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A *N*-oxide-functionalized nanocage-based copper-tricarboxylate framework for selective capture of C_2H_2

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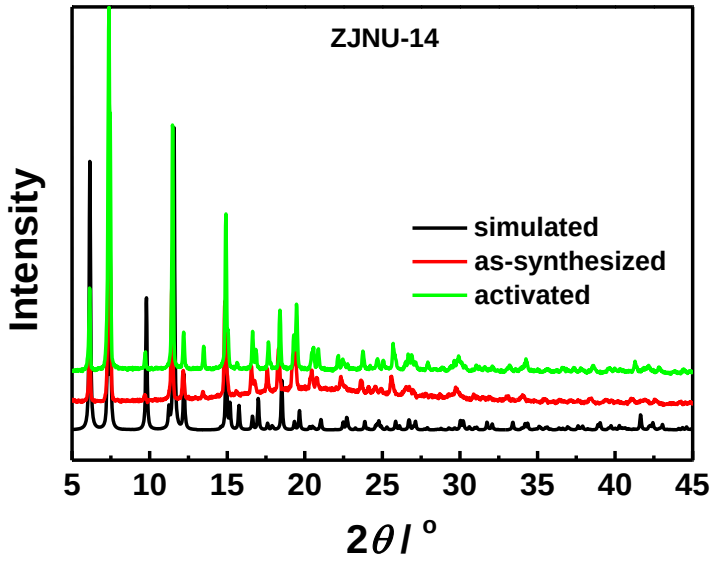


Fig. S1 PXRD patterns of **ZJNU-14**

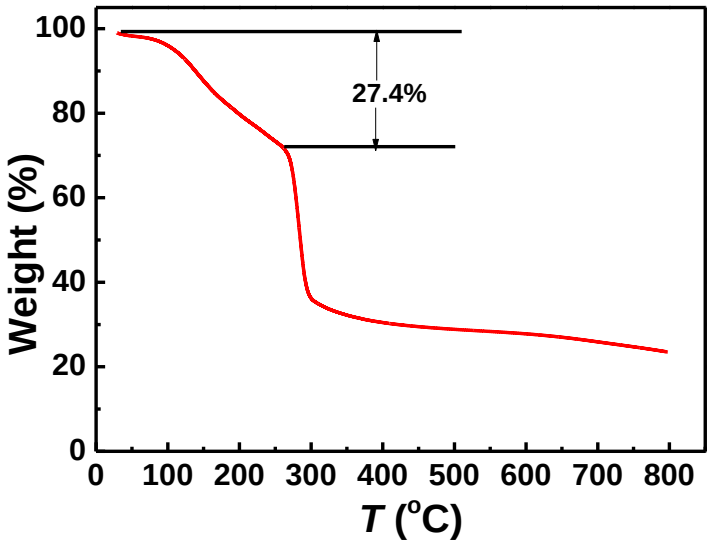


Fig. S2 TGA curve of as-synthesized **ZJNU-14** under N_2 atmosphere

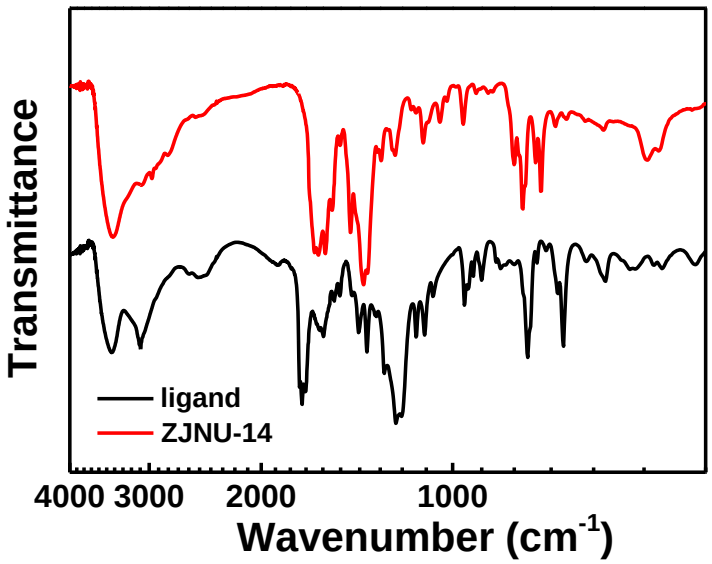
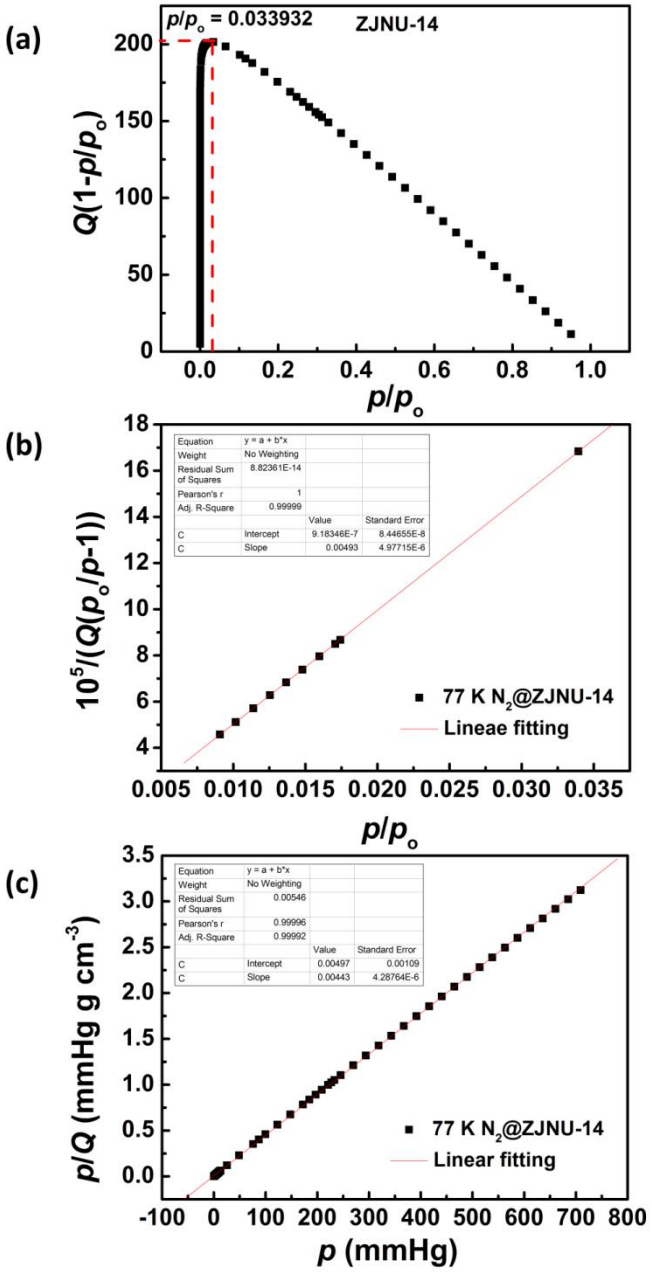


Fig. S3 Comparison of FTIR spectra of the ligand (black) and as-synthesized **ZJNU-14** (red).



S_{BET} = 1/(9.18346×10^{-7}+ 0.00493)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 883 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00443)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 983 m^2 g^{-1}

BET constant C = 1 + 0.00493/9.18346×10^{-7} = 5369

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.013463$$

Fig. S4 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-14**.

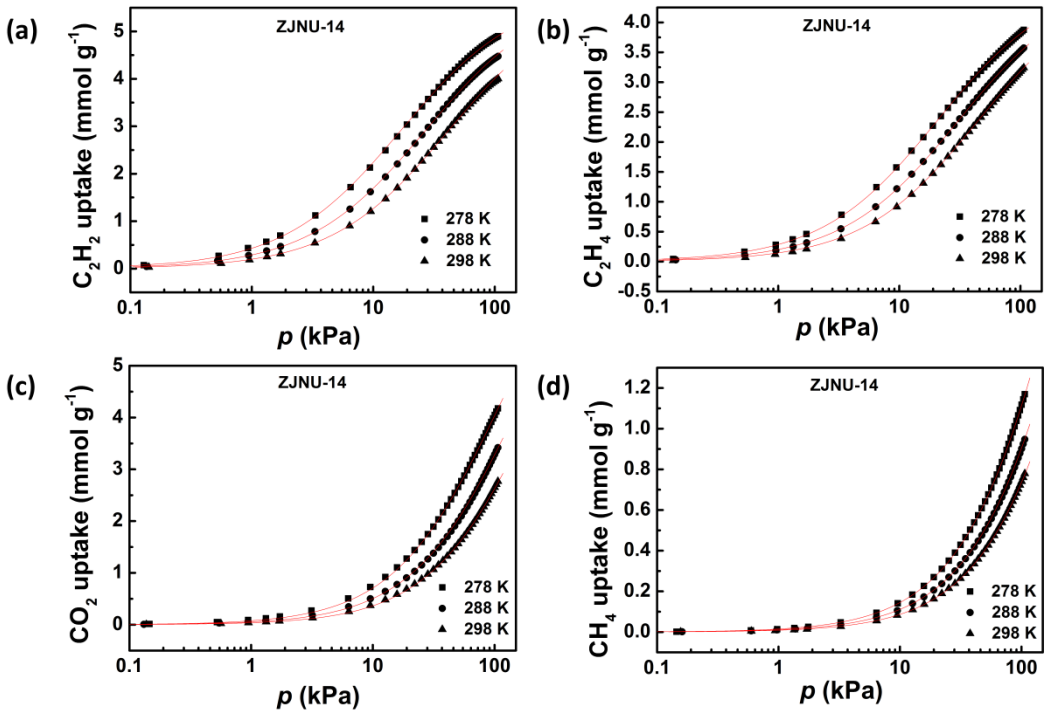
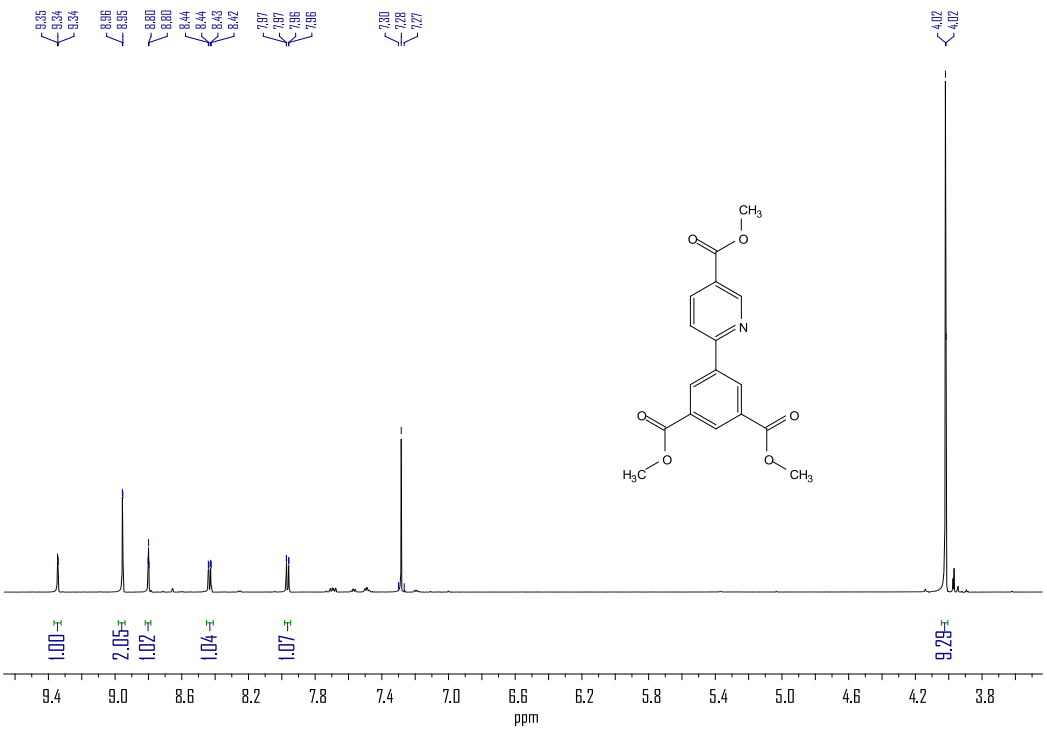


Fig. S5 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) C_2H_4, (c) CO_2, and (d) CH_4 in **ZJNU-14** with the fitted isotherms at 278 K, 288 K, and 298 K.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9.34
8.86
8.85
8.80
8.80
8.44
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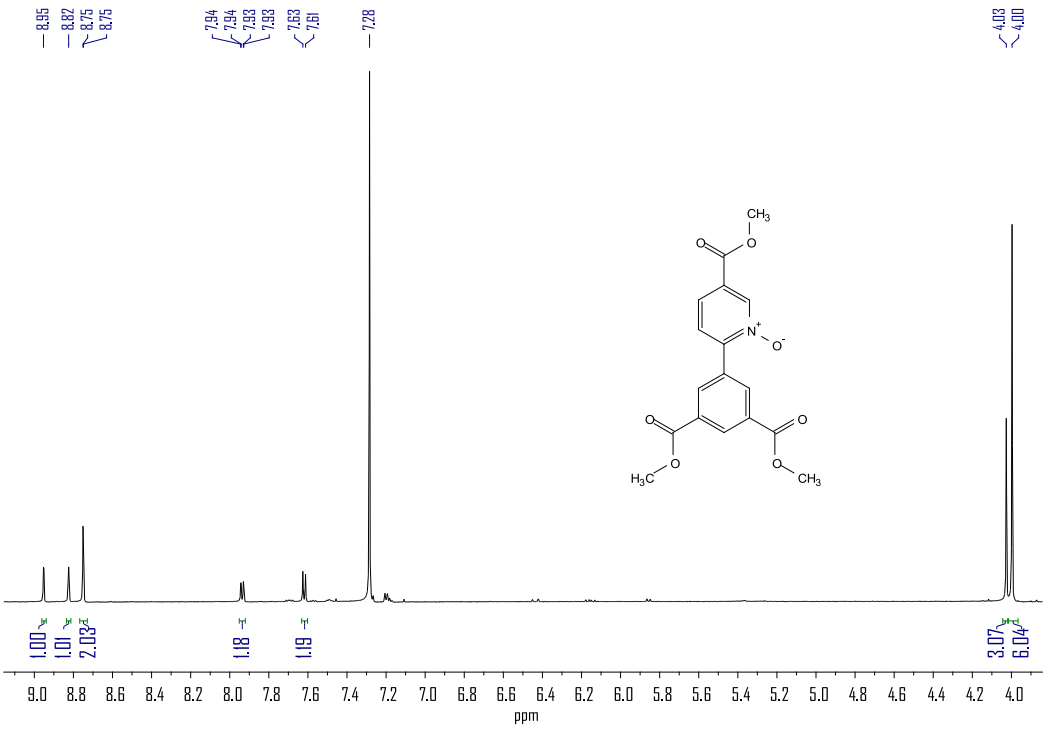
8.43
8.42
7.97
7.97
7.96
7.96
7.30
7.28
7.27
4.02
4.02
1.00
2.05
1.02
1.04
1.07
9.29
9.4
9.0
8.6
8.2
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
ppm


8.95
8.82
8.75
8.75
7.94
7.94
7.93
7.93
7.63
7.61
7.28
4.03
4.00
1.00
1.01
2.03
1.18
1.19
3.07
6.04
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
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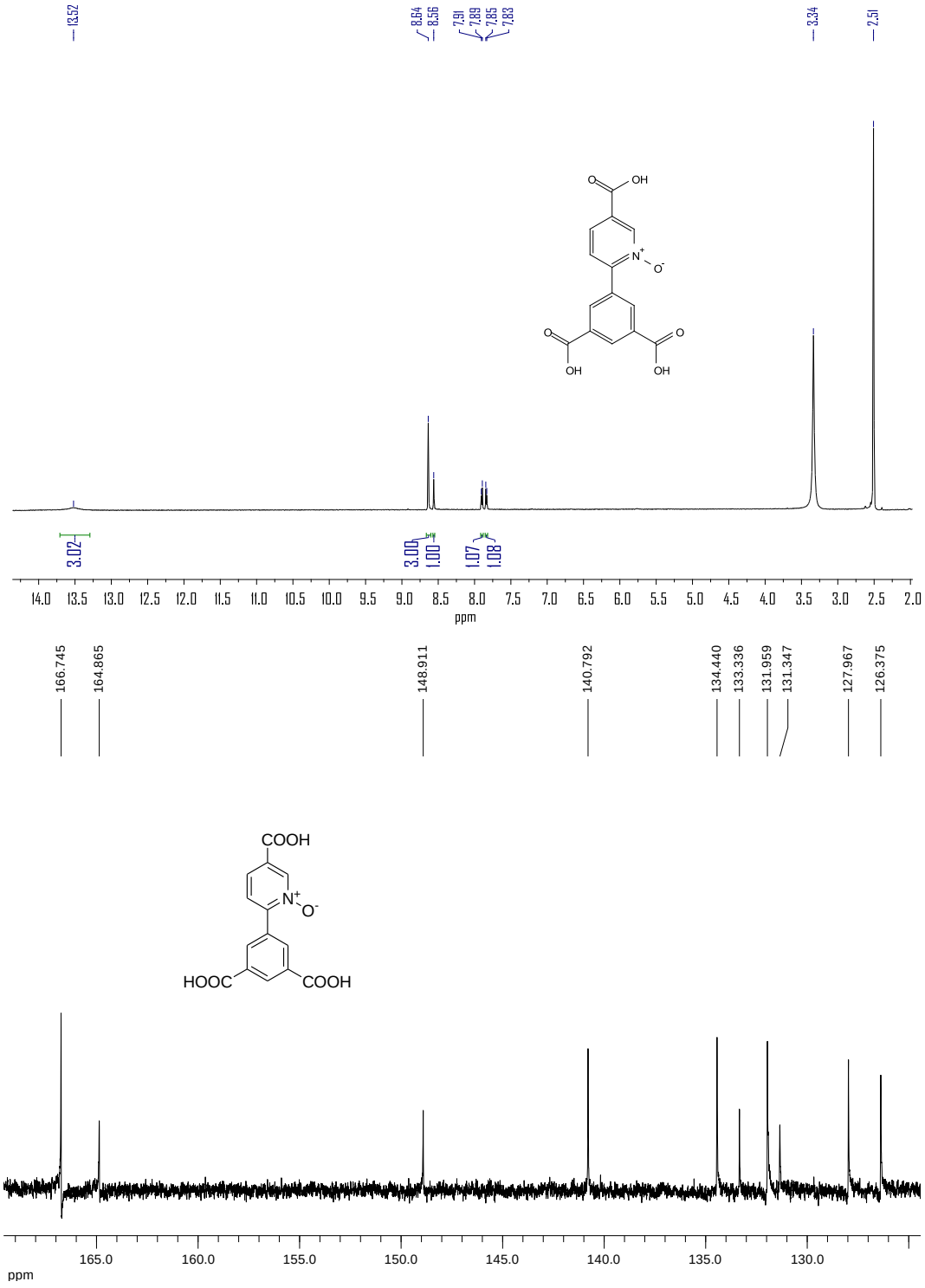

Fig. S6 ^{1}H and ^{13}C NMR spectra.

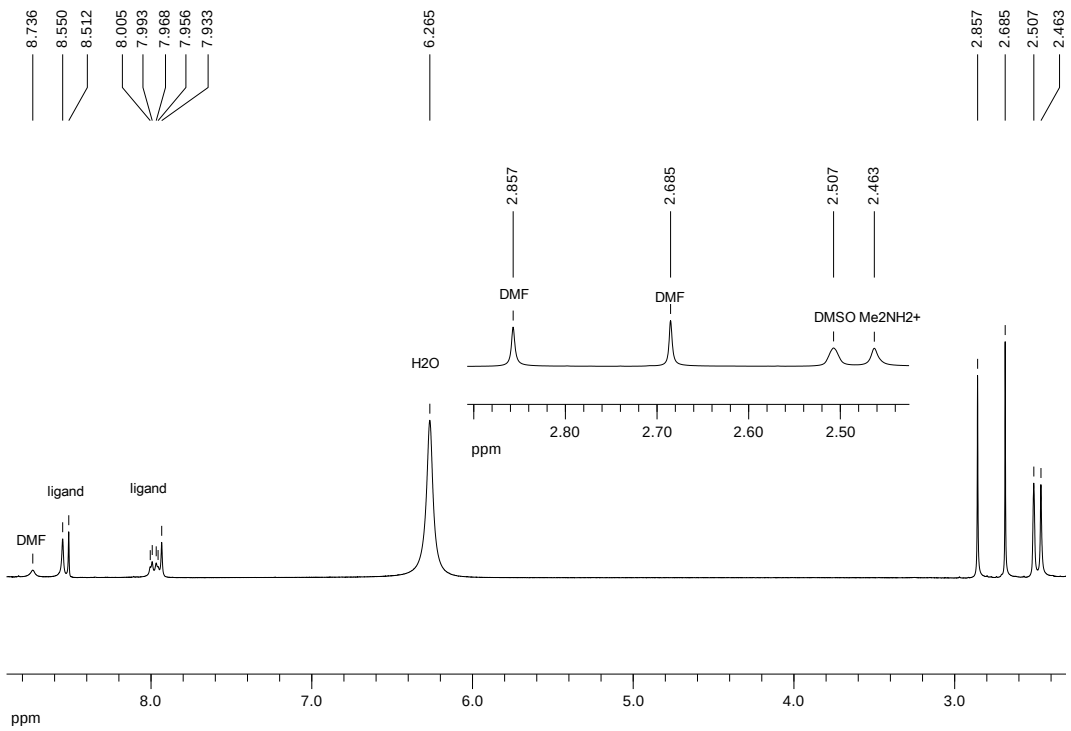

Fig. S7 ^{1}H NMR spectrum of HCl-digested **ZJNU-14** in DMSO-d_6

Table S1 Crystal data and structure refinement for **ZJNU-14**.

MOF	**ZJNU-14**
Empirical formula	$C_{19}H_{23}CuN_3O_9$
Formula weight	500.94
Temperature (K)	150(2)
λ (Å)	0.71073
Crystal system	Trigonal
Space group	*R32:H*
Unit cell dimensions	a = 18.0487(5) Å b = 18.0487(5) Å c = 36.3959(11) Å α = 90° β = 90° γ = 120°
V (Å^3)	10267.7(6)
Z	18
D_c (g cm^{-3})	1.458
μ (mm^{-1})	1.010
F(000)	4662
θ range for data collection (°)	2.257 to 27.484
Limiting indices	$-20 \le h \le 23$ $-22 \le k \le 22$ $-38 \le l \le 47$
Reflections collected / unique	21204 / 5231
R_{int}	0.0287
Max. and min. transmission	0.898 and 0.879
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5231 / 0 / 209
Goodness-of-fit on F^2	1.004
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0241 wR_2 = 0.0669
R indices (all data)	R_1 = 0.026 wR_2 = 0.0682
Largest diff. peak and hole (e·Å^{-3})	0.635 and -0.201
CCDC	2017484

Table S2 Summarizes of physical parameters of C_2H_2, C_2H_4, 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
C_2H_4	169.42	282.34	50.41	4.163	3.3×4.2×4.8	42.52	0	+1.50
CO_2	194.65	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 S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, C_2H_4, CO_2, and CH_4 in **ZJNU-14**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	5.85747	4.51642×10^{-7}	27.904	0.89438	0.99979
C_2H_4	4.7228	1.78752×10^{-6}	24.253	0.9055	0.99993
CO_2	8.45182	2.41297×10^{-7}	24.365	1	0.99973
CH_4	4.30221	1.37872×10^{-6}	18.112	1	0.99995

Table S4 Summaries of gas adsorption properties of **ZJNU-14**

ZJNU-14		298 K	288 K	278 K
Uptake capacity[a] ($cm^3\ g^{-1}$, STP)	C_2H_2	89.7	100.3	109.8
	C_2H_4	72.7	80.1	86.9
	CO_2	62.1	76.6	93.6
	CH_4	17.5	21.2	26.2
IAST adsorption selectivity[a]	C_2H_2/C_2H_4 (*v*/*v*, 1/1)	1.63	1.81	2.05
	C_2H_2/C_2H_4 (*v*/*v*, 1/99)	1.59	1.75	1.95
	C_2H_2/CO_2 (*v*/*v*, 1/1)	3.42	3.46	3.48
	C_2H_2/CH_4 (*v*/*v*, 1/1)	21.9	27.3	35.4
Q_{st}[b] (kJ mol^{-1})	C_2H_2	35.0 ±0.3		
	C_2H_4	31.5 ±0.1		
	CO_2	28.1 ±0.7		
	CH_4	19.2 ±0.7		

[a] at 1 atm; [b] at near zero surface coverage; STP = standard temperature and pressure