

**Pillar-Layer Zn-Triazolate-Dicarboxylate Frameworks with
Customized Pore Structure for Efficient Ethylene
Purification from Ethylene/Ethane/Acetylene Ternary
Mixtures**

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Supporting Information

Material and General characterization

All chemicals were commercially available without further purification. Single-crystal X-ray diffraction data were recorded by Bruker D8 VENTURE system with PHOTON II CPAD detector and a Ga-target Liquid METALJET D2 PLUS X-ray Source ($\lambda = 1.34139 \text{ \AA}$). The structure was solved by SHELXT (version 2018/2) and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3) through the OLEX2 graphical interface. powder X-ray diffraction patterns were recorded with an X-ray diffractometer (D8 Advance Bruker) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) in a 2θ range of $3\text{-}40^\circ$ with a scan speed of $5^\circ/\text{min}$ and the operating power was 40 kV/40 mA. Thermogravimetric analysis measurements were performed in a static N₂ atmosphere on a thermal analyzer (TGA 550, TA Instruments) with a ramping rate of $10 \text{ }^\circ\text{C min}^{-1}$. Single-component gas adsorption isotherms were collected by automated volumetric adsorption apparatus (Micromeritics, 3Flex). About 50 mg adsorbent was degassed under vacuum at $100 \text{ }^\circ\text{C}$ for 5 h prior to the adsorption measurements and all gases were of a 99.99% purity.

Synthesis of HIAM-210

Zn(NO₃)₂·6H₂O (0.5 mmol), 1,2,4-triazole (0.5 mmol), and 1, 4-naphthalene dicarboxylic acid (0.5 mmol) were dissolved in DMF/H₂O (0.5/4.5 mL), and the mixture was transferred to a 20-mL Teflon-lined stainless-steel autoclave and left in a 423 K oven for 48 h to form yellow crystals suitable for structure resolution by single-crystal X-ray crystallography. The as-synthesized HIAM-210 was harvested by filtration and washed with fresh DMF and water five times and then exchanged with

methanol by Soxhlet extraction overnight. Finally, the crystals were activated at 373 K in dynamic vacuum for 12 h to yield activated sample.

Topology analysis

The selection of node and linker was as following

Sc = {C8N12Zn3} cluster

Sc1 = {Zn4, Zn5, Zn2}, Sc2 = {Zn1, Zn6, Zn10}

Zn1 = {Zn9}

Zn2 = {Zn7}

Zn3 = {Zn8}

Zn4 = {Zn3}

Organic ligand acts as two-connection node or linker

Sc serves as a six-connection node

Adsorption selectivity calculation

The dual site Langmuir-Freundlich isotherm model was adopted to fit the adsorption isotherms of HIAM-210, which was described as follows:

$$q = q_{A,sat} \frac{b_A P^{v_A}}{1 + b_A P^{v_A}} + q_{B,sat} \frac{b_B P^{v_B}}{1 + b_B P^{v_B}} \quad (1)$$

with T-dependent parameters b_A , and b_B

$$b_A = b_{AO} \exp\left(\frac{E_A}{RT}\right); b_B = b_{BO} \exp\left(\frac{E_B}{RT}\right) \quad (2)$$

where q represents the adsorption amount of adsorbents with units of mol·kg⁻¹, $q_{A,sat}$ and $q_{B,sat}$ represent the saturated adsorption amount for adsorption sites A and B, respectively, b_A and b_B are constants for species i at adsorption sites A and B,

respectively, p is the total pressure of the bulk gas at the adsorption equilibrium, and v_A and v_B are the Freundlich exponent for sites A and B, respectively.

Taking the C_2H_6/C_2H_4 selectivity as example, the IAST selectivity is defined by:

$$S_{ads} = \frac{q_1/q_2}{y_1/y_2} \quad (3)$$

where q_1 and q_2 represents the adsorption amounts of C_2H_6 and C_2H_4 upon the sample under equilibrium condition, which are usually expressed with units of $mmol \cdot g^{-1}$, y_1 and y_2 are the corresponding mole fractions in the gas phase for the mixtures. The calculated IAST adsorption selectivity for the C_2H_6/C_2H_4 ($C_2H_6/C_2H_4 = 1/1$; v/v) mixtures taking the mole fractions $y_1 = 0.5$ and $y_2 = 1 - y_1 = 0.5$ for a total pressure of 101 kPa at 298 K.

Isosteric heat of adsorption

To determine the affinity between the scaffold and the adsorbates, the Virial equation was employed to calculate the adsorption heat for C_2H_2 , C_2H_6 and C_2H_4 on HIAM-102, which was defined as follows:

$$\ln(P) = \ln(N) + \frac{1}{T} \sum_{i=0}^m a_i N_i + \sum_{i=0}^n b_i N_i \quad (4)$$

$$Q_{st} = -R \sum_{i=0}^m a_i N_i \quad (5)$$

where N is the adsorption amount, and m and n determine the number of items required to precisely fit the adsorption isotherms.

Multicomponent column breakthrough tests

Breakthrough tests were carried out in an auto mixed-gas breakthrough apparatus (3P Mixsorb S). The mass of adsorbents filled into the column (I.D. 6 mm, length 100

mm) was 0.82 g. The adsorbents were activated at 373 K for 10 h under helium purging (10 ml/min). When the temperature cooled down to 298 K, helium flow was stopped and the binary or ternary feed mixed gases at a flow rate of 1 mL/min were introduced to the adsorption column. The outlet gas was analyzed by using a mass spectrometer (MKS circus 3). After the adsorption reached dynamic equilibrium, the column was purged with helium (10 mL/min) at 100 °C for 5 h for regeneration.

The C₂H₄ purity productivity was calculated by the following method: the gas breakthrough gas amount (q_i) was calculated by integrating the breakthrough curve $f(t)$ as following equation.

$$q_i = \frac{\int_0^{t_0} f(t) dt}{m} \times c_i \quad (6)$$

Where the m represents the adsorbent mass and c_i represents the fraction of components in the feed gas mixture.

And then the purity (c) of breakthrough gas was calculated by the following equation.

$$c = \frac{q_{C_2H_4}}{q_{C_2H_2} + q_{C_2H_6} + q_{C_2H_4}} \quad (7)$$

Calculations and simulation details

The GCMC simulations were performed with Materials studio 2020. All simulations were performed using the Sorption, within the CompassIII force field. The electrostatic and van der Waals were Ewald and Atom based respectively. The

adsorption process was simulated at 298 K and 1 bar.

The density functional theory (DFT) calculations were performed using a Dmol3 module of Material Studio 2020. The generalized gradient approximation (GGA) method with Perdew-Burke-Ernzerhof (PBE) function was employed to describe the interactions between core and electrons. The force and energy convergence criterion were set to 0.002 Ha Å⁻¹ and 10⁻⁵ Ha, respectively.

The binding energy (ΔE) was calculated as

$$\Delta E (E_v) = 27.212 * (E_{\text{total}}(\text{Ha}) - E_1(\text{Ha}) - E_2(\text{Ha})) \quad (8)$$

where the E_{total} is the energy of the optimized system; E_1 is the energy of the MOF; E_{molecule} is the energy of C₂H₂, C₂H₄ and C₂H₆.

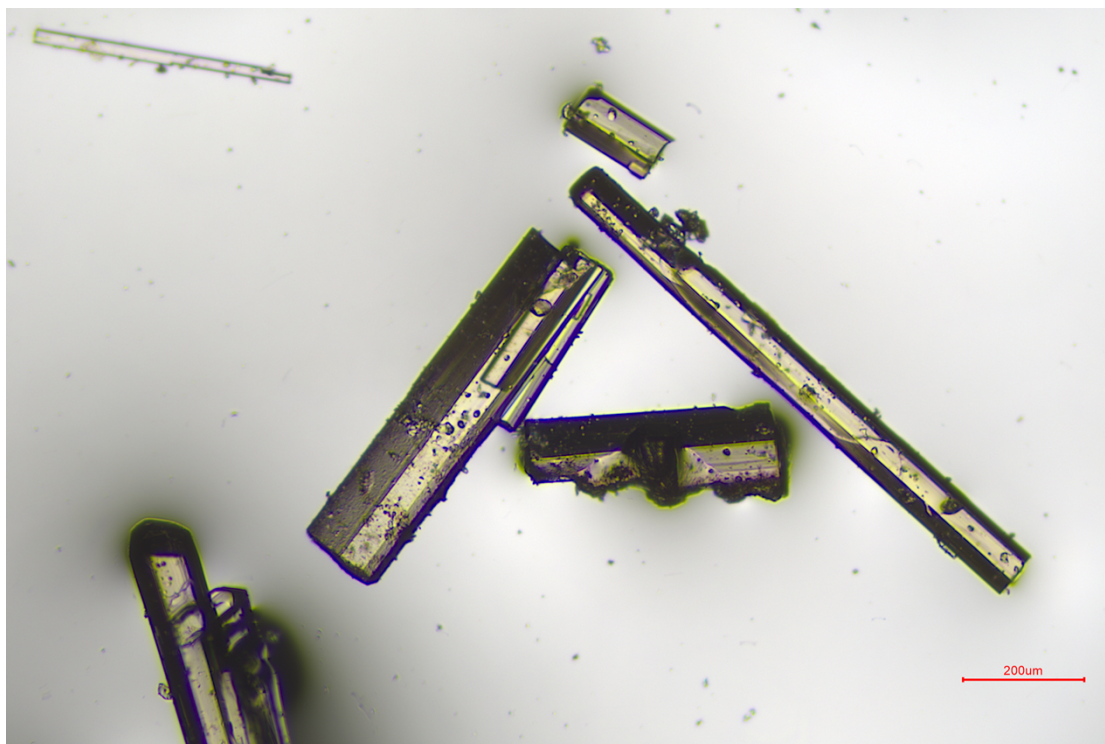


Fig. S1 The optical image of the as-synthesized HIAM-210 crystals.

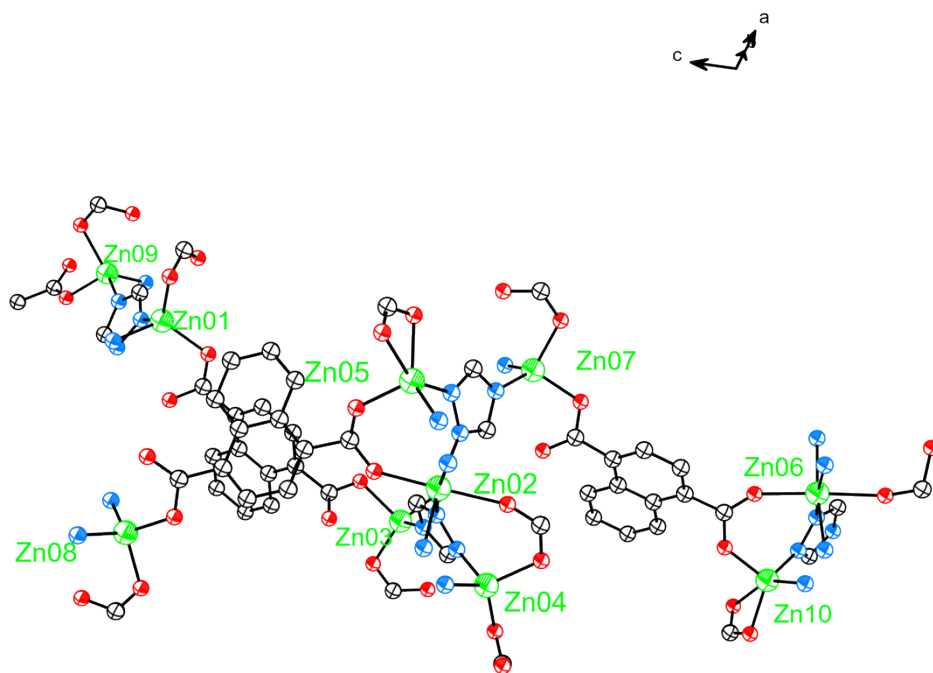


Fig. S2 The coordination environment of the independent Zn(II) ions in the crystal structure of HIAM-210.

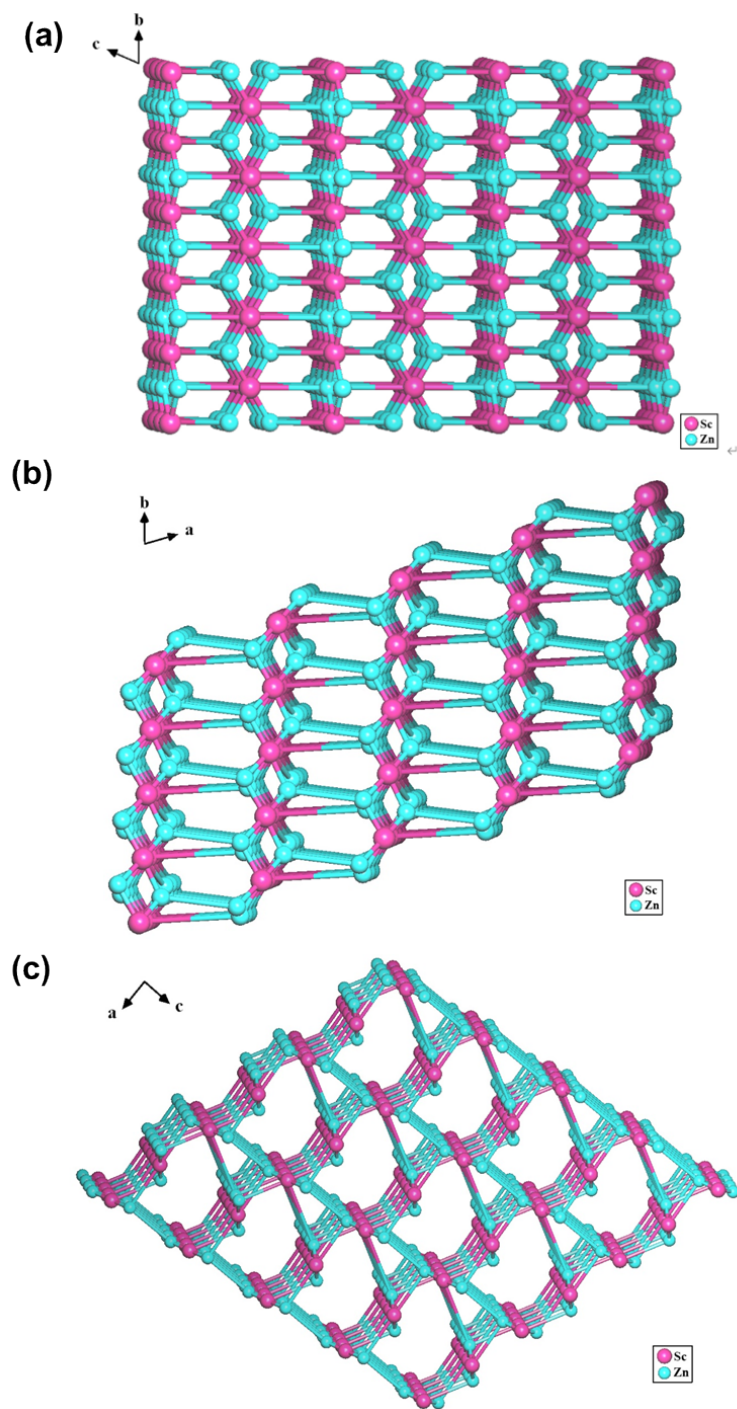


Fig. S3 (a) The 3-D topological view of HIAM-210 along a axis, (b) The 3-D topological view along c axis, (c) The 3-D topological view along b axis.

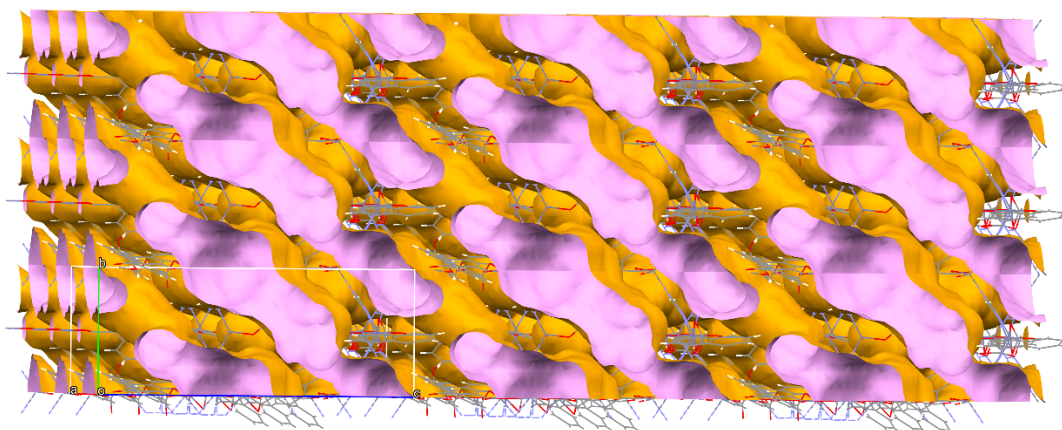


Fig. S4 The pore structure of the as-synthesized HIAM-210.

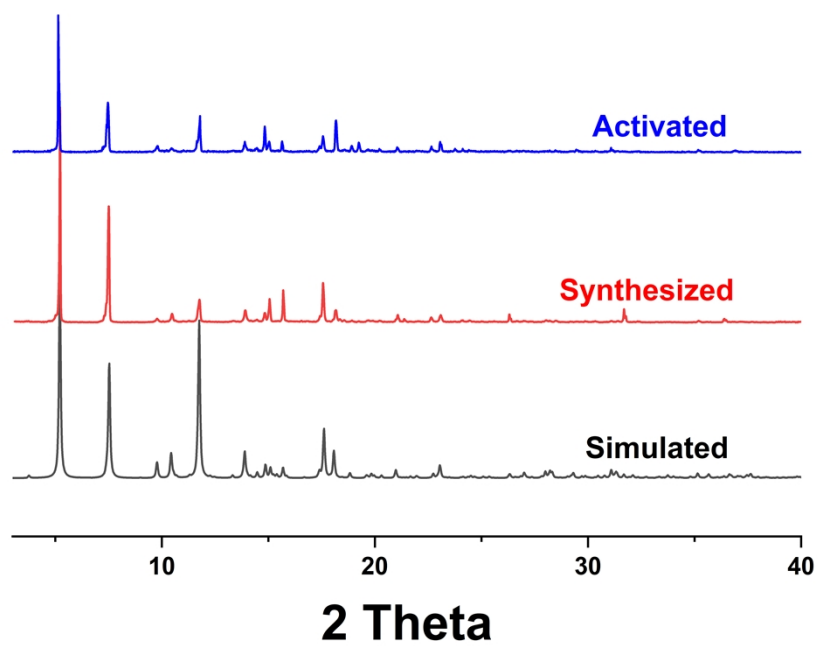


Fig. S5 The comparison of PXRD patterns of the synthesized, activated sample and the simulated one.

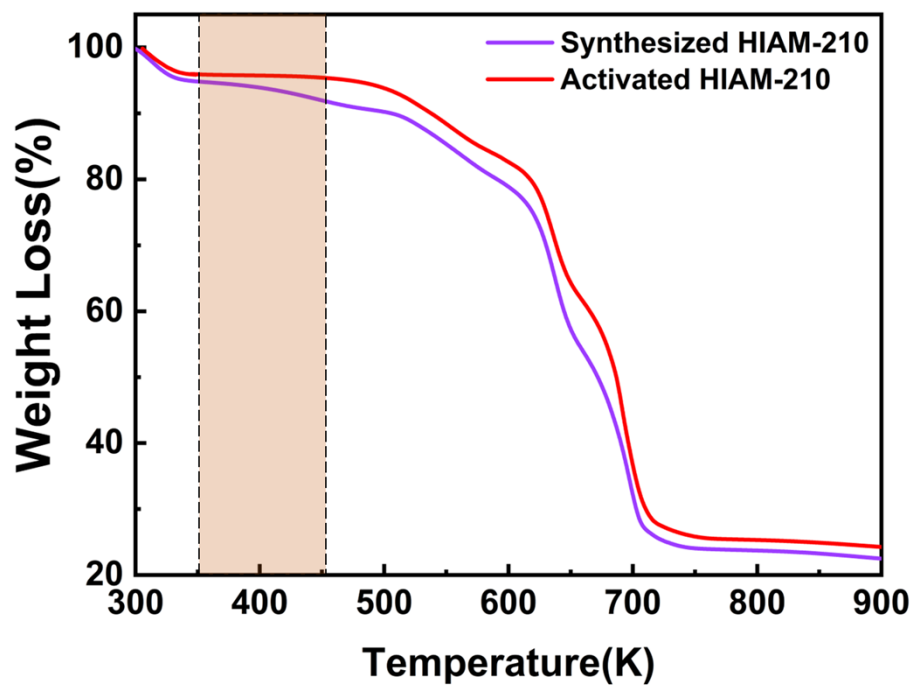


Fig. S6 TG curve of synthesized and activated HIAM-210.

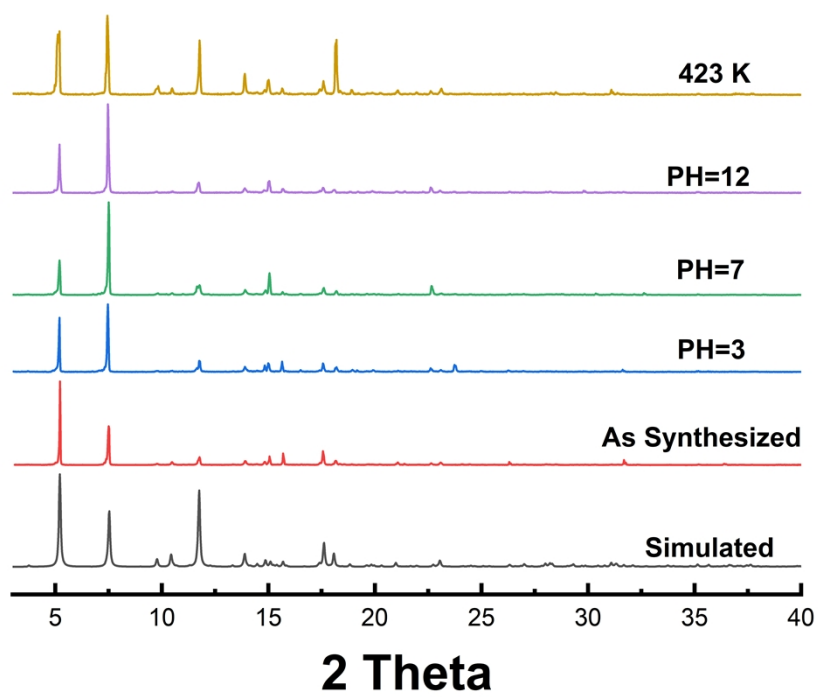


Fig. S7 PXR D patterns of HIAM-210 samples after being treated in different environments for 3 days.

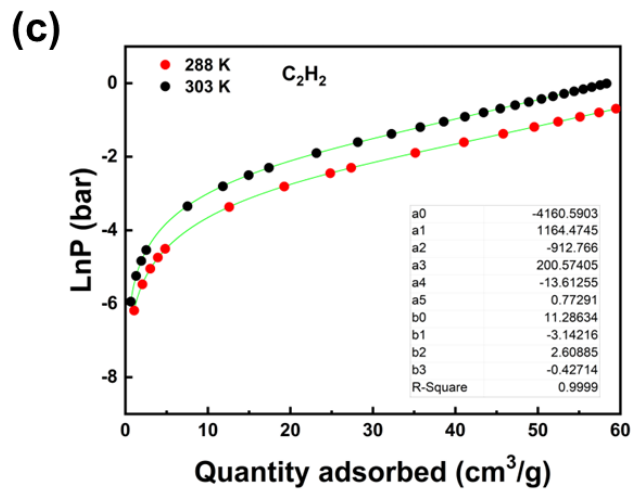
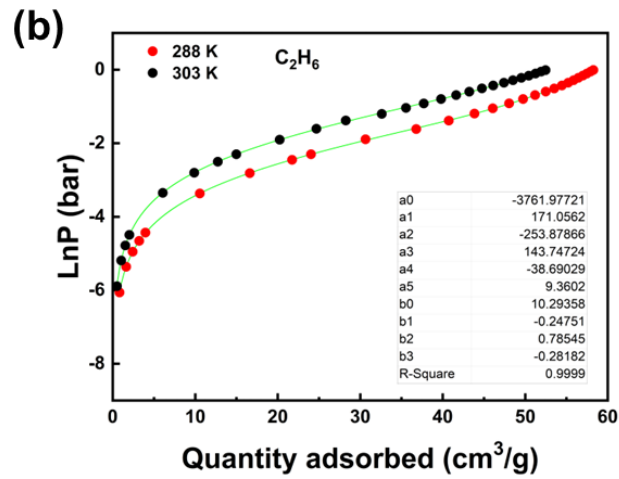
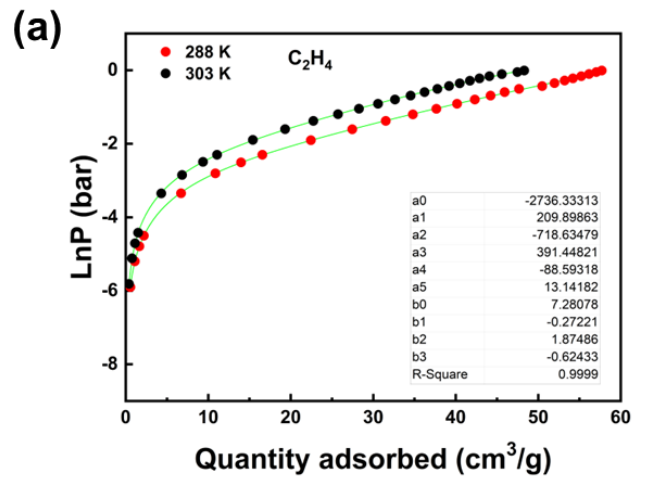


Fig. S8 The fitting parameters of Virial equation for adsorption isotherms of C_2H_2 , C_2H_4 and C_2H_6 on HIAM-210.

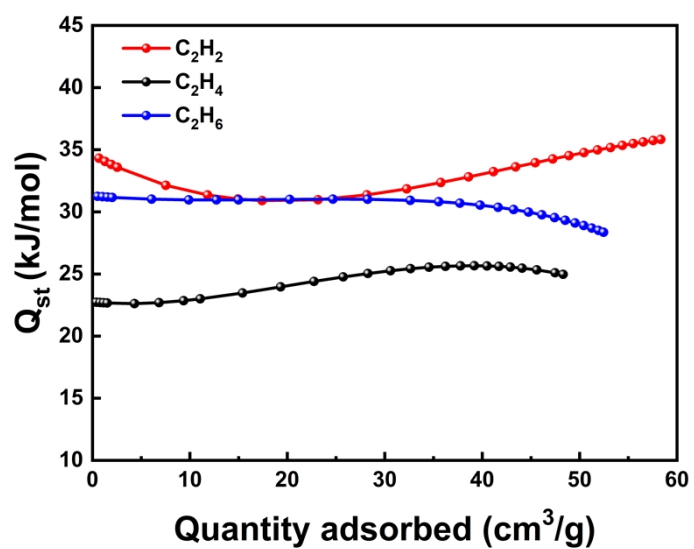


Fig. S9 The isosteric heats of adsorption (Q_{st}) of C_2H_2 , C_2H_4 and C_2H_6 for HIAM-210.

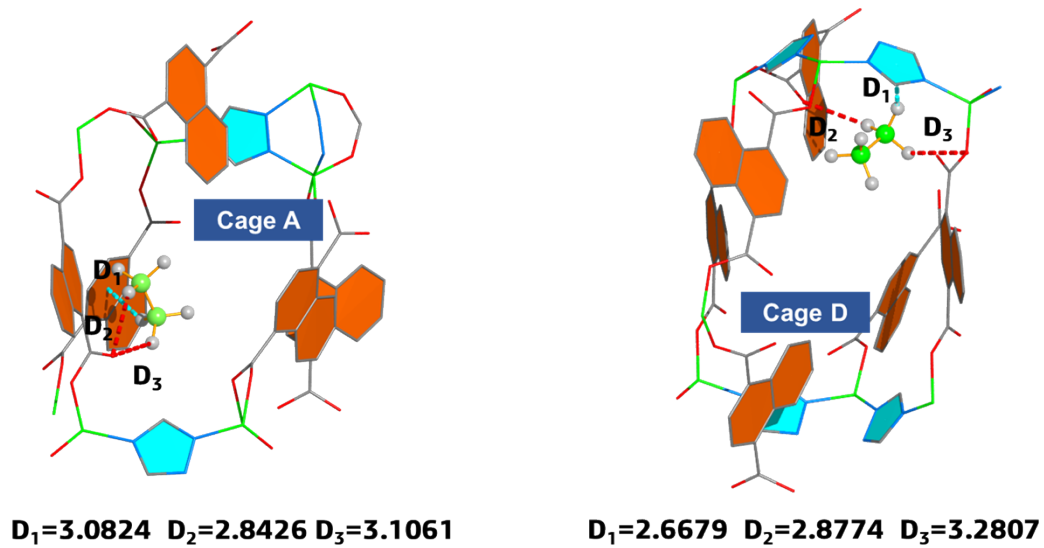


Fig. S10 The preferential adsorption sites for C₂H₆ in Cage A and Cage D, the C-H \cdots π and C-H \cdots O interactions are presented by blue and red dashed line respectively.

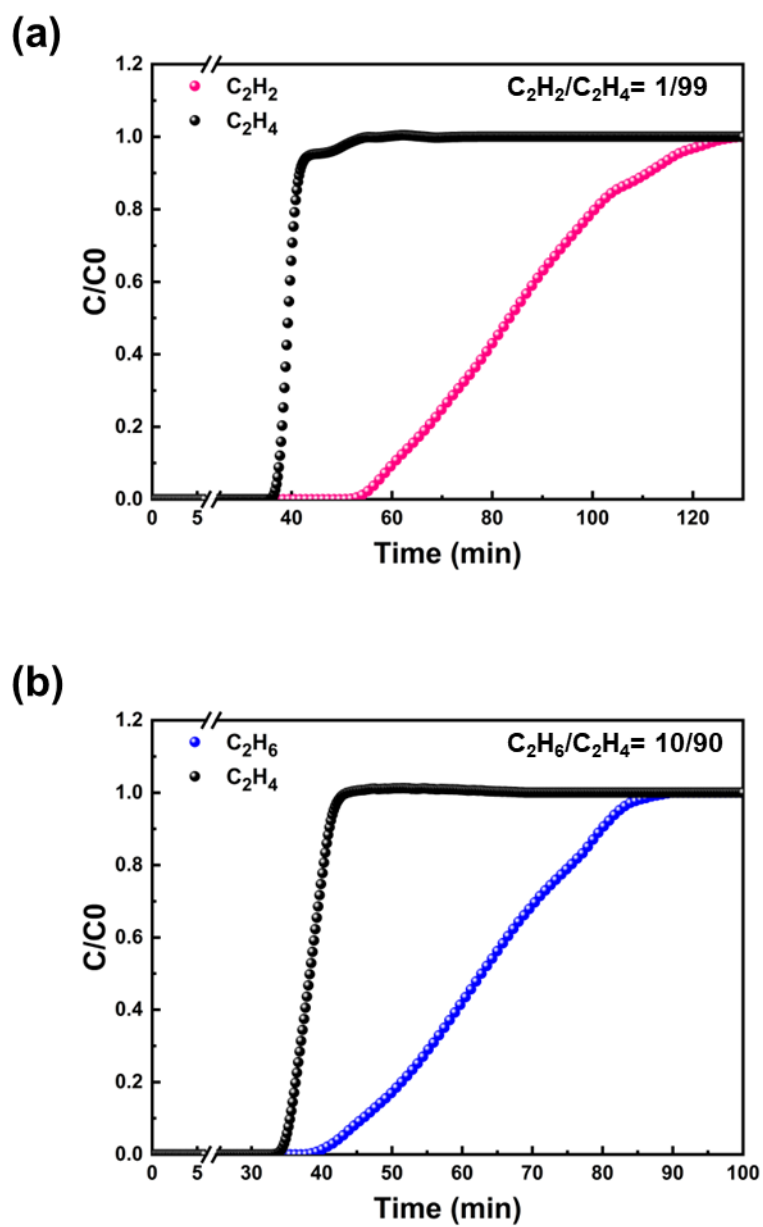


Fig. S11 The breakthrough curves for binary mixture with the composition of (a) $C_2H_2/C_2H_4(1/99, v/v)$ and (b) $C_2H_6/C_2H_4(10/90, v/v)$.

Table S1 Comparison of molecular sizes and physical properties of C₂H₆, C₂H₂, and C₂H₄.

Molecular	Dimension (Å)			Kinetic diameter (Å)	Polarizability × 10 ²⁵ cm ³	Quadrupole moment × 10 ²⁶ /esu cm ²	Bolling point (K)
	X	Y	X				
C ₂ H ₂	3.32	3.34	5.70	3.33	39.3	7.2	188.4
C ₂ H ₄	3.28	4.18	4.84	4.16	42.5	1.5	169.4
C ₂ H ₆	3.81	4.08	4.82	4.44	44.3-44.7	0.65	184.6

Table S2 Crystal data and structure refinement of HIAM-210.

Empirical formula	$C_{112}H_{67}N_{24}O_{32}Zn_{10}$	
Formula weight	2914.59	
Temperature	150(2) K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	Pm	
Unit cell dimensions	$a = 18.0460(17)$ Å	$\alpha = 90^\circ$.
	$b = 9.8055(10)$ Å	$\beta = 110.269(4)^\circ$.
	$c = 24.994(3)$ Å	$\gamma = 90^\circ$.
Volume	$4148.8(7)$ Å ³	
Z	1	
Density (calculated)	1.167 Mg/m ³	
Absorption coefficient	1.377 mm ⁻¹	
F(000)	1463	
Crystal size	0.200 x 0.100 x 0.100 mm ³	
Theta range for data collection	1.639 to 56.964°.	
Index ranges	$-22 \leq h \leq 21, 0 \leq k \leq 12, 0 \leq l \leq 31$	
Reflections collected	8983	
Independent reflections	8983 [R(int) = ?]	
Completeness to theta = 53.594°	99.60%	
Refinement method	Full-matrix least-squares on F ²	

Data / restraints / parameters	8983 / 3684 / 1220
Goodness-of-fit on F ²	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1826
R indices (all data)	R1 = 0.0618, wR2 = 0.1847
Absolute structure parameter	0.03(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.447 and -0.865 e.Å ⁻³

Table S3 Fitting parameters of Dual-site Langmuir-Freundlich isotherm model for single gas adsorption on HIAM-210 at 298K.

	$q_{sat, A}$	b_A	ν_A	$q_{sat, B}$	b_B	ν_B	R-Square
	cm ³ ·g ⁻¹	kPa ⁻¹	dimensionless	cm ³ ·g ⁻¹	kPa ⁻¹	dimensionless	
C ₂ H ₂	98.78	2.10	0.94	0.4	371667.84	99.943	0.9999
C ₂ H ₄	70.23	2.07	0.99	0.19	2095021.04	7.69	0.9999
C ₂ H ₆	44.52	2.41	0.77	21.93	27.21	1.70	0.9999

Table S4 detailed data of multiple breakthrough tests.

Feed gas composition	Humidity / RH	Eluting time of C ₂ H ₄ /min	Retention time* /min	C ₂ H ₄ productivity / L/kg	
Binary	C ₂ H ₂ /C ₂ H ₄ = 50/50	0	40 th	16	9.70
	C ₂ H ₂ /C ₂ H ₄ = 1/99	0	36 th	17	33.20
	C ₂ H ₆ /C ₂ H ₄ = 50/50	0	34 th	6	3.44
	C ₂ H ₆ /C ₂ H ₄ = 10/90	0	33 rd	7	4.15
Ternary	C ₂ H ₂ /C ₂ H ₄ /C ₂ H ₆ = 34/33/33	0	33 rd	5	0.87
	C ₂ H ₂ /C ₂ H ₄ /C ₂ H ₆ = 1/90/9	0	30 th	8	2.56
	C ₂ H ₂ /C ₂ H ₄ /C ₂ H ₆ = 1/90/9	50 %	32 nd	8	2.52

* The time interval between the breakthrough of ethylene and the subsequent gas.