

Supplementary Information

Ultramicroporous Metal–Organic Framework with Inert Pore Surfaces for Inversed Separation of Ethylene from C₂ Hydrocarbons Mixtures

Hai-Yu Duan,^a Xiu-Yuan Li,^{*a} Rajamani Krishna^b and Chaozheng He^{*a}

^aShaanxi Key Laboratory of Optoelectronic Functional Materials and Devices, School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an, 710021, P. R. China.

E-mail: lixiuyuan@xatu.edu.cn; hecz2019@xatu.edu.cn

^bVan 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands.

Table S1 Physical properties of C₂H₂, C₂H₄, and C₂H₆

Molecular formula	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
Melting point (K)	189.1	103.9	89.8
Boiling point (K)	189.3	169.4	184.4
Critical temperature (K)	308.3	282.6	305.4
Critical pressure (MPa)	6.191	5.076	4.884
Molecular dimension (Å ³)	3.32×3.34×5.70	3.28×4.18×4.84	3.81×4.08×4.82
Polarizability ×10 ⁻²⁵ (cm ³)	33.3-39.3	42.52	44.3-44.7
Quadrupole moment ×10 ⁻²⁶ (esu cm ²)	7.2	1.5	0.65
Kinetic diameter (Å)	3.3	4.163	4.443

Table S2 Crystal Data and Structure Refinement for **1**.

Complex	1
Molecular Formula	C ₅₄ H ₅₈ Co ₃ N ₆ O ₂₅
Formula Weight	1367.86
Temperature (K)	170.00
Crystal System	Cubic
Space Group	<i>P</i> $\bar{4}3n$
<i>a</i> (Å)	21.5197(3)
<i>b</i> (Å)	21.5197(3)
<i>c</i> (Å)	21.5197(3)
α (°)	90°
β (°)	90°
γ (°)	90°
<i>V</i> (Å ³)	9965.7(4)
<i>Z</i>	8
D _c (g·cm ⁻³)	1.387
<i>F</i> (000)	4200
Reflections collected	28162
Goodness-of-fit on <i>F</i> ²	1.056
<i>R</i> ₁ ^a [<i>I</i> >2σ(<i>I</i>)]	0.0683
w <i>R</i> ₂ ^b [<i>I</i> >2σ(<i>I</i>)]	0.1987

$${}^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad {}^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S3 Selected bond distances (Å) and angles (°) for **1**.

Co(1)-O(1)	2.071(7)	Co(1)-O(2)#1	2.137(7)
Co(1)-O(3)#2	2.077(6)	Co(1)-O(4)#3	2.133(7)
Co(1)-O(6)	2.0528(18)	Co(1)-N(1)	2.154(8)

Symmetry transformations used to generate equivalent atoms: #1 *y*, -*z*+1, -*x*+1; #2 *x*-1/2, *z*-1/2, *y*+1/2; #3 -*y*+1/2, *x*-1/2, -*z*+3

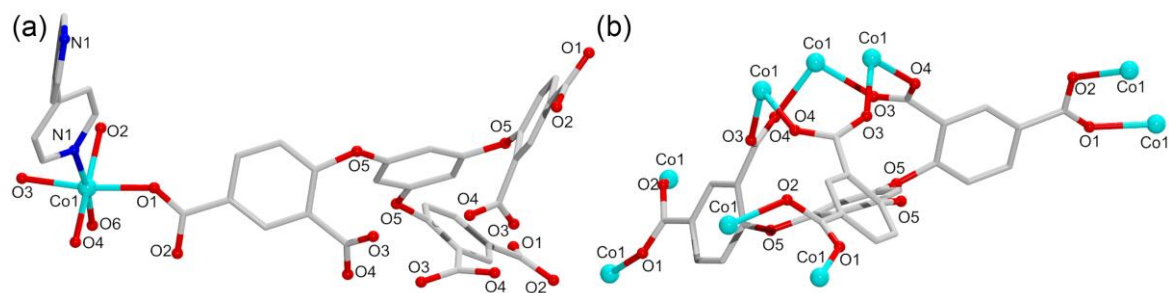


Figure S1. (a) Coordination environment of Co^{2+} ion in **1**; (b) Coordination environment of H_2tipa in **1**.

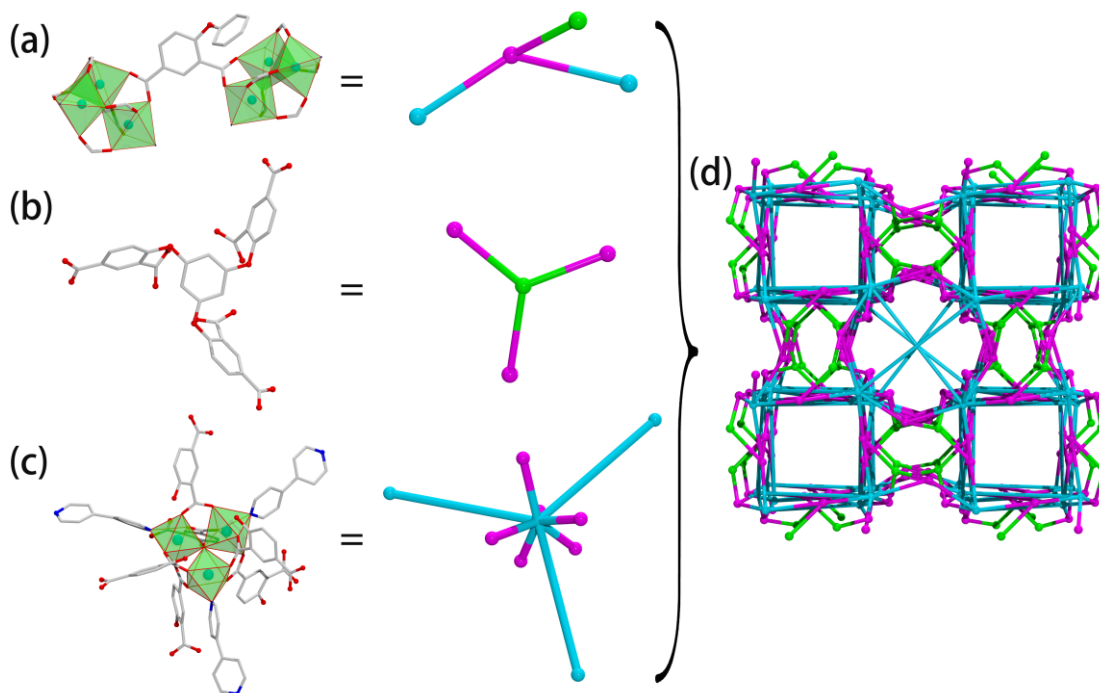


Figure S2. (a-c) Ball-and-stick and schematic representations of 3-connected nodes and 9-connected node, respectively. (d) Schematic representation of a trinodal (3,3,9)-connected network.

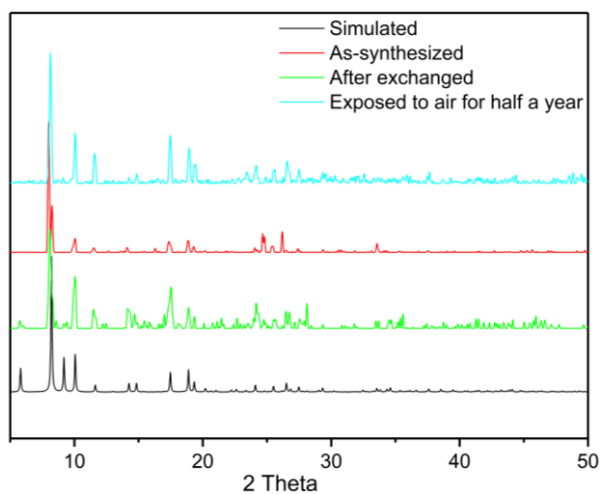


Figure S3. PXRD patterns for as-synthesized, after-exchanged and exposed to air for half a year of **1**.

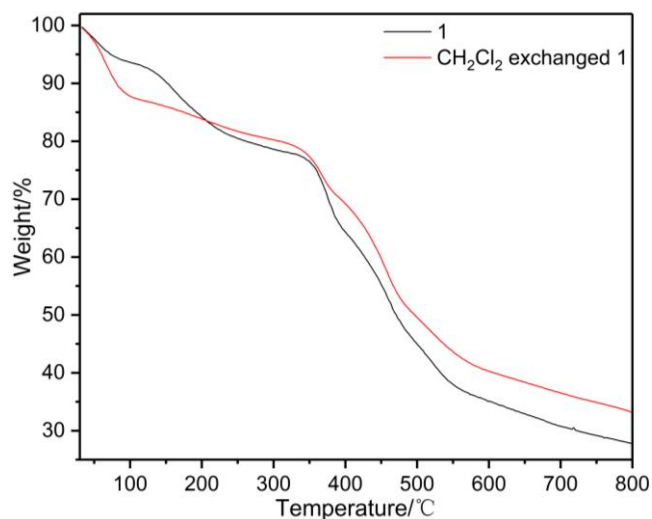


Figure S4. TGA curves for as-synthesized and after CH₂Cl₂ exchanged samples of **1**.

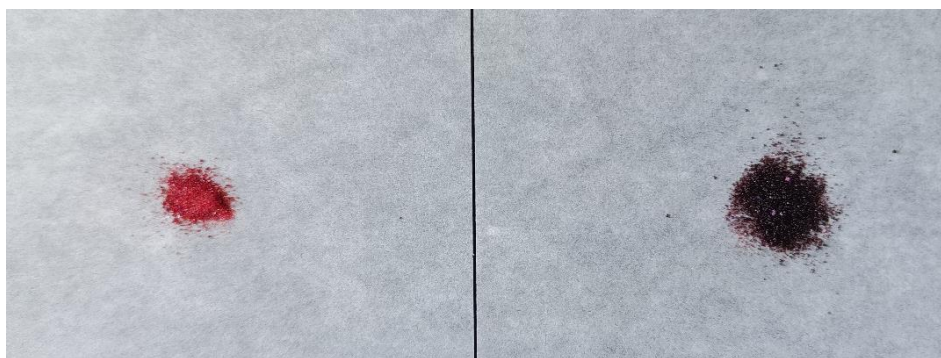


Figure S5. As-synthesized samples of **1** (left) and desolvated samples of **1** (right).

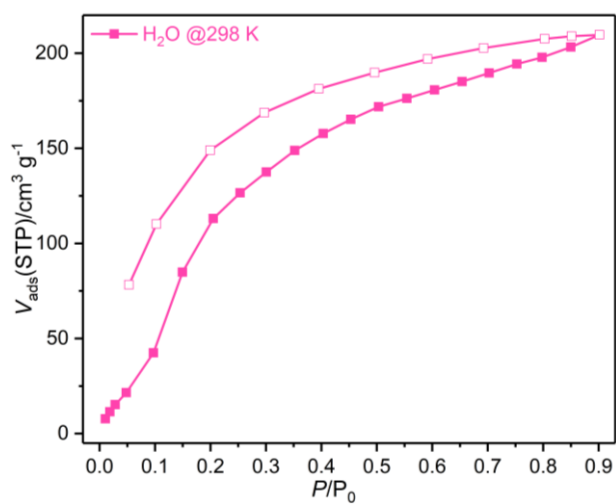


Figure S6. Water adsorption and desorption isotherm of **1a** at 298 K.

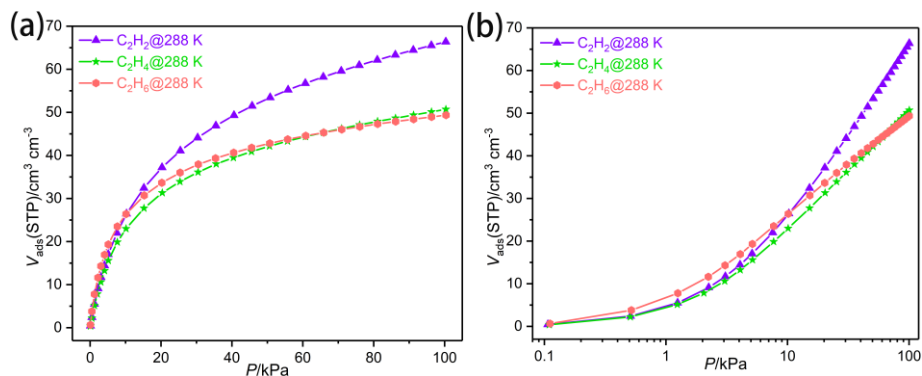


Figure S7. Gas sorption isotherms for C₂ hydrocarbons at 288 K.

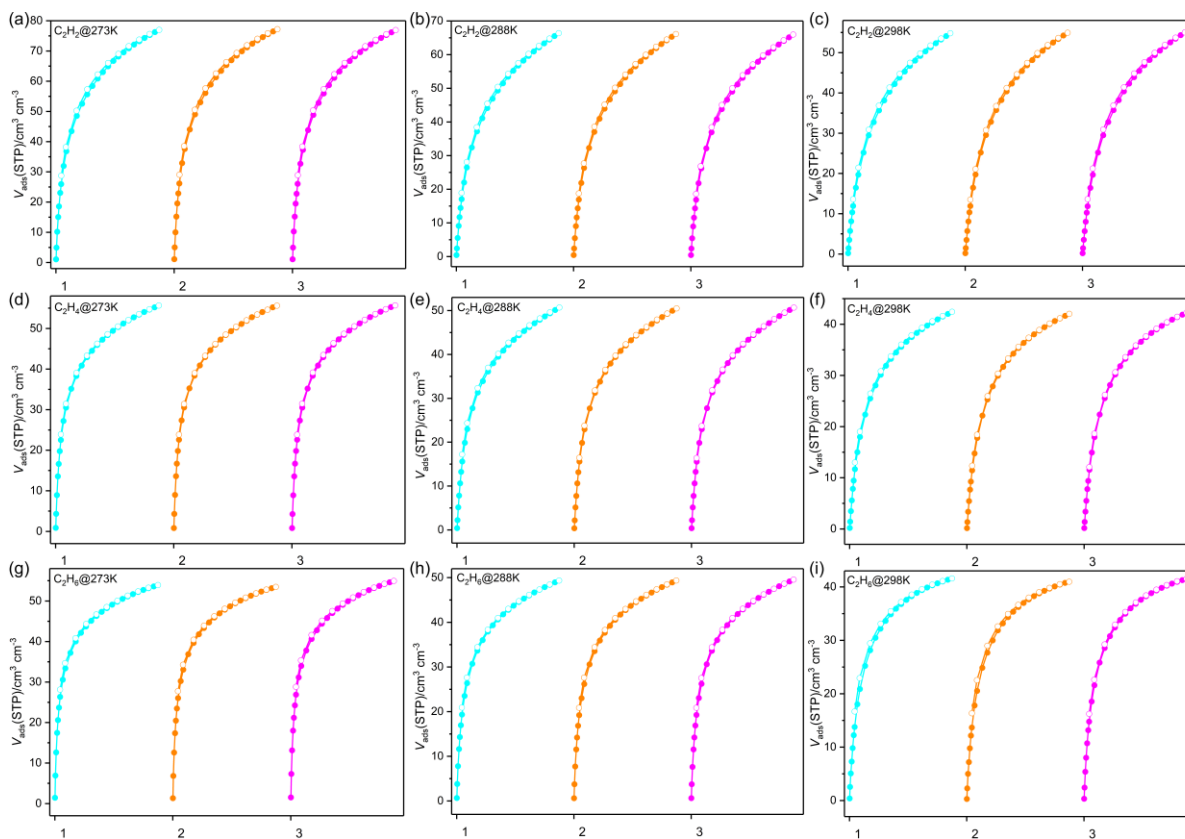


Figure S8. Cyclic gas sorption isotherms for C₂ hydrocarbons at (a), (d), (g) 273 K, (b), (e), (h) 288 K and (c), (f), (i) 298K.

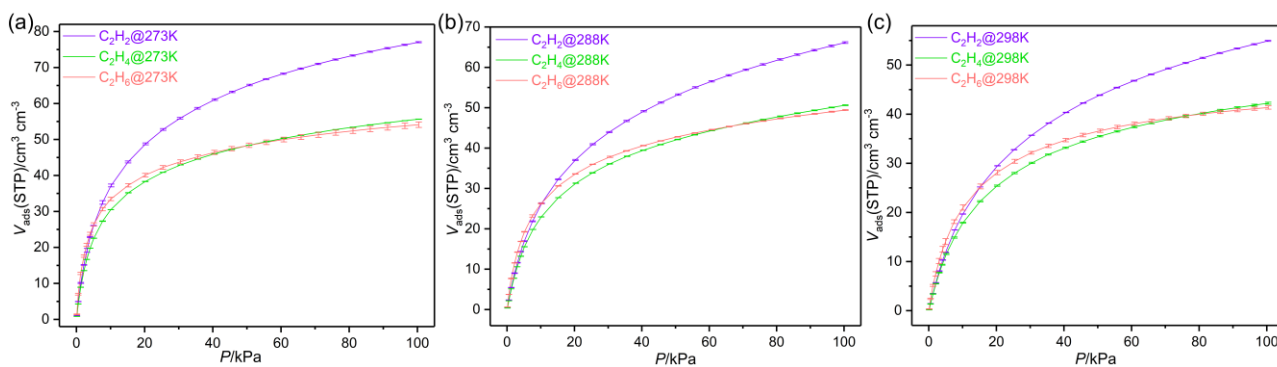


Figure S9. Error analysis of C₂ hydrocarbon at (a) 273 K, (b) 288 K and (c) 298 K.

Calculation of Sorption Heat using Virial 2 Model

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad Q_{st} = -R \sum_{i=0}^m a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1a** at 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i are virial coefficients, and m and n are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

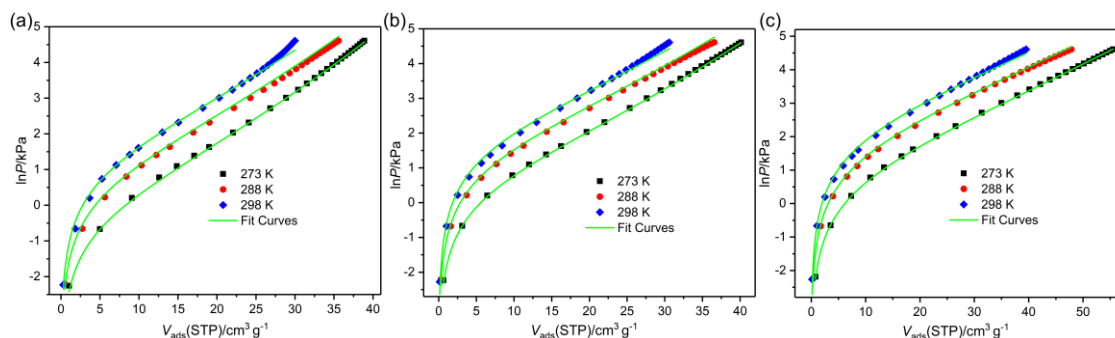


Figure S10. (a) C₂H₆, (b) C₂H₄ and (c) C₂H₂ adsorption isotherms of **1a** with fitting by Virial 2 model.

Table S4 Parameters obtained from the Virial 2 model fitting of the single-component adsorption isotherms at 298 K.

	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
a0	-4482.39984	-4047.95268	-4228.31485
a1	9.34792	7.07374	8.29308
a2	0.37417	0.29991	0.08261
b0	13.92107	12.92457	13.4647
Chi²	9.176E-03	8.046E-03	5.769E-03
R²	0.997	0.998	0.998

Calculation of Sorption Heat using Clausius-Clapeyron Equation

The experimental isotherm data for pure C₂-hydrocarbon were fitted using a Langmuir-Freundlich (L-F) model:

$$q = \frac{a \cdot b \cdot p^c}{1 + b \cdot p^c}$$

Where q and P are adsorbed amounts and the pressure of component i , respectively.

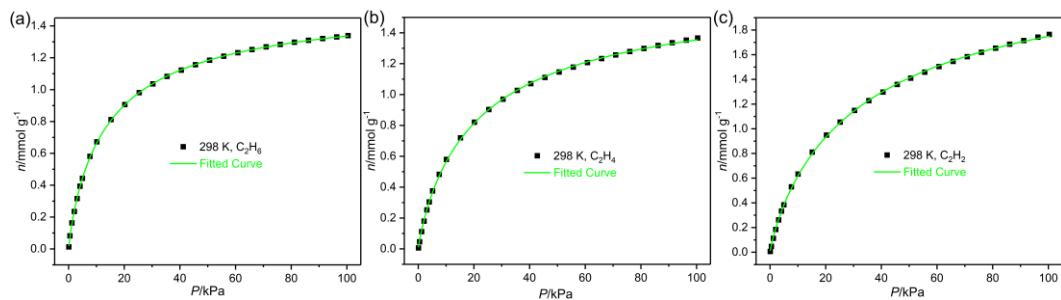


Figure S11. Adsorption isotherms of **1a** fitting by L-F model.

Table S5 Parameters obtained from the Langmuir-Freundlich fitting of the single-component adsorption isotherms.

298 K	C₂H₆	C₂H₄	C₂H₂
a	1.57862	1.71937	2.47231
b	0.09439	0.06408	0.04581
c	0.88335	0.88113	0.86135
Chi²	1.133E-05	5.452E-05	8.078E-05
R²	1.000	1.000	1.000

The isosteric heat of adsorption (Q_{st}) can be calculated via the Clausius-Clapeyron equation:

$$Q_{st} = -R \left[\frac{\partial \ln p}{\partial (1/T)} \right]_N \quad (E1)$$

where p is the pressure, T is the temperature, N is the amount adsorbed, R is the universal gas constant. Integrating equation (E1) gives:

$$(\ln p)_N = -\left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C \quad (E2)$$

where C is a constant. Here an isotherm is first fitted to a high-order polynomial equation to obtain an expression for N as a function of p . Then the values of p at a given N for each T can be interpolated from the fitted equation. At each given N , the isostere plot of $(\ln p)_N$ as a function of $(1/T)$, which is obtained from linear regression, matches with the form of equation (E2), and therefore the Q_{st} values can be computed from the slopes of the isostere plot.

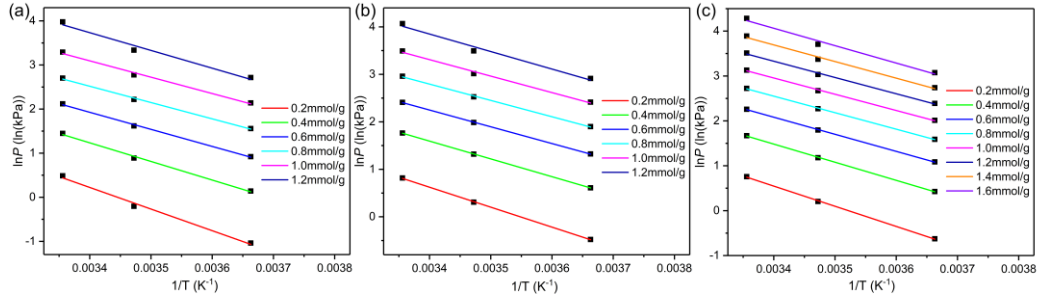


Figure S12. Linear relationship between $\ln P$ and $1/T$ for (a) C_2H_6 , (b) C_2H_4 and (c) C_2H_2 .

Gas Selectivity Prediction via IAST

The experimental isotherm data for pure C2-hydrocarbon were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * p^{c1}}{1 + b_1 * p^{c1}} + \frac{a_2 * b_2 * p^{c2}}{1 + b_2 * p^{c2}}$$

Where q and P are adsorbed amounts and the pressure of component i , respectively.

The adsorption selectivities for binary mixtures defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j * y_i}$$

were respectively calculated using IAST. Where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk.

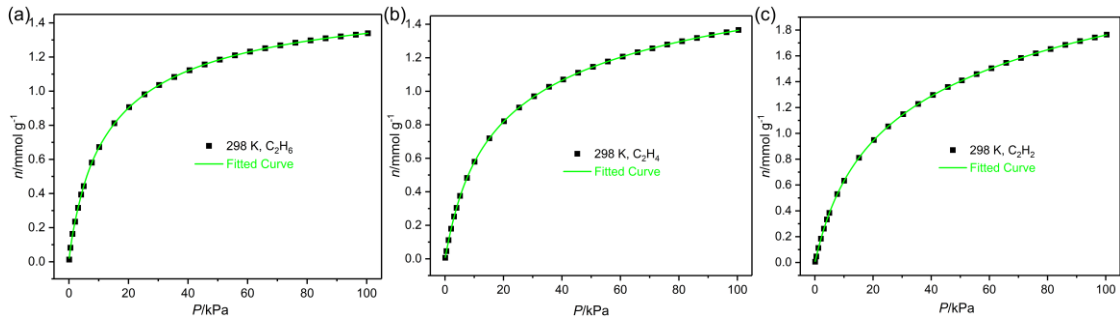


Figure S13. Adsorption isotherms of **1a** fitting by dual L-F model.

Table S6 Parameters obtained from the dual Langmuir-Freundlich fitting of the single-component adsorption isotherms.

298 K	C_2H_6	C_2H_4	C_2H_2
a1	0.03009	0.89496	1.16086
b1	0.00228	0.09147	0.07187

c1	3.78086	1.05394	1.02086
a2	1.57029	0.96401	1.60733
b2	0.0942	0.01588	0.00955
c2	0.86222	0.95055	0.97014
Chi^2	6.408E-06	1.723E-06	1.915E-06
R^2	1.000	1.000	1.000

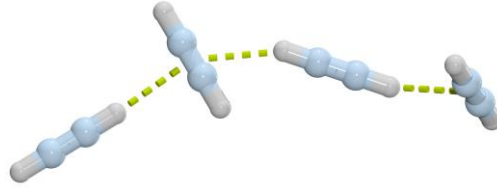


Figure S14. Packing of C₂H₂ molecules in channels at 100 kPa and 298 K.

Transient Breakthrough Simulations

Transient breakthrough simulations were carried out using the methodology described in earlier publications.¹⁻⁵ The following mixtures were simulated:

binary 50/50 C₂H₄/C₂H₆ mixtures

binary 90/10 C₂H₄/C₂H₆ mixtures

ternary 89/10/1 C₂H₄/C₂H₆/C₂H₂ mixtures

For these simulations we choose: length of packed bed, $L = 0.3$ m; cross-sectional area, $A = 1$ m²; volumetric flow rate of gas mixture at the entrance to the bed, $Q_0 = 0.04$ m³ s⁻¹; voidage of the packed bed, $\varepsilon = 0.4$.

The total volume of the bed is $V_{bed} = LA$. The volume of MOF used in the simulations is $V_{ads} = LA(1 - \varepsilon)$. It

is important to note that the volume of adsorbent, V_{ads} , includes the pore volume of the adsorbent material. If

ρ is the crystal framework density, the mass of the adsorbent in the bed is

$m_{ads} = (1 - \varepsilon) \times (L \text{ m}) \times (A \text{ m}^2) \times (\rho \text{ kg m}^{-3})$ kg. The dimensionless concentrations in the exit, c_i/c_{i0} are

plotted as a function of the parameter $\frac{(Q_0 = \text{flow rate L s}^{-1}) \times (\text{time in s})}{(\text{kg MOF packed in tube})} = \frac{Q_0 t}{m_{ads}} = \text{L kg}^{-1}$.

c_i molar concentration of species i , mol m⁻³

c_{i0}	molar concentration of species i in fluid mixture at inlet, mol m ⁻³
Q_0	volumetric flow rate of gas mixture, m ³ s ⁻¹
L	length of packed bed adsorber, m
m_{ads}	mass of adsorbent in packed bed, kg
t	time, s
T	absolute temperature, K
ε	voidage of packed bed, dimensionless
ρ	framework density, kg m ⁻³

GCMC Simulation Methodology

Grand Canonical Monte Carlo (GCMC) simulations were performed to assess adsorption performance. The 2×2×2 supercell was used for the simulations. The partial charges for atoms of the framework were derived from QEq method.⁶ All the parameters for atoms of MOF except metal atoms were modeled with the DREIDING forcefield, while metal atoms were modeled with the universal forcefield.^{7,8} The LJ potential parameters for guests were taken from the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) force field.⁹ A cutoff distance of 10.5 Å was used for LJ interactions, and the Coulombic interactions were calculated by using Ewald summation. For each run, the 5 × 10⁶ equilibration steps, 5 × 10⁶ production steps were employed.

Table S7 The partial charges for atoms of the framework.

Atoms	Charges	Atoms	Charges
Co1	1.236422	H6A	0.1966151
O1	-0.5497197	C7	-0.2122157
O2	-0.5309756	H7	0.1416356
O3	-0.5241014	C8	0.526795
O4	-0.5717756	C9	0.2056871
O5	-0.5834603	C10	-0.078951
O6	-0.5438796	H10	0.1181861
H6	0.2732708	C11	0.02673708
N1	-0.2540275	H11	0.1450907
C1	0.5537508	C12	-0.1562251

C2	-0.003346623	H12	0.1200169
C3	-0.1856025	C13	0.02374584
H3	0.1350813	C14	-0.1435138
C4	0.01159217	H14	0.1274724
C5	0.2757868	C15	0.02096594
C6	-0.1145076	H15	0.1330442

References

- (1) Krishna, R. The Maxwell-Stefan Description of Mixture Diffusion in Nanoporous Crystalline Materials. *Microporous Mesoporous Mater.* **2014**, *185*, 30-50.
- (2) Krishna, R. Methodologies for Evaluation of Metal-Organic Frameworks in Separation Applications. *RSC Adv.* **2015**, *5*, 52269-52295.
- (3) Krishna, R. Screening Metal-Organic Frameworks for Mixture Separations in Fixed-Bed Adsorbers using a Combined Selectivity/Capacity Metric. *RSC Adv.* **2017**, *7*, 35724-35737.
- (4) Krishna, R. Methodologies for Screening and Selection of Crystalline Microporous Materials in Mixture Separations. *Sep. Purif. Technol.* **2018**, *194*, 281-300.
- (5) Krishna, R. Metrics for Evaluation and Screening of Metal-Organic Frameworks for Applications in Mixture Separations. *ACS Omega* **2020**, *5*, 16987–17004.
- (6) Rappe, A. K.; Goddard, W. A. Charge Equilibration for Molecular Dynamics Simulations. *J. Phys. Chem.* **1991**, *95*, 3358-3363.
- (7) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. DREIDING: a Generic Force Field for Molecular Simulations. *J. Phys. Chem.* **1990**, *94*, 8897-8909.
- (8) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024-10035.
- (9) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225-11236.