

Electronic Supplementary Information (ESI) for:

Crystal transformation synthesis of high stable porous phosphonate-based MOF for selective adsorption of CO₂

Fupeng Zhai, Qingshu Zheng, Zhenxia Chen*, Yun Ling, Xiaofeng Liu, Linhong
Weng, Yaming Zhou*

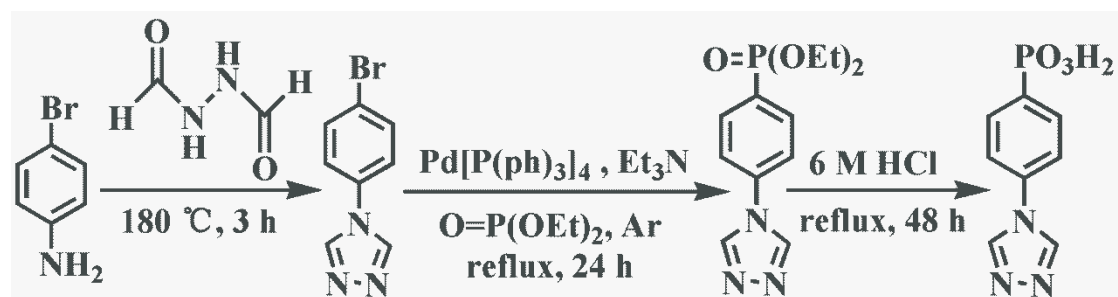
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1. General

All reagents were purchased from commercial sources and used without further purification. 4-(1,2,4-triazol-4-yl)phenylphosphonic acid (H_2ptz) was prepared as shown in Scheme S1. 1H -NMR spectra were recorded on a JEOL ECA NMR spectrometer (400 MHz), chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in D_2O as an internal standard. Fourier transform infrared (FT IR) were recorded on a Nicolet 470 FT-IR spectrometer in the range $4000-400\text{ cm}^{-1}$. C, H, and N elemental analyses were determined on the Elemental Vario EL III. The phase purity of the samples was confirmed by powder X-ray diffraction (PXRD) collected on a Bruker D8 powder diffractometer with $Cu-K\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). Thermogravimetry (TG) studies were carried out on a TGA/SDTA 851 thermoanalyzer in the temperature range of $30-800\text{ }^\circ\text{C}$ under N_2 flow at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. CO_2 and N_2 adsorption were performed on ASAP 2020 gas adsorption analyzer. Samples were activated at $120\text{ }^\circ\text{C}$ for 8 h before gas adsorption.

2. Experiment details

H_2ptz was synthesized according to the route shown in scheme S1.



Scheme S1. Synthesis process of the ligand H_2ptz .

Synthesis of H_2ptz : The first step, a mixture of 4-bromoaniline (17.3 g, 0.1 mol) and N,N' -diformylhydrazine (8.8 g, 0.1 mol) was heated at $180\text{ }^\circ\text{C}$ for 3 h. After cooling

down to room temperature and concentrating under vacuum, the residue was purified by flash chromatography to afford 10 g (45%) of 4-(4-bromophenyl)-1,2,4-triazole. Next step, a mixture of 4-(4-bromophenyl)-1,2,4-triazole (10 g, 45 mmol), diethyl phosphite (7.0 g, 51 mmol), triethylamine (6.0 g, 59 mmol), tetrakis(triphenylphosphine)palladium(0) (3.0 g, 2.6 mmol) was added to the solution of toluene (200 mL), after stirring at 90 °C for 24 h under argon, the mixture was cooled to room temperature and concentrated under vacuum, the residue was purified by flash chromatography. Last step, diethyl 4-(1,2,4-triazol-4-yl)phenylphosphonate was hydrolyzed in 6 M HCl solution at 110 °C for 48 h. 5.5 g of H₂ptz was obtained with yield of 55%. ¹H NMR (400 MHz, D₂O): δ = 7.74 (d, J = 7.8 Hz, 2H), δ = 7.96-7.97 (m, 2H), δ = 9.51 (s, 2H). FT IR frequencies (KBr) (cm⁻¹): 3122 (w), 3043 (w), 2582 (m), 1562 (s), 1535 (w), 1362 (w), 1228 (w), 1186 (m), 1138 (s), 1097 (m), 1022 (m), 983 (m), 924 (s), 836 (m), 745 (m), 623 (w), 566 (m), 540 (m), 482 (w), 434 (m).

Synthesis of [Ni₃(Hptz)₆·6H₂O] · 12H₂O (1): A mixture of NiSO₄·6H₂O (0.040 g, 0.15 mmol), H₂ptz (0.068 g, 0.3 mmol), and deionized water (5 mL) was placed in a teflon-lined stainless steel autoclave (15 mL) and was stirred at room temperature for 1 h (The pH value was 1.0). The mixture was then heated at 180 °C for 24 h, followed by cooling down to room temperature. Light purple block crystals were collected by filtration (Yield 61% based on H₂ptz). Elemental analysis calcd. for C₄₈H₇₈N₁₈Ni₃O₃₆P₆ (1845.23): C, 31.24; H, 4.26; N, 13.66 %. Found: C, 31.11; H, 4.45; N, 13.79 %.

Synthesis of [Ni(Hptz)₂]·10H₂O (2): A mixture of [Ni₃(Hptz)₆·6H₂O] · 12H₂O (1) (0.047 g, 0.025 mmol) and aqueous HOAc (5 mL, pH = 3.0) was placed in a teflon-lined stainless steel autoclave (15 mL) and was stirred at room temperature for 1 h. The mixture was then heated at 180 °C for 7 h, followed by cooling down to room temperature. Green block crystals were collected by filtration (Yield 62%, based on 1). Elemental analysis calcd. for C₁₆H₃₄N₆NiO₁₆P₂ (687.14): C, 27.97; H, 4.99; N, 12.23 %. Found: C, 27.91; H, 5.05; N, 12.27 %.

3. Single-crystal X-ray crystallography

Single crystal data of 1 and 2 were collected at room temperature using a Bruker APEX diffractometer equipped with a normal focus, 3.0 kW sealed tube X-ray source (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$). Data reduction and cell refinement were performed with the SAINT program,^{S1} and the absorption correction program SADABS was employed to correct the data for absorption effects. The structures were solved by direct methods and refined using full-matrix least-squares treatment (SHELXTL-97)^{S2} with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms on the phenyl were theoretically added. O-bonded H atoms were placed in idealized positions and constrained to ride on their parent atoms. Selected bond distances and bond angles are given in Table S1 and Table S2.

Table S1. Selected bond lengths (Å) and angles (deg) for 1

1			
Ni(1)-N(1)#1	2.098(3)	N(1)-Ni(1)-N(1)#4	180.00(18)
Ni(1)-N(1)#2	2.098(3)	N(1)#1-Ni(1)-N(1)#5	90.43(11)
Ni(1)-N(1)#3	2.098(3)	N(1)#2-Ni(1)-N(1)#5	89.57(11)
Ni(1)-N(1)	2.098(3)	N(1)#3-Ni(1)-N(1)#5	180.00(17)
Ni(1)-N(1)#4	2.098(3)	N(1)-Ni(1)-N(1)#5	90.43(11)
Ni(1)-N(1)#5	2.098(3)	N(1)#4-Ni(1)-N(1)#5	89.57(11)
Ni(2)-O(4)#1	2.053(3)	O(4)#1-Ni(2)-O(4)#5	87.25(12)
Ni(2)-O(4)#5	2.053(3)	O(4)#1-Ni(2)-O(4)	87.25(12)
Ni(2)-O(4)	2.053(3)	O(4)#5-Ni(2)-O(4)	87.25(12)
Ni(2)-N(2)#1	2.056(3)	O(4)#1-Ni(2)-N(2)#1	90.45(13)
Ni(2)-N(2)#5	2.056(3)	O(4)#5-Ni(2)-N(2)#1	91.07(13)
Ni(2)-N(2)	2.056(3)	O(4)-Ni(2)-N(2)#1	177.21(12)
		O(4)#1-Ni(2)-N(2)#5	177.21(12)
N(1)#1-Ni(1)-N(1)#2	180.00(19)	O(4)#5-Ni(2)-N(2)#5	90.45(13)
N(1)#1-Ni(1)-N(1)#3	89.57(11)	O(4)-Ni(2)-N(2)#5	91.07(13)
N(1)#2-Ni(1)-N(1)#3	90.43(11)	N(2)#1-Ni(2)-N(2)#5	91.17(12)
N(1)#1-Ni(1)-N(1)	90.43(11)	O(4)#1-Ni(2)-N(2)	91.07(13)
N(1)#2-Ni(1)-N(1)	89.57(11)	O(4)#5-Ni(2)-N(2)	177.21(12)
N(1)#3-Ni(1)-N(1)	89.57(11)	O(4)-Ni(2)-N(2)	90.45(13)
N(1)#1-Ni(1)-N(1)#4	89.57(11)	N(2)#1-Ni(2)-N(2)	91.17(12)
N(1)#2-Ni(1)-N(1)#4	90.43(11)	N(2)#5-Ni(2)-N(2)	91.17(12)
N(1)#3-Ni(1)-N(1)#4	90.43(11)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+y+2, -x+1, z$
 #2 $x-y, x-1, -z$ #3 $y+1, -x+y+1, -z$ #4 $-x+2, -y, -z$ #5 $-y+1, x-y-1, z$

Table S2. Selected bond lengths (Å) and angles (deg) for 2

2			
Ni(1)-O(2)#1	2.075(5)	O(2)#2-Ni(1)-N(3)#3	93.6(2)
Ni(1)-O(2)#2	2.075(5)	N(3)-Ni(1)-N(3)#3	180.000(1)
Ni(1)-N(3)	2.082(6)	O(2)#1-Ni(1)-N(1)#3	85.7(2)
Ni(1)-N(3)#3	2.082(6)	O(2)#2-Ni(1)-N(1)#3	94.3(2)
Ni(1)-N(1)#3	2.085(6)	N(3)-Ni(1)-N(1)#3	88.1(2)
Ni(1)-N(1)	2.085(6)	N(3)#3-Ni(1)-N(1)#3	91.9(2)
		O(2)#1-Ni(1)-N(1)	94.3(2)
O(2)#1-Ni(1)-O(2)#2	180.00(17)	O(2)#2-Ni(1)-N(1)	85.7(2)
O(2)#1-Ni(1)-N(3)	93.6(2)	N(3)-Ni(1)-N(1)	91.9(2)
O(2)#2-Ni(1)-N(3)	86.4(2)	N(3)#3-Ni(1)-N(1)	88.1(2)
O(2)#1-Ni(1)-N(3)#3	86.4(2)	N(1)#3-Ni(1)-N(1)	180.0(3)

Symmetry transformations used to generate equivalent atoms: #1 $x+1,y,z$
#2 $-x,-y,-z+2$ #3 $-x+1,-y,-z+2$ #4 $x-1,y,z$ #5 $x,-y+1/2,z$ #6 $x,-y+3/2,z$

Figure S1. (a) A view of the molecule structure of 1 (b) the packing structure of 1 along c axis.

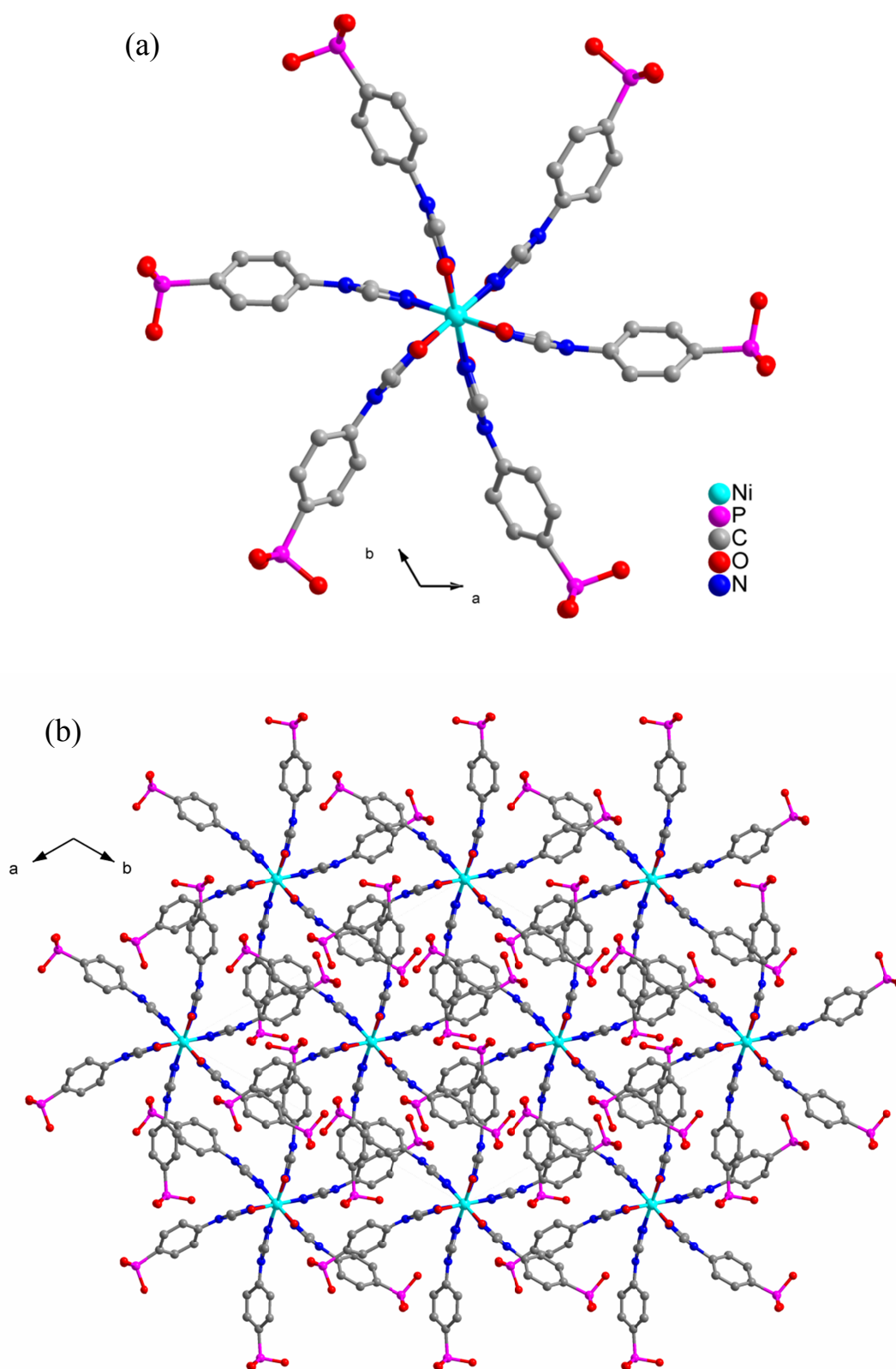
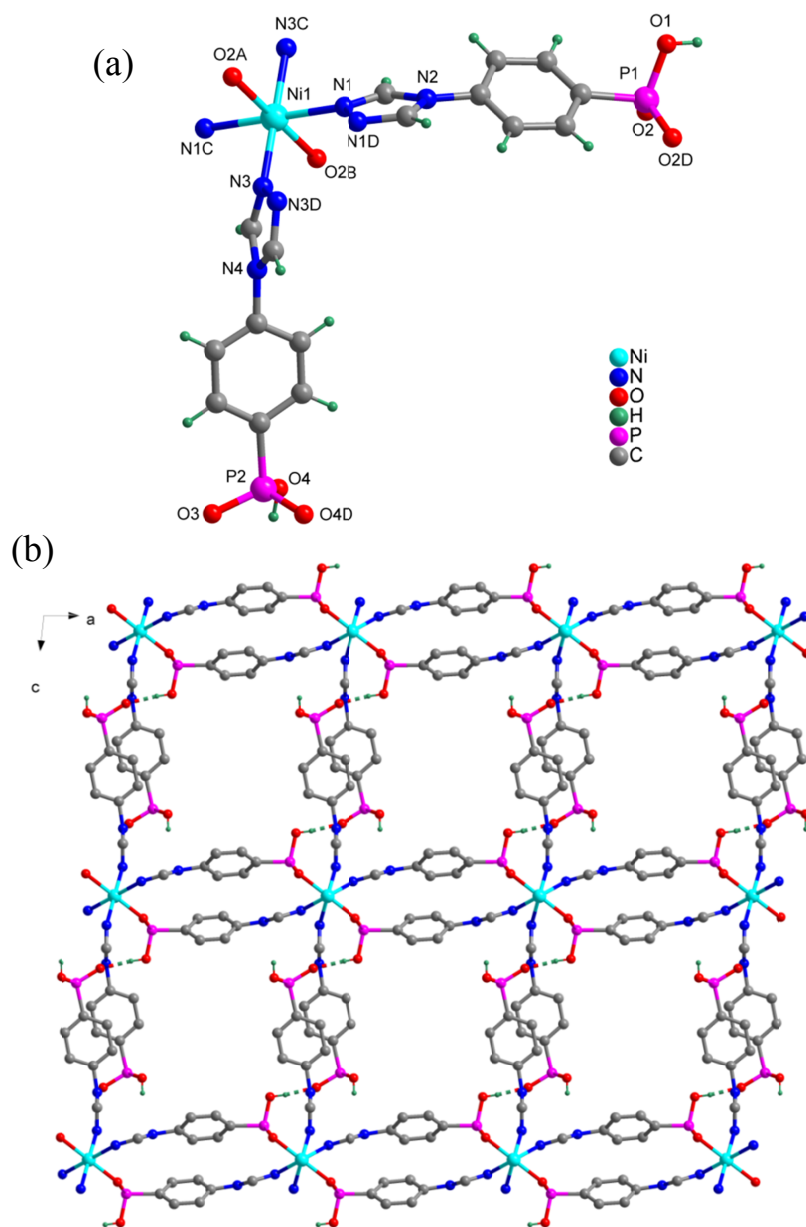


Figure S2. (a) The structural motif of 2 (symmetry code: A: 1+x, y, z; B: -x, -y, 2-z; C: 1-x, -y, 2-z; D: x, 1/2-y, z). (b) view of the 2×2 packing structure and hydrogen bonds of 2 along b axis.



Hydrogen bonds of 2

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(3)#7	0.82	1.70	2.519(10)	174.7

Symmetry transformations used to generate equivalent atoms: #7 x-1,y,z+1.

Figure S3. TGA curve for 2.

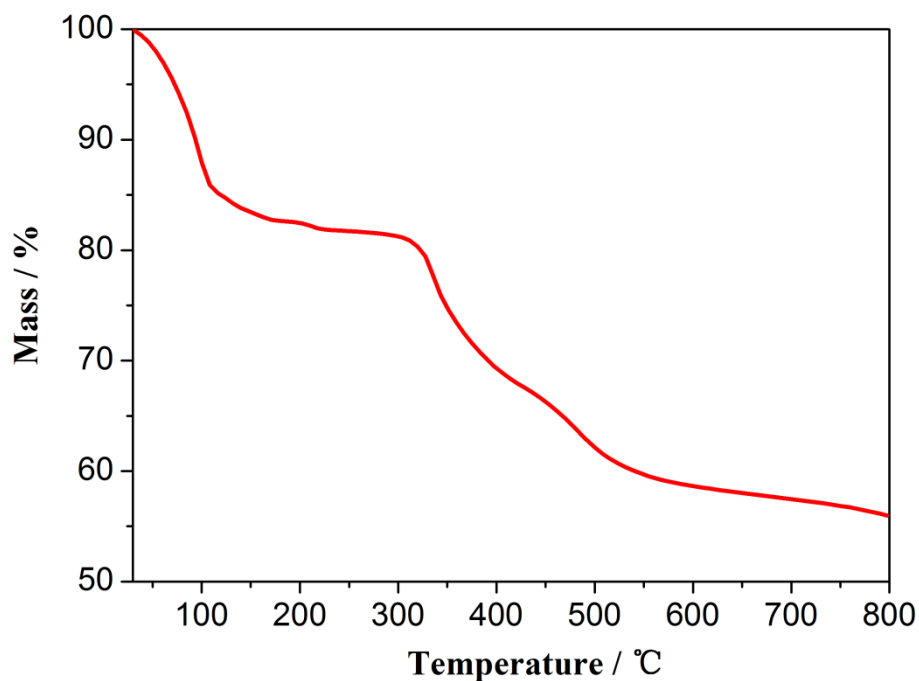


Figure S4. Variable temperature powder X-ray diffraction patterns for 2.

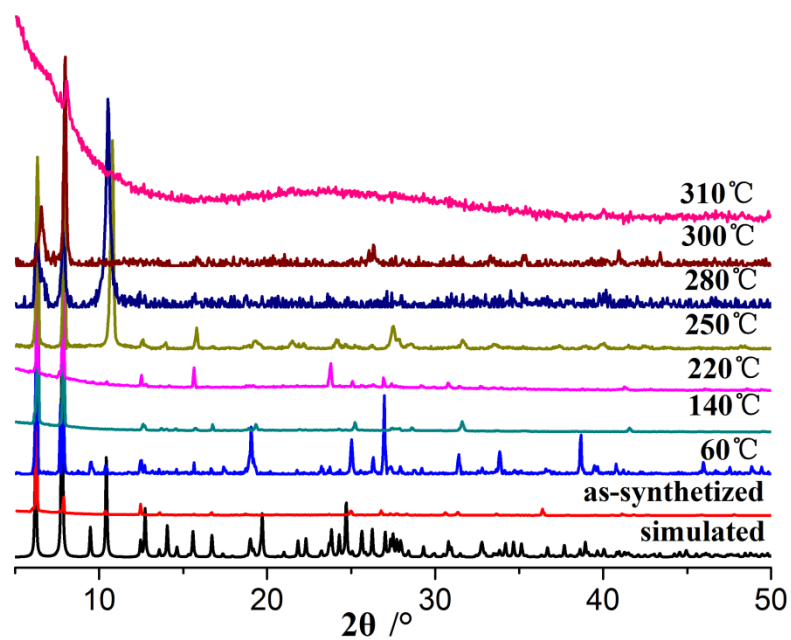


Figure S5. Powder X-ray diffraction patterns for 1 after treatment in room temperature acid aqueous and boiling water for 7 days.

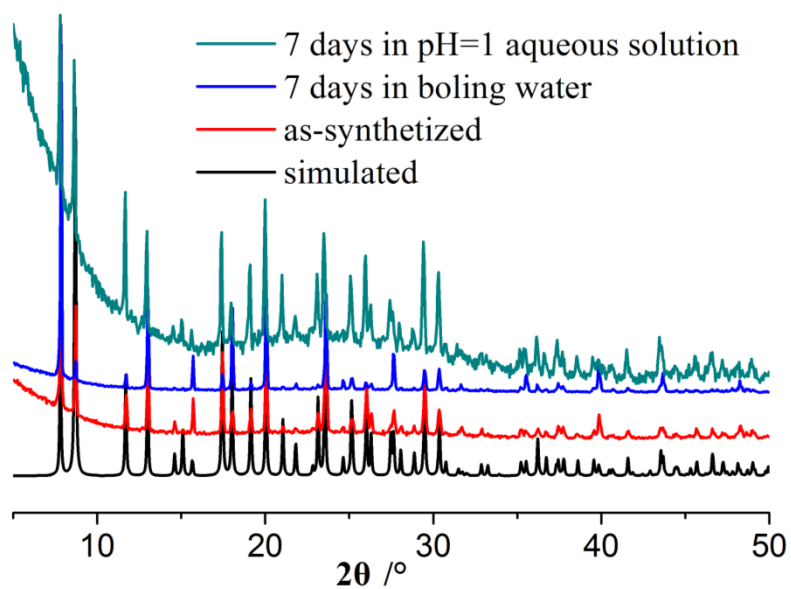


Fig. S6. The PXRD patterns for 2 measured during chemical stability tests. (a) In refluxing toluene at 110°C for up to 7 days. (b) In refluxing EtOH at 80°C for up to 7 days.

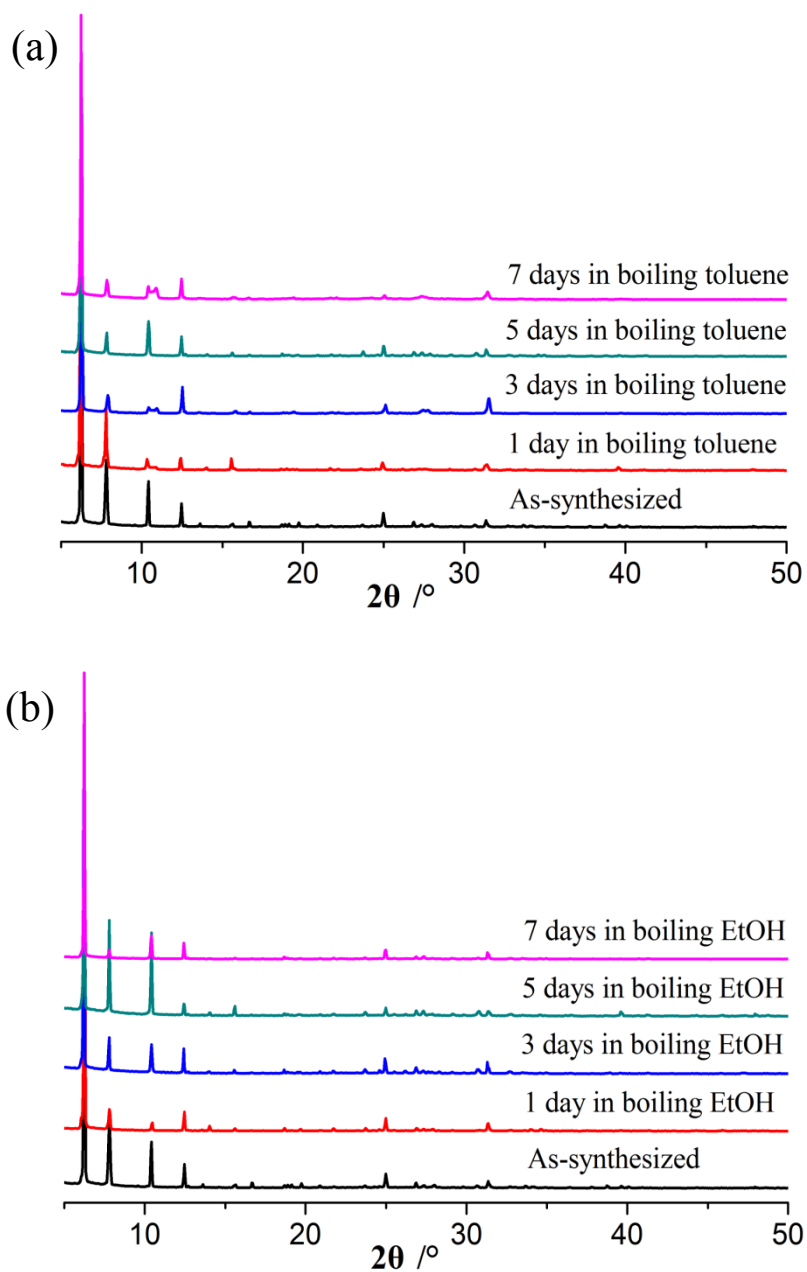


Figure S7: CO₂ adsorption isotherm at 298 K of MOF 2 and 2 after soaking in boiling water for 7 days.

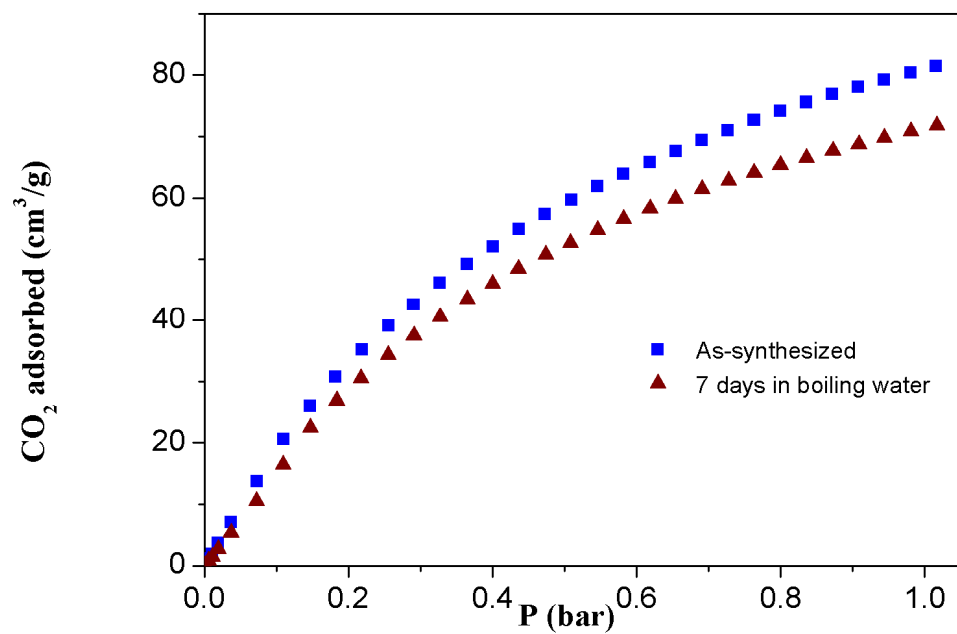


Table S3. CO₂ adsorption capacities of phosphonate-based porous materials.

Chemical formula	Common name	Capacity (wt %)	Pressure (bar)	Temperature (K)	Ref
	HMSnP-1	4.0	1	298	S3
Zn(1,4-benzenediphosphonate-bis(monoethyl ester))	Zn(BDPEt)	4.7	1	273	S4
Cu(1,4-benzenediphosphonate-bis(monoalkyl ester))	Cu(BDPMe)	6.1	1	273	S5
Ni ₂ (pbmp)	Ni-STA-12	9.9	1	304	S6

Table S4. CO₂ adsorption and selectivity capacities of some ZIF Materials at 298 K.

Common name	CO ₂ uptake at 1 bar (mmol g ⁻¹)	CO ₂ /N ₂	Common name	CO ₂ uptake at 1 bar (mmol g ⁻¹)	CO ₂ /N ₂
ZIF-68 ^a	1.7	18.7	ZIF-81 ^a	1.7	23.8
ZIF-69 ^a	1.8	19.9	ZIF-82 ^a	2.4	35.3
ZIF-70 ^a	2.5	17.3	ZIF-95 ^b	0.9	18 ± 1.7
ZIF-78 ^a	2.3	50.1	ZIF-100 ^{b,c}	1.5	24 ± 2.4
ZIF-79 ^a	1.5	23.2			

^aReported in ref S7. ^bReported in ref S8. ^cAdsorption data measured at 273 K.

4. References

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