Electronic Supplementary Information

Scalable Reflux Synthesis of Bimicroporous Hydrogen-Bonded Frameworks with Specific Molecule Recognition Ability for One-Step Ethylene Purification

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1. Experiments Section

1.1 Materials and Methods

In(NO₃)₃·xH₂O, Ni(NO₃)₂·6H₂O, 4,5-dicyanimidazole (H₃ImDCN), 2-amino-1H-imidazole-4,5-dicarbonitrile (AH₃ImDCN), 4,5-imidazoledicarboxylic acid (H₃ImDC), N.N'dimethylformide (DMF), N,N'-dimethylacetamide (DMA), N-Methylpyrrolidone (NMP) and HNO₃ (65%-68%). All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) studies were carried out with a MiniFlex 600 X-ray diffractometer with a scan speed of 0.02 s/deg at room temperature. Specific surface area measurements at 77 K were carried out using a Micromeritics 3 Flex adsorption porosimeter (Micromeritics Instrument Corp., USA) with N₂ gas. C₂H₂, C₂H₄, and C₂H₆ adsorption/desorption isotherms under different temperatures were also measured by the Micromeritics 3 Flex adsorption porosimeter and all gases used in the adsorption experiments are of ≥99.9% purity. The dynamic breakthrough experiments were carried out on a self-built instrument and the mass spectrometry is the gas detector.

1.2 X-Ray Single Crystal Structure Determinations

SNNU-520, SNNU-520-NH₂ and SNNU-521 were all collected on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphitemonochromated Cu K α radiation at 153 K. The structures of them were solved through the XT method and refined through the XS method with the Olex 2 program. All non-hydrogen atoms were refined anisotropically. Both the specific crystallographic data and the parameters of structure refinement were summarized in Table S1.

1.3 NMR Spectroscopy

Liquid ¹³C NMR spectroscopy: around 10 mg of organic ligand samples (H₃ImDCN, AH₃ImDCN, and H₃ImDC) soaked in 0.5 mL of DMSO- d_6 (H₃ImDC was digested in 1 mL of 35% HCl). The spectra were acquired immediately on a Bruker AVANCE III 400 MHz spectrometer. Solid state ¹³C NMR spectroscopy: the activated MOF samples were used directly to obtain the spectra. The solid state ¹³C cross polarization magic angle spinning (CP/MAS) S3S4 NMR spectroscopy was analyzed on a JNM-ECZ400R/S1 spectrometer operating at 400 MHz.

1.4 Gas Adsorption

To explore the permanent porosity of SNNU-520, SNNU-520-NH₂, and SNNU-521, N₂ adsorption and desorption isotherms at 77 K were measured. The adsorption and desorption isotherms of SNNU-520 and SNNU-520-NH₂ for single-component C_2H_2 , C_2H_4 and C_2H_6 at 0 - 1 atm with activated samples were conducted at 273, 283, 298 and 308 K, respectively and SNNU-521 for single-component C_2H_2 , C_2H_4 and C_2H_6 at 0 - 1 atm with activated samples were conducted at 273, 283, 298 and 308 K, respectively and SNNU-521 for single-component C_2H_2 , C_2H_4 and C_2H_6 at 0 - 1 atm with activated samples were conducted at 273 and 298 K. Kinetic adsorption data of C_2H_2 , C_2H_4 , and C_2H_6 at 298 K were collected using an Intelligent Gravimetric Analyzer (IGA 001).

1.5 Breakthrough Separation Experiments and Procedures

The breakthrough experiments were carried out with dynamic gas breakthrough equipment (the equipment was built by cooperating with instrument manufacturers according to the basic principles reported in the literature). A stainless-steel column with an internal diameter of about 0.5 cm, and a length of 12 cm was used for sample packing. Activated crystalline samples (1.2 g and 1.16 g for SNNU-520 and SNNU-520-NH₂) were packed into the column and degreasing cottons were used to seal the ends of the steel column. The column was placed in a circulating jacket connected to a thermostatic bath (temperature ranged from 263 to 323 K). The mixed gas flows and pressure were controlled by using a pressure controller valve and a mass flow controller. Outlet effluent from the column was continuously monitored using a gas analytical mass spectrometer (Hiden, HPR-20 R&D). The column packed with pre-activated sample was firstly purged with He flow (30 mL/min) for 30 minutes at room temperature. The gas flows were controlled at the inlet by a mass flow meter, and before every breakthrough experiment, we activated the sample by flushing the adsorption bed with helium gas (30 mL/min) for 1 hour at 298 K. Subsequently, the column was allowed to equilibrate at the measurement rate before we switched the gas flow.

2. Calculation Section

2.1 Isosteric Analysis of the Heat of Adsorption (Virial method)

To extract the coverage-dependent isosteric heat of adsorption, the data were modeled with a virial-type expression^{S1} composed of parameters a_i and b_i that are independent of temperature:

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$
 (S1)

where P is pressure, N is the amount adsorbed (or uptake), T is temperature, and m and n determine the number of terms required to adequately describe the isotherms.

$$Q_{st} = -\mathbf{R} \sum_{i=0}^{m} a_i N^i$$
 (S2)

where *R* is the universal gas constant. The coverage dependencies of Q_{st} calculated from fitting the 273 K, 283 K and 298 K (under the pressure range from 0-1 bar) data are presented graphically below.

2.2 Isosteric Analysis of the Heat of Adsorption (Clausius-Clapeyron method) ^{S2}

The unary isotherms for C_2H_2 , C_2H_4 and C_2H_6 of SNNU-520, and C_2H_2 and C_2H_4 of SNNU-520-NH₂ measured at two different temperatures (273 and 298 K) were fitted with excellent accuracy using the single-site Langmuir model:

$$q = q_{sat,A} \frac{b_A p}{1 + b_A p} \tag{S3}$$

The unary isotherms for C_2H_6 of SNNU-520-NH₂ measured at two different temperatures (273 and 298 K) were fitted with excellent accuracy using the single-site Langmuir-Freundlich model.

$$q = \frac{q_{sat,A} b_A p^{\nu A}}{1 + b_A p^{\nu A}} \tag{S4}$$

In eq (S3 and S4), the Langmuir parameters b_A are temperature dependent.

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right) \tag{S5}$$

In eq (S5), E_A is the energy parameter. The isosteric heat of adsorption, Q_{st} , is defined as

$$Q_{st} = -R(T_1 T_2) \left(\frac{\ln p_1 - \ln p_2}{T_1 - T_2} \right)$$
(S6)

where the derivative in the right member of eq (S6) is determined at constant adsorbate loading, q. The calculations are based on the Clausius-Clapeyron equation."

2.3 Selectivity Prediction for Binary Mixture Adsorption

Ideal adsorbed solution theory (IAST)^{S3} was used to predict binary mixture adsorption from the experimental pure-gas isotherms. To perform the integrations required by IAST, the single component isotherms should be fitted by a proper model. The dual-site Langmuir-Freundlich (DSLF) equation was found to be the best fit of the experimental pure isotherms for C_2H_2 , C_2H_4 and C_2H_6 .

$$q = q_{m1} * \frac{b_1 * p^{1/n_1}}{1 + b_1 * p^{1/n_1}} + q_{m2} * \frac{b_2 * p^{1/n_2}}{1 + b_2 * p^{1/n_2}}$$
(S7)

where *p* is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), *q* is the adsorbed amount per mass of adsorbent (mmol g⁻¹), q_m is the saturation capacities of site (mmol g⁻¹), *b* is the affinity coefficients of site (1/kPa), and *n* represent the deviations from an ideal homogeneous surface.

Based on the above equation parameters of pure gas adsorption, the IAST model was used to investigate the separation of C_2H_2/C_2H_4 and C_2H_6/C_2H_4 for SNNU-520 and SNNU-520-NH₂ and the adsorption selectivity is defined by

$$s_{A/B} = \frac{x_A / y_A}{x_B / y_B} \tag{S8}$$

where x_i and y_i are the mole fractions of component *i* (*i* = A and B) in the adsorbed and bulk phases, respectively.

2.4 Gas Equilibrium Adsorption Capacity and Separation Factor (α).

The complete breakthrough of C_2H_2 was indicated by the downstream gas composition reaching that of the feed gas. Based on the mass balance, the amount of gas adsorbed *i* (qi) is calculated from the breakthrough curve using the following:

$$q_i = \frac{C_i V}{m} \times \int_0^t \left(1 - \frac{F}{F_0}\right) dt$$
(S9)

Where q_i is the equilibrium adsorption capacity of gas *i* (cm³ g⁻¹), C_i is the feed gas concentration, *V* is the volumetric feed flow rate (cm³ min⁻¹), *t* is the adsorption time (min), F_0 and *F* are the inlet and outlet gas molar flow rates, respectively, and *m* is the mass of the adsorbent (g).

The separation factor (α) of the breakthrough experiment is determined as:

$$\alpha = \frac{q_1}{q_2} \times \frac{n_1}{n_2}$$
(S10)
(S10)
(S10)

in which yi is the molar fraction of gas i (i = A, B) in the gas mixture.

2.5 Kinetic Selectivity

Diffusional time constants (D', D/r^2) were calculated by the short-time solution of the diffusion equation assuming a step change in the gas-phase concentration, clean beds initially, and micropore diffusion control:

$$\frac{q_t}{q_{\infty}} = \frac{6}{\sqrt{\pi}} \cdot \sqrt{\frac{D}{r^2}} \cdot t$$
(S11)

Where q_t is the gas uptake at time t, q_{∞} is the gas uptake at equilibrium, D is the diffusivity and r is the radius of the equivalent spherical particle. The slopes of q_t/q_{∞} versus \sqrt{t} are derived from the fitting of the plots in the low gas uptake range.

3. Theoretical Section

3.1 Grand canonical Monte Carlo (GCMC) Simulations

The adsorption of molecules in MOF structure was performed using the grand canonical Monte Carlo (GCMC) simulation method. Periodic boundary conditions were applied in all three directions (unit cell: 40.23 Å × 40.23 Å × 20.11 Å). The interatomic interactions were described by the condensed-phase-optimized molecular potentials for atomistic simulation studies (COMPASS) force field. The Ewald & Group summation method has an Ewald accuracy of 10^{-5} kcal·mol⁻¹ when used for calculating electrostatic potential energy. To achieve an equilibrium state, 10^7 Monte Carlo steps were carried out. The framework with a rigid structure was considered. The metropolis scheme was used at a constant loading and constant temperature.

3.2 Molecule Dynamic (MD) Simulations for Density Distribution Maps

The starting SNNU-520 crystallographic structure was collected through single crystal measurements. The TraPPE^{S4} united atom force field^{S5, 6} was applied to describe adsorbate-adsorbate interactions for ethane, ethylene, and acetylene. The bonds in these molecules were flexible and charges were not considered. All calculations were carried out in $1 \times 1 \times 1$ SNNU-520 unit cell simulation volume with periodic boundary conditions (PBCs), which was loaded with 40 ethane, 40 ethylene, and 40 acetylene. Lorentz–Berthelot mixing rules described all adsorbate-framework 12–6 LJ interactions in MD simulations. Lennard–Jones potential interactions were truncated at a spherical radius of 16.5 Å and analytical tail corrections were applied. Ewald summation was used to compute long-range Coulombic interactions with a desired relative error in forces of 10–6. In every case, the simulation volumes used were charge neutral.

MOFs	SNNU-520	SNNU-520-NH ₂	SNNU-521	SNNU-520-NH ₂ -a
Empirical formula	C ₆₀ H ₁₂ In ₈ N ₂₄ O ₄₈	C ₆₀ H ₂₄ In ₈ N ₃₆ O ₄₈	C ₇₆ H ₇₆ N ₃₂ Ni ₈ O ₄₈	C ₆₀ H ₂₄ In ₈ N ₃₆ O ₄₈
Formula weight	2755.50	2935.62	2675.36	2935.71
Temperature/K	153.0	153.0	153.0	293(2)
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	Im-3m	Pm-3n	Im-3	Im-3m
<i>a</i> (Å)	20.0896(10)	20.1065(9)	22.2335(9)	20.2126(2)
<i>b</i> (Å)	20.0896(10)	20.1065(9)	22.2335(9)	20.2126(2)
<i>c</i> (Å)	20.0896(10)	20.1065(9)	22.2335(9)	20.2126(2)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
$V(Å^3)$	8108.0(12)	8128.5(6)	10990.7(13)	8257.8(2)
Ζ	2	2	2	2
$D_{\text{calcd}}(\mathbf{g}\cdot\mathbf{cm}^{-3})$	1.129	1.199	0.808	1.181
μ (mm ⁻¹)	9.476	9.502	1.184	1.163
<i>F</i> (000)	2632.0	2839.9	2728.0	2824.0
2θ for data collection (deg)	6.222 to 136.528	6.22 to 136.54	5.622 to 136.18	4.03 to 61.188
parameters	50	64	56	56
GOF on F ²	1.195	1.115	1.454	1.060
$R_{l}^{a}, wR_{2} [I \ge 2\delta (I)]$	0.0612, 0.2165	0.0544, 0.1661	0.0991, 0.3105	0.0462, 0.1348
R_{l}, wR_{2}^{b} (all data)	0.0679, 0.2334	0.0596, 0.1886	0.1110, 0.3454	0.0568, 0.1410
$ ho_{fin}(\max/\min)$ (e·Å ⁻³)	1.06/-0.89	2.06/-0.96	1.10/-0.55	0.87/-0.45
CCDC number	2262090	2262102	2262091	-

Table S1. Crystal data and structure refinements for SNNU-520, SNNU-520-NH₂, SNNU-521, and SNNU-520-NH₂-a.

 $\overline{{}^{a} R_{l} = \Sigma(|F_{o}| - |F_{c}|) / \Sigma|F_{o}|}. {}^{b}wR^{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})^{2}]^{1/2}.$

MOFs	SNNU-520·C ₂ H ₂	SNNU-520·C ₂ H ₄	SNNU-520·C ₂ H ₆
Empirical formula	$C_{80}H_{31}In_8N_{24}O_{48}$	$C_{85.5}H_{63}In_8N_{24}O_{48}$	$C_{85.7}H_{89.1}In_8N_{24}O_{48}$
Formula weight	3014.85	3113.16	3141.86
Temperature/K	160.00(10)	139.8(3)	160.00(8)
Crystal system	Cubic	Cubic	Cubic
Space group	Im-3m	Im-3m	Im-3m
<i>a</i> (Å)	20.2722(7)	20.3709(3)	20.2513(4)
<i>b</i> (Å)	20.2722(7)	20.3709(3)	20.2513(4)
<i>c</i> (Å)	20.2722(7)	20.3709(3)	20.2513(4)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V(Å3)	8331.1(9)	8453.4(3)	8305.4(5)
Ζ	2	2	2
$D_{\text{calcd}}(\text{g}\cdot\text{cm}^{-3})$	1.202	1.223	1.256
$\mu(\text{mm}^{-1})$	1.153	1.138	1.159
F(000)	2910.0	3040.0	3095.0
2θ for data collection (deg)	4.018 to 61.31	3.998 to 61.22	4.022 to 61.22
parameters	68	50	50
GOF on F ²	1.037	1.107	0.974
R_I^a , wR^2 [I >= 2 δ (I)]	0.0647, 0.1657	0.0443, 0.1299	0.0731, 0.1799
R_1 , wR_2^b (all data)	0.1190, 0.1923	0.0565, 0.1362	0.1055, 0.1919
$\rho_{\rm fin}({ m max/min})~({ m e}\cdot{ m \AA}^{-3})$	1.39/-0.69	0.98/-0.46	1.84/-0.68

Table S2. Crystal data and structure refinements for SNNU-520 \cdot C₂H₂, SNNU-520 \cdot C₂H₄, and SNNU-520 \cdot C₂H₆.

Table S3. The C_2H_2 , C_2H_4 , and C_2H_6 uptakes (cm³ g⁻¹) of SNNU-520 at 1 atm and different temperatures.

	273 K	283 K	298 K	308 K
C_2H_2	149.7	123.7	106.1	79.2
C_2H_4	127.7	109.6	93.2	77.3
C_2H_6	131.1	115.9	104.2	89.6

	273 K	283 K	298 K	308 K
C_2H_2	127.8	110.2	88.9	76.1
C_2H_4	109.8	92.5	79.0	68.8
C_2H_6	112.3	98.3	90.9	79.3

Table S4. The C_2H_2 , C_2H_4 , and C_2H_6 uptakes (cm³ g⁻¹) of SNNU-520-NH₂ at 1 atm and different temperatures.

Table S5. The $-Q_{st}$ value of C_2H_2 , C_2H_4 and C_2H_6 based on the virial method and IAST selectivity of C_2H_2/C_2H_4 (v/v = 50/50) and C_2H_6/C_2H_4 (v/v = 50/50) for SNNU-520 and SNNU-520-NH₂ at 298 K and 1 bar.

Compound	SNNU-520	SNNU-520-NH ₂
$-Q_{st}$ of C ₂ H ₂ (kJ mol ⁻¹)	25.2	29.5
$-Q_{st}$ of C ₂ H ₄ (kJ mol ⁻¹)	24.7	27.9
$-Q_{st}$ of C ₂ H ₆ (kJ mol ⁻¹)	27.6	29.2
IAST Selectivity of C_2H_2/C_2H_4	0.98	1.00
IAST Selectivity of C_2H_6/C_2H_4	1.62	1.69

Compound	C ₂ H ₂ /C ₂ H ₄ (50/50)	C ₂ H ₆ /C ₂ H ₄ (50/50)	Ref
NTUniv-59	17.2 ^[a]	-	S7
BUT-150	1.82	1.15	0.0
BUT-151	1.61	1.26	58
Zn-atz-oba	1.43	1.27	S9
$[Co_3(\mu_3-OH)(tipa)(bpy)_{1.5}]\cdot 3DMF\cdot 6H_2O$	-	1.3	S10
UPC-613	1.39	1.45	S 11
UPC-612	1.05	1.4	511
Azole-Th-1	1.0	1.46	S12
CAU-23	1.5	1.54	S13
ZJNU-115-TPA ^[b]	2.70	1.53	C14
ZJNU-115 ^[b]	2.05	1.56	514
UIO-67-(NH ₂) ₂ ^[c]	2.1	1.7	S15
Al-PyDC	4.3 ^[c]	1.9	S16
UiO-66-CF ₃	1.4	1.9	S17
HIAM-326	1.6	1.9	S18
HIAM-210	2.0	2.0	S19
Zn-trz-ox	2.2	2.1	S20
CuTiF ₆ -TPPY	5.03 ^[c]	2.12 ^[e]	S21
TJT-100 ^[d]	1.8	2.2	S22
$Zn(BDC)(H_2BPZ)$	1.6	2.2	S23

Table S6. Comparison of the IAST selectivity of C_2H_2/C_2H_4 and C_2H_6/C_2H_4 at 298 K and 1 bar with reported MOFs for $C_2H_2/C_2H_4/C_2H_6$ ternary mixtures separation.

Zn(ad)(int)	1.61 ^[c]	2.4 ^[e]	S24
Zr-TCA	5.6 ^[c]	2.72	S25
NPU-1	1.4	1.32	
NPU-2	1.25	1.52	S26
NPU-3	1.32	3.21	
SNNU-520-NH ₂	1.01	1.69	This
SNNU-520	0.98	1.62	work

^[a] $C_2H_2/C_2H_4 = 1/99$ at 308 K. ^[b] $C_2H_2/C_2H_4 = 1/99$ at 1.08 bar. ^[c] $C_2H_2/C_2H_4 = 1/99$. ^[d] $C_2H_2/C_2H_4 = 1/99$ and $C_2H_6/C_2H_4 = 1/99$. ^[e] $C_2H_6/C_2H_4 = 10/90$.

Table S7. Comparison of the uptakes for C_2H_2 , C_2H_4 , and C_2H_6 at 298 K and 1 bar and experimental breakthrough interval time of C_2H_4 from $C_2H_2/C_2H_4/C_2H_6$ (1/1/1) ternary mixture at 298 K and 1 bar for SNNU-520 with literatures.

Compound	C ₂ H ₂ uptake (cm ³ g ⁻¹)	C ₂ H ₄ uptake (cm ³ g ⁻¹)	C ₂ H ₆ uptake (cm ³ g ⁻¹)	Breakthrough separation time (min g ⁻¹) / Total gas flow rate (mL min ⁻¹)	Ref
MOF-808-Bzz	66.8	32.0	49.3	12.2 / 1	S27
NTUniv-59	41.4 ^[a]	32.1 ^[a]	32.6 ^[a]	1.9 / 2 ^[b]	S7
Zn-atz-oba	62	45.5	45.9	1.9 / 2.1	S9
Zn(ad)(int)	~68	~48	52.0	14.8 / 2	S24
CuTiF ₆ -TPPY	81.1	54.2	63.2	11[1] / 2.5	S21
UPC-66-a	~71 ^[m]	~54 ^[m]	~63 ^[m]	18.86 / 2	S28
UPC-613	63.4	51.7	57.1	~12 / 2	011
UPC-612	67.44	62.58	80.11	16 / 2	511
NTUniv-64	106	70	79	8.8 ^[e] / 2	S29
Zn(BDC)(H ₂ BPZ)	100.0	73.6	81.4	6.1 / 7	S23
Al-PyDC	184.6 ^[g]	77.1 ^[g]	94.1 ^[g]	41.2 ^[e,g] / 10	S16
TJT-100	~102	~78	~85	10 ^[d] / 2	S22
Azole-Th-1	~80.7	80.7	100.2	~5 ^[e] / 10	S12
BUT-151	107.5	83.3	89.4	1.2 / 2 ^[k]	S8
ZJNU-115	122.9 ^[c]	84 ^[c]	103.6 ^[c]	$10.6^{[f]} / 2$	S14
CAU-23	105.3	85.1	89.6	~4[1] / 3	S13
HAM-111	108.88	88.79	112.17	0.5 ^[1] / x	S30
NPU-1	114.2	94.08	100.8	2.4 / 2.1	S26
UIO-67-(NH ₂) ₂	132.16 ^[g]	96.77 ^[g]	119.16 ^[g]	13.8 / 1.25	S15
MOF-303	177.9 ^[g]	~112 ^[g]	112.2 ^[g]	19.1 / 1.25 ^[g]	S31
SNNU-520	106.0	93.1	104.1	13 / 1	This work

^[a] at 308 K. ^[b] $C_2H_2/C_2H_4/C_2H_6 = 1/90/9$ at 308 K. ^[c] at 1.05 atm. ^[d] $C_2H_2/C_2H_4/C_2H_6 = 0.5/99/0.5$. ^[e] $C_2H_2/C_2H_4/C_2H_6 = 1/9/90$. ^[f] $C_2H_2/C_2H_4/C_2H_6 = 1/90/9$. ^[g] at 296 K. ^[k] at 273 K. ^[l] the unit is min. ^[m] at 293 K.

Compound	C_2H_4 Productivity ($C_2H_2/C_2H_6/C_2H_4$ ratio)	Reference
SNNU-520	0.36 mmol/g (1/1/1)	This work
HIAM-111	0.001 mmol/g (1/9/90)	S30
HIAM-210	0.039 mmol/g (34/33/33)	S19
Ni-BDC-INA	0.1 mmol/g (1/1/1)	S32
LIFM-XYY-6	0.14 mmol/g (1/90/9)	S33
BUT-150	-	
BUT-151	0.32 mmol/g (1/1/1)	S8
UPC-612	0.47 mmol/g (1/1/1)	011
UPC-613		811
HIAM-326	0.50 mmol/g (1/1/1)	S18
MOF-303	0.55 mmol/g (1/49.5/49.5)	S31
TJT-100	0.69 mmol/g (0.5/0.5/99)	S22
Zn-ATA	0.72 mmol/g (1:10:89)	S34
PCP-FDCA	0.95 mmol/g (1/1/1)	S35
CAU-23	1.12 mmol/g (15/1/1)	S13
Azole-Th-1	1.34 mmol/g (1/9/90)	S12
Zn(ad)(int)	1.43 mmol/g (1/1/1)	S24
Al-PyDC	1.57 mmol/g (1/1/1)	S16
Zn-trz-ox	1.742 mmol/g (1.2/9.3/89.5)	S20
UPC-66-a	2.01 mmol/g (1/1/98)	S28

Table S8. Comparison of the C_2H_4 productivity at 298 K with reported MOFs for $C_2H_2/C_2H_4/C_2H_6$ ternary mixtures separation.



Figure S1. The asymmetric unit of SNNU-520 (H atom have been omitted).



Figure S2. The double disordered $[In_8(HImDC)_{12}]$ cube of SNNU-520 (green: In, blue: N).



Figure S3. The asymmetric unit of SNNU-520-NH₂ (double disordered of N atom for $-NH_2$ and H atom have been omitted).



Figure S4. The 3D structure of SNNU-520-NH₂.



Figure S5. The asymmetric unit (a) and $[Ni_8(HImDC)_{12}]$ cube (b) of SNNU-521 (H atom have been omitted).



Figure S6. The 3D structure of SNNU-521.



Figure S7. a) The $[In_8(HImDC)_{12}]$ cage of SNNU-520. b) The 3D structure of SNNU-520. c) The simplified structure of SNNU-520. d) The $[In_8(AHImDC)_{12}]$ cage of SNNU-520-NH₂. e) The 3D structure of SNNU-520-NH₂. f) The simplified structure of SNNU-520-NH₂. g) The $[Ni_8(HImDC)_{12}]$ cage of SNNU-521. h) The 3D structure of SNNU-521. i) The simplified structure of SNNU-521.



Figure S8. FT-IR spectra of desolvated SNNU-520 and 4,5-dicyanimidazole ligand (a), and desolvated SNNU-520-NH₂ and 2-amino-1H-imidazole-4,5-dicarbonitrile ligand (b).



Figure S9. ¹³C-NMR spectra of activated SNNU-520 and 4,5-dicyanimidazole ligand (a), and activated SNNU-520-NH₂ and 2-amino-1H-imidazole-4,5-dicarbonitrile ligand (b).



Figure S10. ¹³C-NMR spectra of desolveted SNNU-521 and 4,5-imidazoledicarboxylic acid ligand.



Figure S11. PXRD patterns of SNNU-520.



Figure S12. PXRD patterns for simulated and as-synthesized SNNU-520 at scale through reflux.



Figure S13. PXRD patterns of SNNU-520-NH₂.



Figure S14. PXRD patterns of SNNU-521.



Figure S15. PXRD patterns of SNNU-520 for a) soaked in different pH solutions (pH = 3, 6, 8, 10, 11) for 4 days and b) soaked in H_2O for different times (1-5 days).



Figure S16. N_2 adsorption and desorption isotherms (a) and pore size distributions (b) of SNNU-520 after different treatments.



Figure S17. TGA curves of SNNU-520 (a) and SNNU-520- NH_2 (b) before and after solvent exchange, and c) as-synthesized SNNU-521.



Figure S18. PXRD patterns of SNNU-520 a) and SNNU-520-NH₂ b) after heating at 300 and 380 °C compared with simulated and synthesized samples.



Figure S19. Pore size distribution of SNNU-520 and SNNU-520-NH₂ through H-K method.



(c)

Figure S20. Adsorption and desorption isotherms of C_2H_2 (a), C_2H_4 (b), and C_2H_6 (c) of activated SNNU-520-NH₂ at 273, 283, 298, and 308 K.



Figure S21. Adsorption and desorption isotherms of C_2H_2 , C_2H_4 , and C_2H_6 for activated SNNU-521 at 273 K.



Figure S22. The comparison of C_2H_2 uptake at 298 K and 1 bar for SNNU-520 with those MOF for ternary $C_2H_2/C_2H_4/C_2H_6$ mixture separation (*: 296 K, **: 293 K, #: estimated).^{S8, 9, 11-13, 16, 19, 21-24, 26, 27, 29-31, 33-40}



Figure S23. Virial fittings of adsorption isotherms of SNNU-520 at 273 K, 283K, and 298 K for a) C_2H_2 , b) C_2H_4 , and c) C_2H_6 respectively.



Figure S24. Virial fitting of adsorption isotherms of SNNU-520-NH₂ at 273 K, 283K, and 298 K for a) C_2H_2 , b) C_2H_4 , and c) C_2H_6 respectively.



Figure S25. DSLF fit of the C_2H_2 adsorption isotherms at a) 273 K, b) 283 K, c) 298K, and d) 308 K of SNNU-520.



Figure S26. DSLF fit of the C_2H_4 adsorption isotherms at a) 273 K, b) 283 K, c) 298K, and d) 308 K of SNNU-520.



Figure S27. DSLF fit of the C_2H_6 adsorption isotherms at a) 273 K, b) 283 K, c) 298K, and d) 308 K of SNNU-520.



Figure S28. DSLF fit of the C_2H_2 adsorption isotherms at a) 273 K, b) 283 K, c) 298K, and d) 308 K of SNNU-520-NH₂.



Figure S29. DSLF fit of the C_2H_4 adsorption isotherms at a) 273 K, b) 283 K, c) 298K, and d) 308 K of SNNU-520-NH₂.



Figure S30. DSLF fit of the C_2H_6 adsorption isotherms at a) 273 K, b) 283 K, c) 298K, and d) 308 K of SNNU-520-NH₂.



Figure S31. Experimental dynamic breakthrough curves of SNNU-520 at 273 K for a) C_2H_4/C_2H_6 separation (1:1 mixture; total gas pressure of 1 atm; total gas flow of 2 mL min⁻¹) and b) $C_2H_2/C_2H_4/C_2H_6$ separation (1:1:1 mixture; total gas pressure of 1 atm; total gas flow of 1 mL min⁻¹). Experimental dynamic breakthrough curves of SNNU-520-NH₂ at 273 K for c) C_2H_4/C_2H_6 separation (1:1 mixture; total gas pressure of 1 atm; total gas flow of 2 mL min⁻¹) and d) $C_2H_2/C_2H_4/C_2H_6$ separation (1:1:1 mixture; total gas pressure of 1 atm; total gas flow of 2 mL min⁻¹) and d) $C_2H_2/C_2H_4/C_2H_6$ separation (1:1:1 mixture; total gas pressure of 1 atm; total gas flow of 2 mL min⁻¹) and d) $C_2H_2/C_2H_4/C_2H_6$ separation (1:1:1 mixture; total gas pressure of 1 atm; total gas flow of 1 mL min⁻¹) (C, outlet gas concentration; C₀, inlet gas concentration).



Figure S32. Experimental dynamic breakthrough curves in all ranges of SNNU-520 for a-b) C_2H_4/C_2H_6 separation and c-d) $C_2H_2/C_2H_4/C_2H_6$ separation at 273 K and 298 K.



Figure S33. Experimental dynamic breakthrough curves in all ranges of SNNU-520-NH₂ for a-b) C_2H_4/C_2H_6 separation and c-d) $C_2H_2/C_2H_4/C_2H_6$ separation at 273 K and 298 K.



Figure S34. Density maps for C_2H_6 (red), C_2H_4 (blue) and C_2H_2 (green) molecules adsorption in SNNU-520 derived from Monte Carlo simulations with 40 C_2H_6 , 40 C_2H_4 and 40 C_2H_2 molecules per supercell at 298 K. (Note: The presence of blue and red dots in pore | does not mean that ethane and ethylene can enter pore |. Because this is a two-dimensional plan figure, the three types of pores are intersected. Only the green dot in the center can be seen for pore |).



Figure S35. The C_2H_2 -loaded structures of SNNU-520 observed by single-crystal diffraction.

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