

Supplementary Information

A pH-responsive phase transformation of a sulfonated metal-organic framework from amorphous to crystalline for efficient CO₂ capture

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Materials and methods

All the reagents were obtained from commercial suppliers and used without further purification. NMR data were collected on a Bruker Avance 500 MHz NMR spectrometer (DRX500). FTIR spectra were obtained with a Bio-Rad FTS-3500 ARX FTIR spectrometer. Field-emission scanning electron microscope (FE-SEM) analyses were conducted on an FEI Quanta 600 SEM (20 kV) equipped with an energy dispersive spectrometer (EDS, Oxford Instruments, 80 mm² detector). Samples were treated via Pt sputtering before observation. Elemental analyses (EA) were performed on Vario MICRO series CHNOS elemental analyzer. Powder X-ray diffraction patterns were obtained on Bruker D8 Advance X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of 0.02 deg s^{-1} . TGA was performed using Shimadzu DTG-60AH thermal analyzer under flowing N₂ gas, with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Synthesis of UiO-66-SO₃H¹

A 20 mL mixed solvent of N, N-dimethylformamide (DMF) and acetic acid (9:1, v:v) was used to dissolve 180 mg of sodium 2-sulfoterephthalate (SS-BDC), followed by the addition of 160 mg of zirconium (IV) chloride (ZrCl₄). The solution was sonicated for 15 min and subsequently heated at $120 \text{ }^\circ\text{C}$ for 40 h. The solid product was recovered through centrifugation and washed with DMF for 3 times, and then soaked in DMF at $80 \text{ }^\circ\text{C}$ for 12 h. The recovered sample was solvent-exchanged with methanol for 3 days, and was fully activated at $120 \text{ }^\circ\text{C}$ under vacuum for 24 h.

Acidification was subsequently carried out by soaking the sample in 0.1 M of aqueous hydrochloric acid (HCl) solution for 12 h, followed by in ethanol solution of trifluoroacetic acid (10 vol%) for 6 h. The acidified sample was washed and solvent-exchanged with methanol for another 3 days, and then dried under vacuum at $120 \text{ }^\circ\text{C}$ for 24 h to afford the final product of UiO-66-SO₃H.

Neutralization with alkali solution

Neutralization of UiO-66-SO₃H was performed using aqueous alkali hydroxide solutions. The hydroxides include lithium hydroxide (LiOH), sodium hydroxide (NaOH), and potassium hydroxide (KOH). Taking LiOH as an example, a desired concentration was first obtained by dissolving LiOH powder with an appropriate amount of deionized water. 120 mg of UiO-66-SO₃H was subsequently immersed in 20 mL of the prepared solution under room temperature for 2 h. The product was recovered through centrifugation, washed with deionized water, and subsequently underwent solvent exchange with ethanol for 3 days. The final product was recovered after the sample was activated under vacuum at $120 \text{ }^\circ\text{C}$ for 24 h. All UiO-66-SO₃M samples were prepared similarly.

X-ray absorption spectra

Zr K-edge X-ray absorption spectra (XAS) of MOF samples were collected at Kyushu Synchrotron Radiation Center on BL07 (SAGA Light Source, Japan). XASs of powder samples were recorded in transmission mode under ambient conditions, using a double crystal monochromator. Incident and transmitted X-ray fluxes were measured with ion

chambers filled with N₂/Ar (50/50%) and Ar/Kr (75/25%). The data were processed with IFEFFIT.² Fourier transformation was *k*³-weighted in the *k* range from 3.0 to 15.0 Å⁻¹.

Gas sorption measurements

Gas sorption isotherms were measured up to 1 bar using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before the measurements, the samples (~100 mg) were degassed under reduced pressure (< 10⁻² Pa) at 150 °C for 12 h. UHP grade N₂, He, and CO₂ were used for all the measurements. Oil-free vacuum pumps and oil-free pressure regulators were used to prevent contamination of the samples during the degassing process and isotherm measurement. The temperatures of 77, 273 and 298 K were maintained with a liquid nitrogen bath, an ice water bath, and under room temperature, respectively. Pore size distribution data were calculated from the N₂ sorption isotherms at 77 K based on non-local density functional theory (NLDFT) model in the Micromeritics ASAP2020 software package (assuming slit pore geometry).

Calculations of isosteric heat of adsorption (Q_{st})

The CO₂ and N₂ adsorption isotherms measured at 273 K and 298 K were first fitted to a virial equation (Equation 1). The fitting parameters were then used to calculate the isosteric heat of adsorption (Q_{st}) using Equation 2,

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (1)$$

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

where *P* is pressure (mmHg), *N* is adsorbed quantity (mmol g⁻¹), *T* is temperature (K), *R* is gas constant (8.314 J K⁻¹ mol⁻¹), *a_i* and *b_i* are virial coefficients, *m* and *n* represent the number of coefficients required to adequately describe the isotherms (herein, *m* = 5, *n* = 2).

Ideal adsorption solution theory (IAST) selectivity

The CO₂ and N₂ adsorption isotherms were first fitted to a dual-site Langmuir-Freundlich (DSLFL) model (Equation 3),

$$q = \frac{q_{sat,A} b_A p^{\alpha_A}}{1 + b_A p^{\alpha_A}} + \frac{q_{sat,B} b_B p^{\alpha_B}}{1 + b_B p^{\alpha_B}} \quad (3)$$

where *q* is the amount of adsorbed gas (mmol g⁻¹), *p* is the bulk gas phase pressure (bar), *q_{sat}* is the saturation amount (mmol g⁻¹), *b* is the Langmuir-Freundlich parameter (bar^{-α}), *α* is the Langmuir-Freundlich exponent (dimensionless) for two adsorption sites A and B indicating the presence of weak and strong adsorption sites.

IAST starts from the Raoult's Law type of relationship between fluid and adsorbed phase,

$$P_i = P y_i = P_i^o x_i \quad (4)$$

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{P_i}{P_i^o} = 1 \quad (5)$$

where P_i is partial pressure of component i (bar), P is total pressure (bar), y_i and x_i represent mole fractions of component i in gas and adsorbed phase (dimensionless). P_i^0 is equilibrium vapour pressure (bar).

In IAST, P_i^0 is defined by relating to spreading pressure π ,

$$\frac{\pi S}{RT} = \int_0^{P_i^0} \frac{q_i(P_i)}{P_i} dP_i = \Pi \text{ (Constant)} \quad (6)$$

where π is spreading pressure, S is specific surface area of adsorbent ($\text{m}^2 \text{g}^{-1}$), R is gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is temperature (K), $q_i(P_i)$ is the single component equilibrium obtained from isotherm (mmol g^{-1}).

For a dual-site Langmuir-Freundlich (DSLFL) model, we have an analytical expression for the integral,

$$\int_0^{P_i^0} \frac{q_i(P_i)}{P_i} dP_i = \Pi \text{ (Constant)} = \frac{q_{sat,A}}{\alpha_A} \ln[1 + b_A (P_i^0)^{\alpha_A}] + \frac{q_{sat,B}}{\alpha_B} \ln[1 + b_B (P_i^0)^{\alpha_B}] \quad (7)$$

The isotherm parameters will be known from the previous fitting. For a binary component system the unknowns will be Π , P_1^0 , and P_2^0 which can be obtained by simultaneously solving Equations 5 and 7.

The adsorbed amount for each compound in a mixture is

$$q_i^{mix} = x_i q_T \quad (8)$$

$$\frac{1}{q_T} = \sum_{i=1}^n \frac{x_i}{q_i(P_i^0)} \quad (9)$$

where q_i^{mix} is the adsorbed amount of component i (mmol g^{-1}), q_T is the total adsorbed amount (mmol g^{-1}).

The adsorption selectivities S_{ads} were calculated using Equation 10.

$$S_{ads} = \frac{q_1 / q_2}{p_1 / p_2} \quad (10)$$

In this study, IAST calculations were carried out assuming a CO_2/N_2 (molar ratio, 15:85) binary mixed gas at 298 K and pressures up to 1 bar to mimic the composition and condition of flue gas.

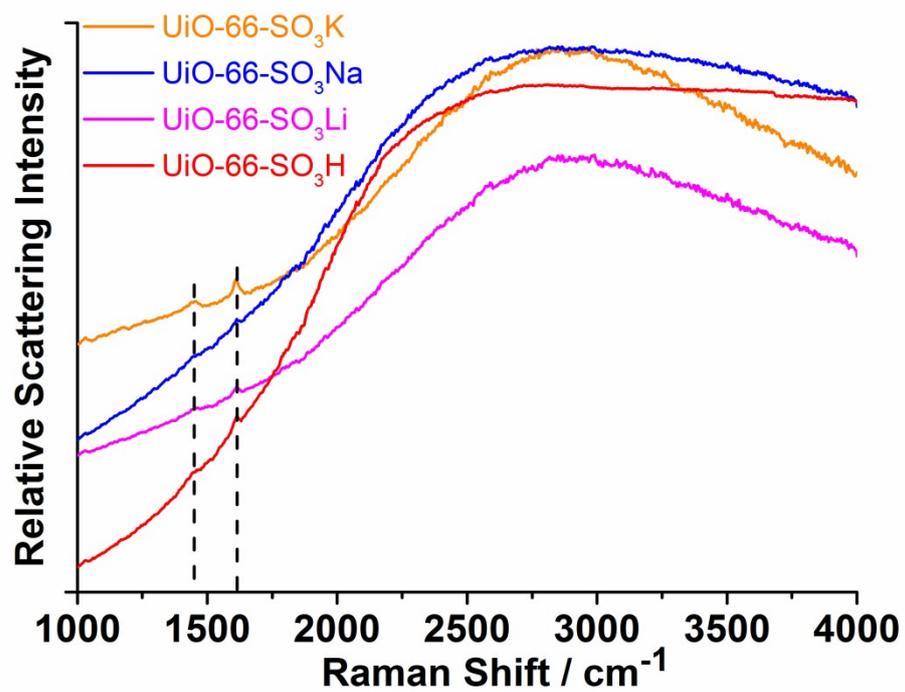


Figure S1. Raman spectra of amorphous UiO-66-SO₃H and recrystallized UiO-66-SO₃M.

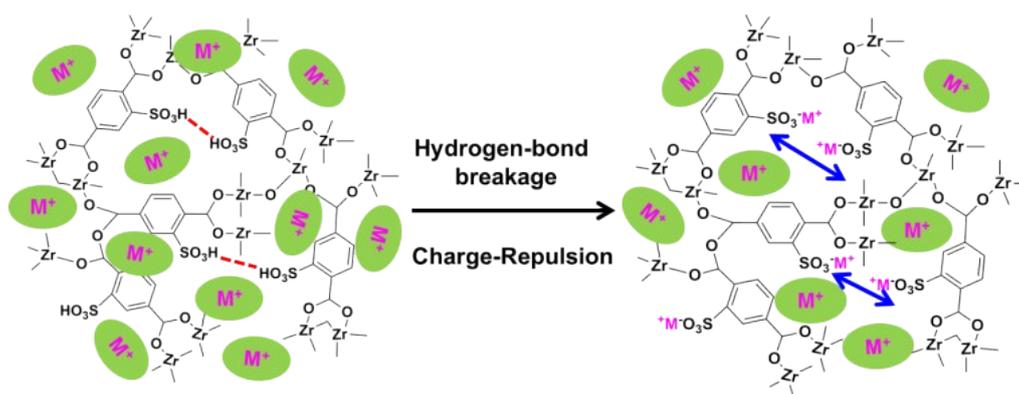


Figure S2. Proposed mechanism of pH-responsive phase transformation from amorphous UiO-66-SO₃H to crystalline UiO-66-SO₃M dominated by the breakage of hydrogen bonds and charge repulsion of metalation.

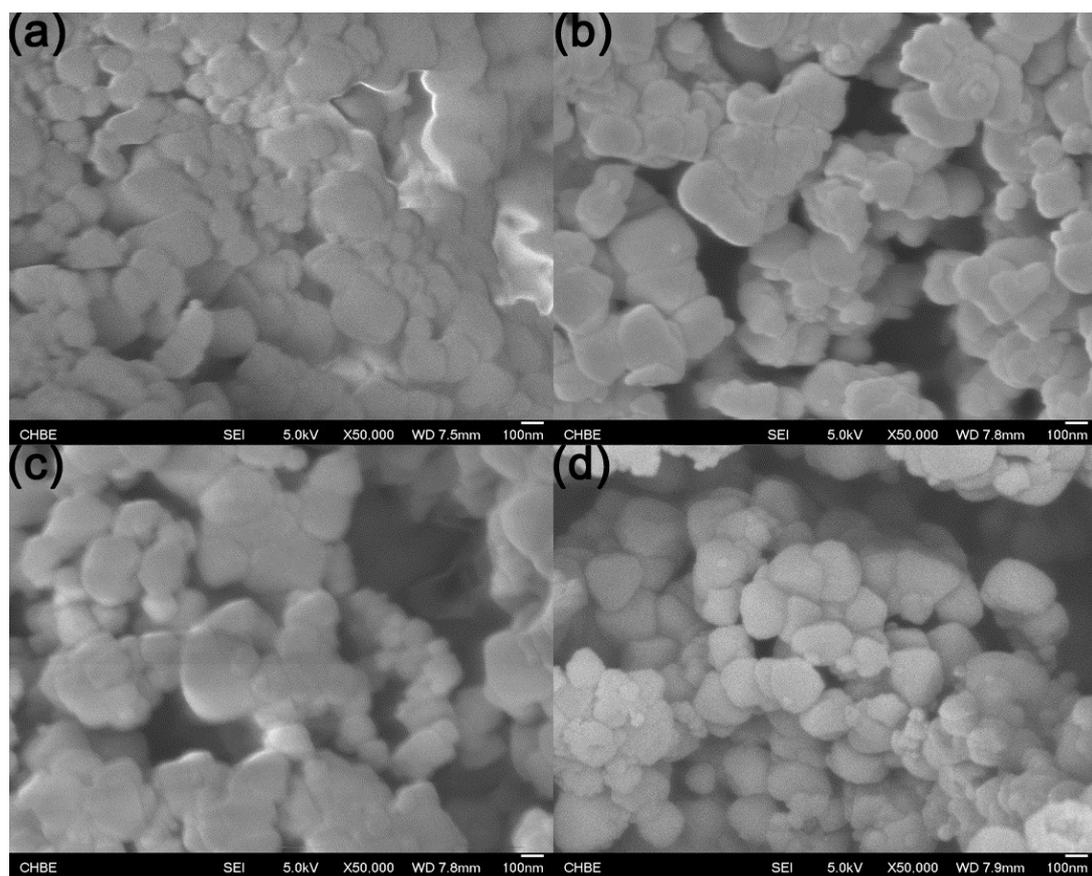


Figure S3. FE-SEM images of (a) amorphous UiO-66-SO₃H, (b) UiO-66-SO₃Li, (c) UiO-66-SO₃Na, and (d) UiO-66-SO₃K.

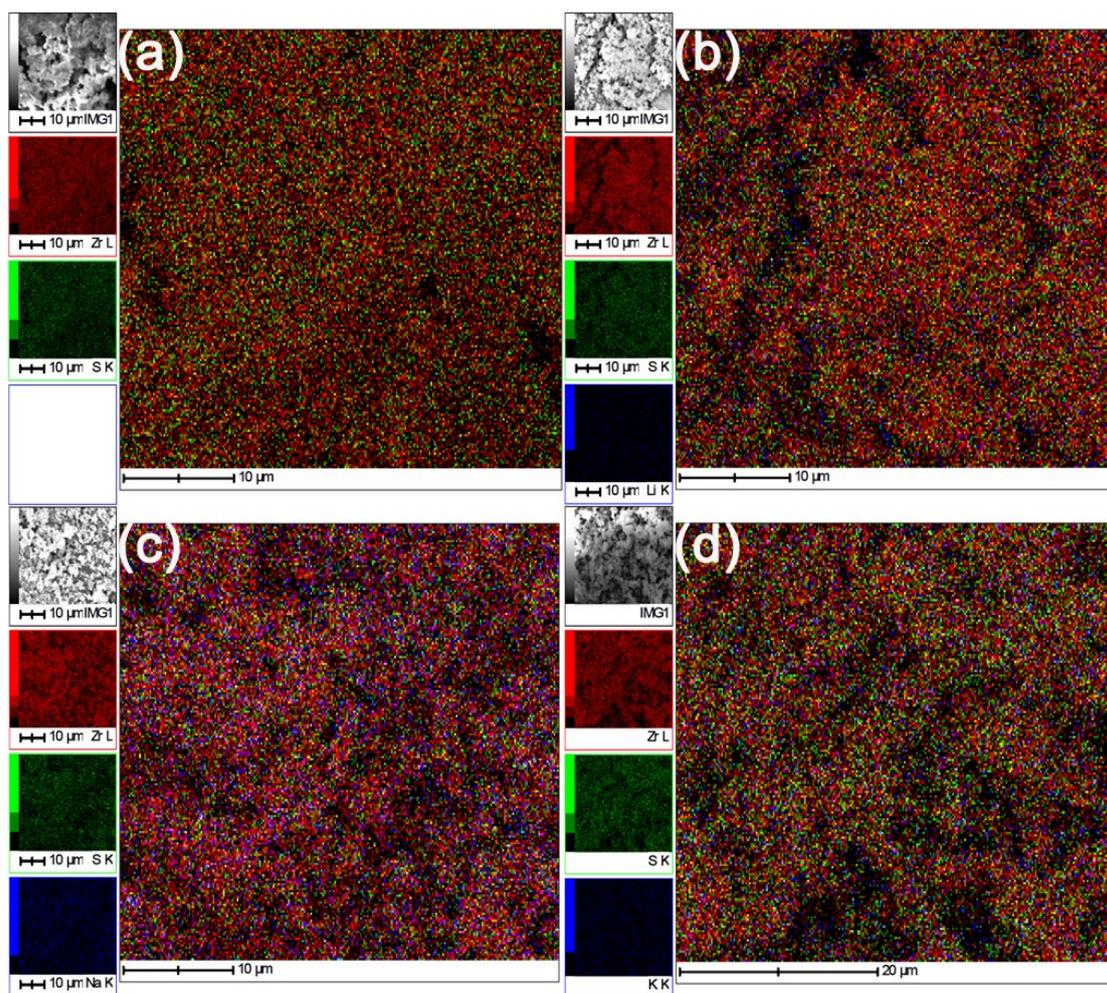


Figure S4. EDS elemental mapping images of (a) amorphous UiO-66-SO₃H, (b) UiO-66-SO₃Li, (c) UiO-66-SO₃Na, and (d) UiO-66-SO₃K.

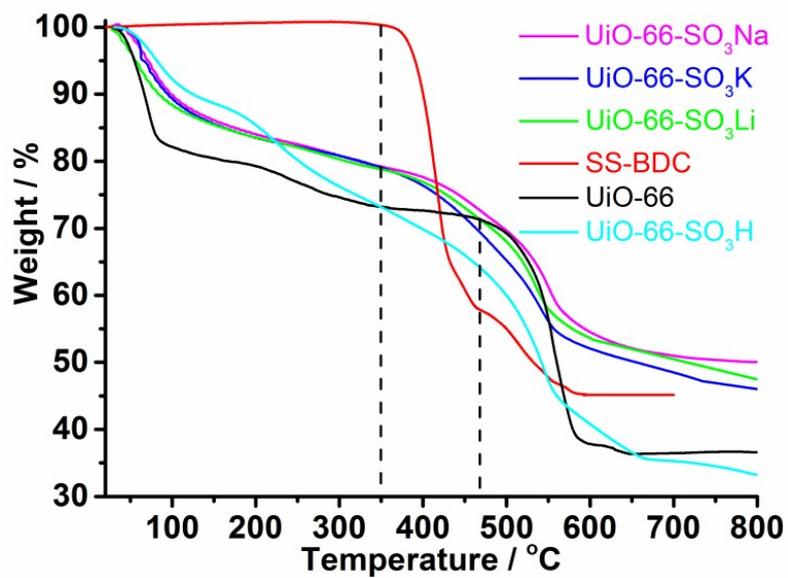


Figure S5. TGA curves of UiO-66-SO₃H and UiO-66-SO₃M.

Table S1. Summary of the amount and critical concentration of alkali hydroxide solutions required for phase transformation as well as the radius of alkali metal cations.

	UiO-66-SO ₃ Li	UiO-66-SO ₃ Na	UiO-66-SO ₃ K
pH value	12.3	12.2	12
MOH concentration ^{a)}	0.02	0.016	0.01
-SO ₃ H content ^{b)}	0.33 ^{c)}	0.33 ^{c)}	0.28 ^{d)}
MOH in total ^{b)}	0.40	0.32	0.25
Diameter of M ⁺ ^{e)} 45	1.80	2.32	3.04
^{a)} mol/L; ^{b)} mmol; ^{c)} 120 mg and ^{d)} 100 mg of UiO-66-SO ₃ H; ^{e)} Å			

Table S2. Summary of porosity, gas uptake, Q_{st} , and IAST CO_2/N_2 selectivity of UiO-66, UiO-66- SO_3H , and UiO-66- SO_3M MOFs.

		UiO-66	UiO-66- SO_3H	UiO-66- SO_3Li	UiO-66- SO_3Na	UiO-66- SO_3K
BET surface area ^{a)}		1525	11	148	95	26
Pore volume ^{b)}		0.66	0.029	0.119	0.106	0.038
CO ₂ uptake at 0.15 bar ^{c)}	298 K	0.37	0.09	0.28	0.22	0.37
CO ₂ uptake at 1 bar ^{c)}	298 K	1.79	0.32	0.89	0.74	0.91
	273 K	3.12	0.67	1.36	1.08	1.95
N ₂ uptake at 1 bar ^{c)}	298 K	0.144	0.046	0.129	0.158	0.076
	273 K	0.235	0.121	0.225	0.251	0.213
Zero-coverage Q_{st} of CO ₂ ^{d)}		24.5	n.d.	26.7	29.8	31.9
Zero-coverage Q_{st} of N ₂ ^{d)}		11.5	16.8	11.6	12.9	17.7
IAST CO ₂ /N ₂ selectivity ^{e)}		19.4	18.7	22.4	34.7	43.3
Metal/sulfur molar ratio ^{f)}		n.d.	n.d.	0.97	0.92	0.84
a) m ² g ⁻¹ ; b) cm ³ g ⁻¹ , c) mmol g ⁻¹ , d) kJ mol ⁻¹ , e) assuming a mixture of CO ₂ /N ₂ (15:85) at 298 K, f) EA analysis, n.d.: not determined.						

References

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2. B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537-541.