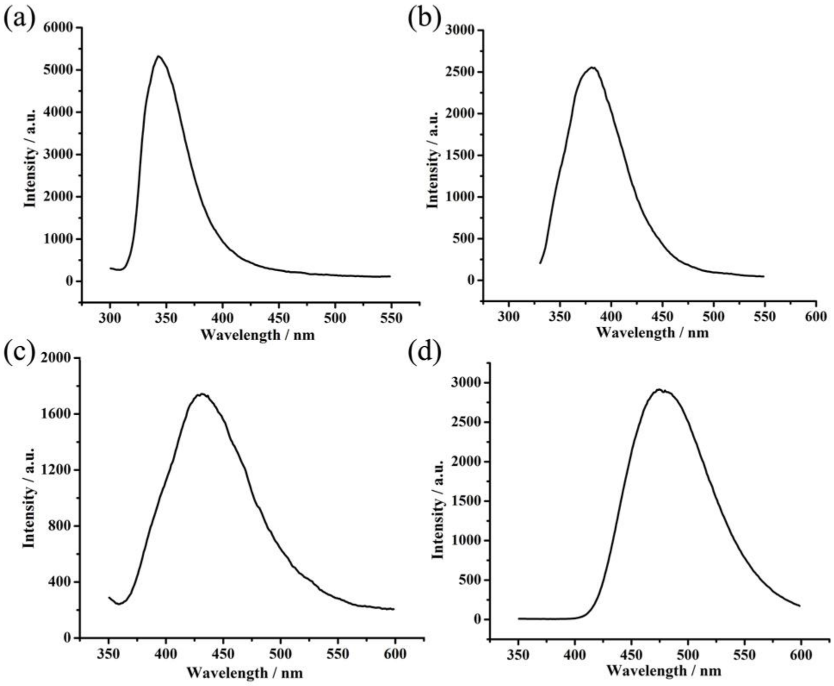


Fig. S22 Solid photoluminescence spectra of (a) H_2btca ligand (λ_{ex} = 280 nm), (b) H_2bdc ligand (λ_{ex}= 320 nm), (c) 2-NH_2-H_2bdc ligand (λ_{ex}= 320 nm), and (d) 1,4-H_2ndc ligand (λ_{ex}= 330 nm) at room temperature.

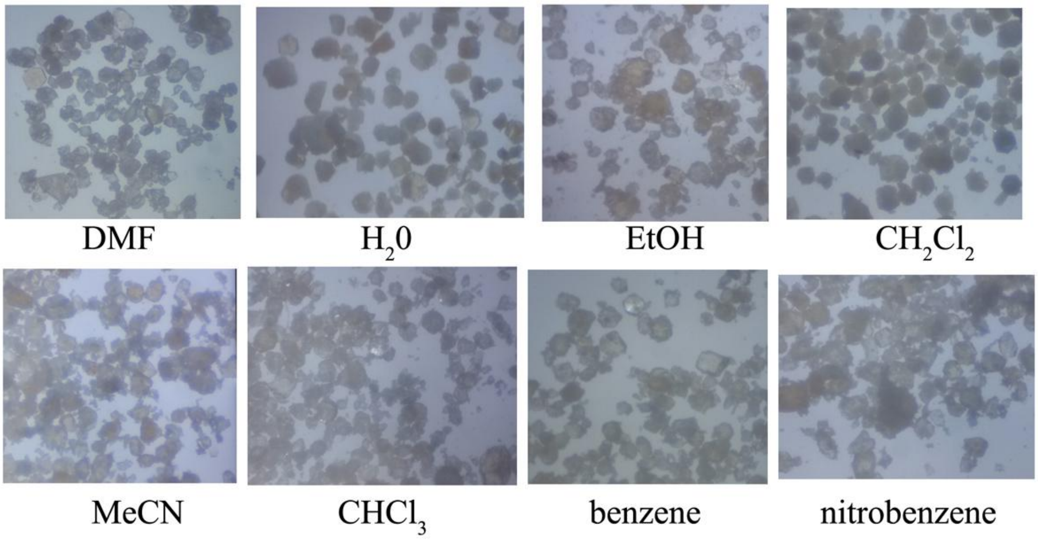


Fig. S23 The microscope pictures of MOF **2** after after solvent (DMF, H_2O, EtOH, CH_2Cl_2, MeCN, $CHCl_3$, benzene, and nitrobenzene) sensing.

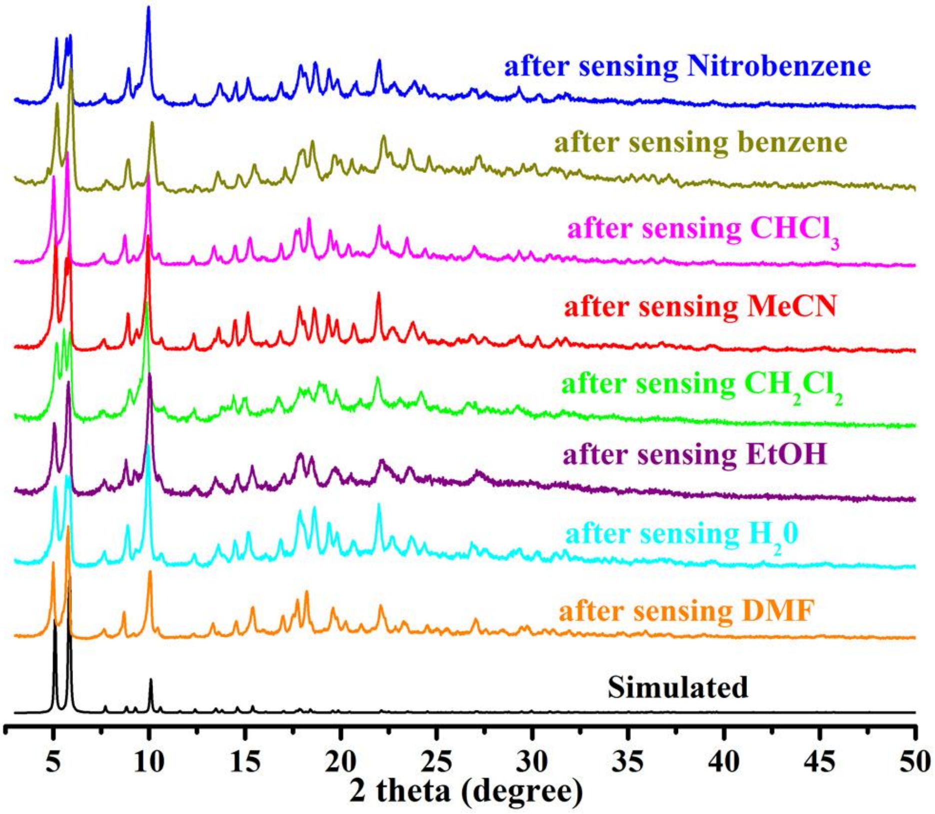


Fig. S24 The PXRDs of MOF **2** after solvent (DMF, H_2O, EtOH, CH_2Cl_2, MeCN, $CHCl_3$, benzene, and nitrobenzene) sensing.

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