Supporting Information

Effect of Modulators on Size and Shape-Controlled Growth of Highly Uniform In-NDC-MOF Particles

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Experimental Section

Chemicals: All of the chemicals and solvents were used as received without further purification. Indium nitrate hydrate ($In(NO_3)_3$, 32-36%, Sigma-Aldrich), 1,4-naphthalenedicarboxylic acid (1,4-NDC, 95%, Tokyo chemical industry), polyvinylpyrrolidone (PVP, MW=40000, Sigma-Aldrich), dimethylformamide (DMF, 99.8%, Vetec), acetonitrile (CH_3CN, 99.8%, Vetec), tetramethylammonium nitrate (TMAN, 96%, Aldrich), triethylamine (TEA, 99%, Sigma-Aldrich), hexadecyl trimethyl ammonium bromide (CTAB, 98%, Sigma), acetic acid (AcOH, 99.7%, Sigma-Aldrich), and deionized water (Millipore, 18.2 MΩ·cm resistivity at 25℃).

Experiment details:

A precursor solution was prepared by mixing $In(NO_3)_3 \cdot \mathbf{x}H_2O$ (25 mg, 0.083 mmol), 1,4-NDC (10 mg, 0.046 mmol), 0.5 mL of PVP (0.4 g/mL in DMF) and 0.1 mL of CTAB, TEA, TMAN (0.1 g/mL in deionized water) or 0.01 mL of AcOH in 1 mL of DMF and 1 mL of CH_3CN. The mixture was heated to 120 ^{o}C and held for 1.5 hour on a hot plate with continuous stirring. The products were harvested by centrifugation and washed with anhydrous ethanol twice.

Characterization: Power X-ray diffraction (XRD) measurements were performed on a D8 focus diffractometer at a scanning rate of 5°/min in the 2θ range from 8° to 40°, with graphite monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm). Thermogravimetric analysis (TGA) data were recorded with Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) with a heating rate of 10°/min in an air flow of 100 mL/min. The morphology of the samples was characterized by using a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi) and a transmission electron microscope (TEM, FEI Tenai G2 S-Twin) equipped with an energy-dispersive X-ray (EDX) spectra and a field emission gun operating at 200 kV. Elemental analyses of C, H, and N were conducted on a Perkin–Elmer 2400 elemental analyzer. Fourier transform infrared spectra were measured on a Vertex PerkinElmer 580BIR spectrophotometer (Bruker) with KBr pellet technique.

Gas Adsorption Analysis

Activation of samples. The as-synthesized samples of In-NDC-MOF were immersed in ethanol solution for 1 day, during which the solution was decanted and freshly replenished every two hours. The resultant samples were degassed under dynamic vacuum and heated at 150 °C for 8 hours.

Low-Pressure Gas Sorption Measurements. Low-pressure gas sorption experiments were carried out on a Quantachrome Autosorb IQ instrument. N_2 isotherms were measured using a liquid nitrogen bath (77 K) and CO_2, CH_4, C_2H_6 and C_3H_8 isotherms were measured at 273 K and 298 K. The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) and Langmuir equation from the N_2 sorption data.

Langmuir-Freundlich Fitting of Pure Component Isotherms. The experimental data of the pure component for CO_2, CH_4, C_2H_6 and C_3H_8 were measured as a function of the excess loading q^{ex}, which is converted to the absolute loading q by Equation (S1).

$$q = q^{ex} + \frac{pV_{pore}}{zRT} \qquad \text{(S1)}$$

Where p is the pressure, V_{pore} is the pore volume, z is the compressibility factor, R is the gas constant, and T is the temperature. The Peng-Robinson equation is used to estimate z.

The single-component isotherm is fitted with the Dual-Site Langmuir-Freundlich (DSLF) adsorption model to correlate the pure-component equilibrium data and predict the adsorption of mixtures by Equation (S2).

$$q = \frac{q_{m1} b_1 p^{1/n1}}{1 + b_1 p^{1/n1}} + \frac{q_{m2} b_2 p^{1/n2}}{1 + b_2 p^{1/n2}} \qquad \text{(S2)}$$

Where p is the pressure of the bulk gas at equilibrium with the adsorbed phase, q is the adsorbed amount per mass of adsorbent, q_{m1} and q_{m2} are the saturation capacities at site 1 and 2, b_1 and b_2 are the affinity coefficients at site 1 and 2, n_1 and n_2 are the deviations from an ideal homogeneous surface.

Calculations of the Isosteric Heats of Gas Adsorption (*Q_{st}*). A virial-type expression (Equation S3)[Ref. S1] is applied to model the adsorption data of CH_4, C_2H_6 and C_3H_8 (at 273 K and 298 K), and to calculate the enthalpies of adsorption.

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j \qquad \text{(S3)}$$

Where P is pressure (Torr); N is the amount adsorbed (mg g^{-1}); T is temperature (K); a_i and b_i are virial coefficients, which are independent of temperature; m and n represent the number of coefficients required to adequately describe the isotherms (m and n are gradually increased until the contribution of extra added a and b coefficients are deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values is minimized). The values of the virial coefficients a_0 through a_m were used to calculate the isosteric heat of adsorption according to Equation (S4).

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad \text{(S4)}$$

Where Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of gas sorption for In-NDC-MOF is determined from the sorption data measured in the pressure range from 0-1 bar (273 and 298 K for gases).

Prediction of adsorption of binary mixture by IAST theory. The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

References:

[S1] Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304-1315.

[S2] Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121-127.

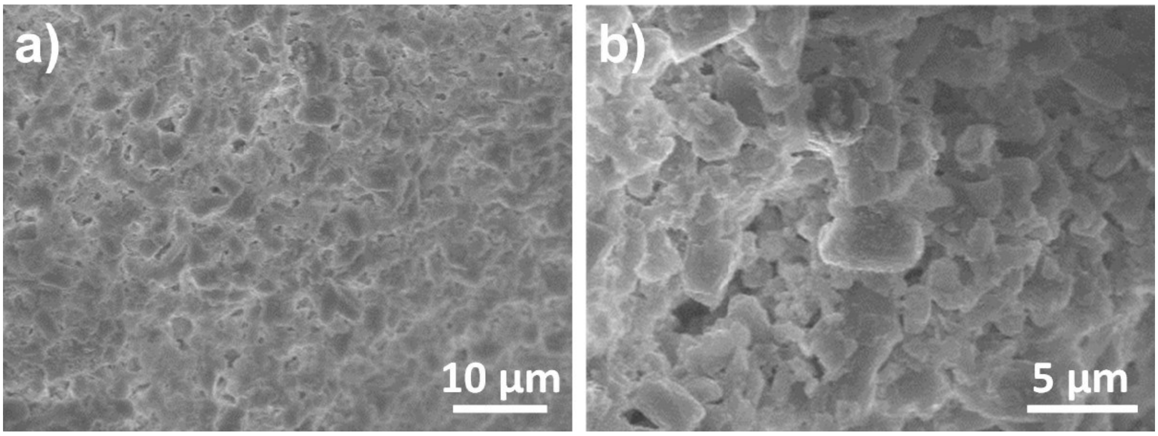


Figure S1. SEM images for In-NDC-MOF particles prepared in the absence of PVP.

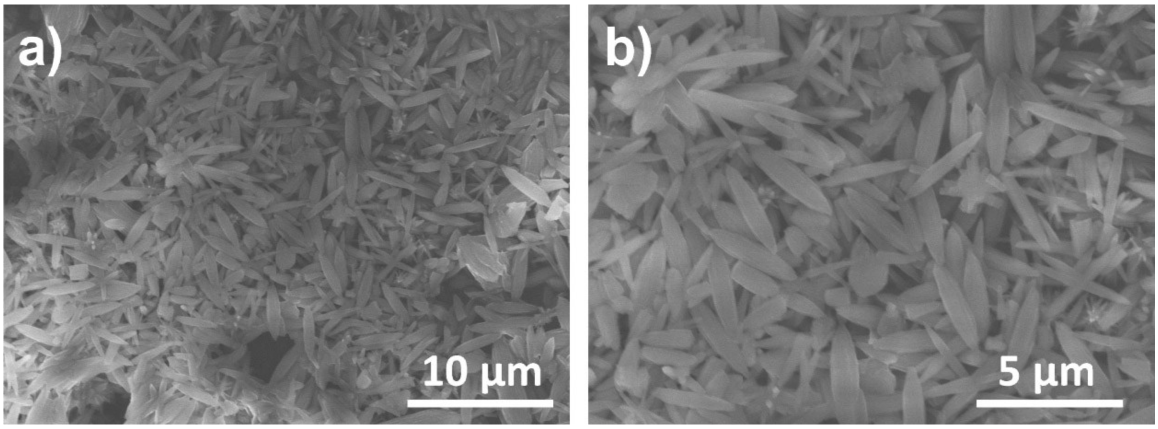


Figure S2. SEM images for In-NDC-MOF particles prepared in the presence of PVP.

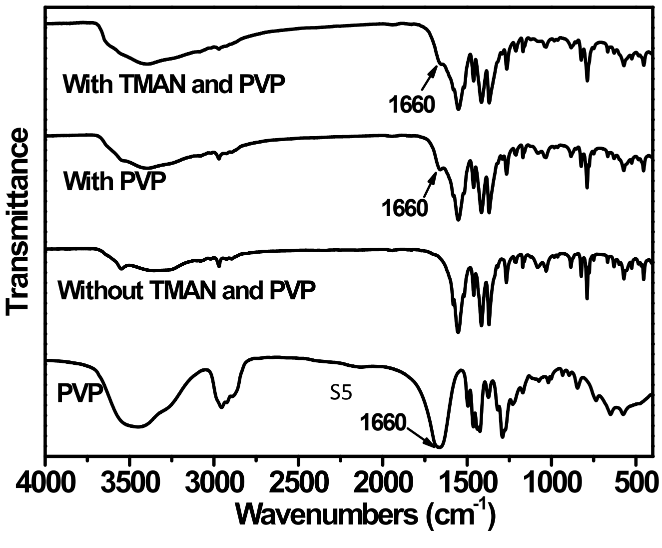


Figure S3. FT-IR spectra for In-NDC-MOF prepared in the absence or presence of PVP.

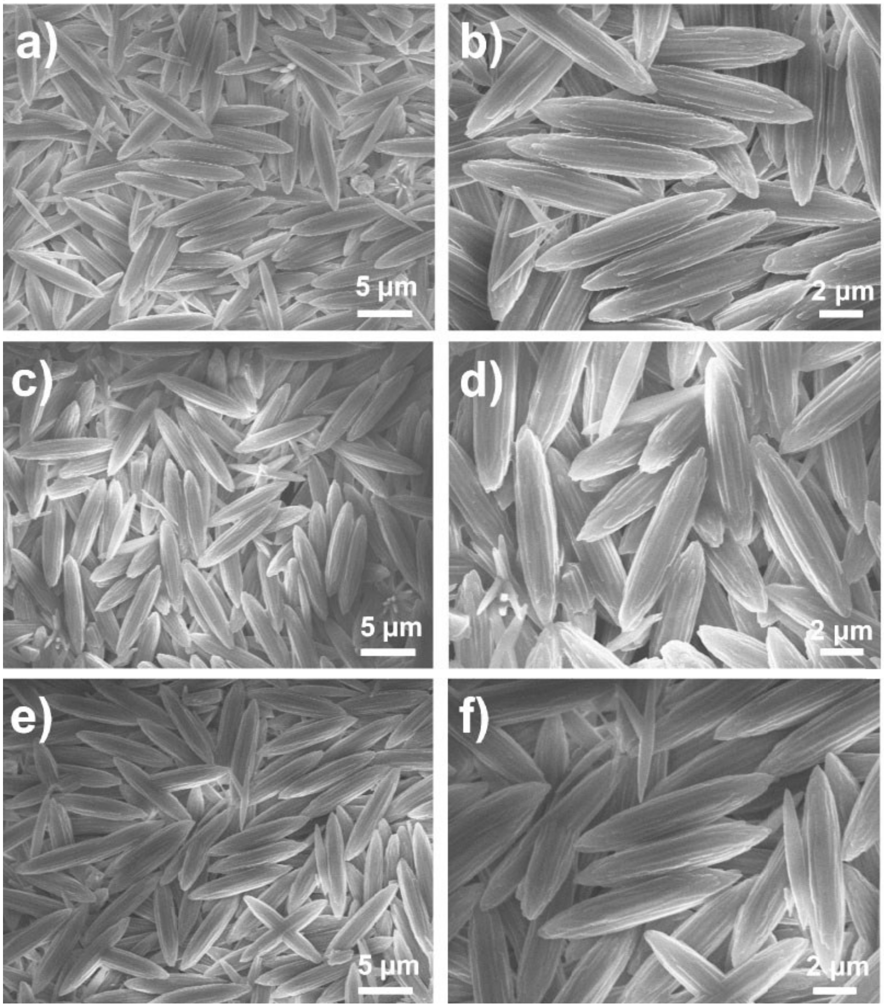


Figure S4. SEM images for In-NDC-MOF particles prepared in the presence of: (a,b) lauric acid, (c,d) benzoic acid, (e,f) fumaric acid.

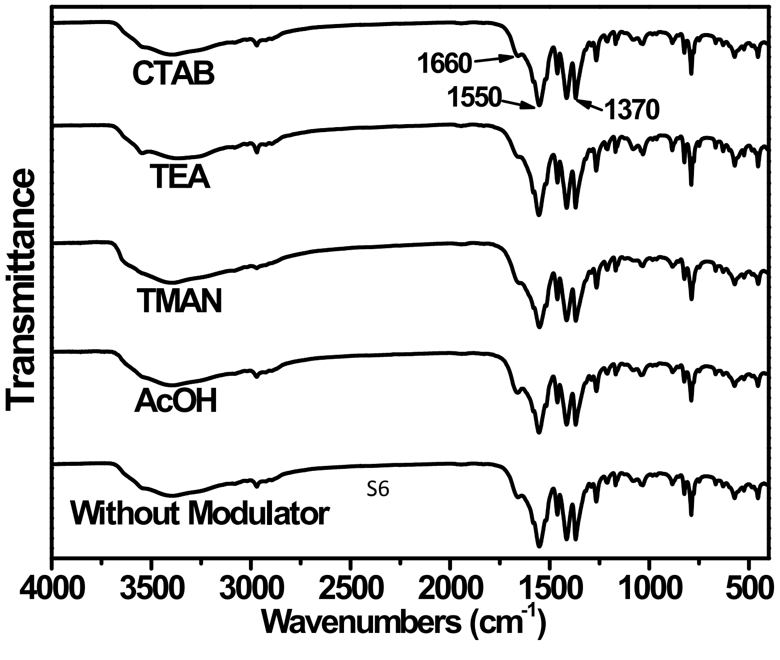
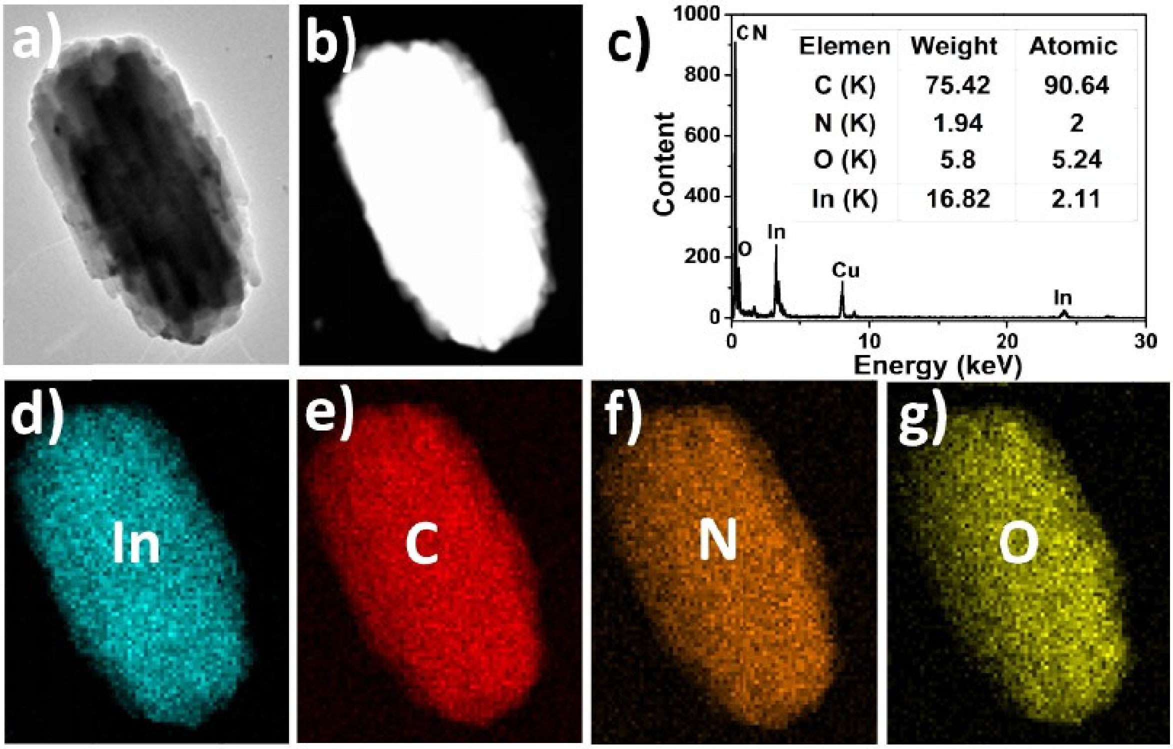


Figure S5. FT-IR spectra for In-NDC-MOF prepared in the absence or presence of different modulators.

Table S1. Elemental analyses result for the as-synthesized In-NDC-MOF.

	N [%]	C [%]	H [%]
1st test	0.97	40.99	3.035
2nd test	0.98	40.90	3.013
Average	0.975	40.945	3.024
Molar ratio	1	48.7	43.2



Elemen	Weight	Atomic
C (K)	75.42	90.64
N (K)	1.94	2
O (K)	5.8	5.24
In (K)	16.82	2.11

Figure S6. (a) TEM, (b) Dark-field STEM image, (c) EDX spectrum, and (d-g) elemental mapping for an individual In-NDC-MOF particle.

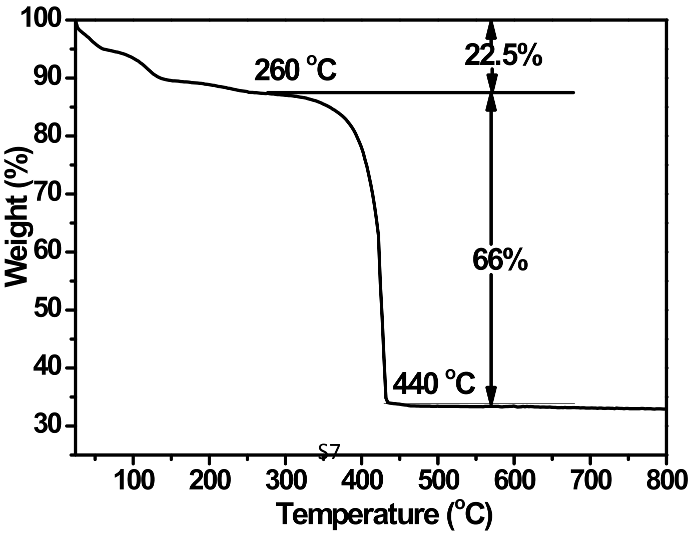


Figure S7. TGA curve for In-NDC-MOF.

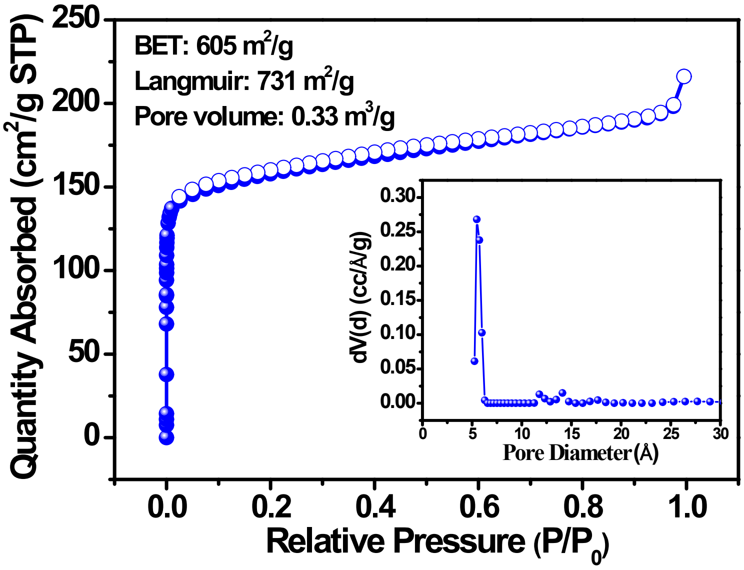


Figure S8. N_2 adsorption-desorption isotherm measured at 77 K for In-NDC-MOF prepared in the absence of modulators.

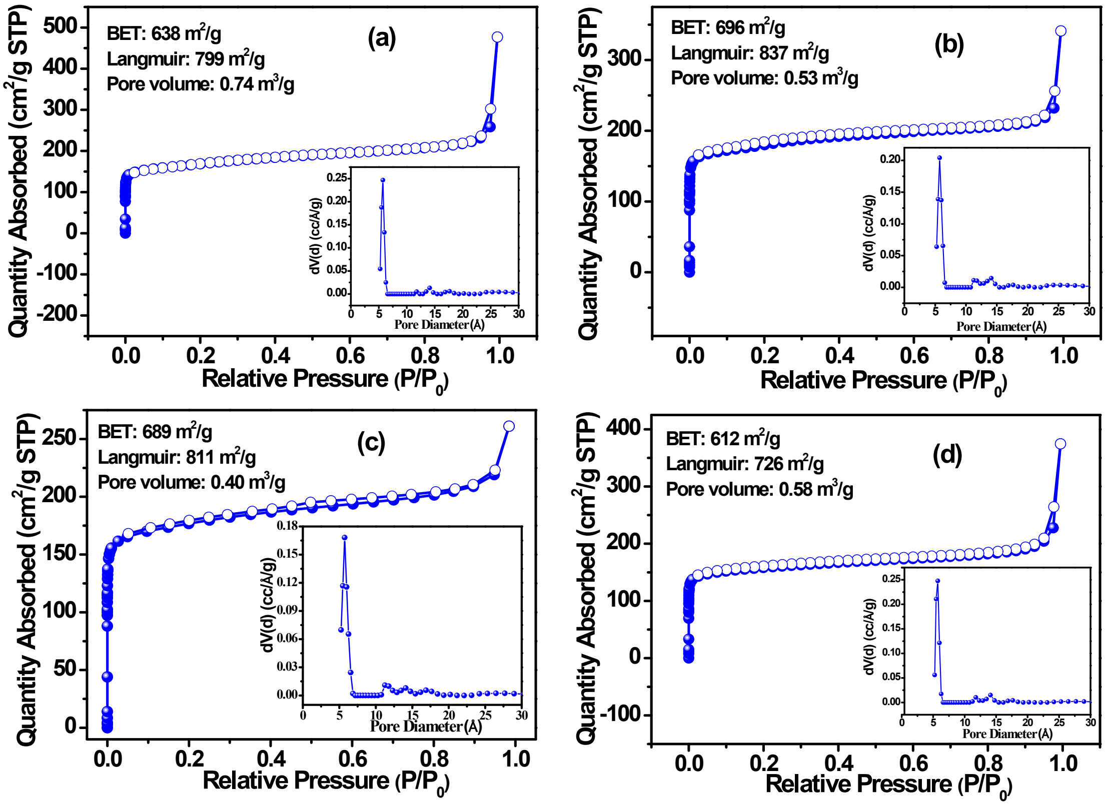


Figure S9. N_2 adsorption-desorption isotherms measured at 77 K for In-NDC-MOF prepared in the presence of (a) CTAB, (b) TEA, (c) TMAN and (d) AcOH, the insert is pore size distribution curve.

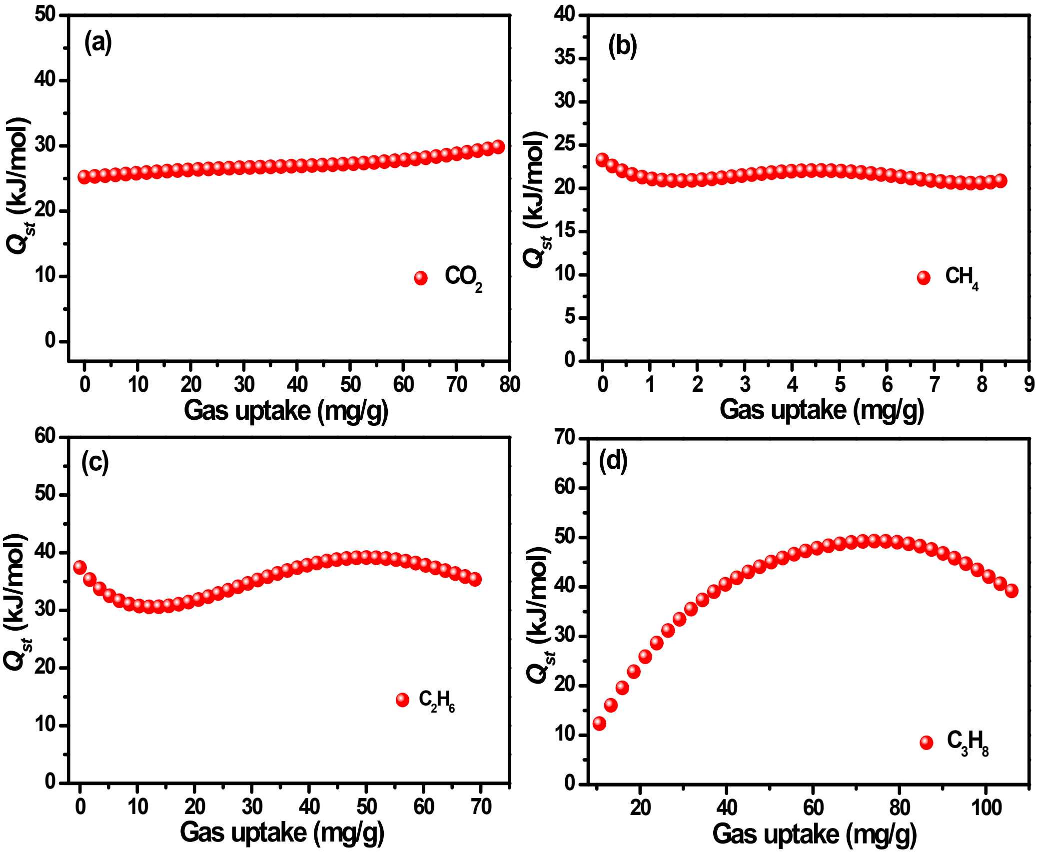


Figure S10. Isosteric heat (Q_{st}) of adsorption of (a) CO_2, (b) CH_4, (c) C_2H_6, and (d) C_3H_8.

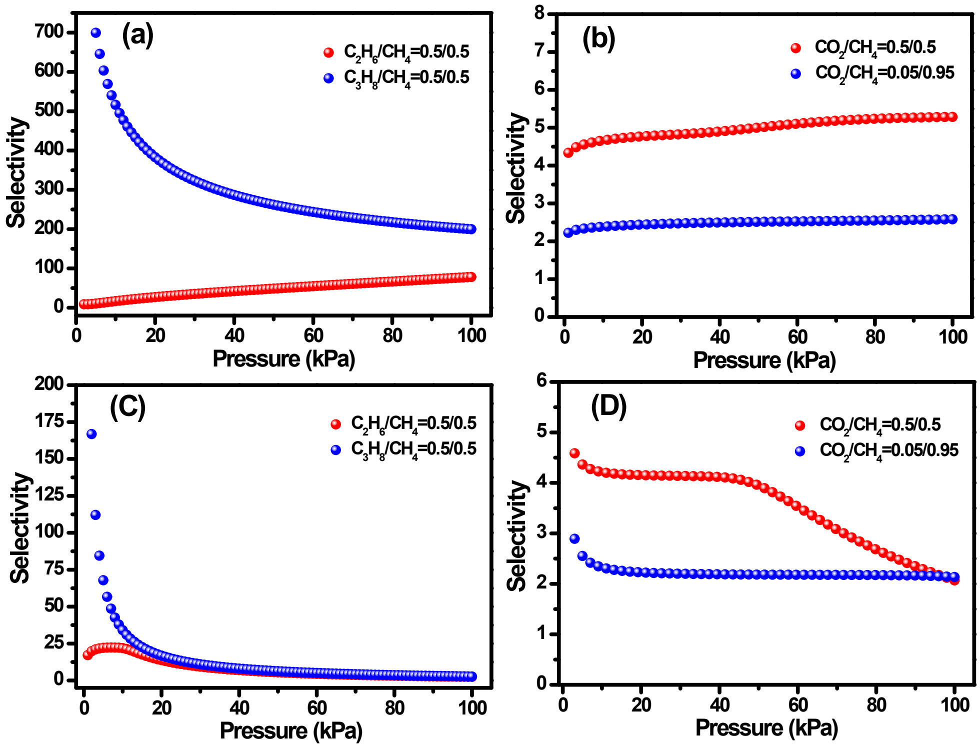


Figure S11. Gas mixture selectivity predicted by IAST at (a,b) 273 K, and (c,d) 298 K under 1 bar for In-NDC-MOF.