Electronic Supplementary Information

Thermal crystal phase transition in zeolitic imidazolate frameworks induced by nanosizing the crystal

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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), ethanol (EtOH), *N*,*N*-dimethylformamide (DMF), acetonitrile (MeCN), propionitrile, zinc (II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 1-methylimidazole (1-MIm), 1allylimidazole (1-Alm), *N*-*tert*-butoxycarbonylimidazole, 2-methylimidazole (2-HMIm), 2-ethylimidazole (2-HEIm), triethylamine (TEA), 1,8-diazabicyclo-[5,4,0]undec-7-ene (1,8-DBU) were purchased from FUJIFILM Wako Pure Chemical Corporation or Tokyo Chemical Industry Co., Ltd..

2. Experimental procedure

2.1 Synthetic procedure of ZIF-8 with different crystal sizes

$Zn(NO_3)_2 \cdot 6H_2O$ (2.47 mmol) and 1-MIm or 1-AIm or *N*-*tert*-butoxycarbonylimidazole (9.87 mmol) were dissolved in solvent (50 mL). MeOH, propionitrile, and DMF were used as a reaction solvent. A second solution was prepared by dissolving 2-HMIm (9.87 mmol) in solvent (50 mL). The latter clear solution was poured into the former clear solution under stirring with a magnetic stirrer (25 ºC, 3 min). After 24 h, the product was centrifuged (10,000 rpm, 10 min), washed several times with MeOH or MeCN, and dried under vacuum (30 ºC, 24 hour) to give a powdery product (white powder).

2.2 Synthetic procedure of ZIF-67 with different crystal sizes

$Co(NO_3)_2 \cdot 6H_2O$ (2.47 mmol) and 1-MIm or 1-AIm (9.87 mmol) were dissolved in solvent (50 mL). MeOH, EtOH, and propionitrile were used as a reaction solvent. A second solution was prepared by dissolving 2-HMIm (9.87 mmol) in solvent (50 mL). The latter clear solution was poured into the former clear solution under stirring with a magnetic stirrer (25 ºC, 3 or 2 min). After 24 or 20 h, the product was centrifuged (10,000 rpm, 10 min), washed several times with MeOH or MeCN, and dried under vacuum (30 ºC, 24 hour) to give a powdery product (purple powder).

2.3 Synthetic Procedure of MAF-6 with different crystal sizes

$Zn(NO_3)_2 \cdot 6H_2O$ (2.47 mmol) and 1-MIm or 1-AIm (9.87 mmol) were dissolved in solvent (50 mL). MeCN and propionitrile were used as a reaction solvent. A second solution was prepared by

dissolving 2-HEIm (9.87 mmol) and TEA or 1,8-DBU in solvent (50 mL). The latter clear solution was poured into the former clear solution under stirring with a magnetic stirrer (25 ºC, 3 min). After 24 h, the product was centrifuged (10,000 rpm, 10 min), washed several times with MeOH or MeCN, and dried under vacuum (30 ºC, 2 or 24 hour) to give a powdery product (white powder).

2.4 Scanning electron microscopy

Scanning electron microscopy (SEM) images were measured on a Hitachi FE-SEM SU-8020 scanning electron microscope. A specimen was prepared by directly placing the bulk powder on a conducting carbon tape.

2.5 Powder X-ray diffraction (XRD) measurement

Powder X-ray diffraction (XRD) measurements were performed using a Rigaku SmartLab SE diffractometer with graphite-monochromatized Cu-K_α radiation (X-ray wavelength: 1.5418 Å) in steps of 0.01° over the 2θ ranged of 5−60°. A sample was set in a standard glass holder or a non-refractive silicon holder (Overseas X-Ray Service, Saitama, Japan).

2.6 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 thermophysical 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 4-7 mg of sample and were sealed in aluminum pans. A heating and cooling cycle were performed under nitrogen atmosphere (flow rate: 100 mL/min).

2.7 Transmission electron microscopy and low-dose selected-area electron diffraction

Transmission electron microscopy (TEM) images were measured on a JEOL JEM-ARM200F NEOARM transmission electron microscope. The camera length for low-dose selected-area electron diffraction was calibrated using a ceria standard. A specimen was prepared by directly drop-casting on a carbon-coated copper grid.

2.8 Thermogravimetry analysis (TGA) measurement

Thermogravimetric analysis (TGA) was performed using a Hitachi STA7200RV. 5 mg of each sample was placed in a platinum pan and heated to the target temperature at 10 K/min under nitrogen atmosphere.

2.9 Nitrogen adsorption-desorption isotherm

Nitrogen adsorption-desorption isotherms were obtained at liquid nitrogen 77 K using BELSORP-mini II instrument (MicrotracBEL Corp.). Before the measurements, the samples were degassed under reduced pressure (<10 Pa) at 200 °C for 18 h.

2.10 ^{1}H-NMR spectroscopy

^{1}H-NMR spectroscopy was performed on a JEOL JNM-ECZ400S spectrometer operated at 400 MHz. Prior to the measurements, the crystal sample was soaked in DCl/D_2O to dissolve completely.

3. Supporting Figures

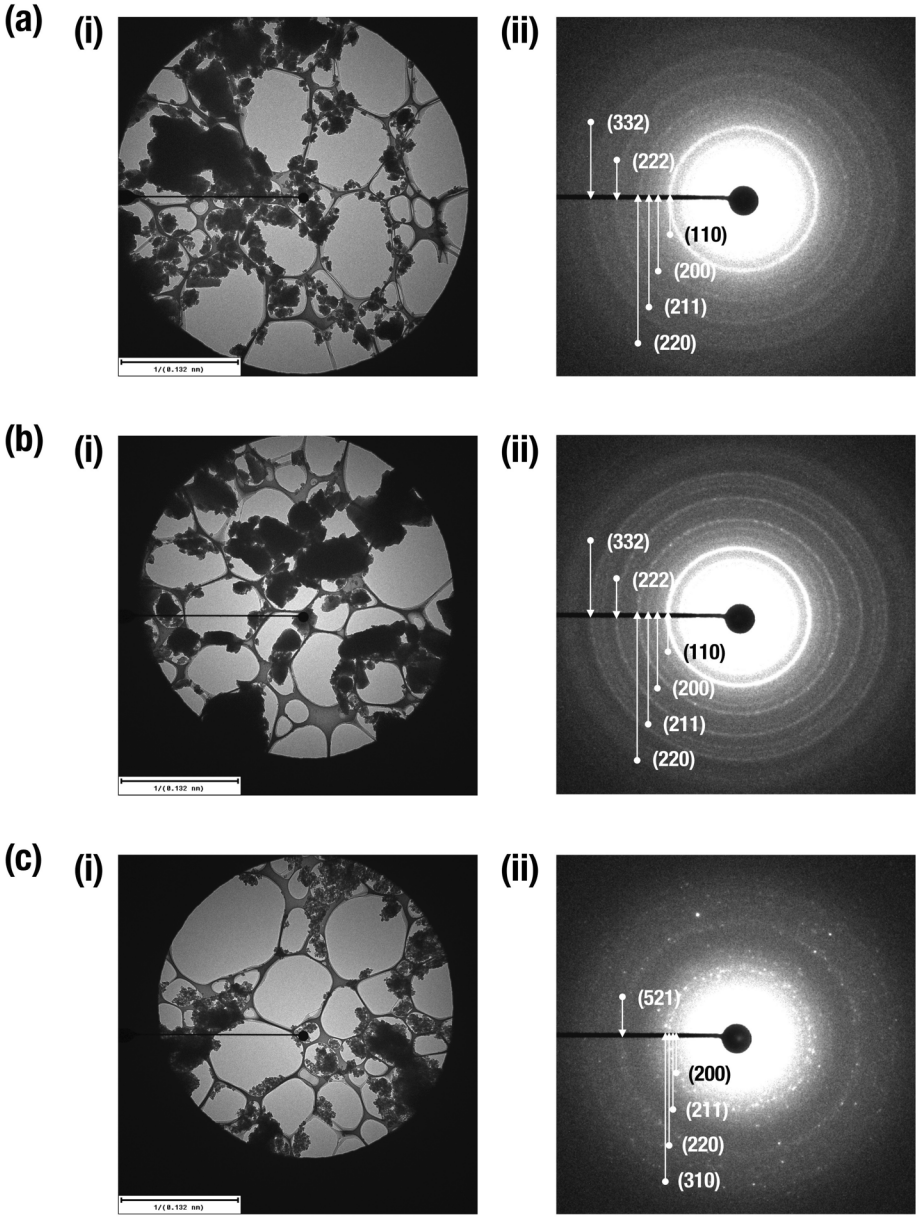

Figure S1. (i) TEM images and (ii) low-dose electron diffraction patterns of (a) 20-nm sized ZIF-8, (b) 20-nm sized ZIF-67, (c) 50-nm sized MAF-6.

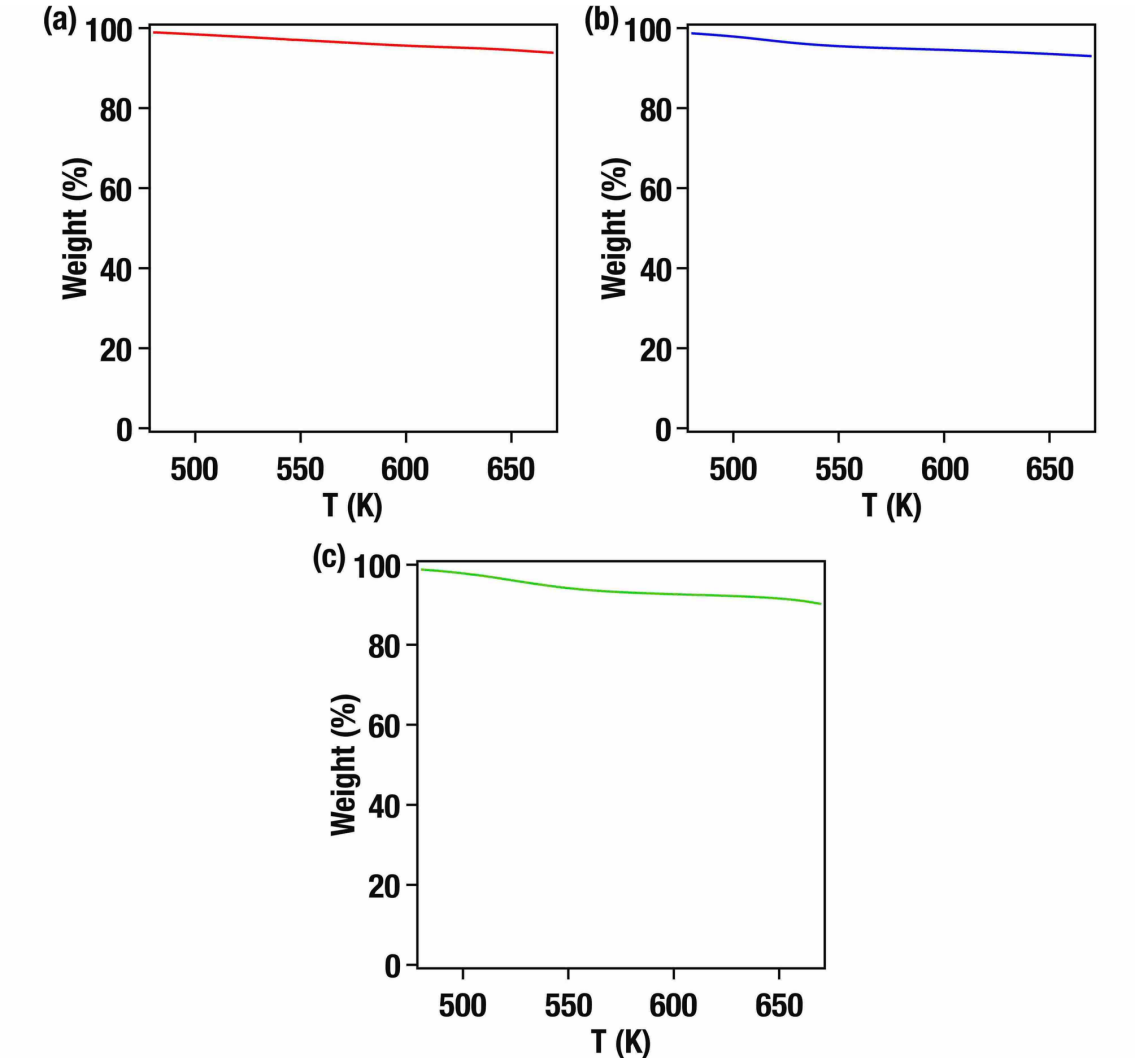

Figure S2. Thermogravimetric analysis (TGA) of the weight loss of (a) 20-nm sized ZIF-8, (b) 20-nm sized ZIF-67, (c) 50-nm sized MAF-6 (heating range: 480-670 K).

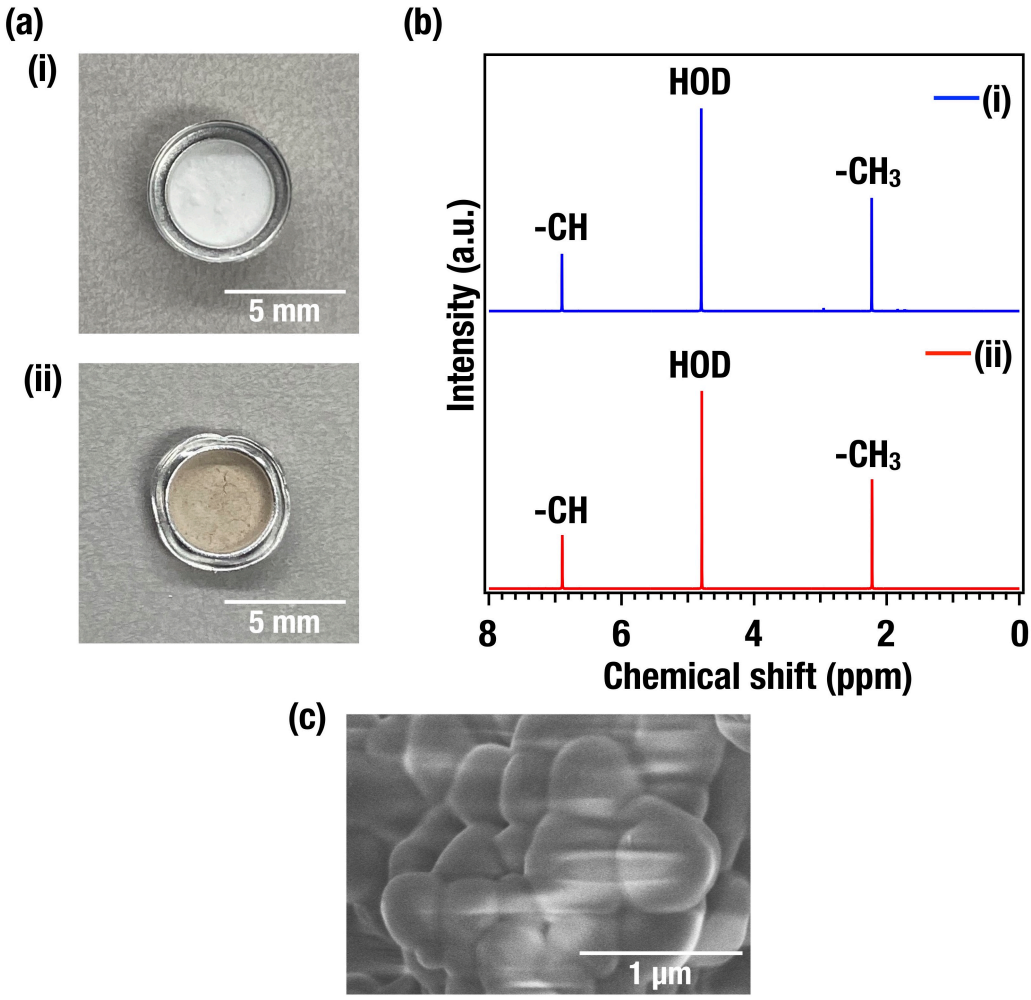

Figure S3. (a) Photographs of the 20 nm-sized ZIF-8 samples (i) before and (ii) after DSC measurement. (b) ^{1}H-NMR spectra (400 MHz, DCl/D_2O) of the recovered 2-methylimidazole from the ZIF-8 crystal (i) before and (ii) after DSC measurement. (c) SEM image of the sample after DSC measurement.

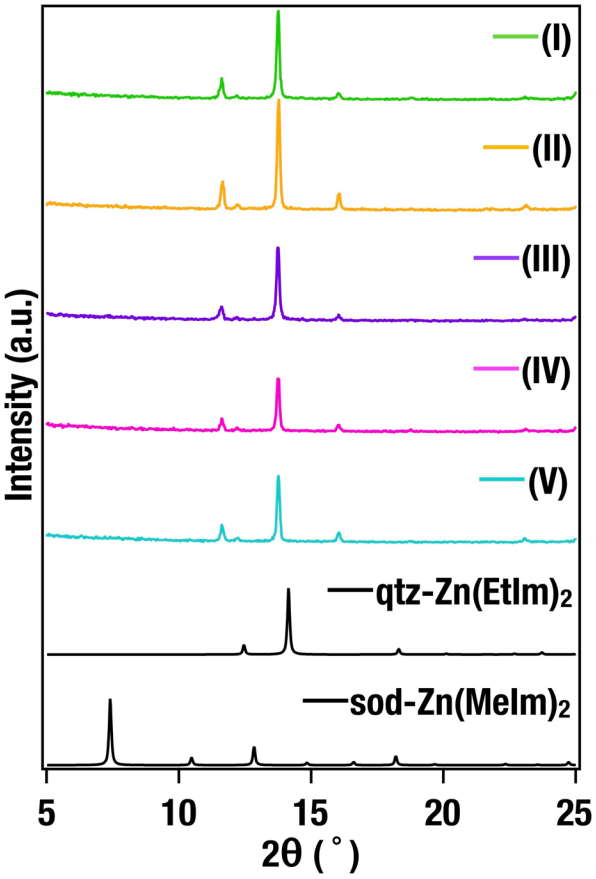

Figure S4. XRD patterns of the samples after DSC measurements at various temperature ramp rate: (I) 10 K/min, (II) 20 K/min, (III) 50 K/min, (IV) 70 K/min, and (V) 100 K/min.

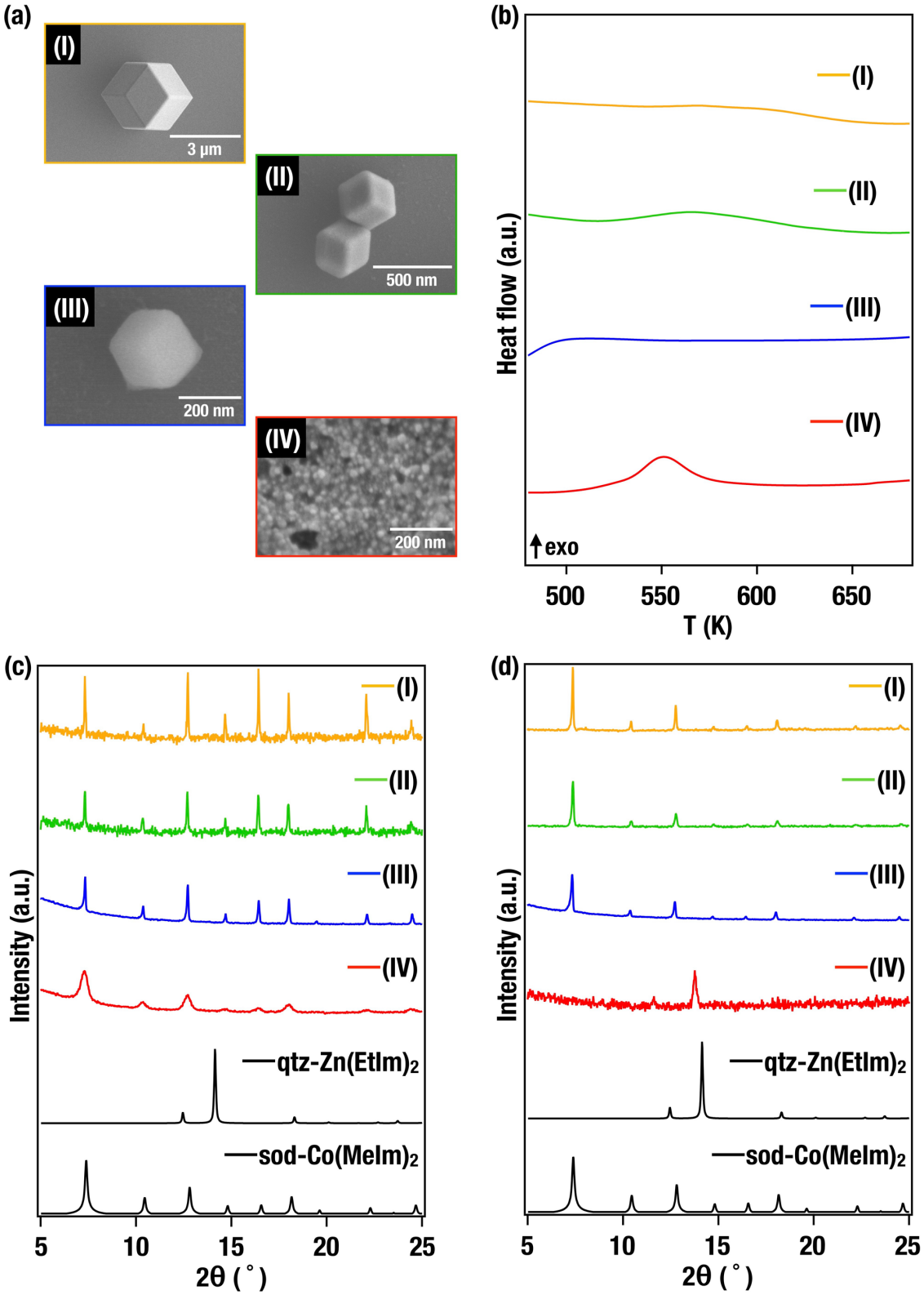

Figure S5. (a) SEM images of the prepared ZIF-67 crystals with different crystal sizes. XRD patterns of four crystal sizes samples (b) before and (d) after DSC measurements compared with the simulated pattern of qtz-Zn(Etlm)$_2$ (CSD code: EHETER), and sod-Co(MeIm)$_2$ (CSD code: GITTOT02). (c) DSC upscans of four crystal sizes samples at a 10 K/min ramp rate. The average crystal sizes are I: 3 μm, II: 400 nm, III: 200 nm, and IV: 20 nm.

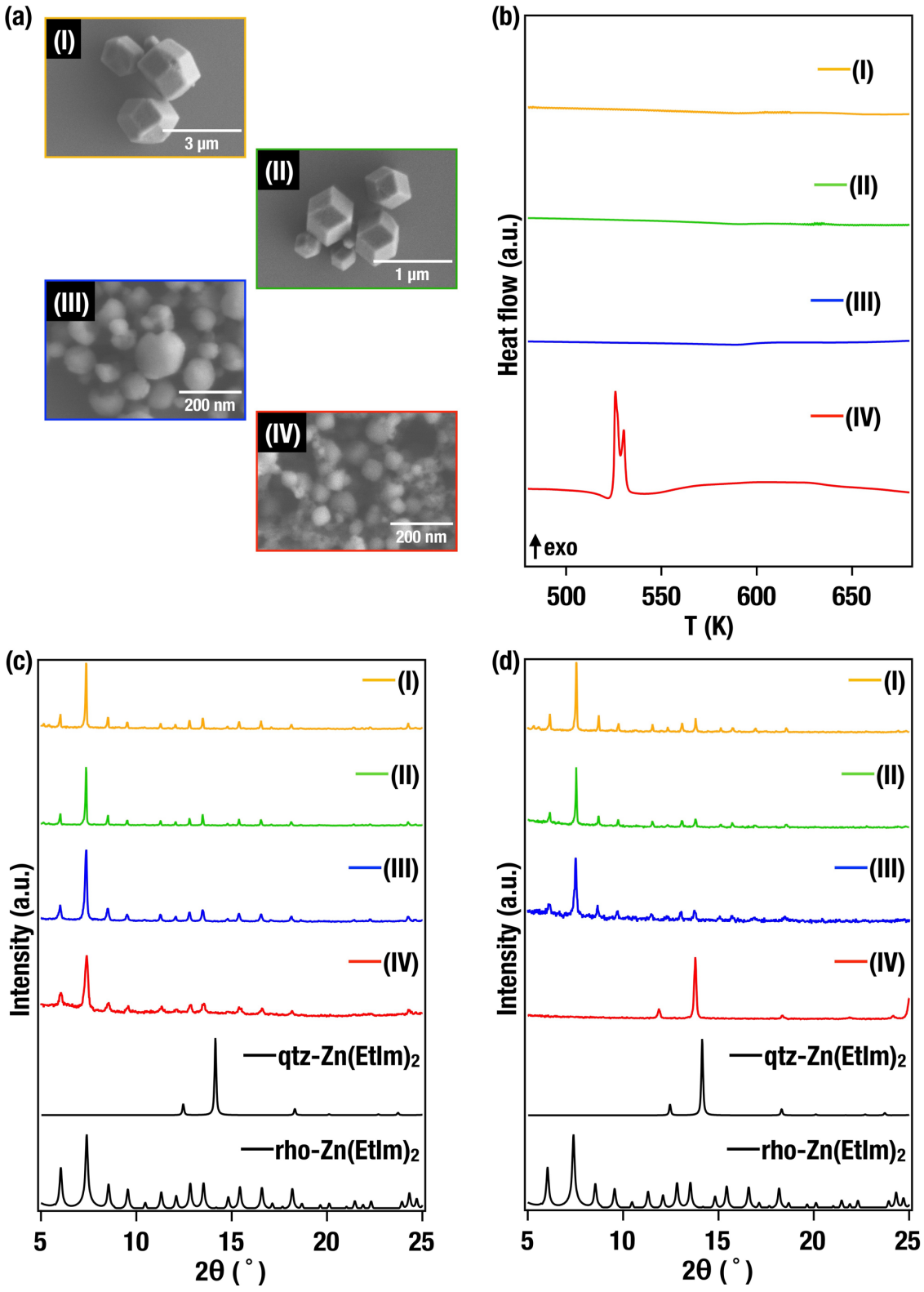

Figure S6. (a) SEM images of the prepared MAF-6 crystals with different crystal sizes. XRD patterns of four crystal sizes samples (b) before and (d) after DSC measurements compared with the simulated pattern of qtz-$Zn(Etlm)_2$ (CSD code: EHETER), and rho-$Zn(EtIm)_2$ (CSD code: MECWOH). (c) DSC upscans of four crystal sizes samples at a 10 K/min ramp rate. The average crystal sizes are I: 1.3 µm, II: 900 nm, III: 90 nm, and IV: 50 nm.

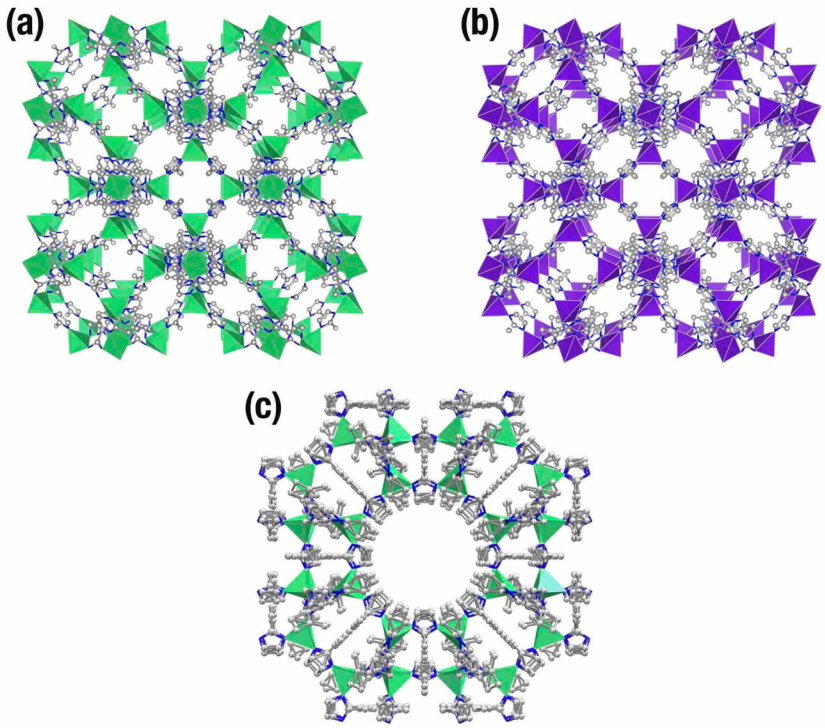

Figure S7. Crystal structures of (a) ZIF-8 (CSD code: OFERUN03), (b) ZIF-67 (CSD code: GITTOT02), and (c) MAF-6 (CSD code: MECWOH).

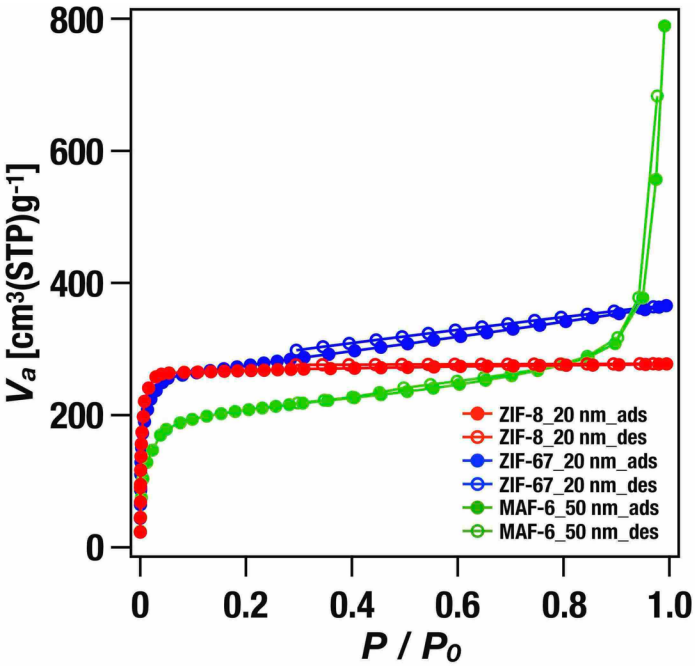

Figure S8. Nitrogen adsorption (solid symbol) and desorption (open symbol) isotherms of samples: (red) 20-nm sized ZIF-8, (blue) 20-nm sized ZIF-67, (green) 50-nm sized MAF-6.

Table S1. Nitrogen gas adsorption/desorption analysis of samples

sample	crystal size (nm)	activation energy: E_a (kJ/mol)	specific surface area, S_{BET} (m^2/g)	pore volume (cm^3/g)	pore diameter (nm)
ZIF-8	**20**	**119 ± 4**	**1160**	**0.42**	**1.5**
ZIF-67	**20**	**145 ± 6**	**1100**	**0.56**	**2.0**
MAF-6	**50**	**193 ± 11**	**806**	**1.20**	**6.0**