

Supporting Information

A Copper-Based Metal-Organic Framework with Suitable Pore Environment for Effective Ethylene Purification

Xiaolai Zhang, ^{*a} Mingyue Fu, ^b Hongyan Liu, ^b Yutong Wang, ^{*b} Yecheng Zou, ^c Li Wang, ^c
Chenhao Li, ^a Yong Lu, ^a Liangliang Zhou ^a and Xiangyu Cui ^a

Email: zhangxlai@sdu.edu.cn; 1067746283@qq.com.

Contents

Section 1. Experimental Section

Section 2. Crystal data, structure and characterization of Complex 1

Section 3. Simulation and calculation for Q_{st} by Clausius-Clapeyron equation

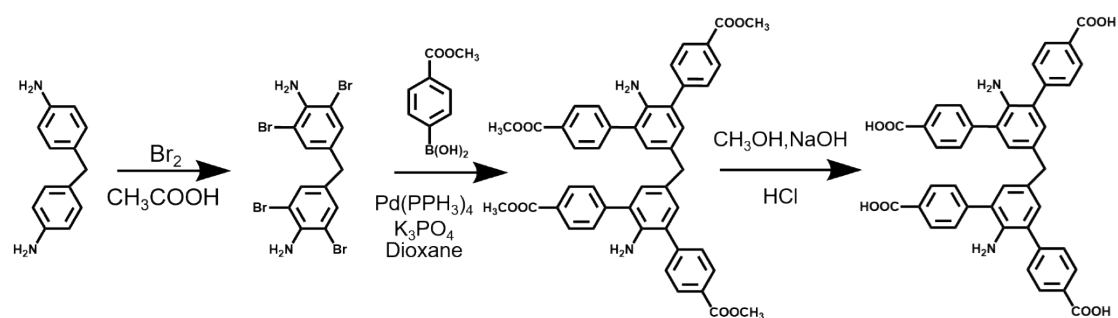
Section 4. Simulation and calculation for gas selectivity by IAST methods

Section 1. Experimental Section

1.1 Materials and characterizations.

All chemical reagents used were available from chemical suppliers and were not purified. The powder XRD diffractograms (PXRD) were acquired on the Panalytical X-Pert PRO diffractometer (Cu-K α). Thermogravimetric analysis (TGA) measurement was conducted on the Mettler Toledo TGA instrument under the N₂ atmosphere within the 40-900 °C region with a heating speed of 10 °C /min. Infrared (IR) spectrum was obtained on the Nicolet 330 FTIR Spectrometer within the range of 4000-400 cm⁻¹. Elementary analyses (C, H, N) were performed on the CE instruments EA 1110 elemental analyzer.()

1.2 Synthesis of L-CH₂¹⁻²



Scheme S1. Synthetic procedures of the L-CH₂ ligand

1.2.1 4,4'-methylenebis(2,6-dibromoaniline)

Bromine (2.0 mL, 40 mmol) was added to acetic acid (5 ml) at room temperature and then slowly added dropwise to acetic acid (50 mL) with 4,4'-methylenedianiline (1.98 g, 10 mmol) The reaction was stirred at 35 °C for 10 min and then poured into cold water (200 mL). It was filtered, washed with cold water, dried and crystallized from ethyl acetate. Yield: 3.85 g, 7.5 mmol, 75%. ¹H NMR (CDCl₃) δ 7.16 (s, 4H) ppm, 3.66 (s, 2H) ppm. Anal. Calc. for C₁₃H₁₀Br₄N₂ (mw513.85): C, 30.39; H, 1.96; Br, 62.20; N, 5.45. Found: C, 29.78; N, 5.33; H, 1.53; Br, 62.33.

1.2.2 5',5'''-methylenebis(2'-amino-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate)

Methyl 4-boronobenzoate (4.32 g, 24 mmol), 4,4'-methylenebis(2,6-dibromoaniline) (2.56 g, 5 mmol), K₃PO₄ (10.64 g, 40 mmol) and Pd(PPh₃)₄ (0.3 g, 0.26 mmol) were placed in a 500 ml two-necked round bottom flask under N₂ atmosphere. The flask was further charged with 220 mL dry 1,4-dioxane, and heated for 50 h. After cooling down to room temperature, the solvent was removed followed by the addition of water. The water phase was washed with CH₂Cl₂. The mixed organic phase was then dried by MgSO₄. After the solvent was removed, the crude product was purified by column chromatography with CH₂Cl₂ as the eluent. Yield 88%. ¹H NMR (400 MHz, CDCl₃) δ 3.91(s, 2H), 3.94(s, 12H), 7.02(s, 4H), 7.56(d, 8H), 8.11(d, 8H) ppm. Anal. Calc. for C₄₅H₃₈NO₈ (mw 734.81): C, 73.56; H, 5.21; N, 3.81; O, 17.42. Found: C, 73.27; H, 5.55; N, 3.57.

1.2.3 5',5'''-methylenebis(2'-amino-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid)

Tetramethyl 5,5''-methylenebis(2'-amino-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate) (3.67 g, 5 mmol) was dissolved in 60 mL MeOH followed by the addition of 60 mL 2 M KOH aqueous solution. The mixture was stirred at 60 °C overnight. The organic phase was removed, while the aqueous phase was acidified with diluted hydrochloric acid. The yellow precipitate was further filtered and washed with water for several S10 times. Yield 98%. ¹H NMR (400 MHz, DMSO-d₆) δ 8.02 (d, 8H), 7.59(d, 8H), 7.07(d, 4H) ppm. Anal. Calc. for C₄₁H₃₀N₂O₈ (mw 678.70): C, 72.56; H, 4.46; N, 4.13; O, 18.86. Found: C, 71.78; N, 3.98; H, 4.27.^{1,2}

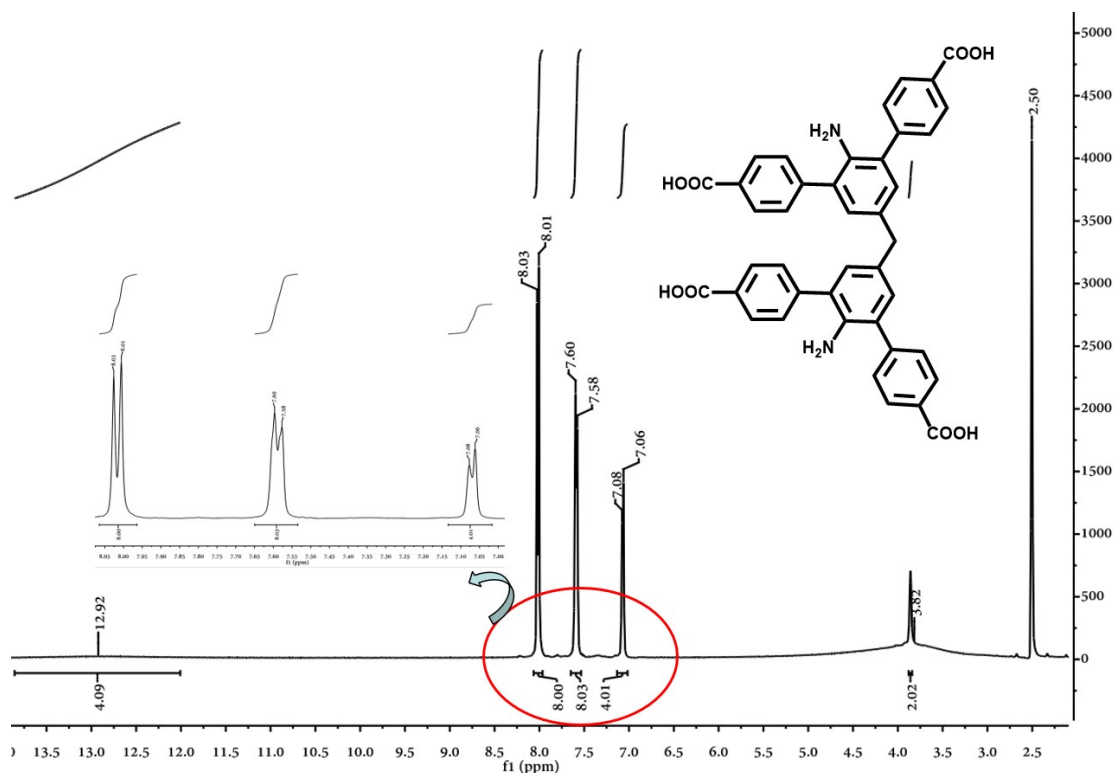


Figure S1. ¹H NMR of L-CH₂.

1.3 Synthesis of Complex 1.

A mixture of L-CH₂ (0.005 g, 0.007mmol) and Cu(NO₃)₂·6H₂O (0.020 g, 0.077mmol) was dissolved in 3ml solution of DMA/EtOH/H₂O (5/2/1) and sealed in a 10 mL glass vial reactor. The vial was heated to 100 °C in 40 min, and maintained at 100 °C for 1440 min. After slowly cooling down to ambient temperature at a speed of 0.1 °C /min, the crystals were collected and then rinsed with DMA/EtOH/H₂O (5/2/1). After dried at ambient condition, the blue block crystals were obtained with a yield of 81% based on copper. The elementary analysis calcd (%) for **Complex 1**: C 58.9; H 5.05; N 5.61. Found: C 61.0; H 5.10; N 5.80. IR (KBr, cm⁻¹): 1611 (s), 1381 (s), 1377 (s), 1222 (m), 725 (m), 627 (w), 583 (w).

1.4 Crystal structure determination.

The Single crystal X-ray diffraction data were collected with the Agilent Technologies SuperNova diffractometer equipped with the graphite monochromatic Cu K α radiation.

The structure was solved by means of the Superflip structure solution program employing the charge flipping method and refined by way of the ShelXL refinement package employing the least squares minimization method. The structure was anisotropically treated, while all hydrogen atoms were located in the calculated ideal positions and refined as riding on respective nonhydrogen atoms.³

1.5 Gas sorption measurements.

The activated samples were prepared by immersing the as-synthesized **Complex 1** in the chromatographic grade CH₃OH and CH₂Cl₂ to exchange solvent. After dried at ambient atmosphere, the samples were heated at 80°C under vacuum for 5 hours. The gas adsorption experiments including N₂ sorption at 77 K as well as the low-pressure C₂H₂, and C₂H₄ sorption experiments at 273 K and 298 K were performed with the help of the JW-BK200 surface area analyzer. The Brunauer-Emmett-Teller (BET) specific surface area and the corresponding pore size distribution were calculated based on N₂ adsorption isotherm at 77 K.

1.6 Breakthrough experiments.

The separation experiments of C₂H₂/C₂H₄ (1/99,10/90,50/50) were completed using fixed beds. Before the experiment, the as-synthesized sample was heated at 80 °C for 12 h accompanied by the He flow (2 ml min⁻¹) for activation. 0.8438 g of activated crystal **Complex 1** was packed into the stainless steel column as the adsorbent bed, and the gas mixture was led into the column at 298K.

1.7 Adsorption sites simulation based on GCMC.

The Grand Canonical Monte Carlo (GCMC) calculations, performed by SORPTION code embedded in the Material Studio software, were carried out to study the C₂H₂/C₂H₄ adsorption capacity of Complex 1 at given adsorption 298 K and 1 atm pressure. The atomic locations were derived from the experimental crystal data. In view of the size of the task to complete the calculations using a whole MOF unit cell, the MOF framework is not geometrically optimized. Periodic boundary conditions were applied in three dimensions. The favorable adsorption sites were simulated by the locate task. In the simulations, we have modeled the framework and gas molecule as rigid and the universal force field (UFF) was applied. Specifically, the van der Waals interactions with a cutoff of 18.5 Å were depicted by the Lennard-Jones potential.

Section 2. Crystal data, structure and characterization of Complex 1

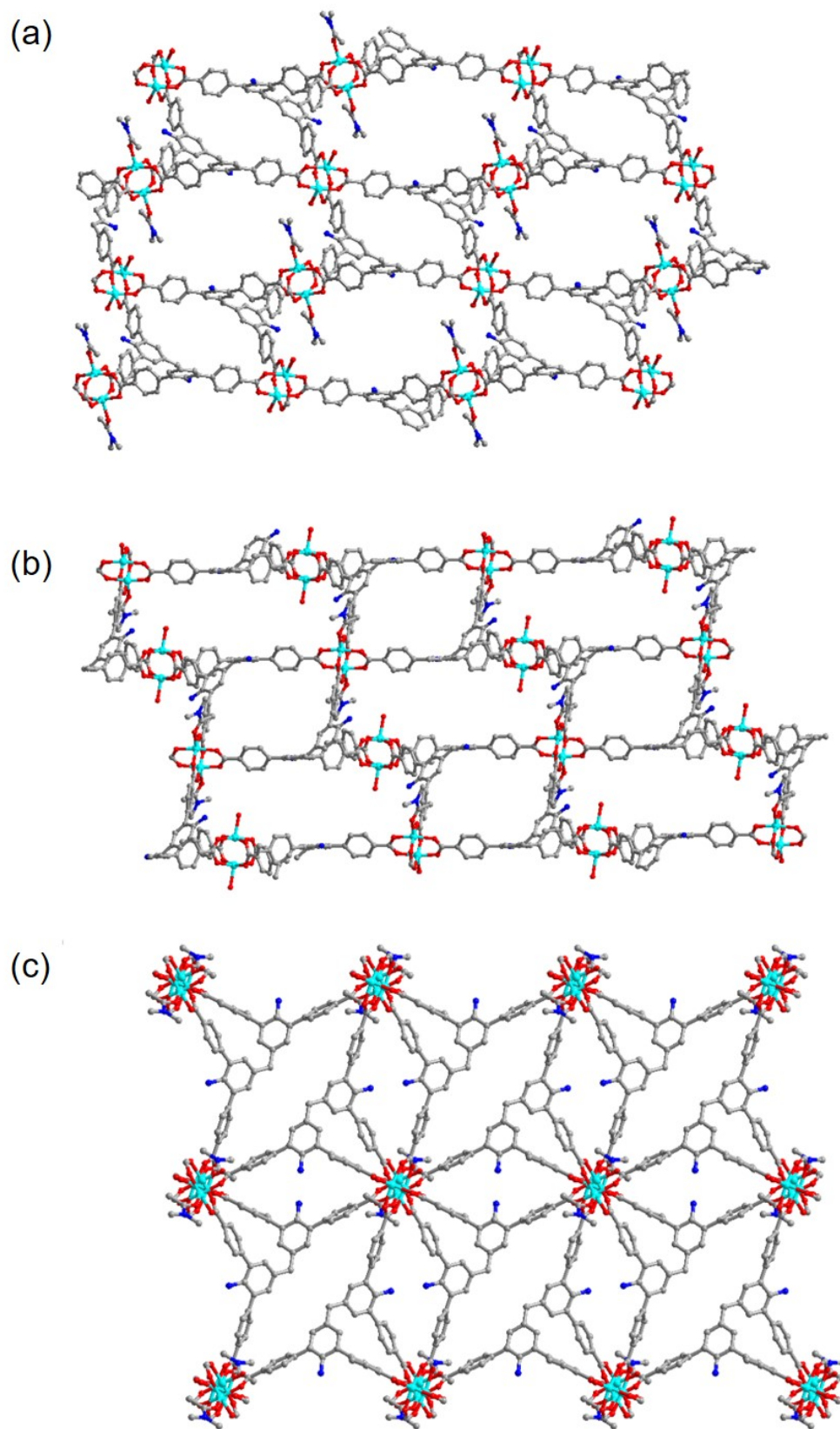
Table S1. Crystal data and structure refinement of **Complex 1**

Identification code	Complex 1
Empirical formula	C _{24.5} H ₂₃ CuN ₂ O _{5.5}
CCDC	2069515
Formula weight	496.99
Temperature/K	150.03(10)
Crystal system	triclinic
Space group	P-1
a/Å	16.5521(5)
b/Å	17.8898(5)
c/Å	20.2377(6)
α /°	110.392(3)
β /°	101.931(3)
γ /°	91.093(2)
Volume/Å ³	5468.5(3)
Z	4
D _c /g cm ⁻³	0.604
μ /mm ⁻¹	0.417
F(000)	1028.0
2 θ range for data	7.238 to 141.318
Reflections collected	37273
Independent reflections	20071 [R _{int} = 0.0706, R _{sigma} = 0.0908]
Data/restraints/parameters	20014/6/604
Goodness-of-fit on F ²	1.021
Final R indexes [I ≥ 2 σ]	R1 = 0.0964, wR2 = 0.2703
Final R indexes [all data]	R1 = 0.1223, wR2 = 0.2986
Largest diff. peak/hole /e	1.15/-0.71

Table. S2 Selected bond lengths (Å) for **Complex 1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu2	Cu2 ¹	2.6369(11)	Cu1	Cu1 ²	2.6569(11)
Cu2	O5	1.957(3)	Cu1	O2	1.955(3)
Cu2	O6	1.984(3)	Cu1	O1	1.969(3)
Cu2	O8	1.954(3)	Cu1	O3 ²	1.961(3)
Cu2	O7	1.964(3)	Cu1	O4	1.953(3)
Cu2	O10	2.123(3)	Cu1	O9	2.135(3)

¹2-X,-1-Y,-Z; ²2-X,1-Y,1-Z; ³1-X,-Y,-Z; ⁴1+X,-1+Y,+Z; ⁵-1+X,+Y,+Z; ⁶-1+X,1+Y,+Z; ⁷1+X,+Y,+Z



Fig

ure S2. Three-dimensional stacking of **Complex 1** along the a, b, and c axes.

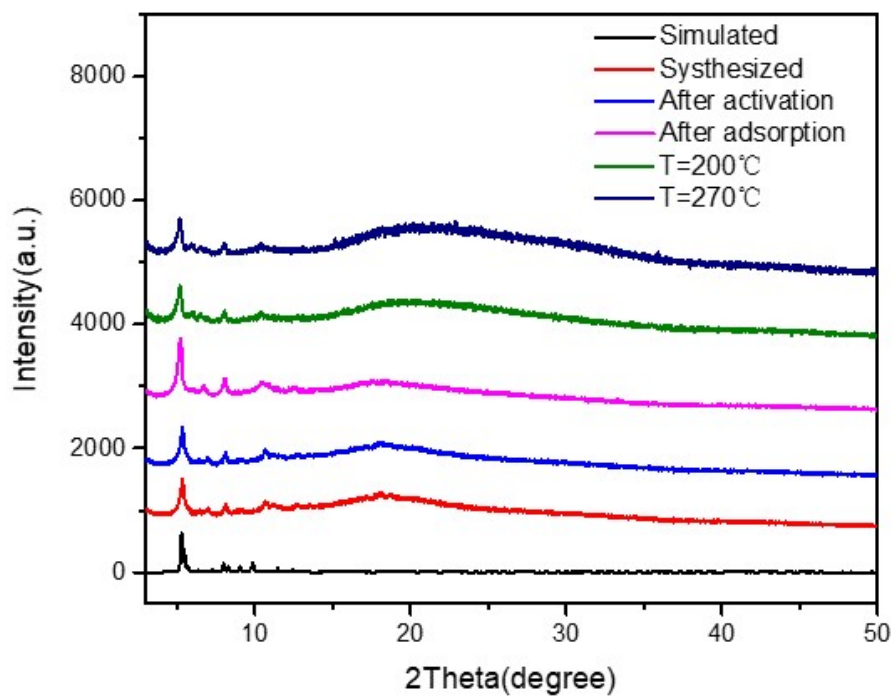


Figure S3. PXRD spectrum of **Complex 1** sample.

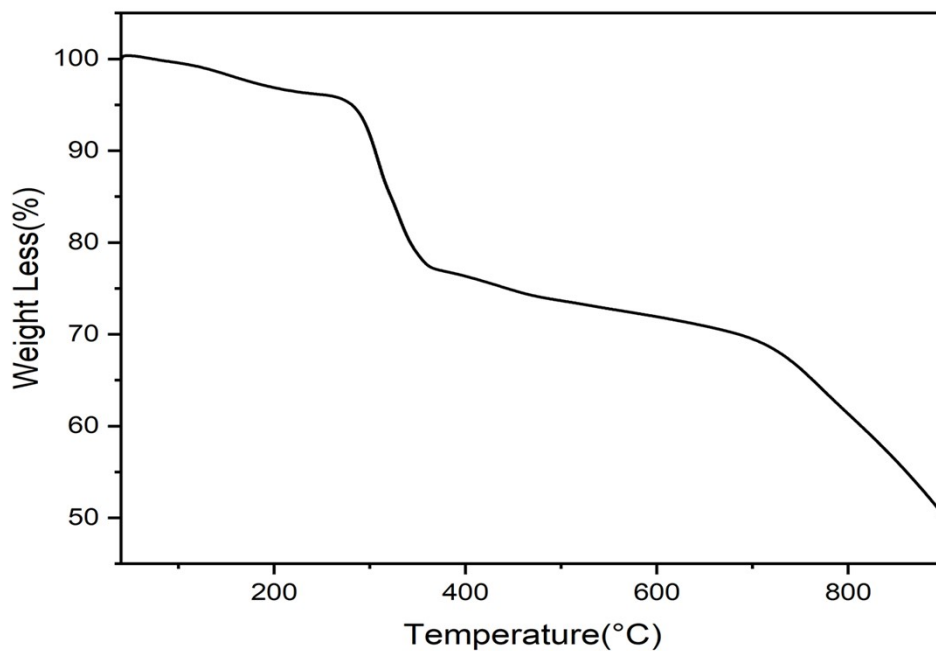


Figure S4. Thermogravimetric spectrum of **Complex 1** sample.

Section 3. Simulation and calculation for Q_{st} by Clausius-Clapeyron equation

Isosteric heat of adsorption (Q_{st})

A Virial equation comprising of the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for C_2H_2 and C_2H_4 in **Complex 1**, which measured at three different temperatures 273K and 293 K.

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N_i + \sum_{j=0}^n b_j N_j$$

Here, P is the pressure expressed in mmHg, N is the amount absorbed in mmol g^{-1} , T is the temperature in K, a_i and b_j are virial coefficients, and m , n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased till the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit. And the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of absorption using the following expression:

$$Q_{st} = -R \sum_{i=0}^m a_i N_i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat enthalpy of C_2H_2 and C_2H_4 sorption for **Complex 1** in this manuscript are determined by using the sorption data measured in the pressure range from 0-1 bar (at 273 K and 293 K).

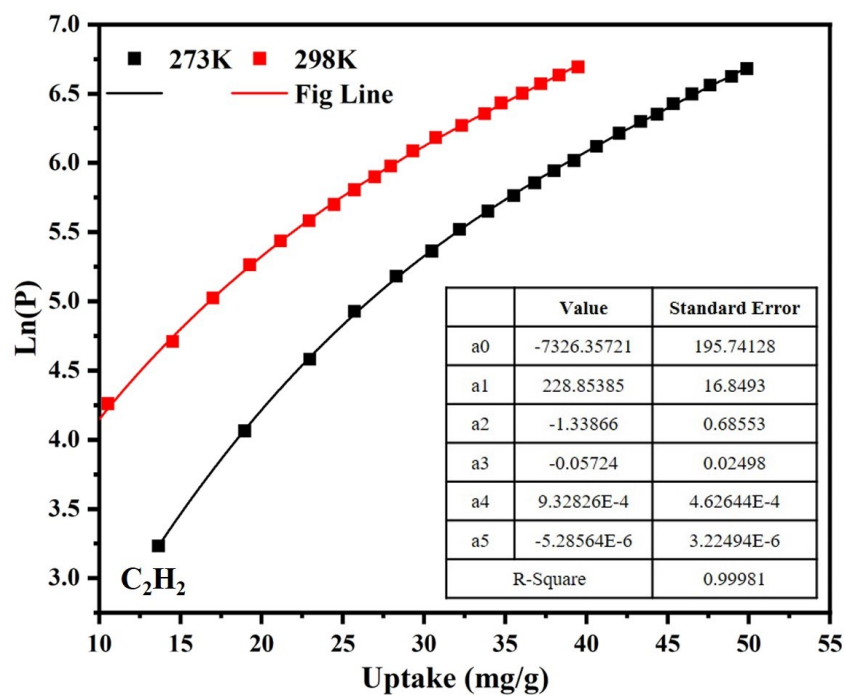


Figure S5. The parameters and optimized adsorption isotherms for calculated Q_{st} of C_2H_2 using a variant of the Clausius-Clapeyron equation.

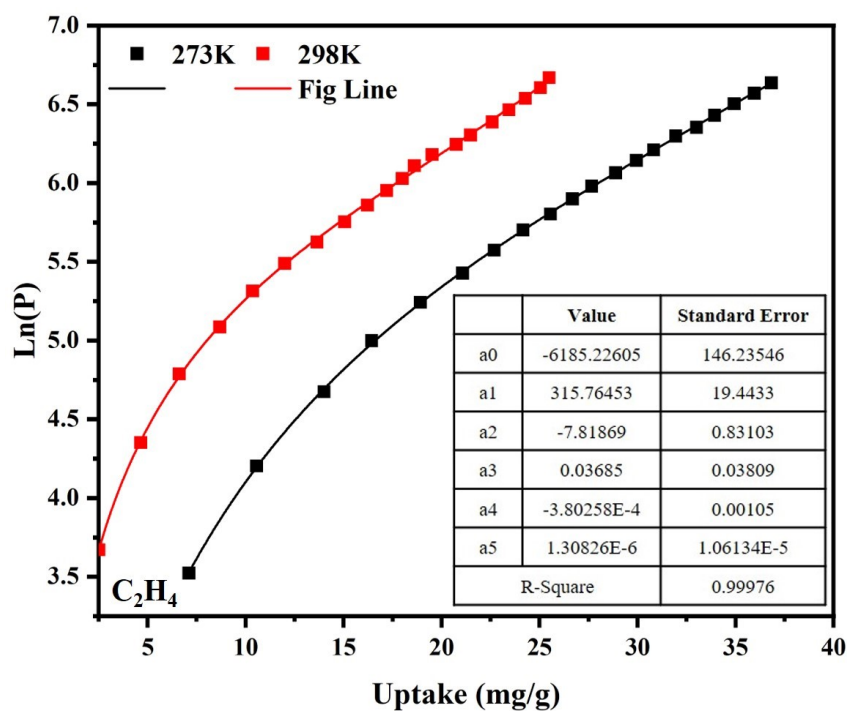


Figure S6. The parameters and optimized adsorption isotherms for calculated Q_{st} of C_2H_4 using a variant of the Clausius-Clapeyron equation.

Section 4. Simulation and calculation for gas selectivity by IAST methods.

IAST calculations of adsorption selectivities

The selectivity of preferential adsorption of component 1 (C_2H_2) over component 2 (C_2H_4) can be defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

Where q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture, and p_1 and p_2 are the component partial pressures. The component loadings and adsorption selectivity S_{ads} for 50/50 $C_2H_2(1)/C_2H_4(2)$ mixtures in **Complex 1** at 293 K were determined using IAST.

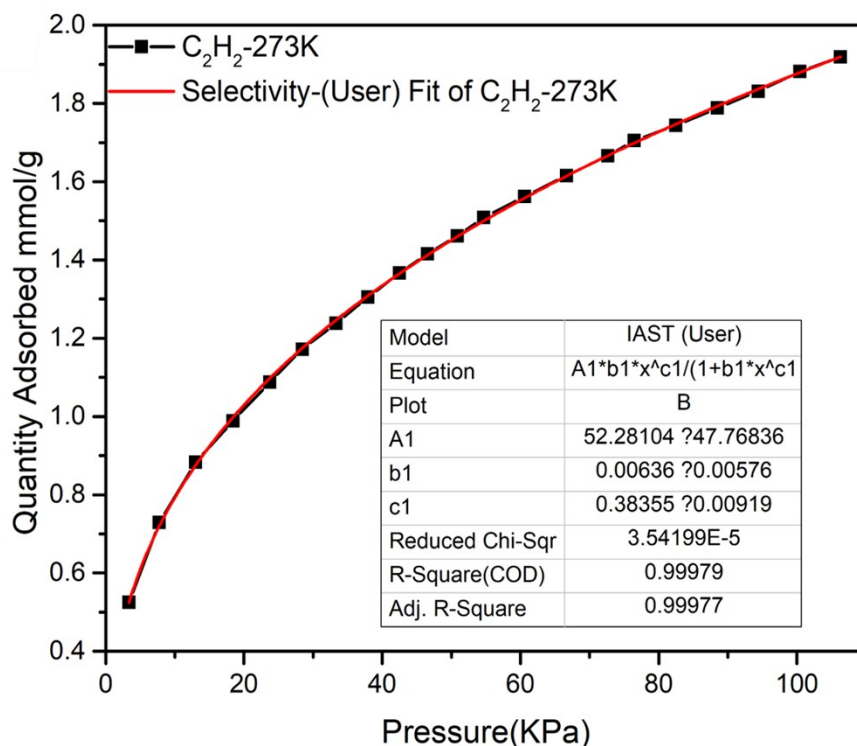


Figure S7. The details of the Virial equation (solid line) fitting the C_2H_2 adsorption data of **Complex 1** at 273K using the IAST method.

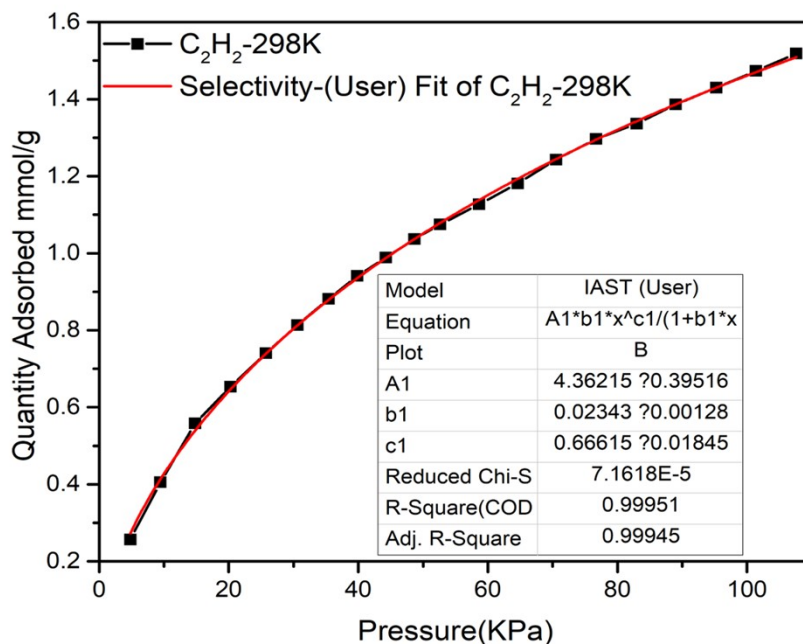


Figure S8. The details of the Virial equation (solid line) fitting the C_2H_2 adsorption data of **Complex 1** at 298K using the IAST method.

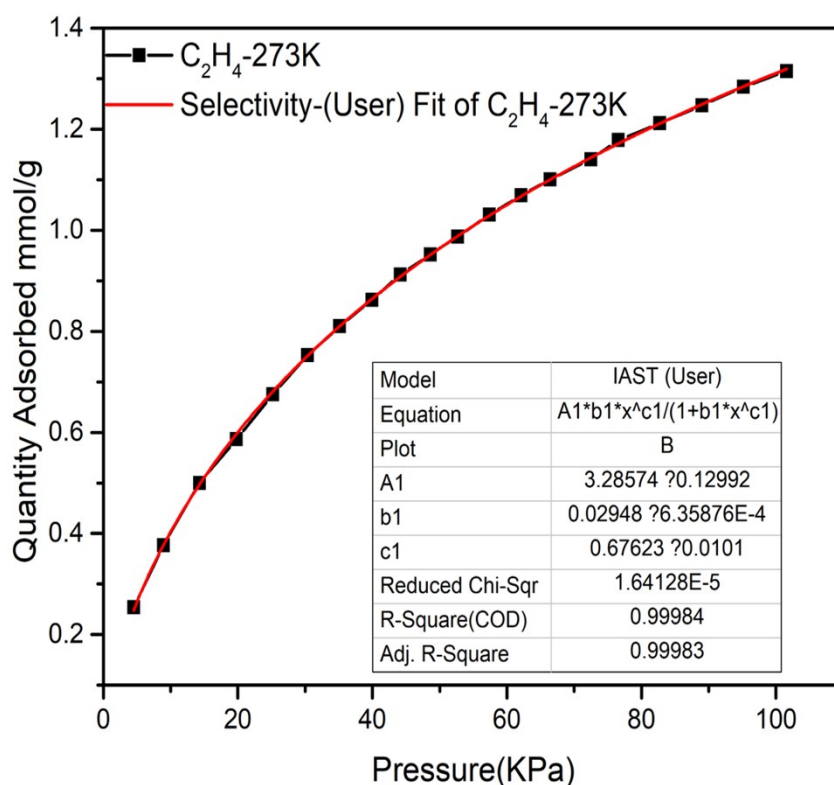


Figure S9. The details of the Virial equation (solid line) fitting the C_2H_4 adsorption data of **Complex 1** at 273K using the IAST method.

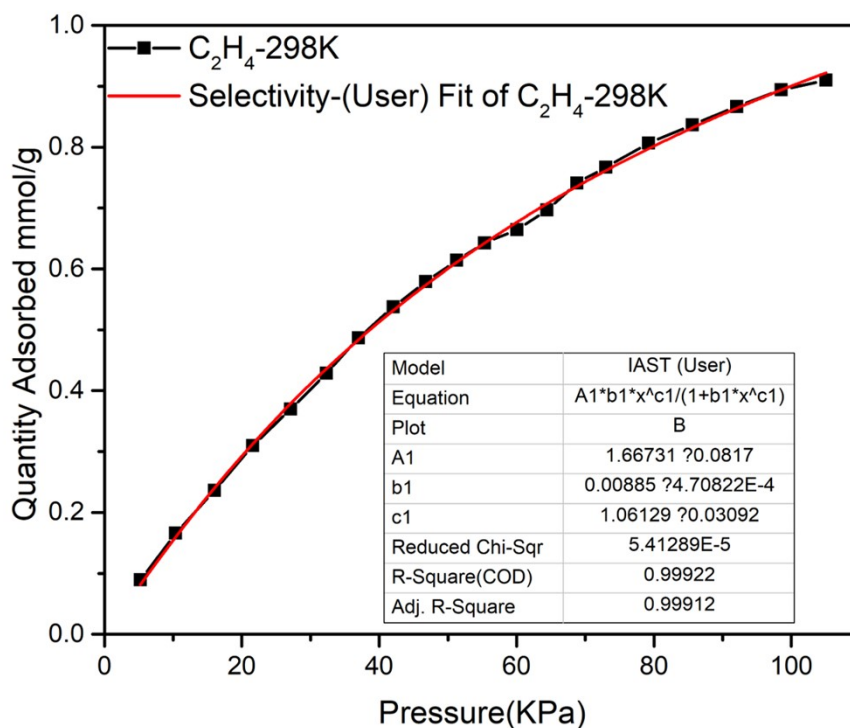


Figure S10. The details of the Virial equation (solid line) fitting the C_2H_2 adsorption data of **Complex 1** at 298K using the IAST method.

References

- [1] Y. T. Wang, L. Feng, K. Zhang, K. Y. Wang, W. D. Fan, X. K. Wang, B. B. Guo, F. N. Dai, L. L. Zhang, D. F. Sun, *Adv. Sci.*, 2019, **6**, 1901855.
- [2] L. Feng, Y. T. Wang, K. Zhang, K. Y. Wang, W. D. Fan, X. K. Wang, J. A. Powell, B. B. Guo, F. N. Dai, L. L. Zhang, R. M. Wang, D. F. Sun and H. C. Zhou, *Angew. Chem. Int. Ed.*, 2019, **58**, 16682-16690.
- [3] G. M., Sheldrick, SHELXTL, Version 6.14, Bruker AXS, Madison, WI, 2003.