Electronic Supplementary Information

Controlled Synthesis of Concave Cuboctahedral Nitrogen-Rich Metal-Organic Framework Nanoparticles Showing Enhanced Catalytic Activation of Epoxides with Carbon Dioxide

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1. Regents and equipment

All starting materials were purchased from Sigma-Aldrich and used without any purification. The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Bruker D8 diffractometer with CuKα radiation (λ = 1.5418 Å) at room temperature. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (JEOL JSM-6700F field emission SEM), and transmission electron microscopy (TEM, JEOL 2010). All TEM samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid. FT-IR spectra were recorded on a Perkin-Elmer 1760-X FT-IR spectrometer with the sample power diluted in KBr (1%). Thermogravimentric analysis (TGA) was carried on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. UV-vis analyses were performed on a Shimadzu UV-3600 spectrophotometer. The gas sorption isotherms were measured on an autosorp-IQ instrument from Quantachrome Instruments Corporation (Boynton Beach, Florida USA).

2. Synthesis of 5,5',5''-(4,4',4''-(Benzene-1,3,5-triyl)tris(1*H*-1,2,3-triazole-4,1-diyl)) triisophthalic acid (H_6-1)

Organic ligand H_6-1 was synthesized according to our previous report. Generally, the ester $^tBu_6$-1 (1.23g, 1.11 mmol) was added into CH_2Cl_2 solution (20 mL). Then, trifluoroacetic acid (TFA, 10 mL) was added into the above solution. The mixture solution was stirred at room temperature over 5 h. The white precipitates were obtained. The suspension was filtered and washed with CH_2Cl_2, and the obtained solid was dried under vacuum to afford the compound H_6-1.

3. Synthesis of concave cuboctahedral N-MOF nanoparticles (Sample 1)

In a typical synthesis, $Cu(NO_3)_2{\cdot}3H_2O$ (0.024 g, 0.1 mmol) was added into a mixture of ethanol/DMF (4.5 mL / 4.5 mL) to form the solution 1. Benzimidazole (0.2 g, 1.7 mmol) was added in the same mixture of ethanol/DMF (4.5 mL / 4.5 mL) to form the solution 2. Then, solution 2 was added into the solution 1, and the mixture solution was stirred at room temperature for 10 min. Compound H_6-1 (0.02 g) was dissolved in the mixture of ethanol/DMF (9 mL / 9 mL) to form the solution 3. The solution 3 was added into the above

mixture solution. The mixture was stirred at 90 °C for 6 h. After reaction, the products were collected by high-speed centrifugation and washed several time with ethanol. The Sample 2 and Sample 3 were synthesized in a similar way where 0.06 g and 1.5 g benzimidazole were used, respectively.

4. Catalysis

The as-prepared MOF catalysts were exchanged with DMF at 70 °C for 6 h, which were dried under vacuum after centrifugation. The catalytic reaction was conducted in a Schlenk tube using epoxides (15 mmol), MOF catalyst (0.75 mmol) calculated based on copper paddlewheel units) and co-catalyst tetra-n-butylammonium bromide (TBAB, 1.5 mmol) with CO_2 purged at 1 atm under solvent free environment at room temperature for 48 h. The products were monitored by ^1H NMR to calculate the yields. The catalyst for recyclability reaction was recycled by centrifugation at 10 000 rpm.

Experiment Results

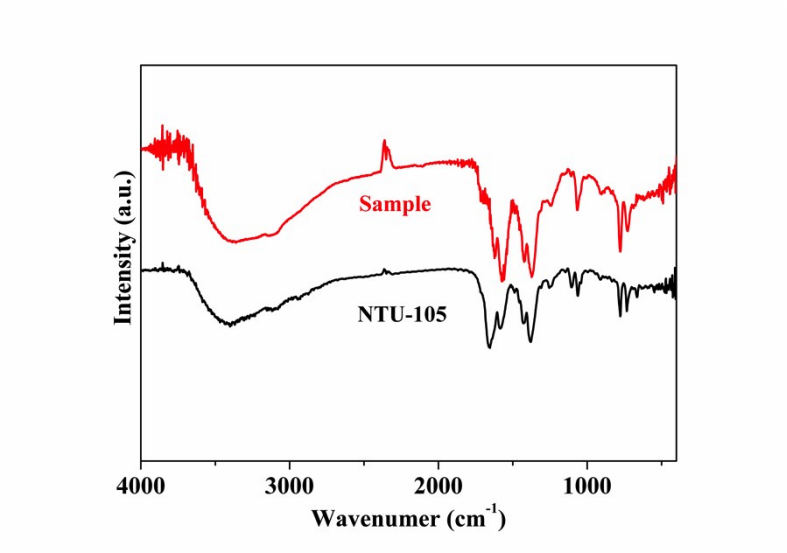

Figure S1. FT-IR spectra of Sample 1 and NTU-105 (N-MOF).

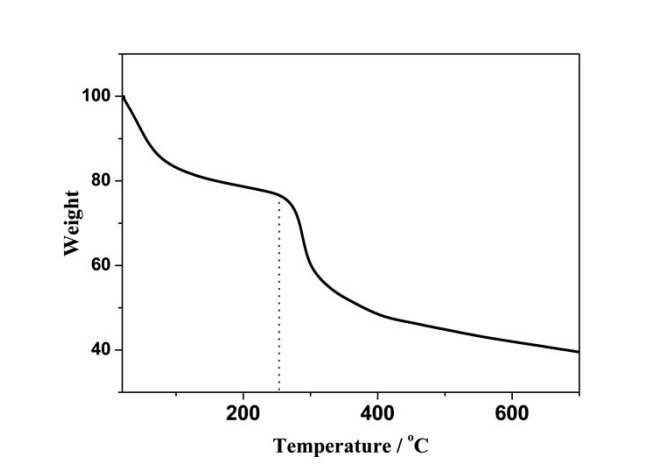

Figure S2. TGA curve of Sample 1, indicating that the sample was stable up to 260 °C.

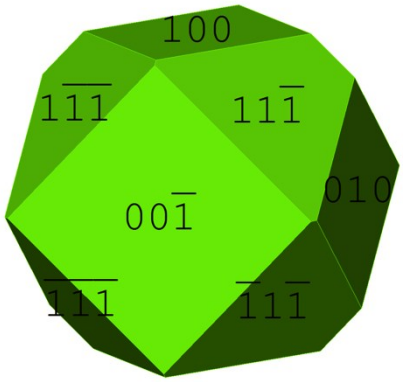

Figure S3. Ideal geometrical model of cuboctahedral shape without concave surface, indicating that the exposed facets mainly include the (001), (100) and (111) facets.

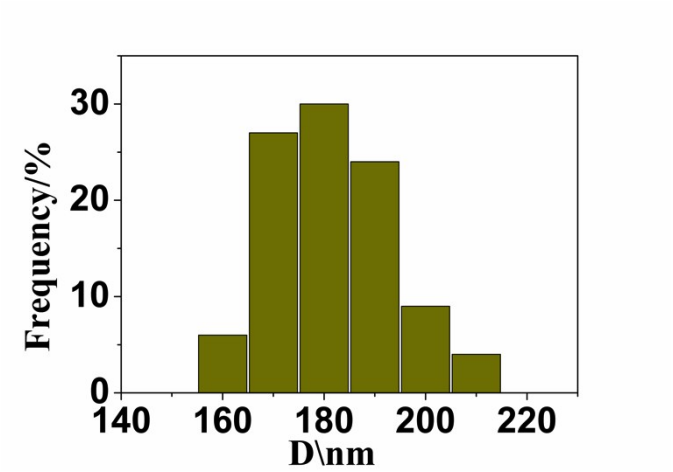

Figure S4. Size distribution of the Sample 1.

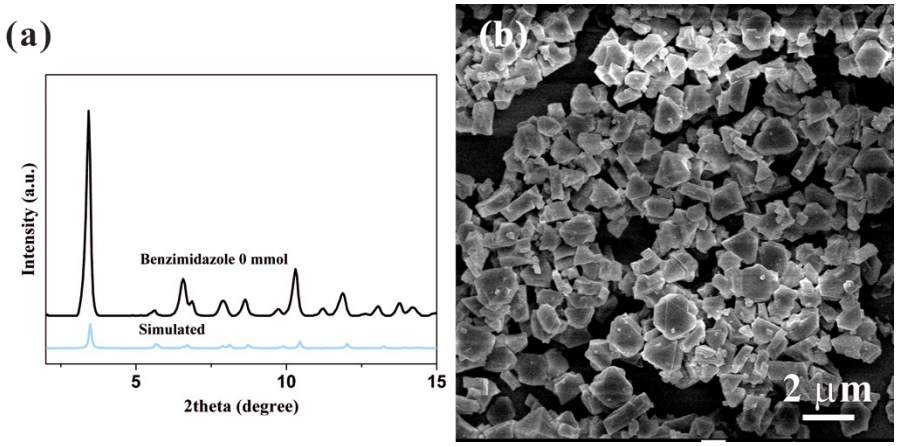

Figure S5. (a) PXRD patterns of the product prepared without benzimidazole and simulated one, (b) SEM image of the product prepared without using benzimidazole as the modulator.

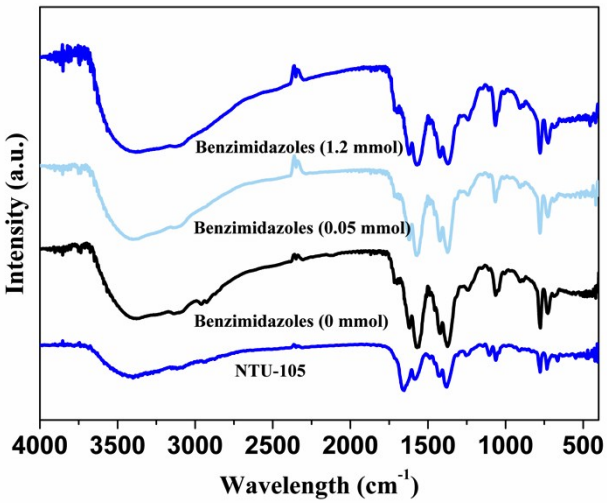

Figure S6. FT-IR spectra of the products prepared using different amount of benzimidazole as well as NTU-105 (N-MOF).

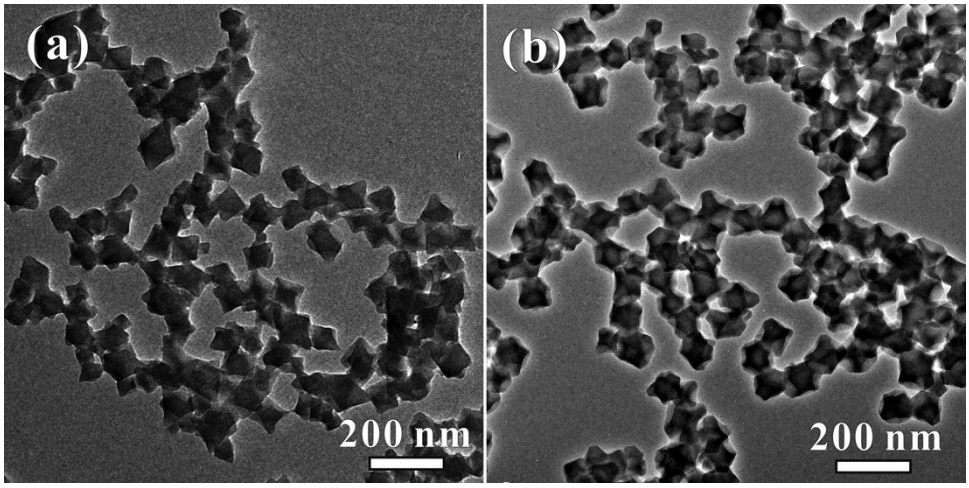

Figure S7. TEM images of the products prepared using different amount of benzimidazole: (a) 0.5 mmol and (b) 1.2 mmol.

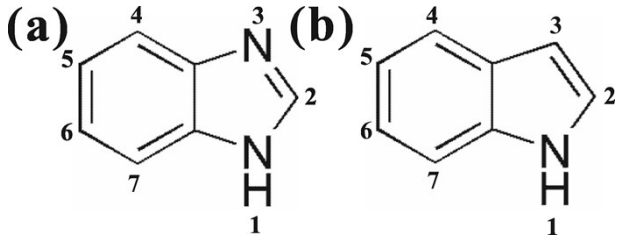

Figure S8. Molecular structural formula of (a) benzimidazole and (b) indole.

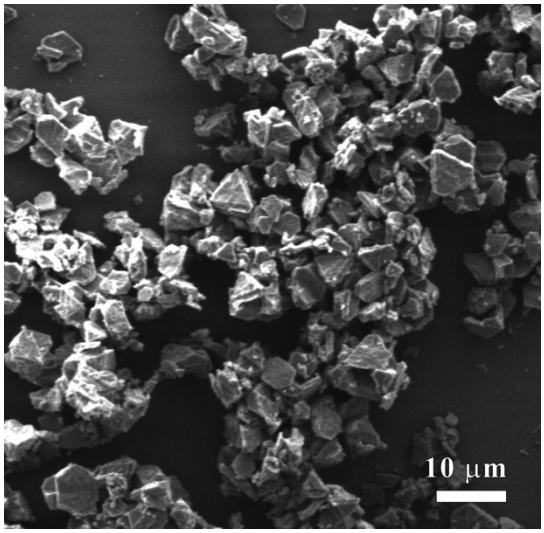

Figure S9. SEM image of the product prepared using indole as the modulator.

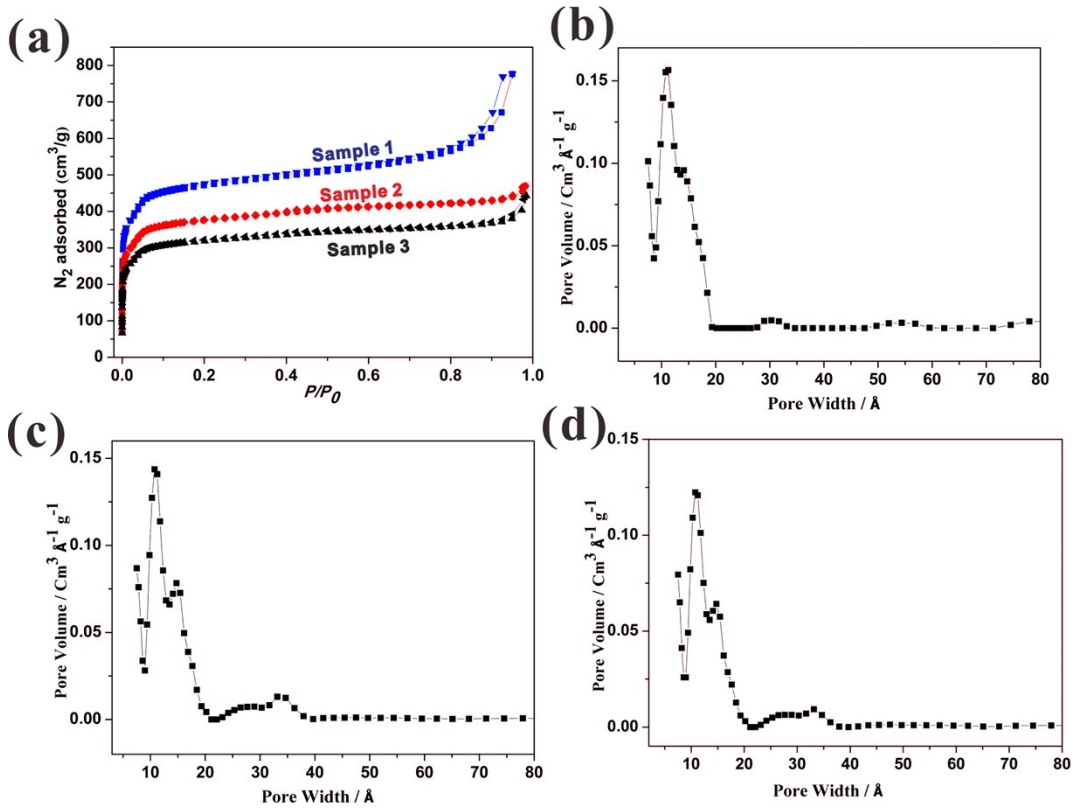

Figure S10. (a) N_2 adsorption isotherms (77 K) of Samples 1-3, as well as pore size distributions of (b) Sample 1, (c) Sample 2, and (d) Sample 3.

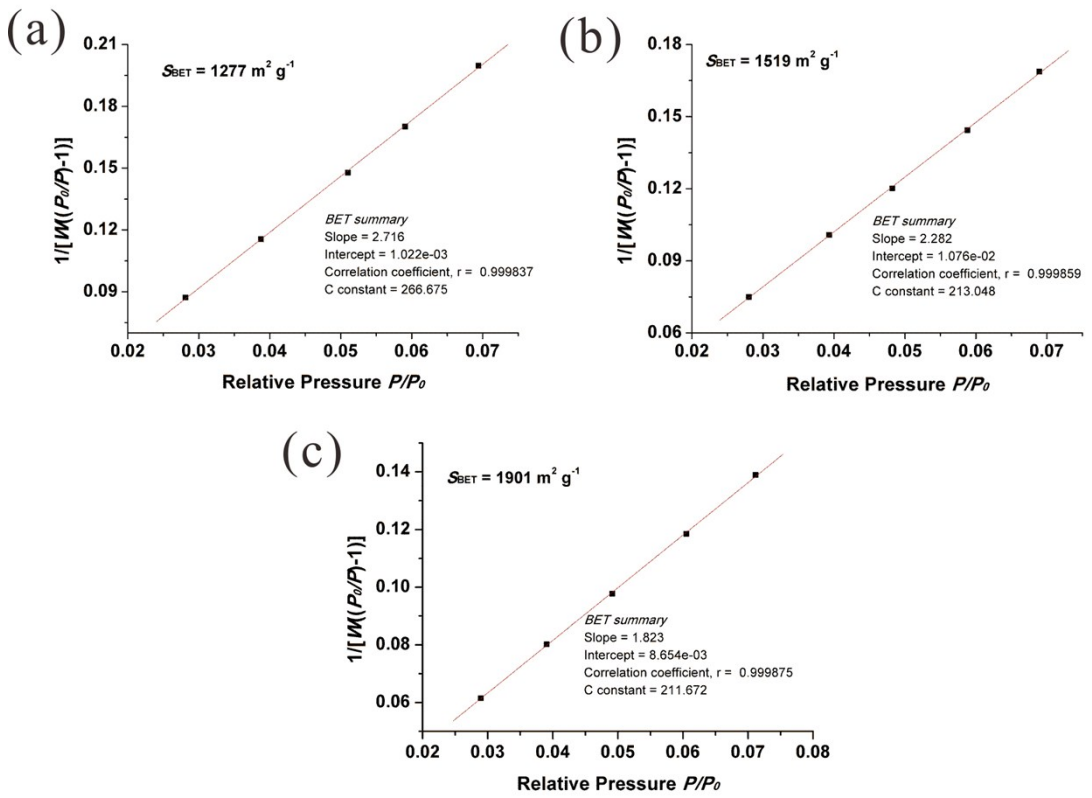

Figure S11. BET linear plots for (a) Sample 3, (b) Sample 2, and (c) Sample 1.

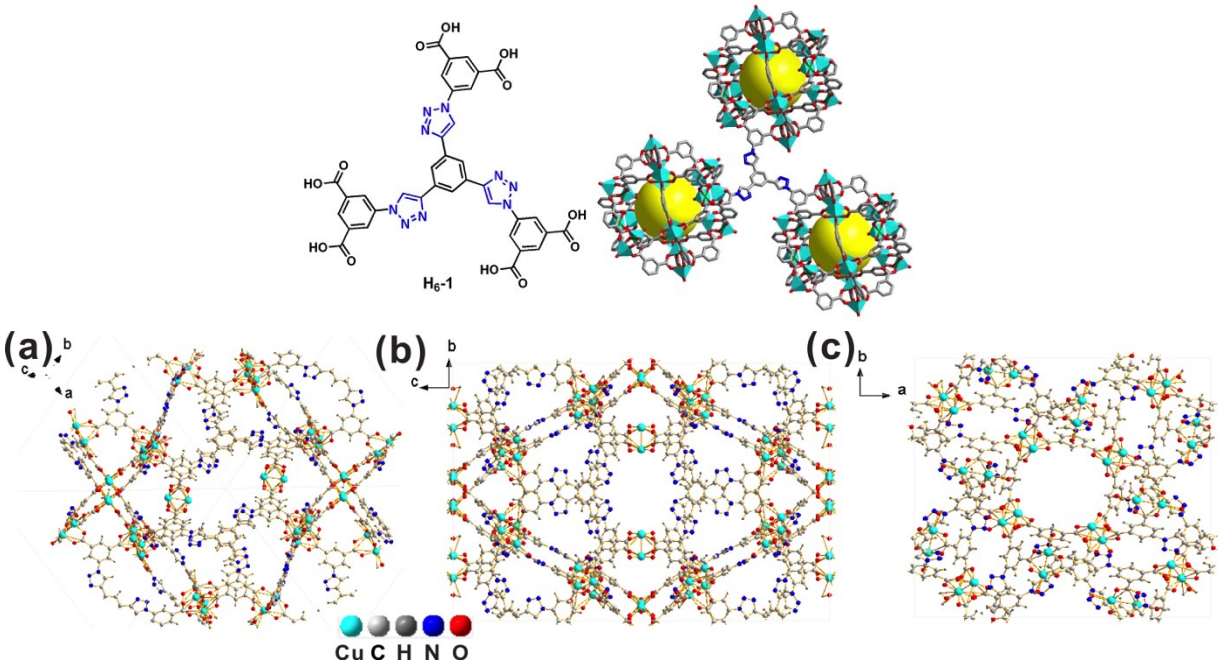

Figure S12. Crystallographic structures of NTU-105 (N-MOF) projected from different directions: (a) (111) direction, (b) (100) direction, and (c) (001) direction.

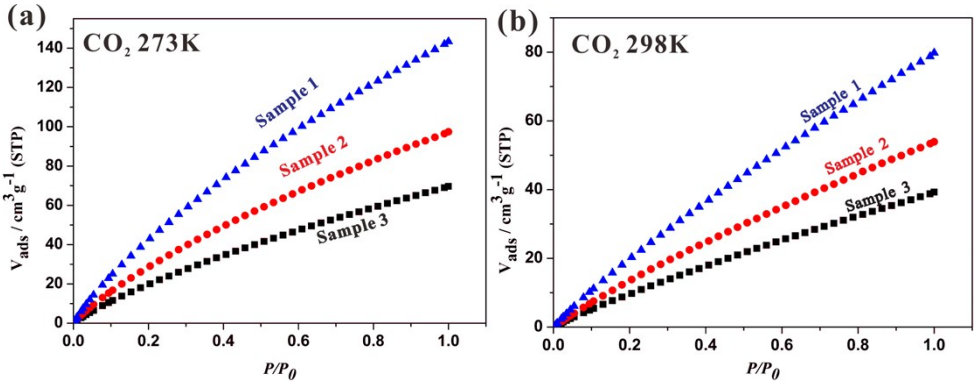

Figure S13. CO_2 adsorption isotherms of Sample 1-3: (a) 273 K, (b) 298K.

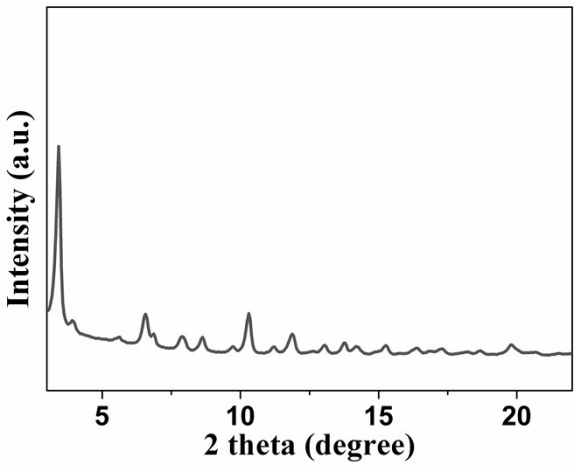

Figure S14. Powder XRD pattern of N-MOF (Sample 1) after catalytic reaction.