Supporting Information

Engineering Ligand conformation by substituent manipulation towards various copper-tricarboxylate frameworks with tuned gas adsorption properties

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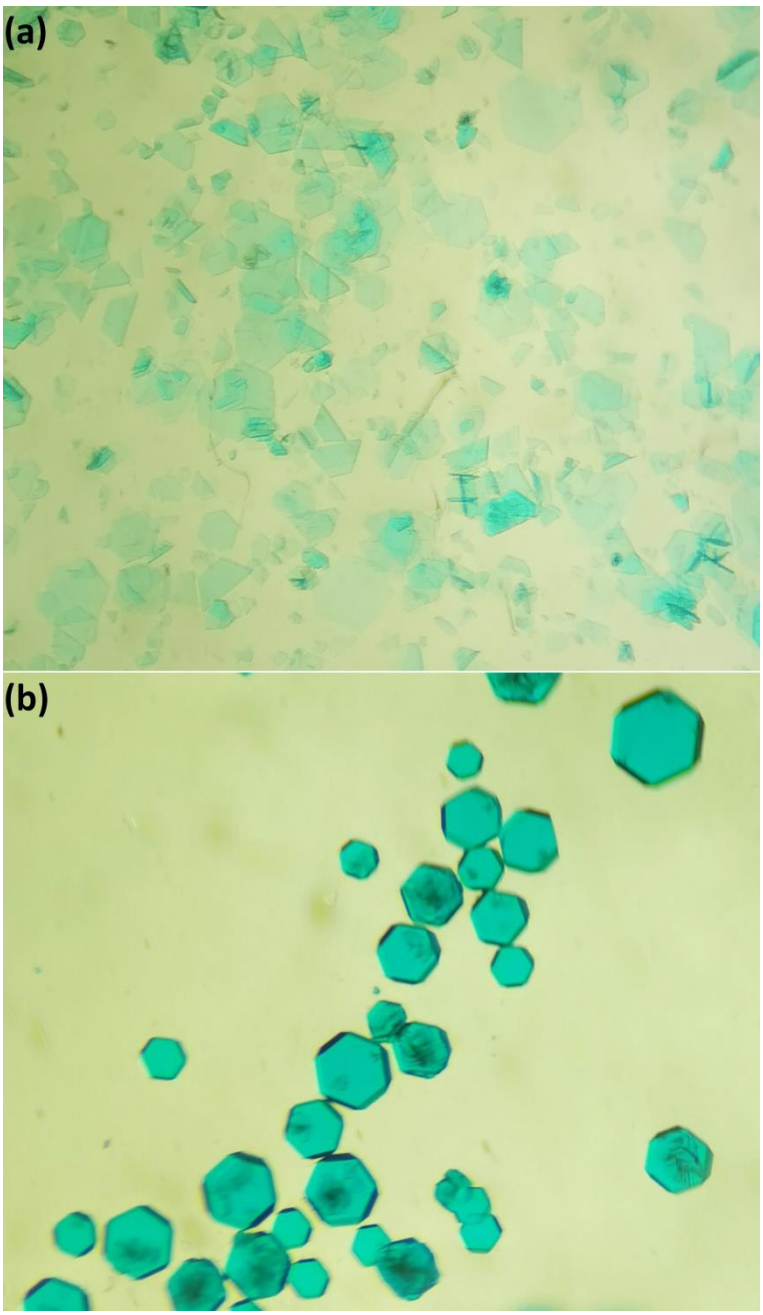


Fig. S1 Electronic photographs of the as-synthesized (a) **ZJNU-109**, and (c) **ZJNU-110**.

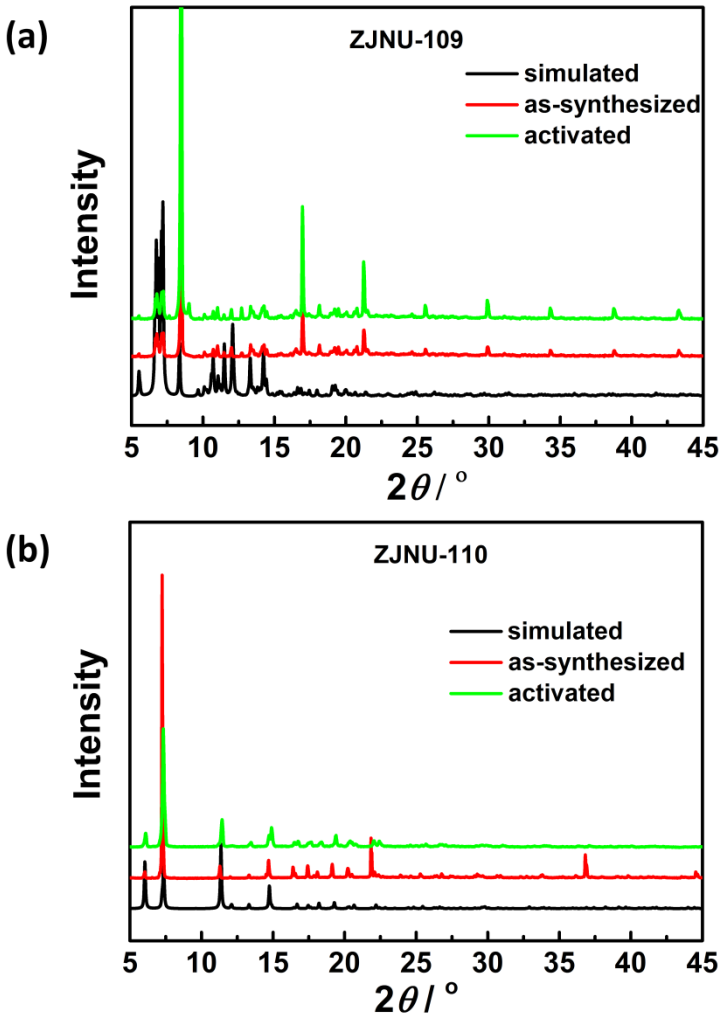


Fig. S2 Experimental and simulated PXRD patterns of (a) **ZJNU-109**, and (b) **ZJNU-110**.

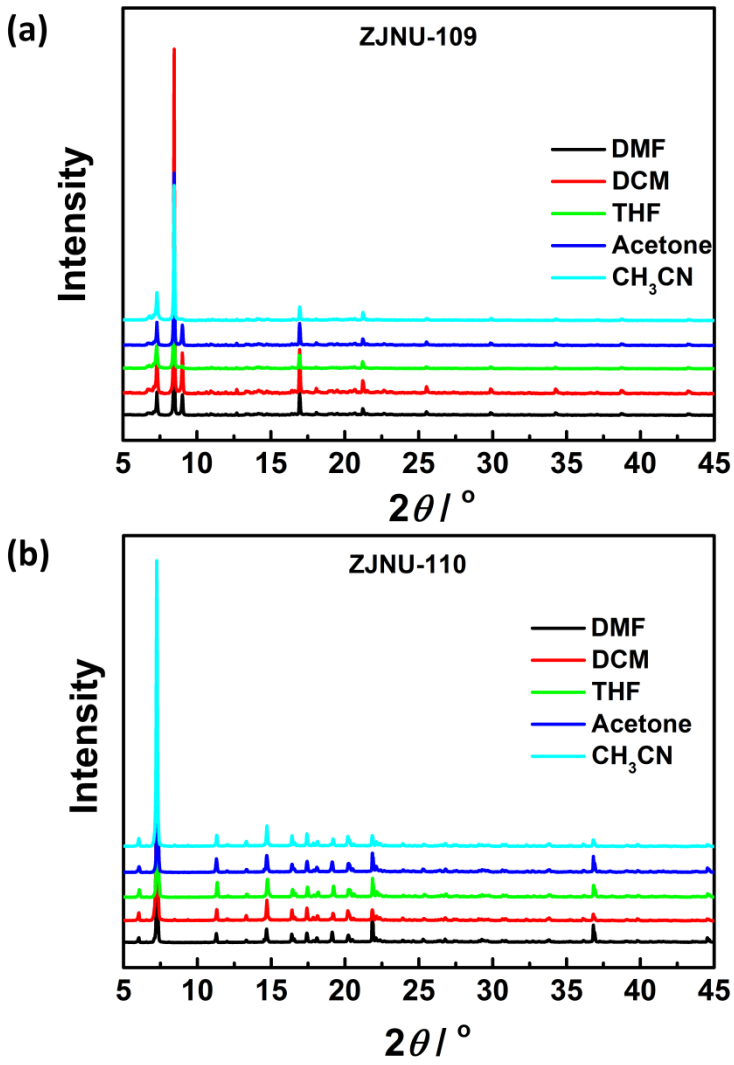


Fig. S3 PXRD patterns for the as-synthesized (a) **ZJNU-109** and (b) **ZJNU-110** immersed in different organic solvents for 24 h at room temperature.

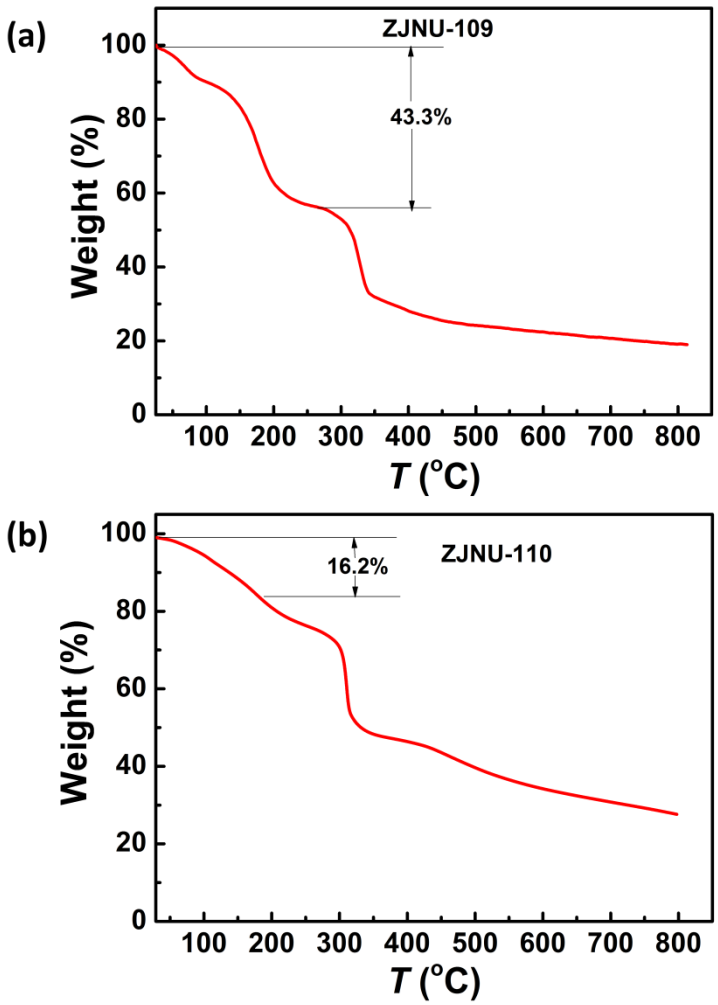


Fig. S4 TGA curves of the as-synthesized (a) **ZJNU-109**, and (b) **ZJNU-110** under N_2 atmosphere with a heating rate of 5 K min^{-1}.

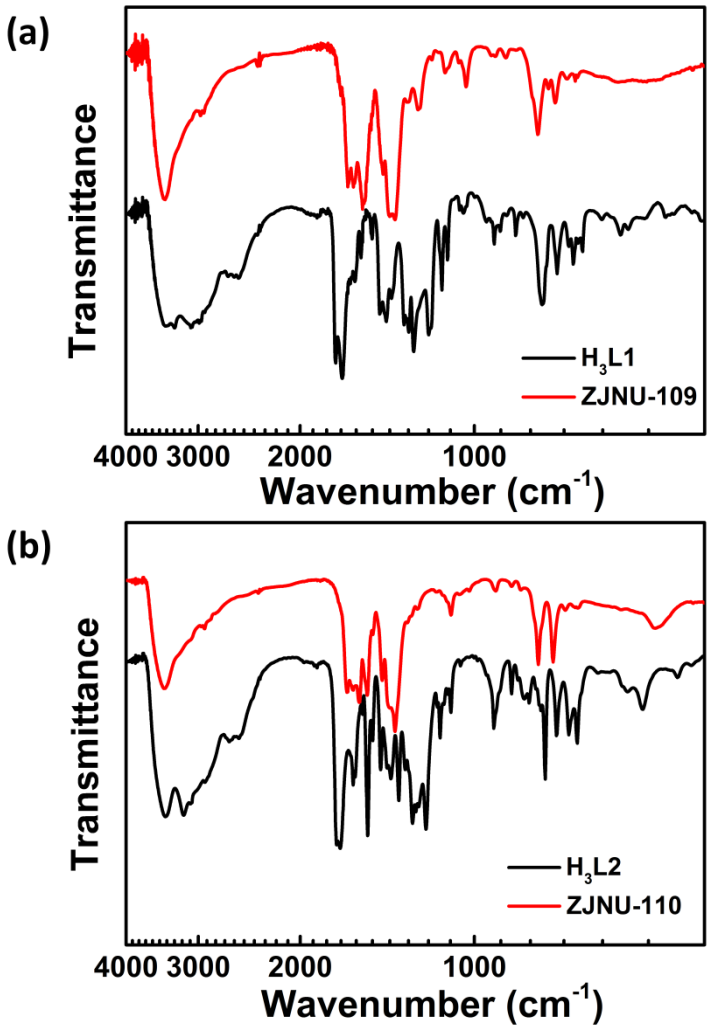
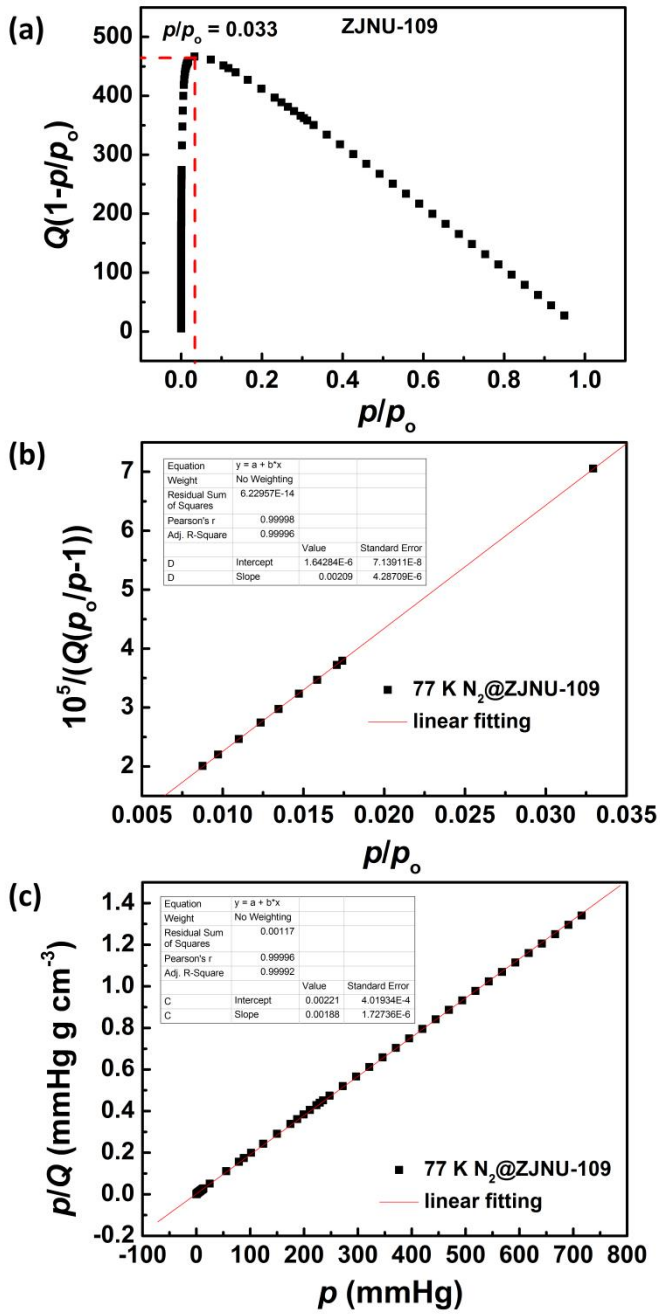


Fig. S5 Comparisons of FTIR spectra of (a) **ZJNU-109** and its ligand H_3L1, and (b) **ZJNU-110** and its ligand H_3L2.



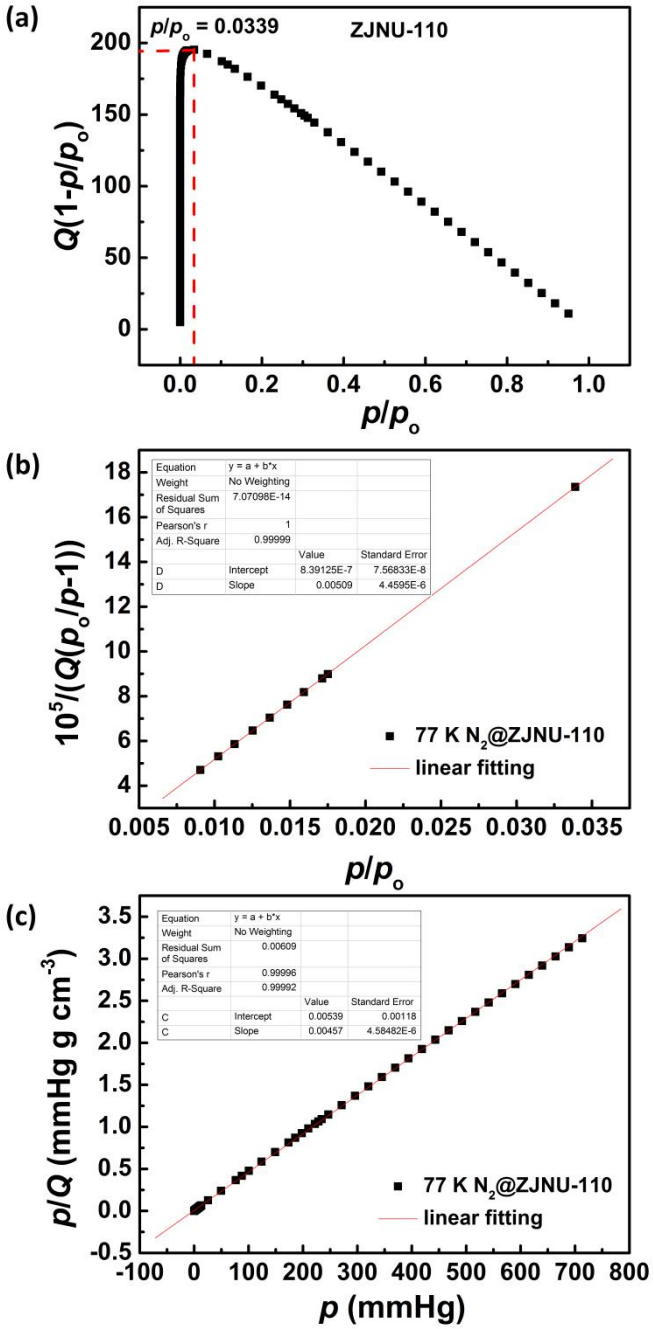
S_{BET} = 1/(1.64284×10^{-6} + 0.00209)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2081 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00188)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2316 m^2 g^{-1}

BET constant C = 1 + 0.00209/1.64284×10^{-6} = 1273

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.02726$$

Fig. S6 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-109**.



S_{BET} = 1/(8.39125×10^{-7} + 0.00509)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 855 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00457)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 953 m^2 g^{-1}

BET constant C = 1 + 0.00509/8.39125×10^{-7} = 6067

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01268$$

Fig. S7 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-110**.

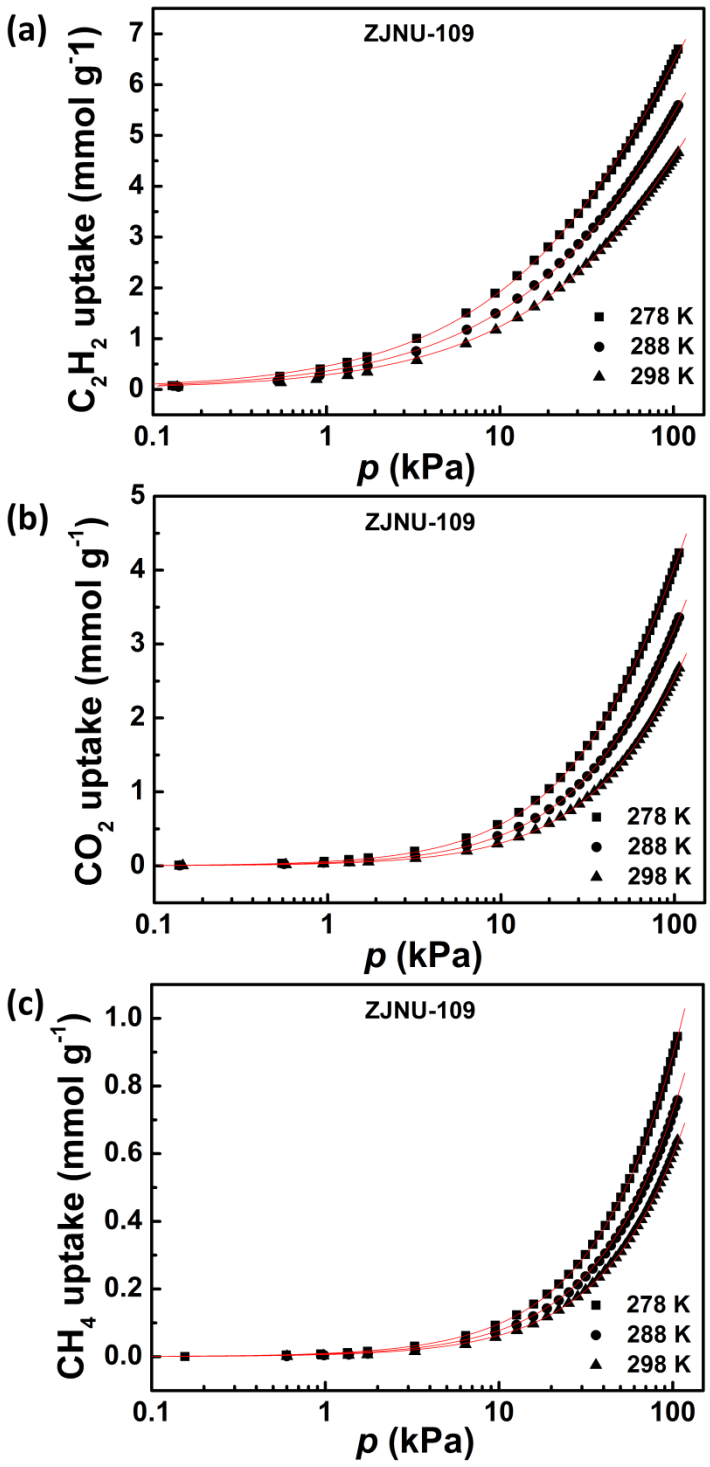


Fig. S8 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-109** with the fitted isotherms at 278 K, 288 K, and 298 K.

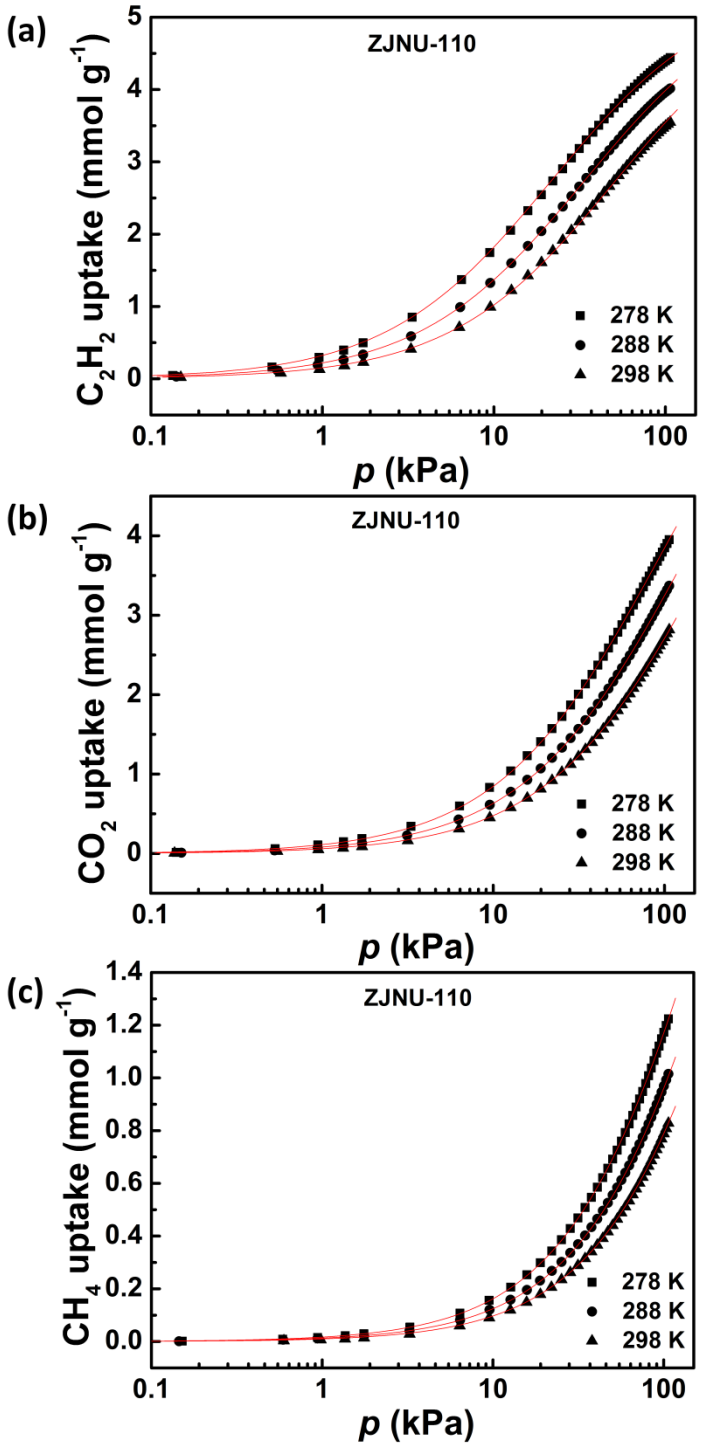


Fig. S9 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-110** with the fitted isotherms at 278 K, 288 K, and 298 K.

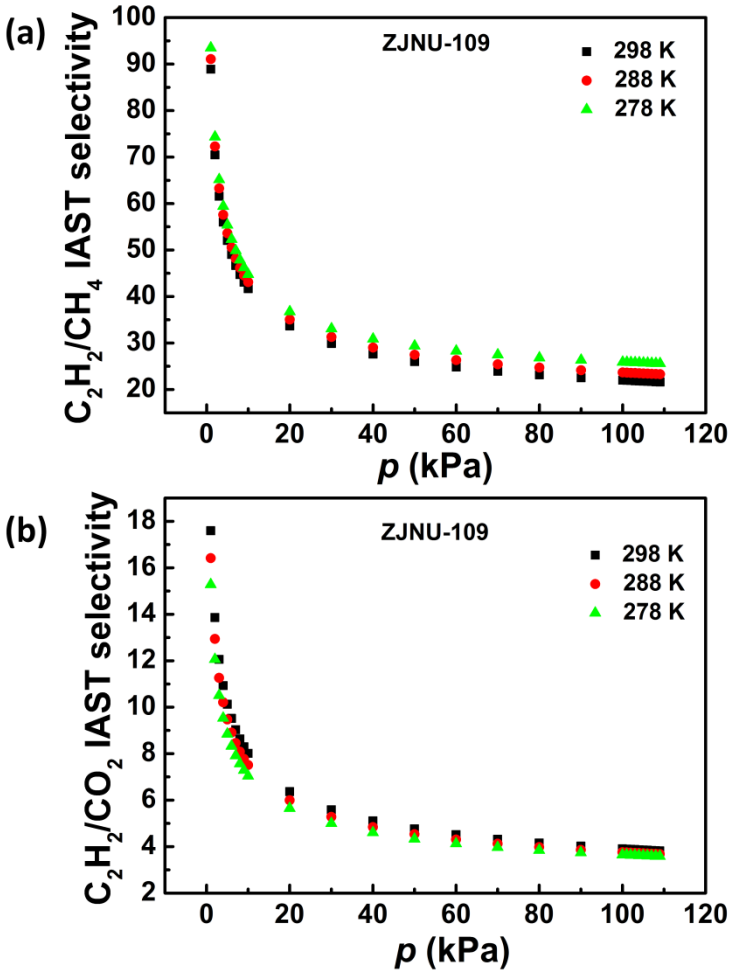


Fig. S10 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) C_2H_2/CO_2 gas mixtures in **ZJNU-109** at three different temperatures of 278 K, 288 K, and 298 K.

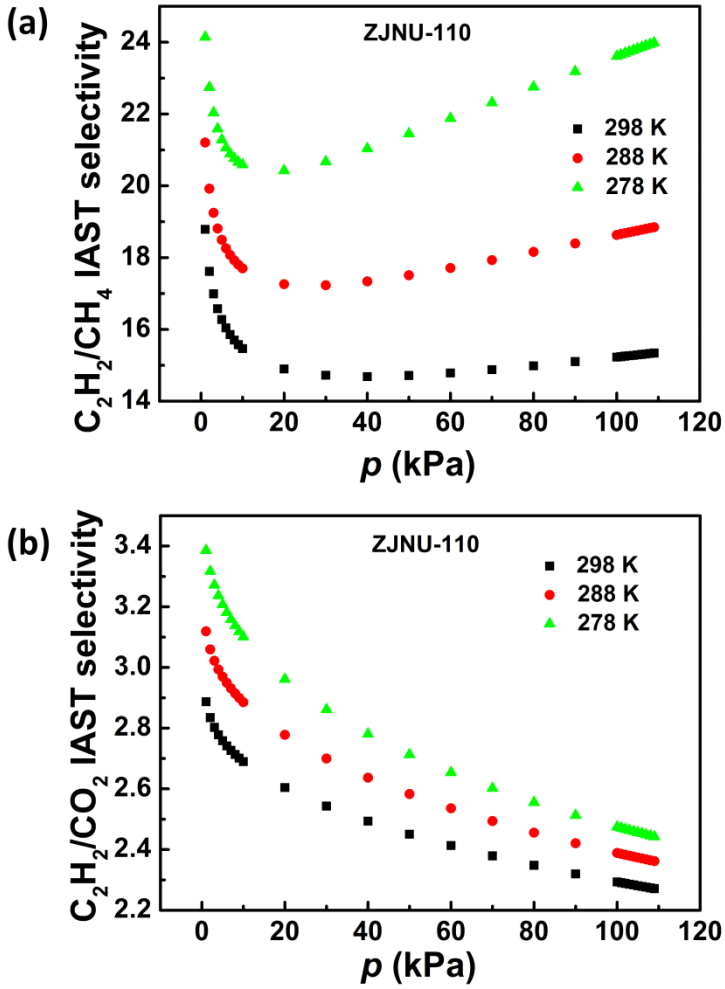
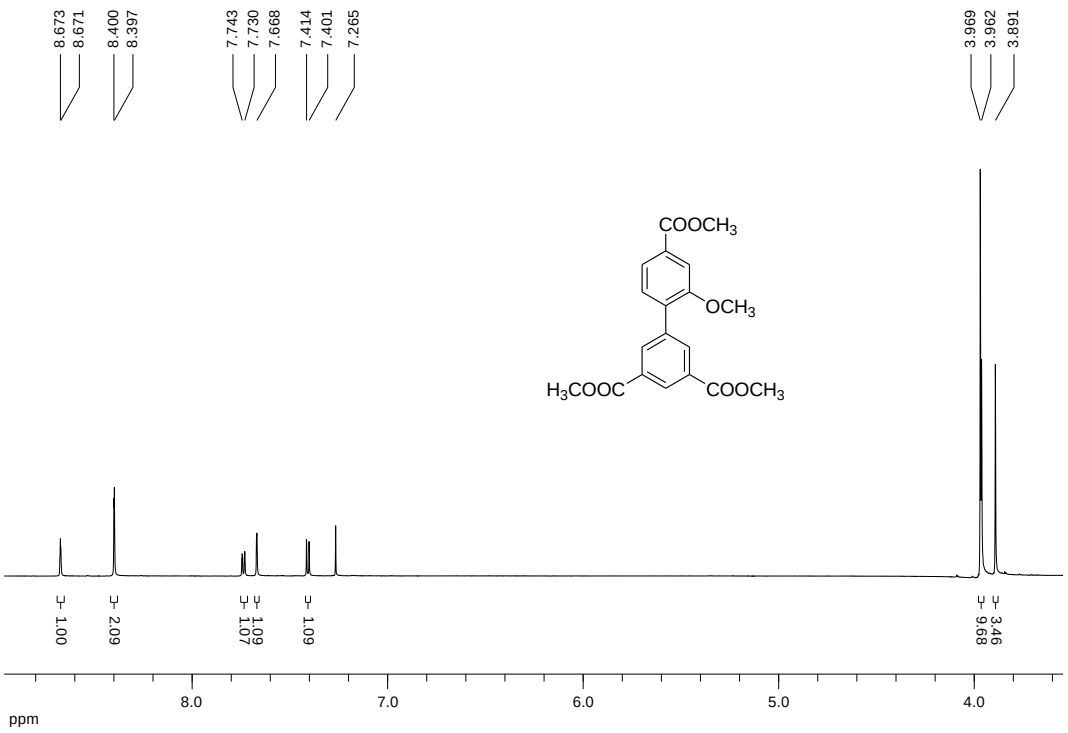


Fig. S11 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) C_2H_2/CO_2 gas mixtures in **ZJNU-110** at three different temperatures of 278 K, 288 K, and 298 K.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7.730
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7.265
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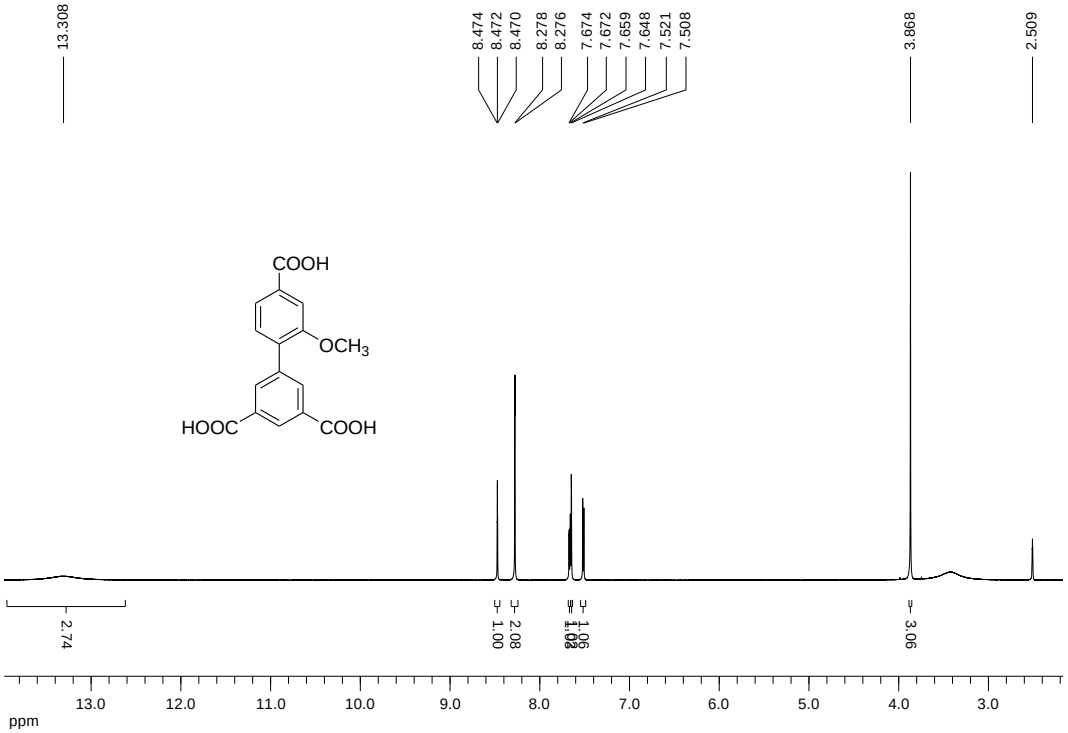
3.962
3.891
COOCH3
OCH3
H3COOC
COOCH3
1.00
2.09
1.09
1.07
1.09
9.68
3.46
8.0
7.0
6.0
5.0
4.0
ppm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7.672
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3.868
2.509
COOH
OCH3
HOOC
COOH
2.74
1.00
2.08
3.06
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6.0
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4.0
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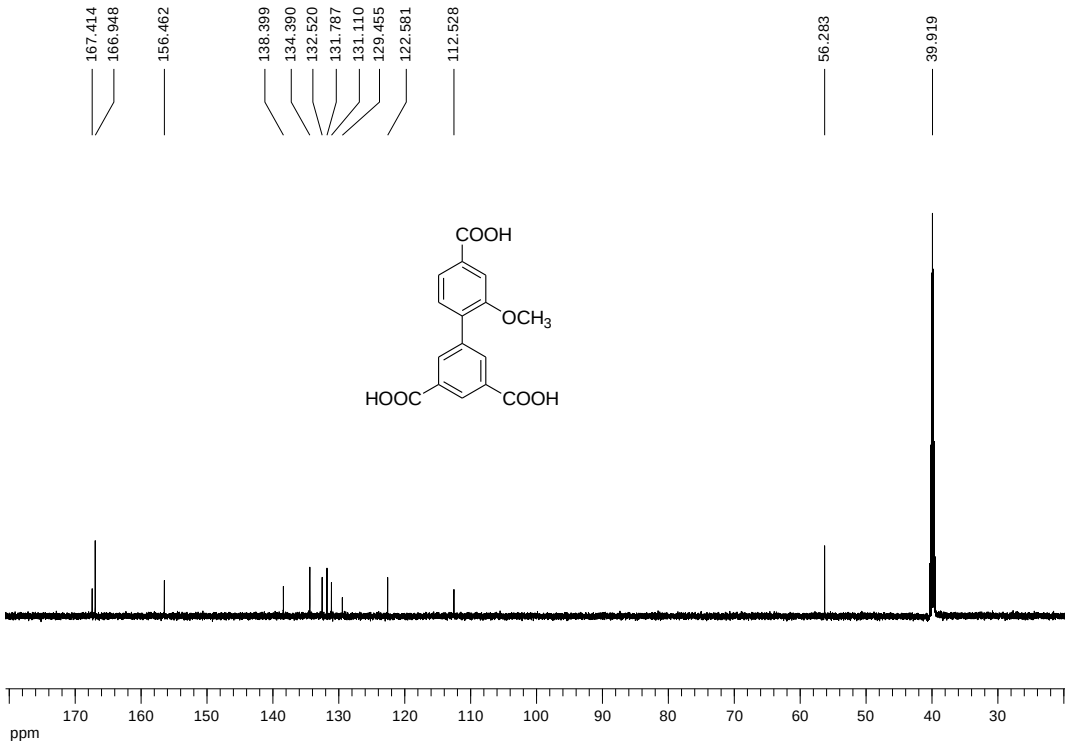
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134.390
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131.110
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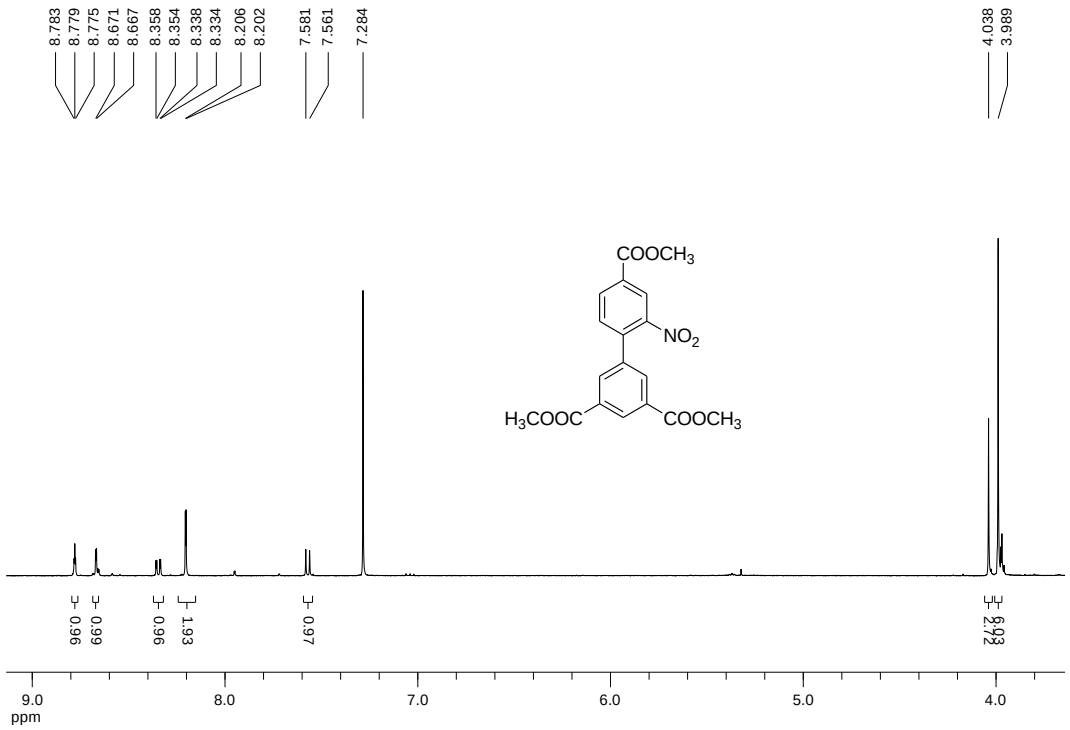
122.581
112.528
56.283
39.919
COOH
OCH3
HOOC
COOH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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7.284
4.038
3.989
COOCH3
NO2
H3COOC
COOCH3
0.96
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7.0
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5.0
4.0
ppm

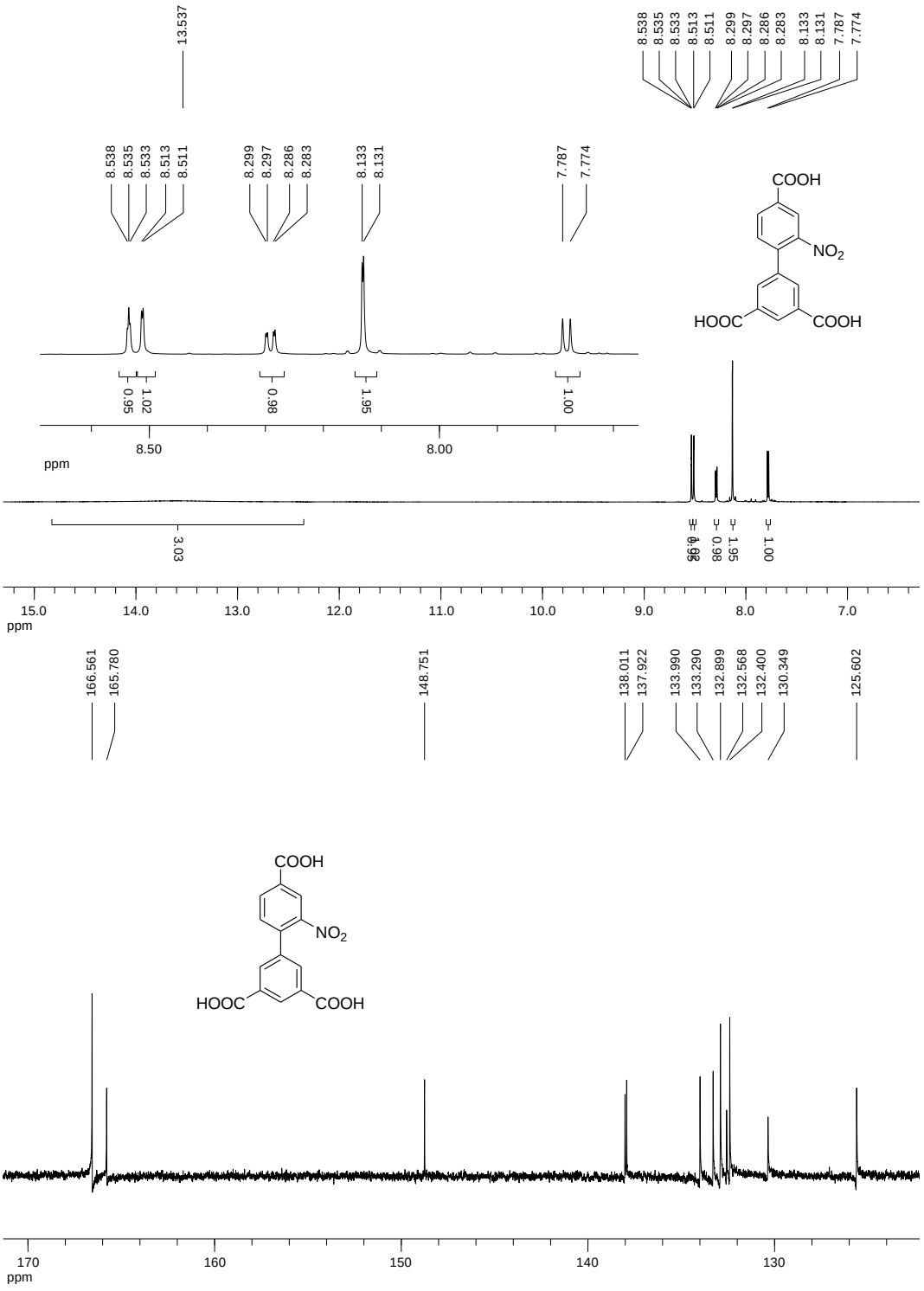

Fig. S12 ^{1}H and ^{13}C NMR spectra.

Table S1. Summarizes of physical parameters of C_2H_2, CO_2, and CH_4

Adsorbates	BP (K)	T_c (K)	p_c (bar)	Kinetic diameter (Å)	Molecular dimension (Å)	Polarizability ($\times10^{25}$ cm^3)	Dipole moment ($\times10^{18}$ esu cm)	Quadruple moment ($\times10^{26}$ esu cm^2)
C_2H_2	188.40	308.30	61.14	3.3	3.3×3.3×5.7	33.3-39.3	0	+7.5
CO_2	216.55	304.12	73.74	3.3	3.2×3.3×5.4	29.11	0	-4.3
CH_4	111.66	190.56	45.99	3.758	3.7×3.7×3.7	25.93	0	0

BP: normal boiling point; T_c: critical temperature; p_c: critical pressure

Table S2 Crystal data and structure refinement for **ZJNU-109**, and **ZJNU-110**.

MOFs	**ZJNU-109**	**ZJNU-110**
Empirical formula	$C_{84}H_{122}Cu_5N_{12}O_{39}$	$C_{53}H_{44}Cu_4N_6O_{28}$
Formula weight	2241.63	1467.10
Temperature (K)	150(2)	150(2)
λ (Å)	1.54178	0.71073
Crystal system	Monoclinic	Trigonal
Space group	*C2/c*	*R -3 m :H*
Unit cell dimensions	a = 32.031(6) Å b = 18.235(5) Å c = 41.925(10) Å α = 90° β = 95.246(12)° γ = 90°	a = 18.3936(7) Å b = 18.3936(7) Å c = 36.5323(14) Å α = 90° β = 90° γ = 120°
V (Å^3)	24385(10)	10703.9(9
Z	8	6
D_c (g cm^{-3})	1.221	1.366
μ (mm^{-1})	1.605	1.255
F(000)	9336	4464
Crystal size (mm)	0.270 × 0.210 × 0.090	0.250 × 0.240 × 0.220
θ range for data collection (°)	2.116 to 68.409	2.214 to 30.512
Limiting indices	$-36 \le h \le 38$ $-21 \le k \le 21$ $-50 \le l \le 50$	$-25 \le h \le 25$ $-24 \le k \le 25$ $-51 \le l \le 49$
Reflections collected / unique	120037 / 22189	35345 / 3885
R_{int}	0.0937	0.0272
Max. and min. transmission	0.7531 and 0.5265	0.2657 and 0.2075
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	22189 / 647 / 812	3885 / 395 / 269
Goodness-of-fit on F^2	1.097	1.021
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0940 wR_2 = 0.2337	R_1 = 0.0768 wR_2 = 0.1767
R indices (all data)	R_1 = 0.1177 wR_2 = 0.2487	R_1 = 0.0896 wR_2 = 0.1837
Largest diff. peak and hole (e·Å^{-3})	2.084 and -1.329	1.030 and -0.952
CCDC	2035071	2035070

Table S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-109**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	19.01133	1.91495×10^{-5}	16.559	0.65755	0.99966
CO_2	12.90022	4.16121×10^{-7}	21.495	1	0.99996
CH_4	9.53946	1.53902×10^{-6}	15.037	1	0.99968

Table S4 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-110**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	5.49258	5.87531×10^{-7}	26.744	0.90145	0.99979
CO_2	7.40873	1.33615×10^{-6}	21.616	0.92265	0.99996
CH_4	3.78056	1.64136×10^{-6}	18.287	1	0.99992

Table S5 Summary of pore textural and gas adsorption properties of **ZJNU-109** and **ZJNU-110**.

MOFs		**ZJNU-109**	**ZJNU-110**
$S_{BET}/S_{Langmuir}$ (m^2 g^{-1})		2081/2316	855/953
V_p (cm^3 g^{-1})		0.8257	0.3403
C_2H_2 uptake[a] (cm^3 g^{-1}, STP)	298 K	104.6	79.5
	288 K	125.4	90.0
	278 K	150.2	99.5
CO_2 uptake[a] (cm^3 g^{-1}, STP)	298 K	60.0	63.2
	288 K	75.4	75.6
	278 K	94.9	88.6
CH_4 uptake[a] (cm^3 g^{-1}, STP)	298 K	14.3	18.6
	288 K	17.0	22.8
	278 K	21.2	27.4
C_2H_2/CH_4 (v/v = 1/1) IAST selectivity[a]	298 K	21.6	15.3
	288 K	23.3	18.9
	278 K	25.6	24.0
C_2H_2/CO_2 (v/v = 1/1) IAST selectivity[a]	298 K	3.8	2.3
	288 K	3.7	2.4
	278 K	3.6	2.4

$S_{BET}/S_{Langmuir}$ = BET and Langmuir surface areas; V_p = total pore volume; [a] at 1 atm; STP = standard temperature and pressure