Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Countercation-Regulated Pore Structure Engineering of fcu-Metal-Organic Frameworks for Enhanced Gas Separation

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Materials

All the materials were purchased from Sigma Aldrich and used as received without further purification.

Synthesis

All reagents were used as purchased from commercial suppliers without further purification. MOF-801 was prepared according to published procedures with slight modifications. Fumaric acid (5.8 g) and $ZrOCl_2·8H_2O$ (16 g) were dissolved in a solvent mixture of N,N-dimethylformamide (DMF)/formic acid (200 mL/70 mL) in a 500-mL screw-capped jar, which was heated at 130 °C for 6 h. White precipitate was filtered using Nylon membrane filters (pore size 0.2-μm), and washed three times with 20 mL of fresh DMF and three times with 50 mL of ethanol. As-synthesized MOF-801 was rinsed three times per day with 50 mL of DMF for three days and immersed in 100 mL of ethanol for three days, during which time the ethanol was replaced three times per day. The solid was then evacuated at 150 °C for 24 hours to yield an activated sample.

Y-MOF was then prepared according to the previous literature procedure with slight modifications to a get better yield. Fumaric acid (305.0 mg) $Y(NO_3)_3{\cdot}6H_2O$ (1010.0 mg), 2-fluorobenzoic acid (3500.0 mg) were dissolved in a solvent mixture of N,N-dimethylformamide (DMF)/ distilled H_2O (85 mL/12.5 mL) in a 200 mL scintillation vial, sealed and heated to 115 °C for 72 h and cooled to room temperature. The colourless polyhedral crystals were then collected by filtration. As-synthesized samples of Y-MOF prepared in different vials were then combined in one big vial, washed with excess DMF, and then solvent exchanged with ethanol for 7 days, during which time the ethanol was replaced three times per day. The solid was then dried at 150 °C under vacuum for 24 h to yield an activated sample.

Supplementary Methods

Synchrotron X-ray Powder Diffraction (PXRD) and Rietveld Refinement. Synchrotron PXRD measurements for structure determination were collected on Beamline 19A at Taiwan Photon Source at the National Synchrotron Radiation Research Centre, Taiwan. High-throughput synchrotron PXRD data were obtained from the MOF samples (loaded in 0.5-mm borosilicate capillaries) using the MYTHEN detectors with 70° aperture. The patterns were collected in the 2θ range 3-40° with 0.001° data binning. Each synchrotron PXRD data was collected for 10 min to produce a good quality pattern with a high signal-to-noise ratio. The synchrotron PXRD data was analysed using the Rietveld refinement method available in TOPAS-v7.0 software.

The lattice parameters were obtained using analytical software, and the background curve was fitted by a Chebyshev polynomial with an average of 2θ coefficients. The Thompson-Cox-Hastings (pseudo-Voigt) function was applied to describe the diffraction peaks. The scale factor and lattice parameters were allowed to vary for all the histograms. Each data histogram's final refined structural parameters were carried out using the Rietveld method with the fractional coordinates (x, y, z) and isotropic displacement factors (Beq) for all atoms.

Thermogravimetric Analysis (TGA). The TGA measurements were performed using a Thermogravimetric analyser/Differential Scanning Calorimeter (Mettler Toledo TGA/DSC3+). Around 10 mg zeolitic sample was weighed and placed in a corundum crucible; the sample was heated from room temperature to 600 K within a ramping rate of 10 K min^{-1} in a flow of N_2 (40 mL min^{-1}). The TGA measurements were performed using the same equipment setup for the methanol preabsorbed on zeolite samples. The apparent activation energy for the desorption of methanol is estimated according to the following modified Arrhenius equation.

$$2lnT_m - ln\beta = \frac{E_{des}}{RT_m} + ln\frac{E_{des}}{AR}$$

where T_m is the peak desorption temperature at a specific β, β is the temperature ramping rate, E_{des} is the desorption energy and A is a numerical constant. Plotting ($2lnT_m - ln\beta$) versus 1/T_m for a series of β values allows the estimation of E_{des}.

Solid-State Nuclear Magnetic Resonance (ssNMR) Spectroscopy. Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were acquired at room temperature on a Bruker Avance III spectrometer operating at a Larmor frequency of 400 MHz for ^{13}C The finely ground MOF powder samples were packed into 4.0 mm outer diameter zirconia rotors and spun at a MAS rate of 10 kHz. The CP/MAS experiments utilized a contact time of 2.0 ms and a recycling delay of 3.0 s, with a total of 1024 scans accumulated.

Fourier Transform Infrared (FT-IR) Spectroscopy. FTIR spectra were recorded on a Thermo Nicolet iS50 spectrometer. The spectra were collected in the range of 4000 to 400 cm^{-1} at room temperature using KBr pellets. To monitor the thermal activation process, the as-synthesized material was heated at 150 °C, 175 °C, and 200 °C under dynamic vacuum for 12 hours prior to spectral acquisition.

IAST selectivity calculation:

The dual site Langmuir-Freundlich model was adopted to fit the adsorption isotherms of Y-MOF and Zr-MOF, which were described as follows:

$$q = q_{A,sat}\frac{b_A P^{vA}}{1 + b_A P^{vA}} + q_{B,sat}\frac{b_B P^{vB}}{1 + b_B P^{vB}} \tag{1}$$

With T-dependent parameters b_A, and b_B

$$b_A = b_{A0}\, exp(\frac{E_A}{RT});\ b_B = b_{B0}\, exp(\frac{E_B}{RT}) \tag{2}$$

Where q represents the adsorption amount of adsorbents with units of $mg{\cdot}g^{-1,}$ $q_{A,sat}$ and $q_{B,sat}$ represent the saturated adsorption amount for adsorption site A and B, respectively, b_A and b_B are constants for species i at adsorption sites A and B, respectively, P is the total pressures of the bulk gas at the adsorption equilibrium, and v_A and v_B are the Freundlich exponent for site A and B, respectively. Taking the CO_2/N_2 selectivity as example, the IAST selectivity is defined by:

$$S = \frac{q_1/q_2}{y_1/y_2} \tag{3}$$

where q_1, and q_2 represents the adsorption amounts of CO_2, and N_2 under equilibrium conditions, which are usually expressed with units of mmol g^{-1}. $y_1$and y_2 are the corresponding mole fractions in the gas phase for the mixtures. The calculated IAST adsorption selectivity for the CO_2/ N_2 (CO_2/ N_2 = 50/50;

v/v) mixtures taking the mole fractions y_1 = 0.50 and y_2 = 0.50 for a total pressure of 1 bar at 298 K.

Isosteric heat of adsorption (*Q*$_{st}$) calculation:

The adsorption heat of each component was determined precisely according to the virial fitting parameters of single-component adsorption isotherms measured at 278, 288,and 298K up to 1 bar.

Q_{st} = -slope × R by drawing the ln(P) versus gas uptakes, which was defined as follows:

$$ln(P) = ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i \tag{4}$$

$$Q_{st} =- R\sum_{i=0}^{m} a_i N_i \tag{5}$$

where N is the adsorption amount, and m and n determine the number of items required to precisely fit the adsorption isotherms.

Supplementary Figures

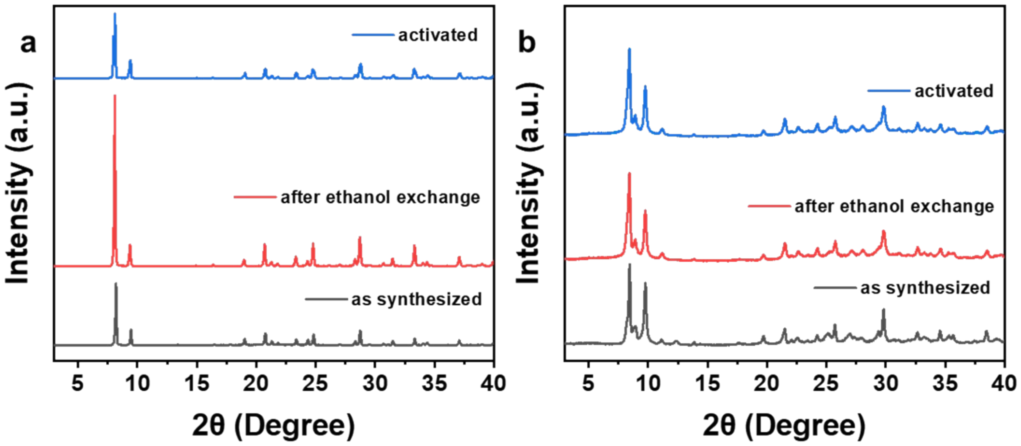

Figure S1. High-resolution PXRD patterns using Cu X-ray radiation (λ = 1.5418 Å; E = 8.04 keV) of (a) Y-MOF and (b) Zr-MOF.

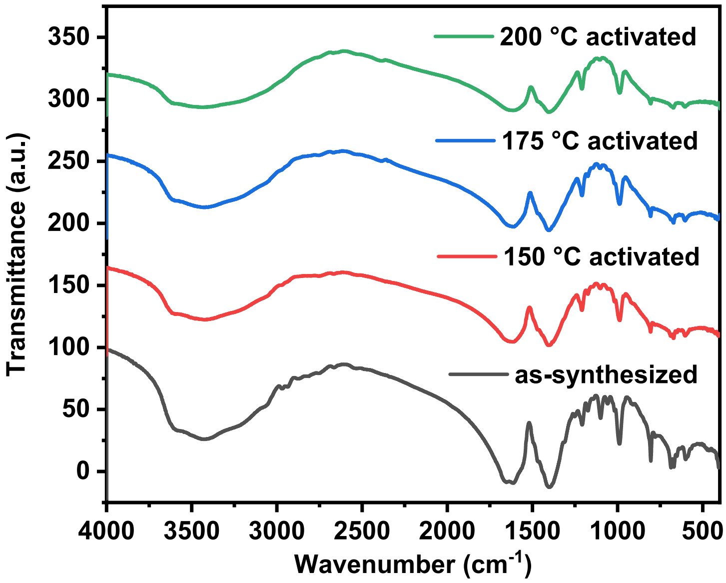

Figure S2. Fourier transform infrared spectroscopy (FTIR) of Y-MOF treated at different temperatures.

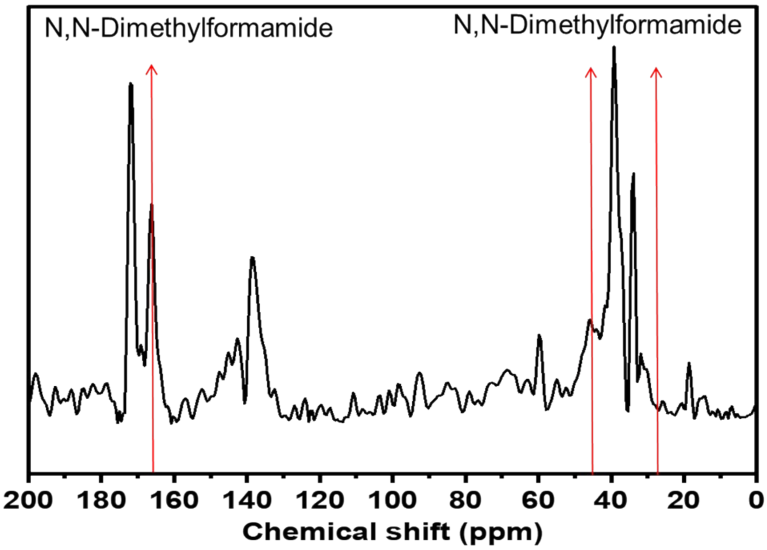

Figure S3. ^{13}C solid-state NMR spectra of Y-MOF.

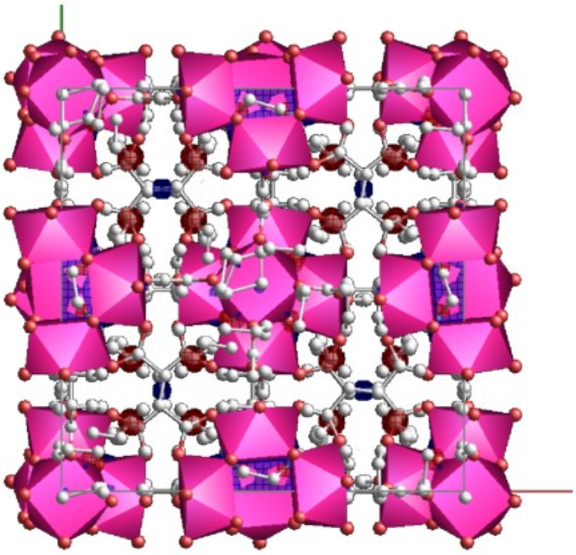

Figure S4. Fourier difference map of Zr-MOF.

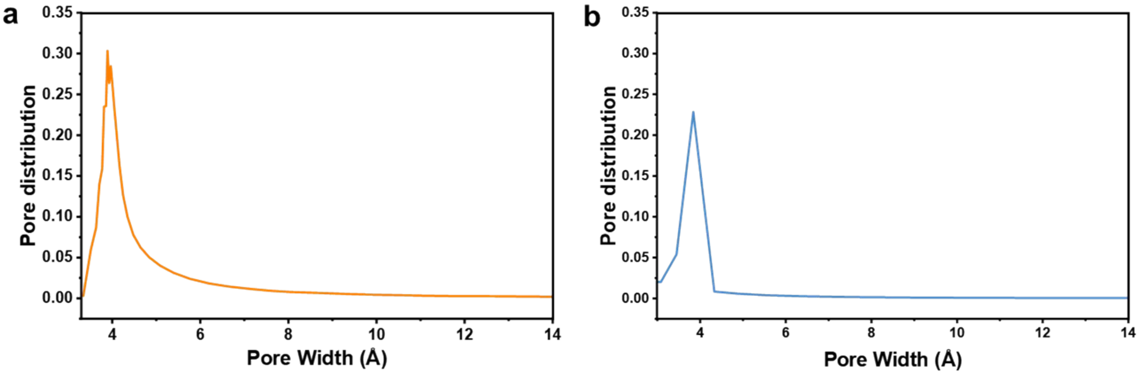

Figure S5. The pore size distribution of (a) Y-MOF and (b) Zr-MOF.

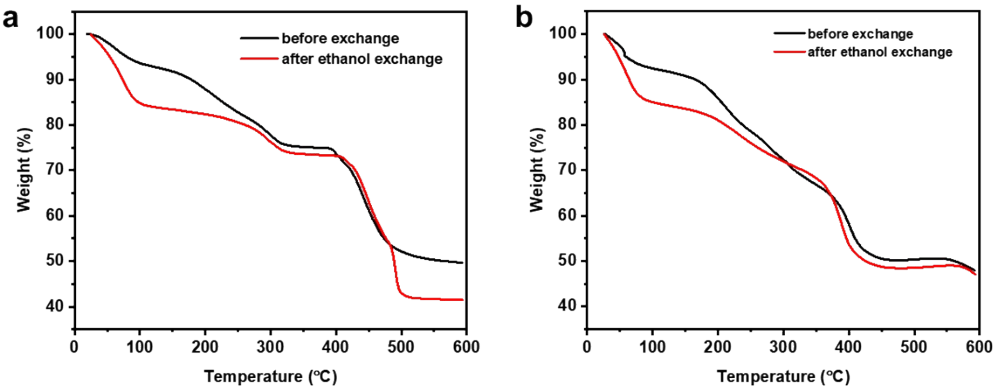

Figure S6. Thermogravimetric analysis (TGA) before and after ethanol exchange of (a) Y-MOF and (b) Zr-MOF.

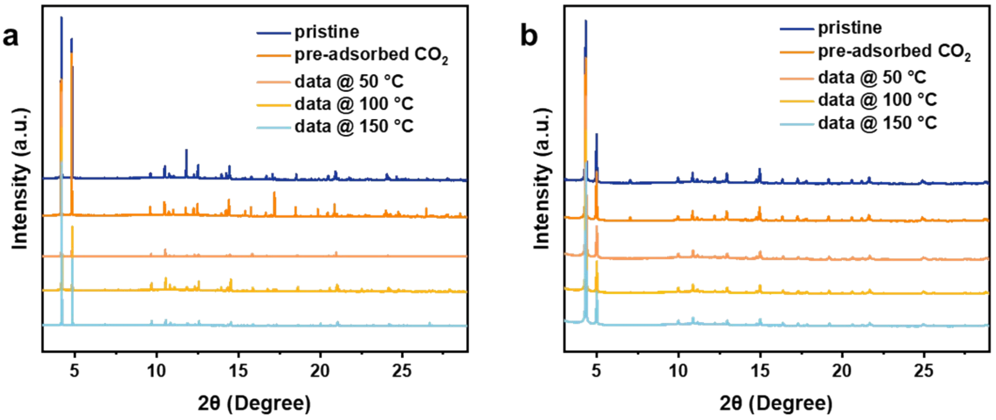

Figure S7. In situ synchrotron PXRD of (a) Y-MOF and (b) Zr-MOF.

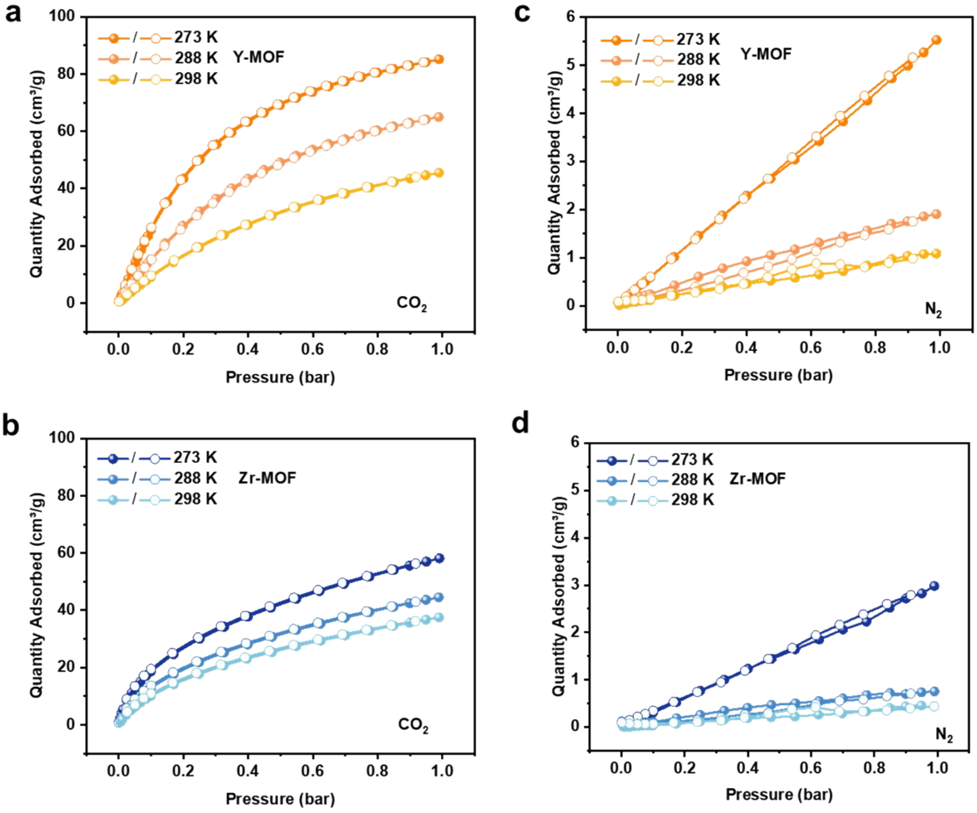

Figure S8. Adsorption-desorption isotherms of CO_2 at 273, 288, and 298 K of (a) Y-MOF and (b)Zr-MOF. Adsorption-desorption isotherms of N_2 at 273, 288, and 298 K of (c) Y-MOF and (d) Zr-MOF.

Table S1. Elemental analysis of Y-MOF and Zr-MOF.

	N [wt%]	**C [wt%]**	**H [wt%]**
Y-MOF	2.78	22.61	3.75
Zr-MOF	3.21	21.25	4.09

Table S2. Refinement details of Y-MOF.

X-ray energy (keV)	20.0
Wavelength (Å)	0.6199
Space group	Pn-3
Crystal system	Cubic
a (Å)	18.5813
b (Å)	18.5813
c (Å)	18.5813
V ($Å^3$)	6415.55
2θ range for refinement (°)	3-40
Number of parameters	26
Number of hkls	1047
Refinement methods	Rietveld
$R_{wp}/R_{exp}/R_p$ (%)	5.501 / 4.002 / 3.842
Gof	1.375

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *Gof*: goodness-of-fit.

Table S3. Atomic parameters of Y-MOF derived from synchrotron PXRD.

Atom	x	y	z	occ	Beq
Y1	0.137	0.511	0.011	1	3.039
O4	0.209	0.408	0.008	1	6.711
O5	0.190	0.624	0.024	1	6.553
O6	0.189	0.507	0.126	1	6.237
O7	0.208	0.523	-0.090	1	6.869
C11	0.160	0.689	0.024	1	6.869
C13	0.214	0.755	0.024	1	11.13
C1	0.190	0.339	0	1	6.474
C2	0.256	0.286	0.001	1	9.869
O1	0.076	0.591	-0.064	1	3.316
O2	0.078	0.421	0.078	1	3.316
C31	0.004	0.182	0.444	0.352	20
N32	-0.020	0.131	0.499	0.352	20
C33	-0.001	0.158	0.571	0.352	20

Table S4. Refinement details of Zr-MOF.

X-ray energy (keV)	20.0
Wavelength (Å)	0.6199
Space group	Pn-3
Crystal system	Cubic
a (Å)	17.9079
b (Å)	17.9079
c (Å)	17.9079
V (Å^3)	5743.01
2θ range for refinement (°)	3-40
Number of parameters	26
Number of hkls	722
Refinement methods	Rietveld
$R_{wp}/R_{exp}/R_p$ (%)	5.501 / 2.148 / 4.0123
Gof	2.561

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *Gof*: goodness-of-fit.

Table S5. Atomic parameters of Zr-MOF derived from synchrotron PXRD.

Atom	x	y	z	occ	Beq
Zr1	0.137	0.511	0.011	1	3.039
O4	0.209	0.408	0.008	1	6.711
O5	0.190	0.624	0.024	1	6.553
O6	0.189	0.507	0.126	1	6.237
O7	0.208	0.523	-0.090	1	6.869
C11	0.160	0.689	0.024	1	6.869
C13	0.214	0.755	0.024	1	11.13
C1	0.190	0.339	0	1	6.474
C2	0.256	0.286	0.000	1	9.869
O1	0.076	0.591	-0.064	1	3.316
O2	0.078	0.421	0.078	1	3.316

Table S6. Crystallographic parameters of Y-MOF pre-adsorbed with CO_2.

X-ray energy (keV)	20.0
Wavelength (Å)	0.6199
Space group	Pn-3
Crystal system	Cubic
a (Å)	18.4280
V (Å^3)	6258.01
2θ range for refinement (°)	3-40
Number of parameters	26
Number of hkls	198
Refinement methods	Rietveld
R_{wp}/R_{exp}/R_p (%)	4.603 / 2.469 / 3.165
Gof	1.864

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *Gof*: goodness-of-fit.

Table S7. Atomic parameters derived from synchrotron PXRD of Y-MOF pre-adsorbed with CO_2.

Atom	x	y	z	occ	Beq
Y1	0.137	0.511	0.011	1	3.039
O4	0.209	0.408	0.008	1	6.711
O5	0.190	0.624	0.024	1	6.553
O6	0.189	0.507	0.126	1	6.237
O7	0.208	0.523	-0.090	1	6.869
C11	0.160	0.689	0.024	1	6.869
C13	0.214	0.755	0.024	1	11.13
C1	0.190	0.339	0	1	6.474
C2	0.256	0.286	0.001	1	9.869
O1	0.076	0.591	-0.064	1	3.316
O2	0.078	0.421	0.078	1	3.316
H31	0.615	0.544	0.245	0.070	10
N32	0.559	0.553	0.245	0.070	10
C33	0.533	0.557	0.170	0.070	10
C34	0.523	0.492	0.283	0.070	10
H35	0.548	0.601	0.272	0.070	10
C21	9.992	0.715	0.346	0.572	10
O22	10.01	0.745	0.399	0.572	10
O23	9.977	0.686	0.293	0.572	10

Table S8. Crystallographic parameters of Zr-MOF pre-adsorbed with CO_2.

X-ray energy (keV)	20.0
Wavelength (Å)	0.6199
Space group	Pn-3
Crystal system	Cubic
a (Å)	17.8910
V (Å^3)	5726.45
2θ range for refinement (°)	3-40
Number of parameters	26
Number of hkls	285
Refinement methods	Rietveld
$R_{wp}/R_{exp}/R_p$ (%)	10.539 / 1.272/ 7.855
Gof	8.280

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *Gof*: goodness-of-fit.

Table S9. Atomic parameters derived from synchrotron PXRD of Zr-MOF pre-adsorbed with CO_2.

Atom	x	y	z	occ	Beq
Zr1	0.137	0.511	0.011	1	3.039
O4	0.209	0.408	0.008	1	6.711
O5	0.190	0.624	0.024	1	6.553
O6	0.189	0.507	0.126	1	6.237
O7	0.208	0.523	-0.090	1	6.869
C11	0.160	0.689	0.024	1	6.869
C13	0.214	0.755	0.024	1	11.13
C1	0.190	0.339	0	1	6.474
C2	0.256	0.286	0.001	1	9.869
O1	0.076	0.591	-0.064	0.500	3.316
O2	0.078	0.421	0.078	0.500	3.316
C21	3.660	0.405	4.078	0.395	5
O22	3.651	0.357	4.120	0.395	5
O23	3.668	0.454	4.036	0.395	5