Electronic Supplementary Material (ESI) for Dalton Transactions.

A lactam-functionalized copper bent diisophthalate framework displaying significantly enhanced adsorption of CO_2 and C_2H_2 over CH_4

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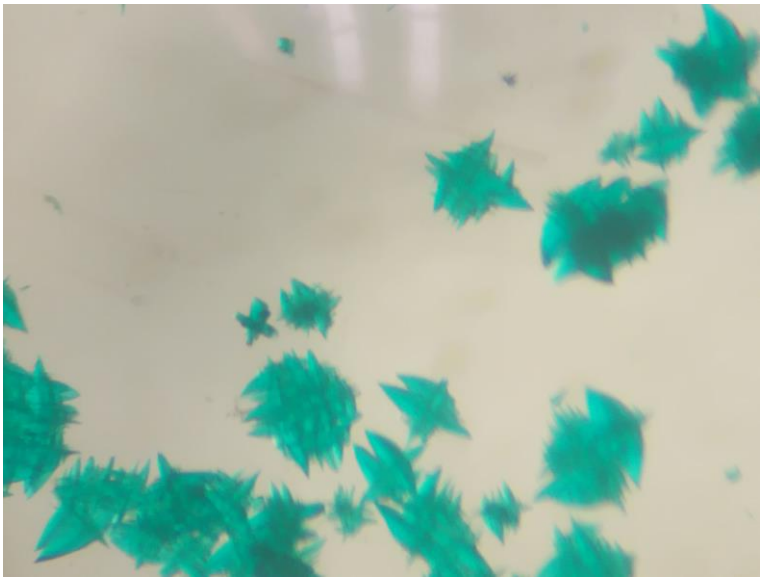


Fig. S0 Electronic photograph of the as-synthesized **ZJNU-99**.

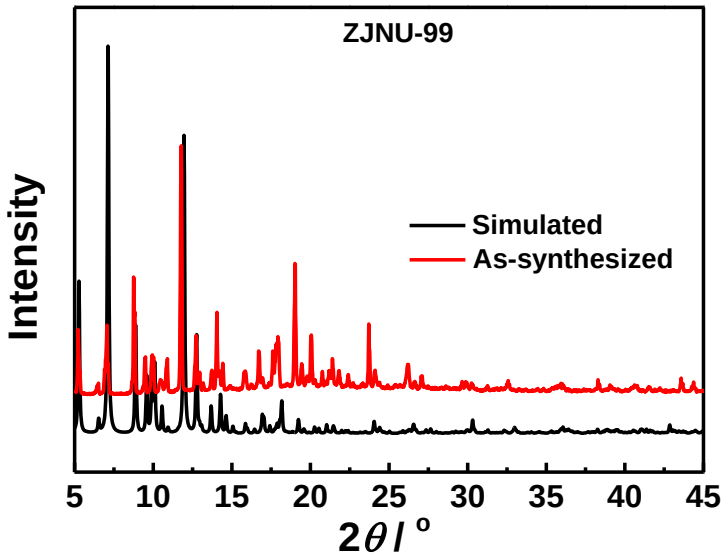


Fig. S1 Comparison of the experimental and simulated PXRD patterns of **ZJNU-99**.

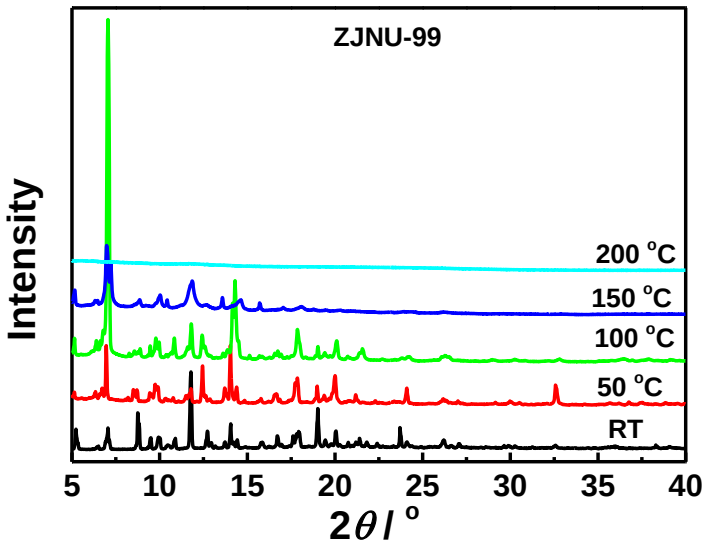


Fig. S2 Variable-temperature PXRD patterns of the as-synthesized **ZJNU-99**.

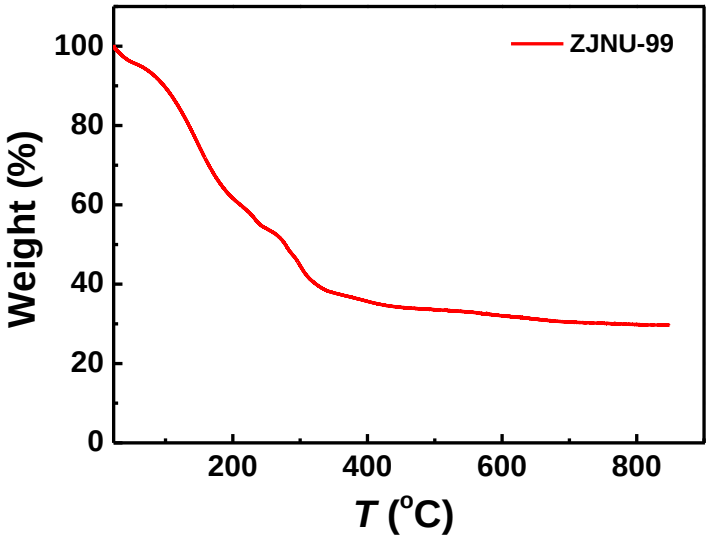


Fig. S3 TGA curve of the as-synthesized **ZJNU-99** under a flowing nitrogen atmosphere.

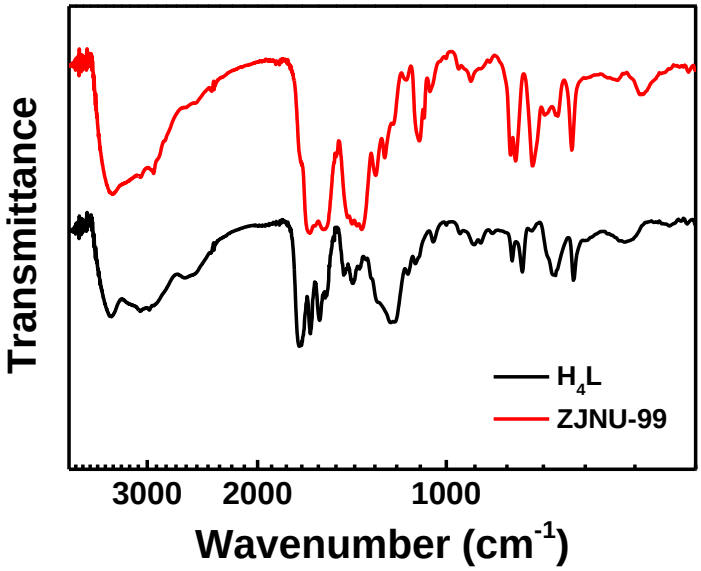
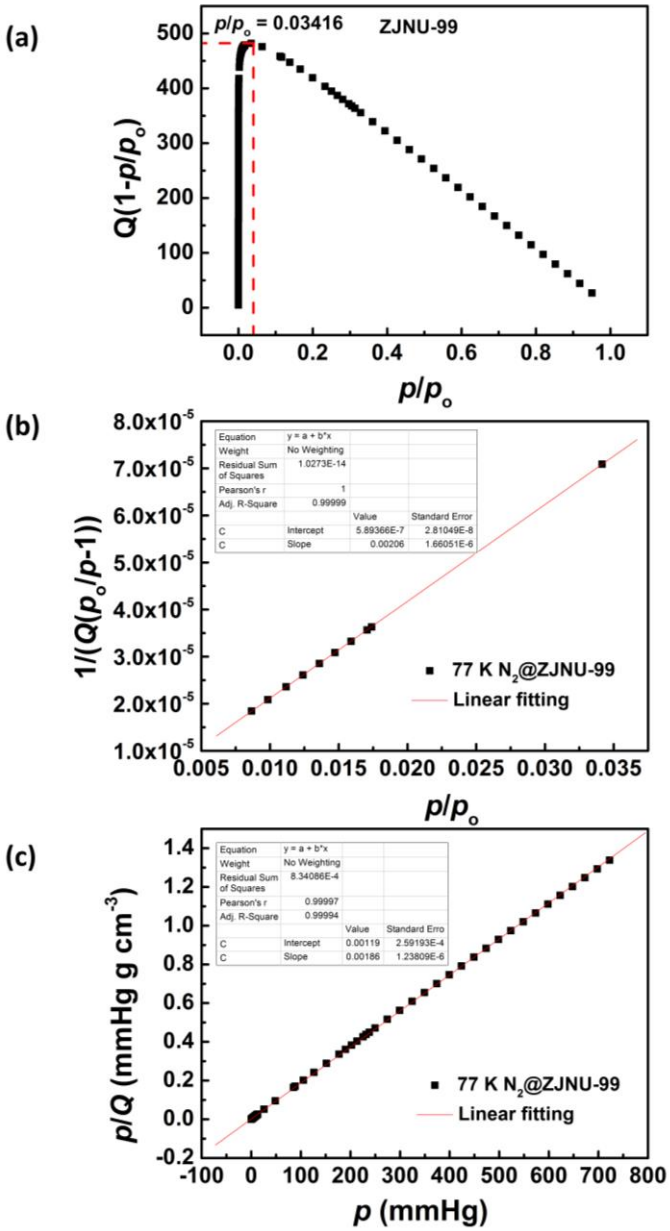


Fig. S4 Comparison of FTIR spectra of the ligand H_4L and its corresponding as-synthesized MOF **ZJNU-99**.



S_{BET} = 1/(5.89366 ×10^{-7}+ 0.00206)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2113 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00186)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2340 m^2 g^{-1}

BET constant C = 1 + 0.00206/5.89366 ×10^{-7} = 3496

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01663$$

Fig. S5 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-99**.

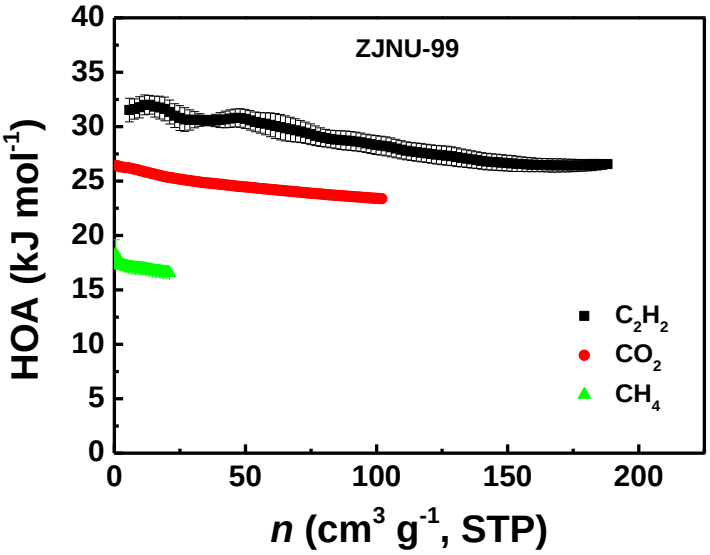


Fig. S6 The isosteric heat of C_2H_2, CO_2, and CH_4 adsorption in **ZJNU-99** as a function of gas loadings.

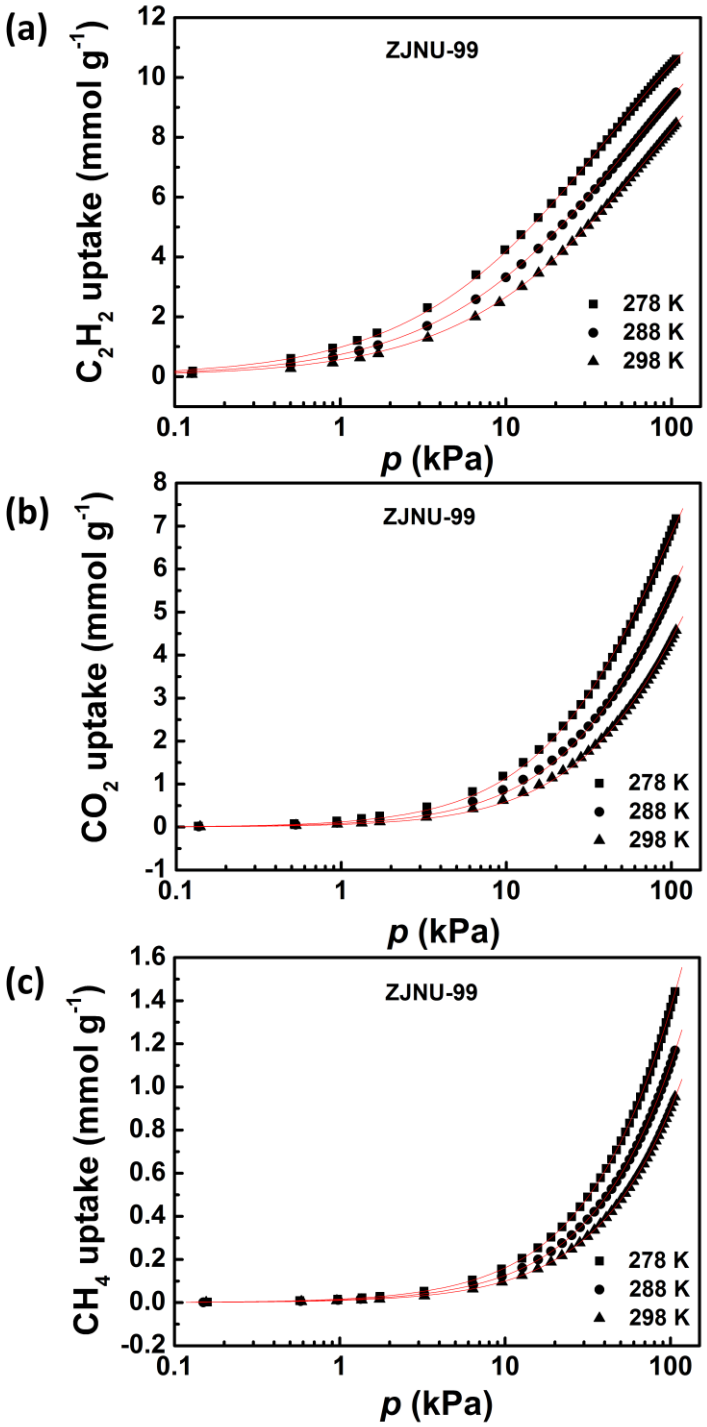


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-99** with the fitted isotherms at 278 K, 288 K, and 298 K.

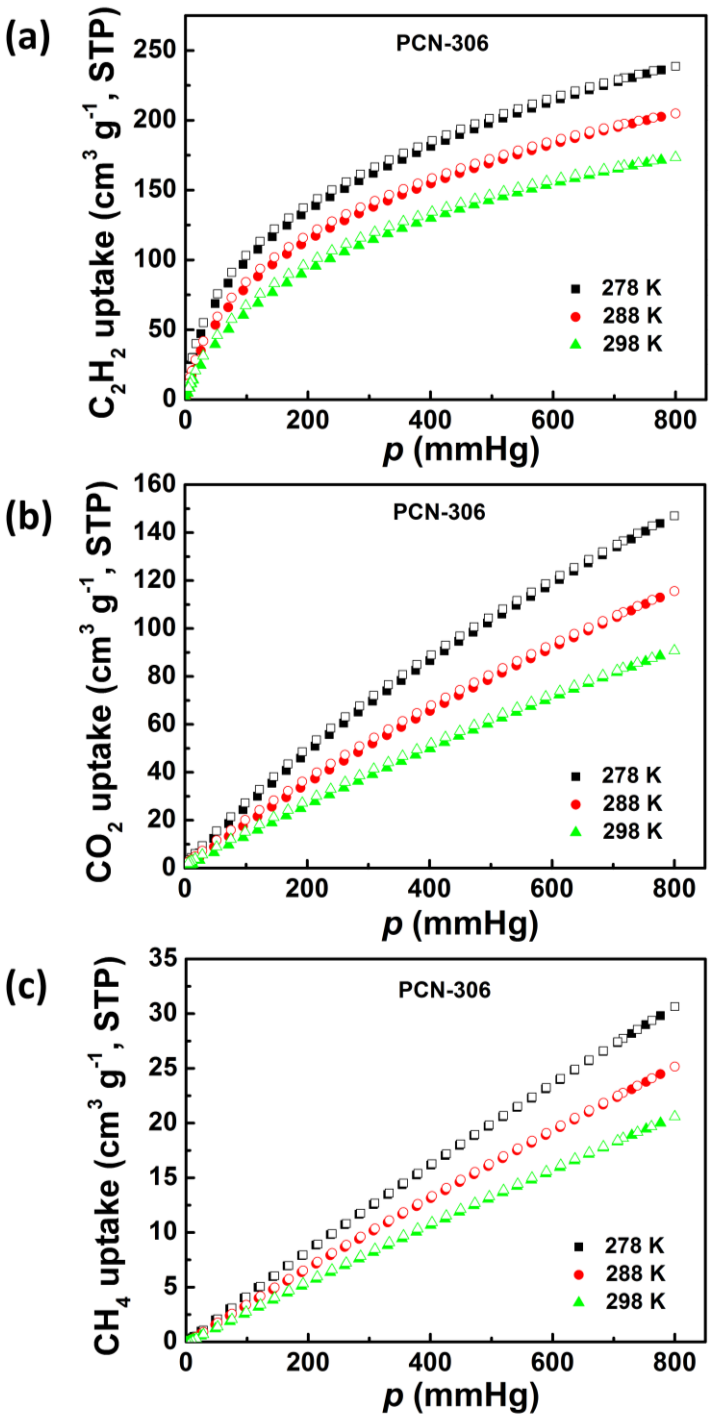


Fig. S8 (a) C_2H_2, (b) CO_2, and (c) CH_4 isotherms of **PCN-306** at 278 K, 288 K, and 298 K.

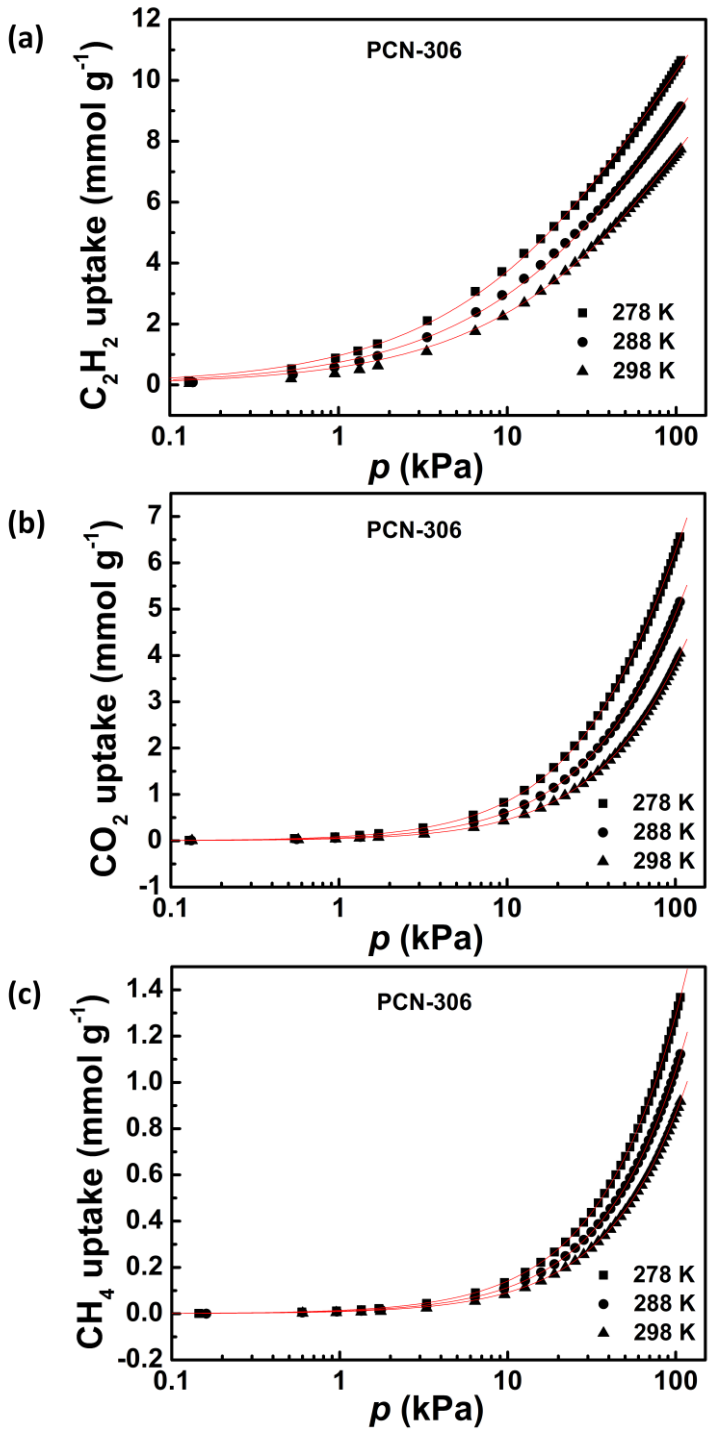


Fig. S9 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **PCN-306** with the fitted isotherms at 278 K, 288 K, and 298 K.

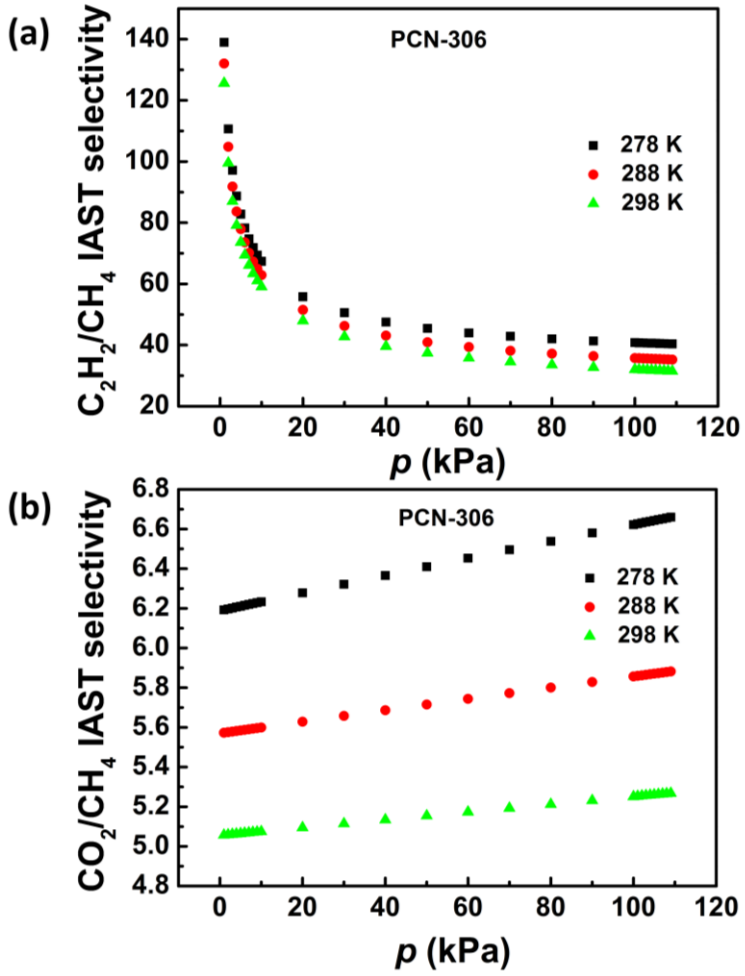
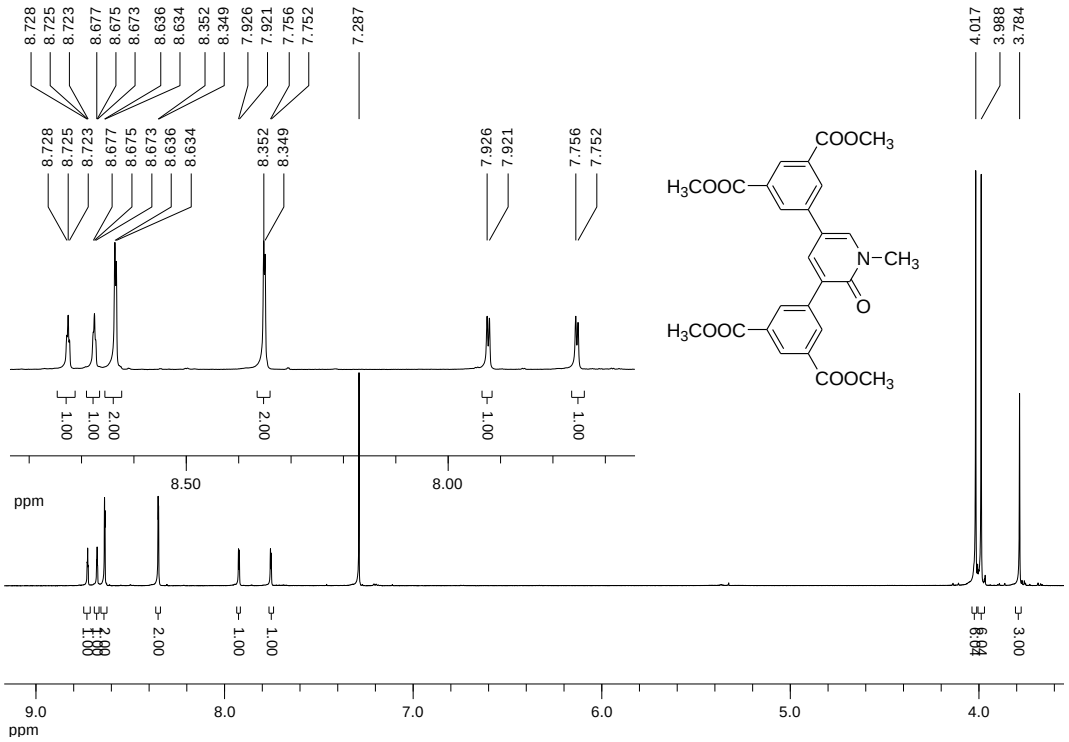


Fig. S10 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) CO_2/CH_4 gas mixtures in **PCN-306** at three different temperatures of 278 K, 288 K, and 298 K.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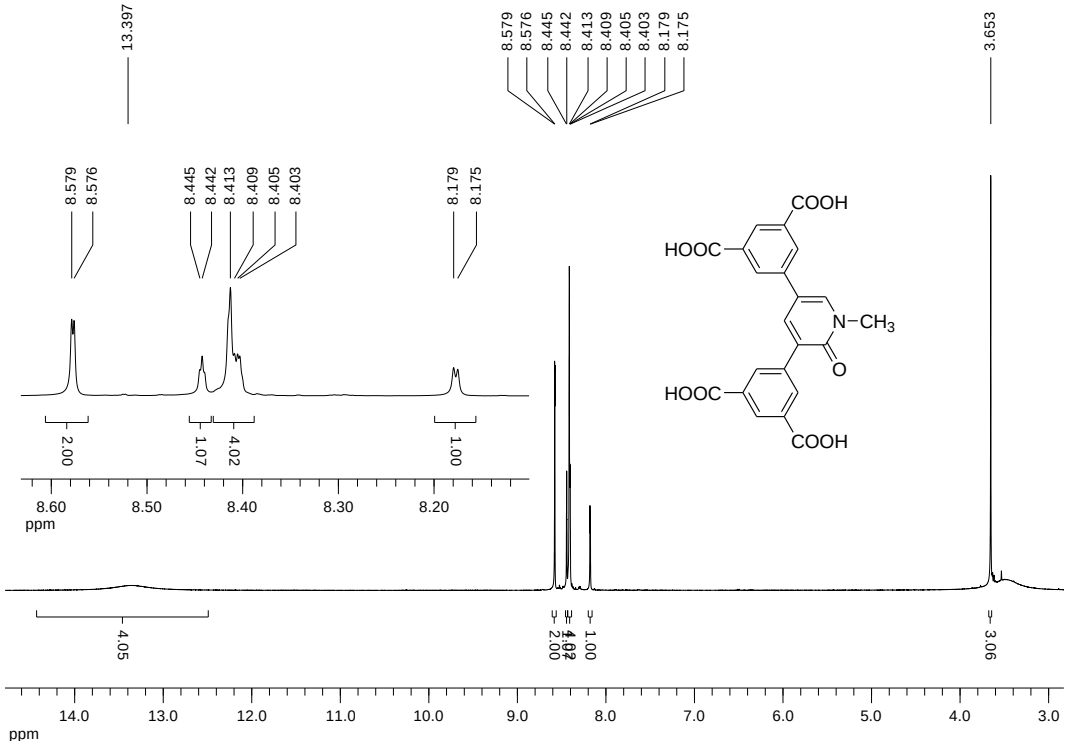
8.723
8.677
8.675
8.673
8.636
8.634
8.352
8.349
7.926
7.921
7.756
7.752
7.287
4.017
3.988
3.784
COOCH3
H3COOC
N−CH3
O
H3COOC
COOCH3
1.00
1.00
2.00
2.00
1.00
1.00
8.50
8.00
ppm
2.00
1.00
1.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
ppm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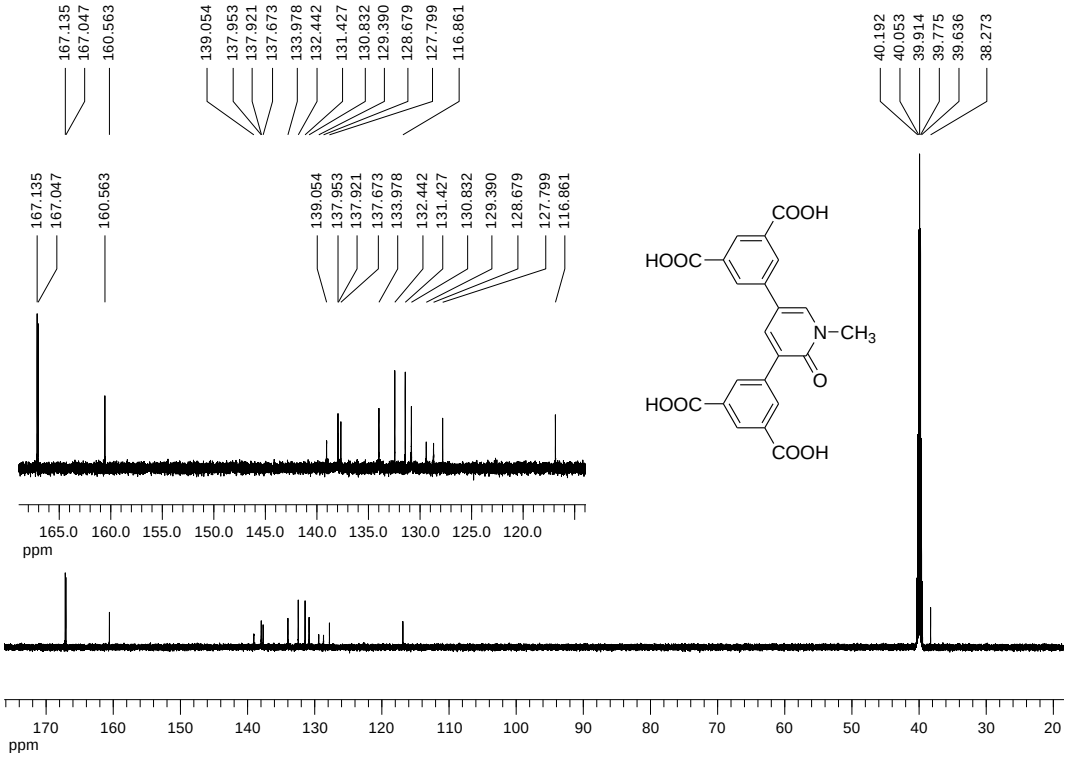
8.579
8.576
8.445
8.442
8.413
8.409
8.405
8.403
8.179
8.175
3.653
COOH
HOOC
N−CH3
O
HOOC
COOH
2.00
1.07
4.02
1.00
8.60
8.50
8.40
8.30
8.20
ppm
4.05
2.00
1.00
3.06
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm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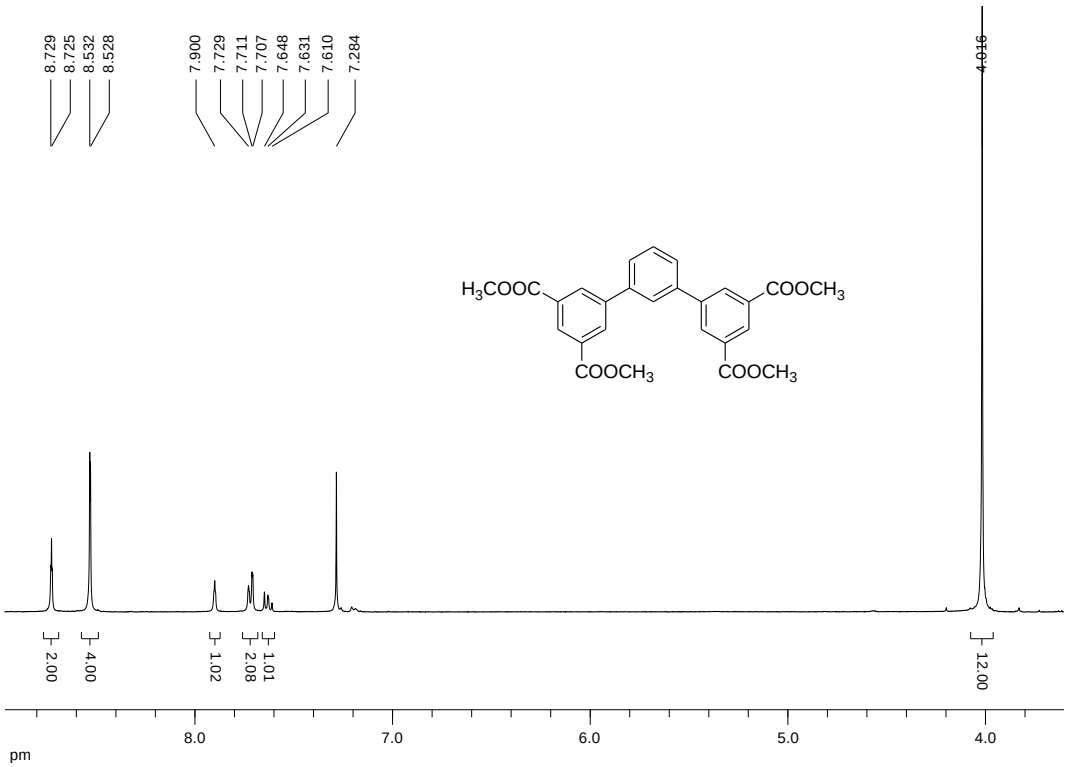
167.047
160.563
139.054
137.953
137.921
137.673
133.978
132.442
131.427
130.832
129.390
128.679
127.799
116.861
40.192
40.053
39.914
39.775
39.636
38.273
COOH
HOOC
N−CH3
O
HOOC
COOH
165.0 160.0 155.0 150.0 145.0 140.0 135.0 130.0 125.0 120.0
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm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8.725
8.532
8.528
7.900
7.729
7.711
7.707
7.648
7.631
7.610
7.284
4.016
H3COOC
COOCH3
COOCH3
COOCH3
2.00
4.00
1.02
2.08
1.01
12.00
8.0
7.0
6.0
5.0
4.0
pm

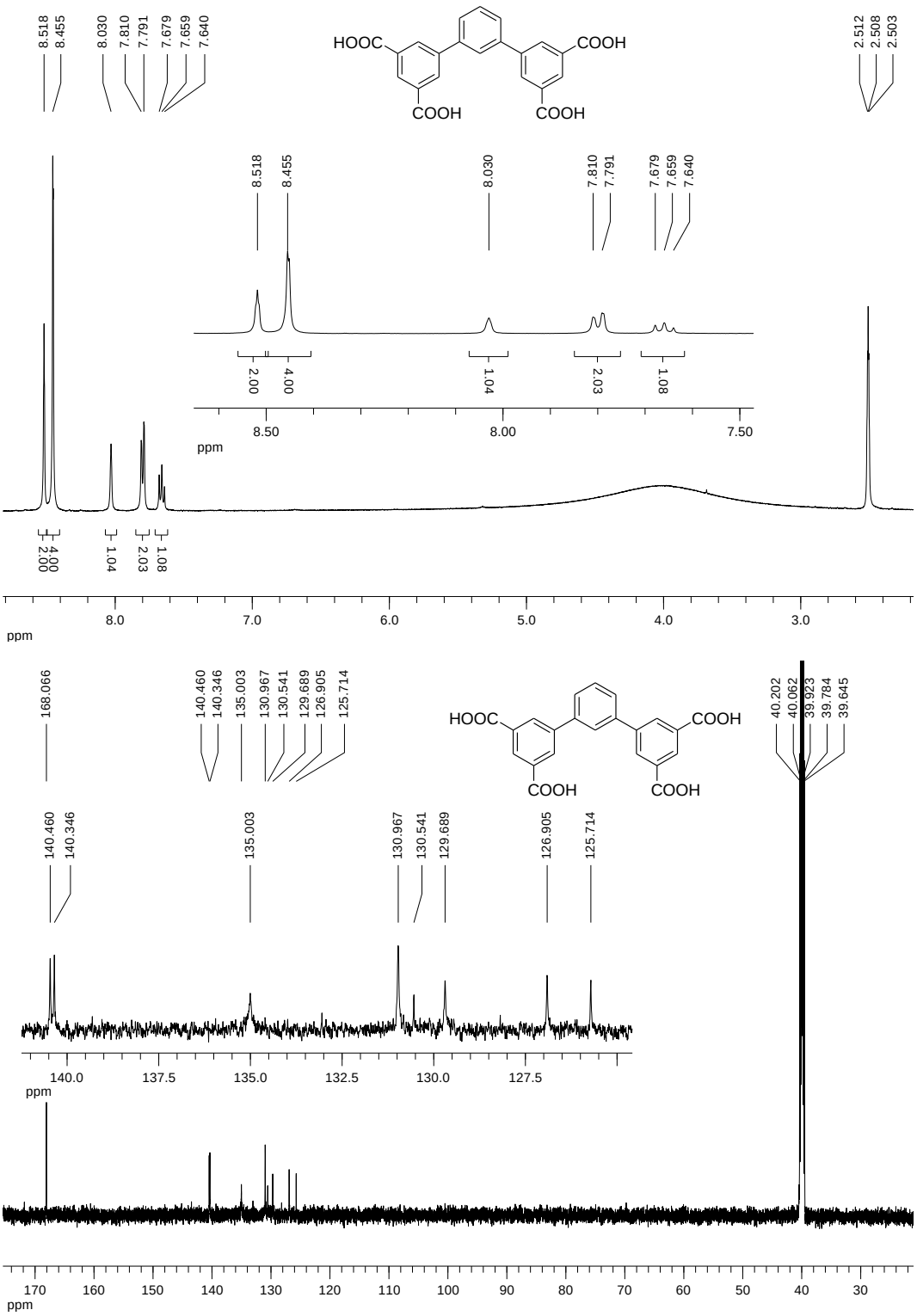

Fig. S11 ^{1}H and ^{13}C NMR spectra.

Table S1 Crystal data and structure refinement for **ZJNU-99**.

MOFs	**ZJNU-99**
Empirical formula	$C_{37}H_{52}Cu_2N_6O_{17}$
Formula weight	979.92
λ (Å)	1.54178
Crystal system	Orthorhombic
Space group	*Cmcm*
Unit cell dimensions	a = 24.7465(12) Å b = 33.4859(14) Å c = 18.4434(8) Å α = 90° β = 90° γ = 90°
V (Å^3)	15283.3(12)
Z	12
D_c (g cm^{-3})	1.278
μ (mm^{-1})	1.610
F(000)	6120
θ range for data collection (°)	3.267 to 65.206
Limiting indices	$-29 \le h \le 27$ $-37 \le k \le 39$ $-19 \le l \le 21$
Reflections collected / unique	30025/6892
R_{int}	0.0552
Max. and min. transmission	0.890 and 0.843
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6892/3/285
Goodness-of-fit on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0688 wR_2 = 0.2074
R indices (all data)	R_1 = 0.0875 wR_2 = 0.2255
Largest diff. peak and hole (e·Å^{-3})	0.688 and -0.393
CCDC	1907360

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-99**.

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	15.73206	1.24379×10^{-5}	19.844	0.73516	0.99988
CO_2	15.14643	2.56684×10^{-7}	23.962	1	0.99951
CH_4	7.92144	1.52239×10^{-6}	16.688	1	0.99999

Table S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **PCN-306**.

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	20.56898	1.83018×10^{-5}	18.245	0.65466	0.99922
CO_2	21.01804	2.96428×10^{-7}	22.109	1	0.99997
CH_4	13.18114	1.6832×10^{-6}	14.953	1	0.99995

Table S4 Summary of gas adsorption properties of **ZJNU-99** and its parent compound **PCN-306**.

MOFs	S_{BET} $S_{Langmuir}$ ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	D_c ($g\ cm^{-3}$)	C_2H_2 uptake[a] ($cm^3 g^{-1}$, STP)			CO_2 uptake[a] ($cm^3 g^{-1}$, STP)			CH_4 uptake[a] ($cm^3 g^{-1}$, STP)			C_2H_2/CH_4 (50/50, *v*/*v*) IAST selectivity[a]			CO_2/CH_4 (50/50, *v*/*v*) IAST selectivity[a]		
				298 K	288 K	278 K	298 K	288 K	278 K	298 K	288 K	278 K	298 K	288 K	278 K	298 K	288 K	278 K
ZJNU-99	2113/2340	0.835	0.731	189.8	212.9	237.7	102.5	128.9	160.7	21.4	26.2	32.3	46.6	56.1	71.1	6.8	7.8	9.2
PCN-306	2825/3087	1.101	0.690	173.5	204.9	238.7	90.8	115.6	147.0	20.6	25.2	30.6	31.5	35.3	40.4	5.3	5.9	6.7

$S_{BET}/S_{Langmuir}$ = BET and Langmuir surface areas; V_p = Pore volume based on 77 K N_2 isotherm; D_c = Framework density calculated from single-crystal X-ray data; [a] at 1 atm.