Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Thermodynamic Analysis of Gate-Opening Carbon Dioxide Adsorption Behavior of Metal–Organic Frameworks

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1. Materials

All the reagents and chemicals used were obtained from commercial sources and used as received, unless otherwise noted. methanol (MeOH), *N*,*N*-dimethylformamide (DMF), zinc (II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), were purchased from FUJIFILM Wako Pure Chemical Corporation or Tokyo Chemical Industry Co., Ltd..

2. Experimental procedure

2.1 Synthetic procedure of ZIF-7-I

$Zn(NO_3)_2 \cdot 6H_2O$ (1.24 mmol) and benzimidazole (BIm, 2.48 mmol) were dissolved in 25 mL of DMF, respectively. The BIm solution was mixed with $Zn(NO_3)_2$ solution. The mixture was heated and stirred in an autoclave at 140 ℃. After 20 h, the product was centrifugation (10,000 rpm, 10 min), washed with DMF and MeOH, and dried under vacuum (40 ℃, 24 hours) to give a powdery product (white powder).

2.2 Synthetic Procedure of ZIF-9

$Co(NO_3)_2 \cdot 6H_2O$ (0.99 mmol) and benzimidazole (1.98 mmol) were dissolved in 25 mL of DMF, respectively. The BIm solution was mixed with $Co(NO_3)_2$ solution. The mixture was heated and stirred in an autoclave at 140 °C. After 20 h, the product was centrifugation (10,000 rpm, 10 min), washed with DMF and MeOH, and dried under vacuum (40 °C, 24 hours) to give a powdery product (yellow-blown powder).

2.3 Powder X-ray diffraction (XRD) measurement

Powder X-ray diffraction (XRD) measurements were performed using a Rigaku SmartLab SE diffractometer with nickel-filtered Cu-K_α radiation (X-ray wavelength: 1.5418 Å) in steps of 0.01° over the 2θ range of 5−50°. A sample was set in a standard glass holder or a non-refractive silicon holder (Overseas X-Ray Service, Saitama, Japan).

In situ heating XRD diffraction measurements were also conducted using a Rigaku SmartLab SE diffractometer with the gas-exchangeable heating unit. For the sample set, a platinum-slit folder was used.

2.4 CO_2 and N_2 adsorption/desorption isotherm

Before the measurements, the samples were degassed reduced pressure (<10 Pa) at 200 °C for 20

h. N_2 adsorption/desorption isotherms were measured at liquid nitrogen 77 K using BELSORP-mini II instrument (MicrotracBEL Corp.). CO_2 adsorption/desorption isotherms were measured at 300 K.

2.5 Differential scanning calorimetry (DSC) measurement

Differential scanning calorimetry (DSC) measurements were performed using a Hitachi DSC7000X with a PS2 cooling system was used to confirm the thermodynamic properties of the samples. The DSC baseline and cell thermal parameters were calibrated using sapphire discs. The temperature and cell constant were calibrated using an indium standard. All DSC samples were prepared using about 5 mg of sample and were sealed in aluminum pans. Pretreatment was performed by heating at 20 K/min under N_2 atmosphere (flow rate: 50 mL/min). Heating and cooling cycles were performed at 2 K/min of heating/cooling rate under CO_2 or N_2 atmosphere (flow rate: 50 mL/min).

2.6 Thermogravimetry analysis (TGA) measurement

Thermogravimetric analysis (TGA) was performed using a Hitachi STA7200RV. 5 mg of each sample was placed in a platinum pan.

3. Supporting Figures

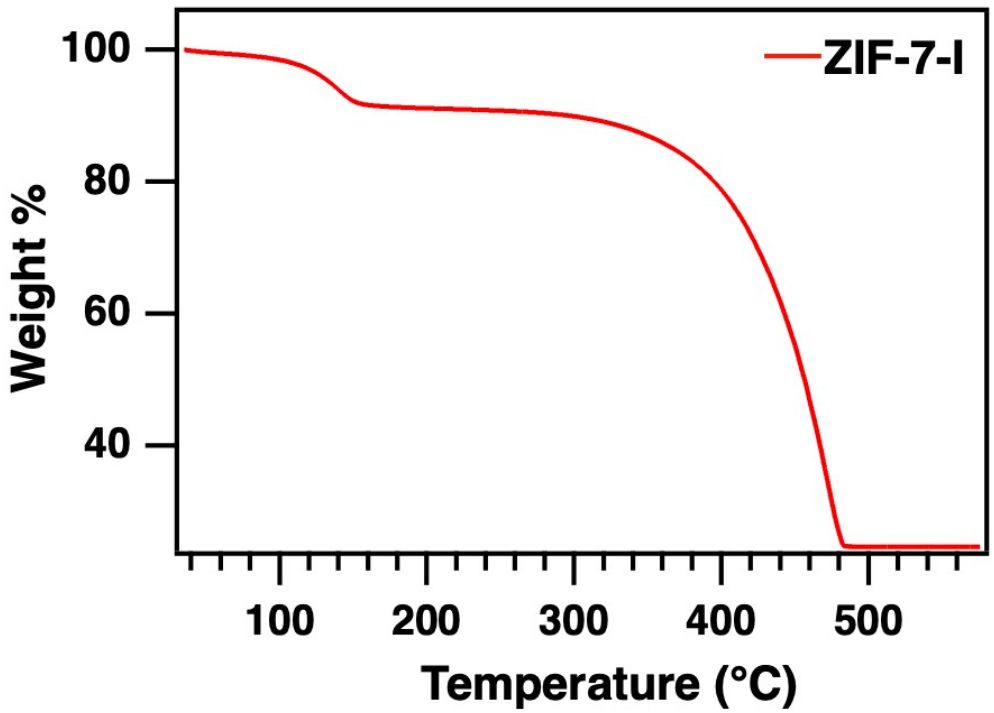

Figure S1. TG curve of ZIF-7-I. The heating rate was of 1 K/min in air flow (100 mL/min).

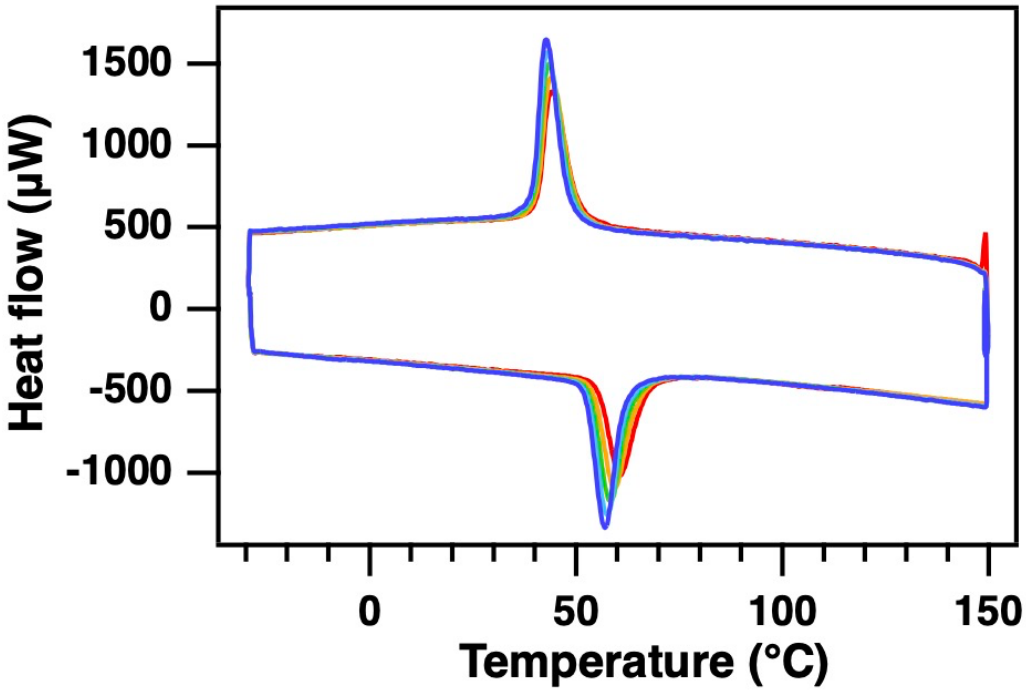

Figure S2. DSC curves of ZIF-7 under CO_2 atmosphere (5 cycles). Prior to the measurements, the sample was pretreated at 150°C under N_2 atmosphere. 1st cycle (red), 2nd cycle (orange), 3rd cycle (yellow green), 4th cycle (light blue), and 5th cycle (blue).

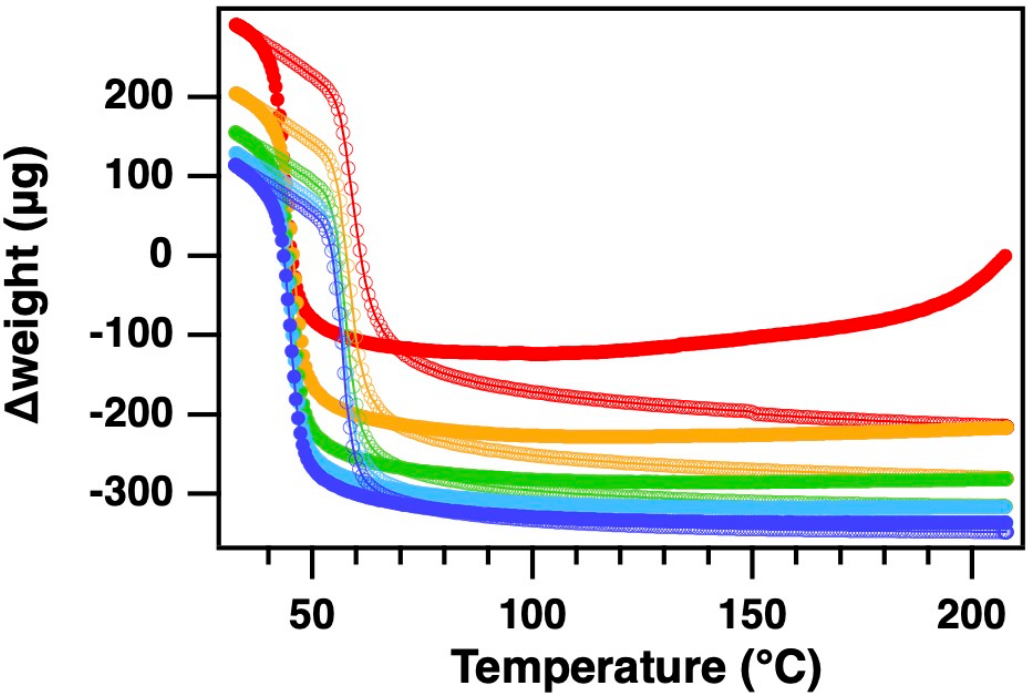

Figure S3. Thermogravimetric curves of ZIF-7 under CO_2 atmosphere (5 cycles). Prior to the measurements, the sample was pretreated at 210°C under N_2 atmosphere. 1st cycle (red), 2nd cycle (orange), 3rd cycle (yellow green), 4th cycle (light blue), and 5th cycle (blue).

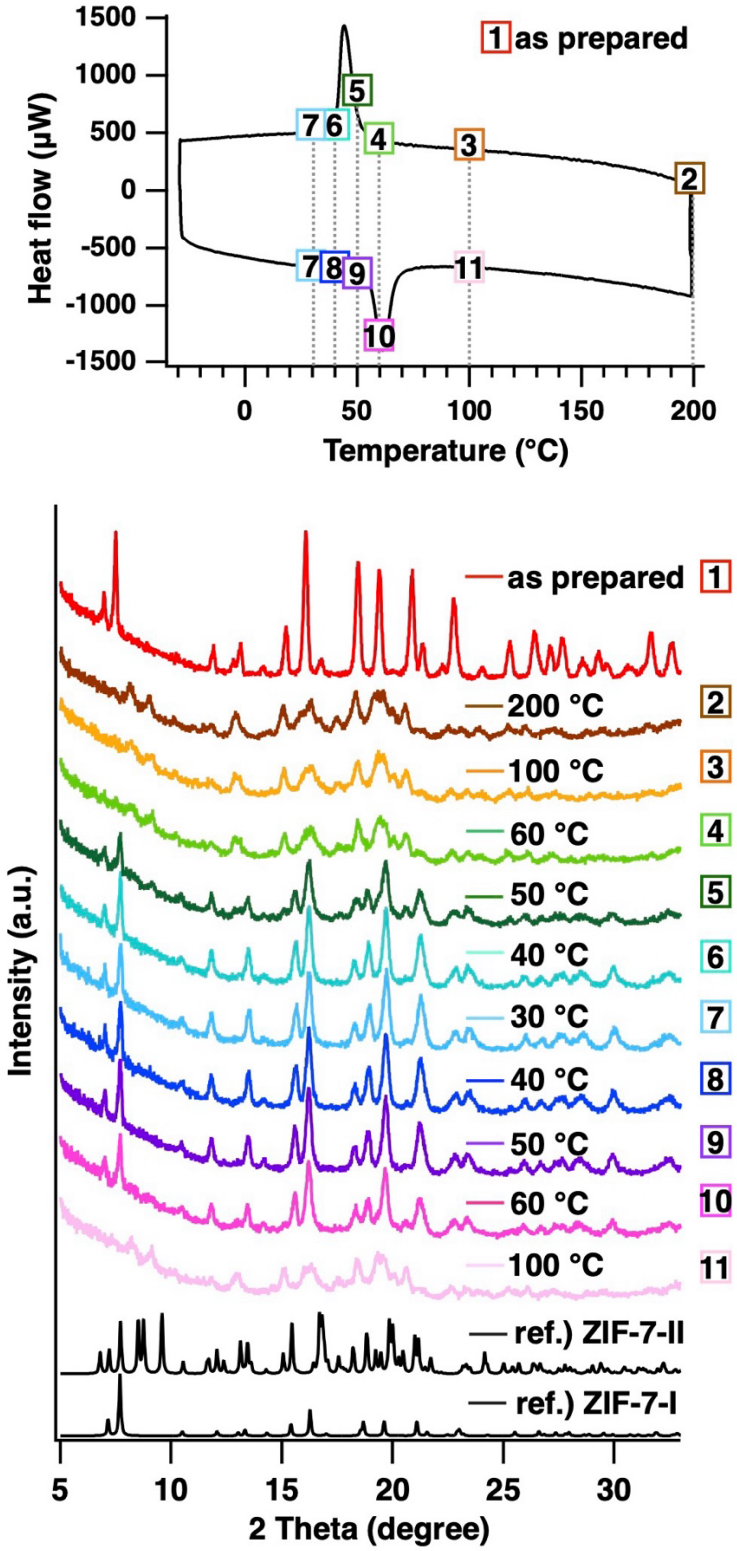

Figure S4. *In situ* heating PXRD patterns of ZIF-7 under CO_2 atmosphere (Figure 2a). The reference XRD patterns of ZIF-7-I and II were simulated from cif files (CCDC: 602541 and 2101613). Cooling and heating steps were performed in the following order: As prepared (red), 200 °C (blown), 100 °C (orange), 60 °C (yellow green), 50 °C (green), 40 °C (aqua green), 30 °C (light blue), 40 °C (blue), 50 °C (purple), 60 °C (pink), and 100 °C (light pink).

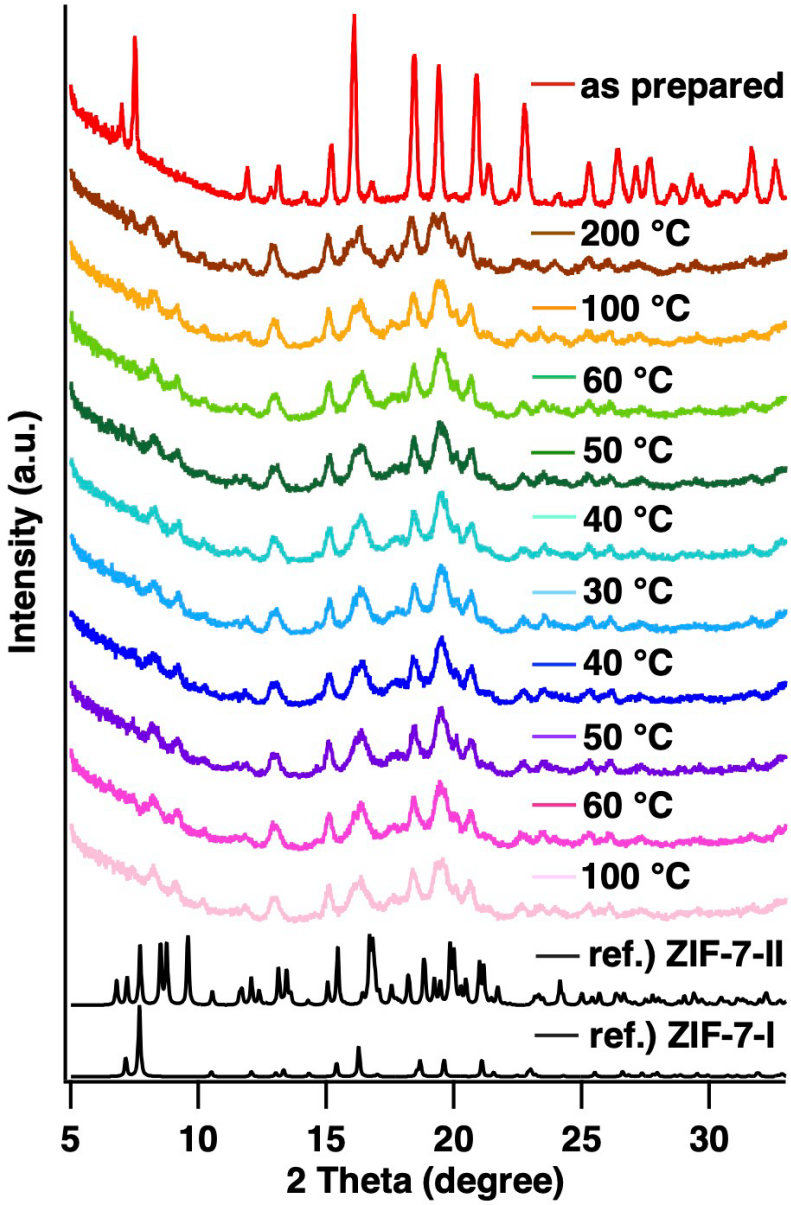

Figure S5. *In situ* heating PXRD patterns of ZIF-7 under N_2 atmosphere. The reference XRD patterns of ZIF-7-I and II were simulated from cif files (CCDC: 602541 and 2101613). Cooling and heating steps were performed in the following order: As prepared (red), 200 °C (blown), 100 °C (orange), 60 °C (yellow green), 50 °C (green), 40 °C (aqua green), 30 °C (light blue), 40 °C (blue), 50 °C (purple), 60 °C (pink), and 100 °C (light pink).

Table S1. Observed adsorption/desorption heat from the DSC peak area in Figure 4a.

$p(CO_2)$	1.0 bar	0.9 bar	0.8 bar	0.7 bar	0.6 bar	0.5 bar
Adsorption heat, $\times 10^{-4}$ kJ	–1.83	–2.02	–2.25	–2.34	–2.41	–2.44
Desorption heat, $\times 10^{-4}$ kJ	1.68	1.75	1.85	1.91	1.99	2.08

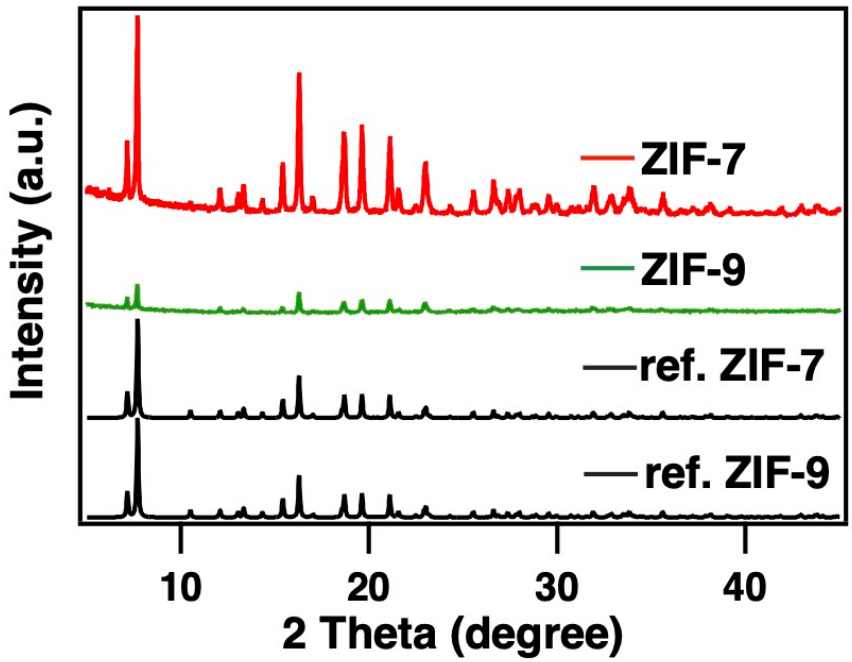

Figure S6. Powder X-ray diffraction measurements of ZIF-7 (red) and ZIF-9 (green). The reference XRD patterns of ZIF-7 and ZIF-9 were simulated from cif files (CCDC: 602541 and 1036076).