Electronic Supplementary Material (ESI) for CrystEngComm.

Construction and gas adsorption properties of two heteroSBU MOFs based on unsymmetrical tetracarboxylate linkers

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Fitting of Pure-Component Isotherm data

The pure-component C_2H_2, CO_2 and CH_4 adsorption isotherms measured at 278 K, 288 K and 298 K were fitted with the single-site Langmuir-Freundlich model

$$q = \frac{q_{sat} b p^{v}}{1 + b p^{v}} \quad \text{, with } T\text{-dependent parameter} \quad b = b_o \exp(\frac{E_a}{RT})$$

where q is the adsorbed amount (mmol g^{-1}), q_{sat} is the monolayer adsorption capacity (mmol g^{-1}), p is the equilibrium pressure (kPa), and b and v is the Langmuir and Freundlich constants. The corresponding fitting parameters are provided in Table S2-3 in the supporting information. Fig S6 in the supporting information provides a comparison of the experimental isotherm data for C_2H_2, CO_2 and CH_4 in **ZJNU-9** with the isotherm fits. Fig S7 in the supporting information provides a comparison of the experimental isotherm data for C_2H_2, CO_2 and CH_4 in **ZJNU-10** with the isotherm fits.

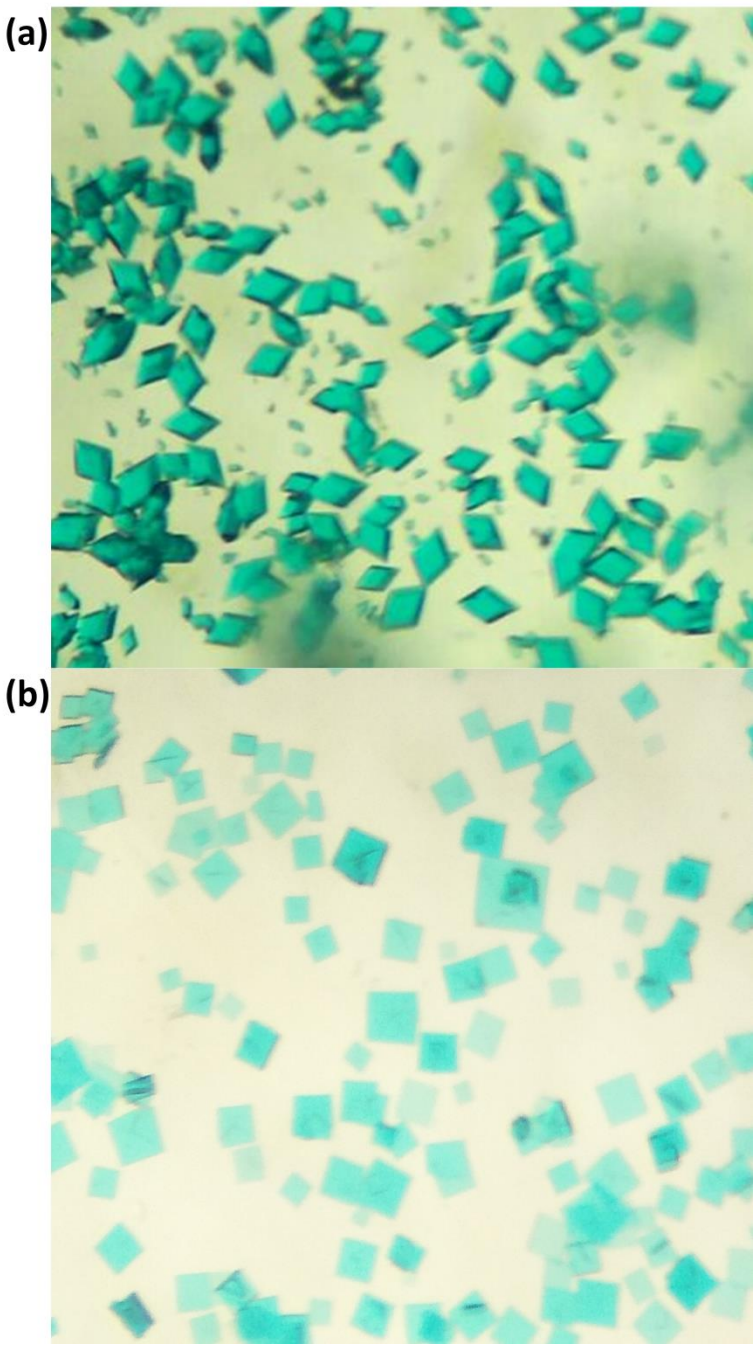


Fig. S1 The electronic photographs of as-synthesized **ZJNU-9** and **ZJNU-10**

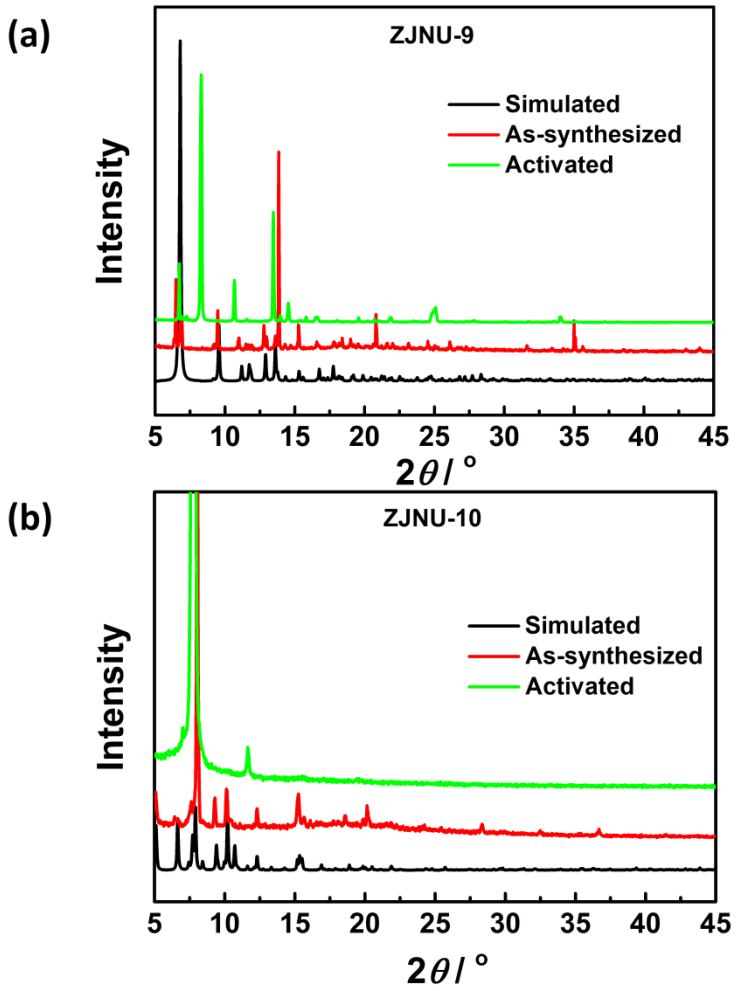


Fig. S2 The experimental and simulated PXRD patterns of (a) **ZJNU-9** and (b) **ZJNU-10**.

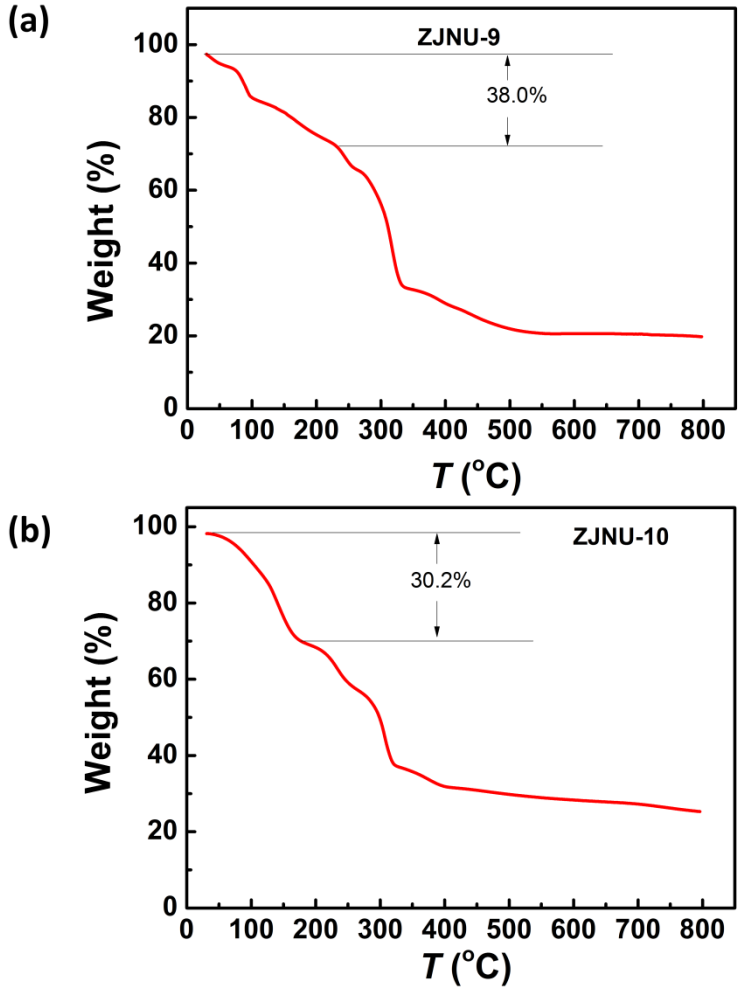


Fig. S3 The TGA curves of the as-synthesized (a) **ZJNU-9** and (b) **ZJNU-10** under N_2 atmosphere. For **ZJNU-9**, the weight loss of 38.0% before 505 K corresponds to the departure of 6.5 DMF and 5 H_2O molecules *per* chemical formula. For **ZJNU-10**, the weight loss of 30.2% before 450 K corresponds to the departure of 11 DMA and 1 H_2O molecules *per* chemical formula.

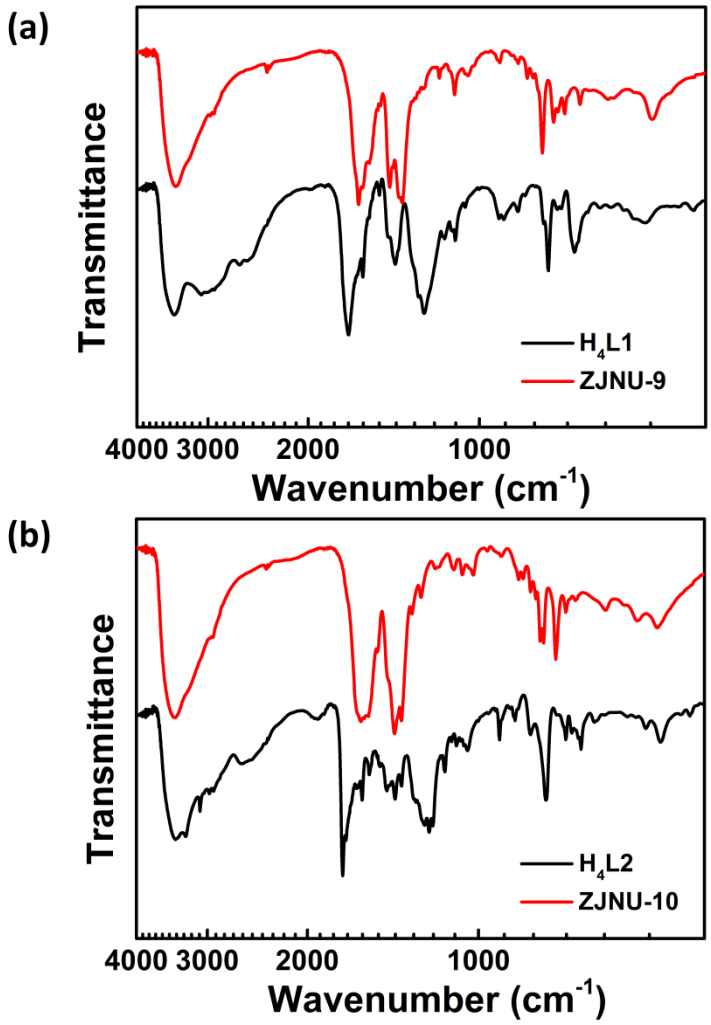
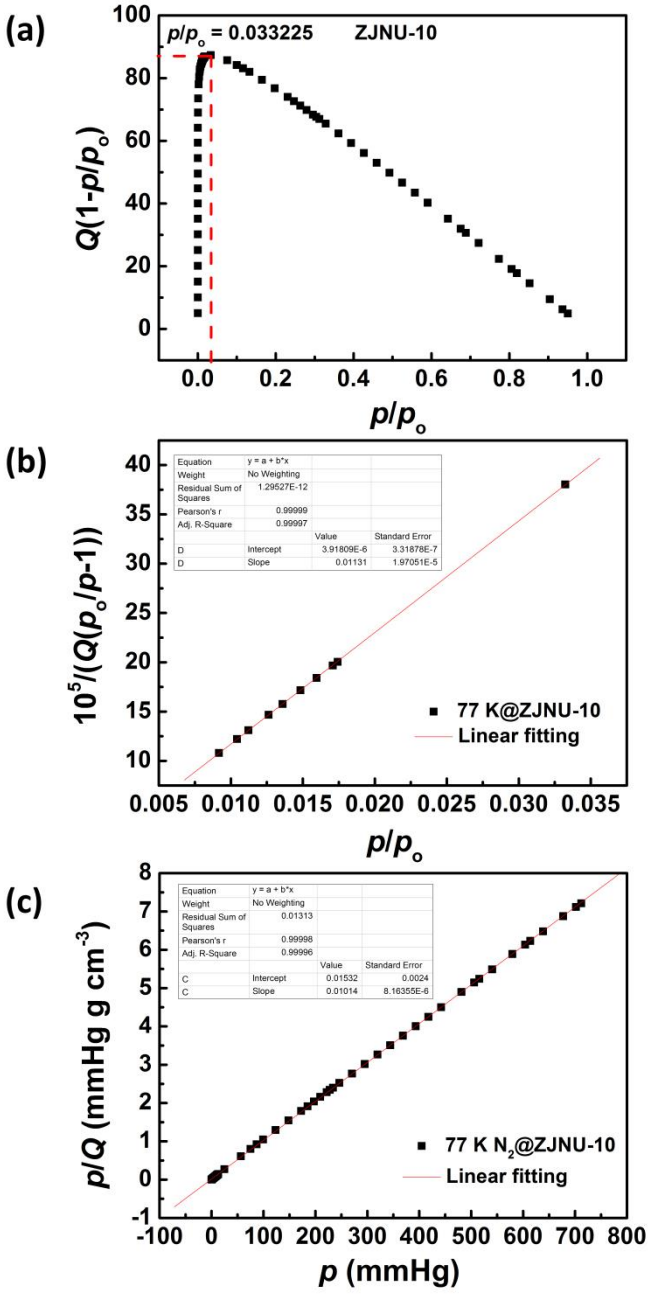


Fig. S4 Comparison of the FTIR spectra of (a) **ZJNU-9** and its ligand H_4L1, and (b) **ZJNU-10** and its ligand H_4L2.



S_{BET} = 1/(3.91809×10^{-6}+ 0.01131)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 385 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.01014)/22414 ×6.023 ×10^{23} ×0.162 ×10^{-18} = 429 m^2 g^{-1}

BET constant C = 1 + 0.01131/3.91809×10^{-6} = 2888

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01827$$

Fig. S5 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-10**.

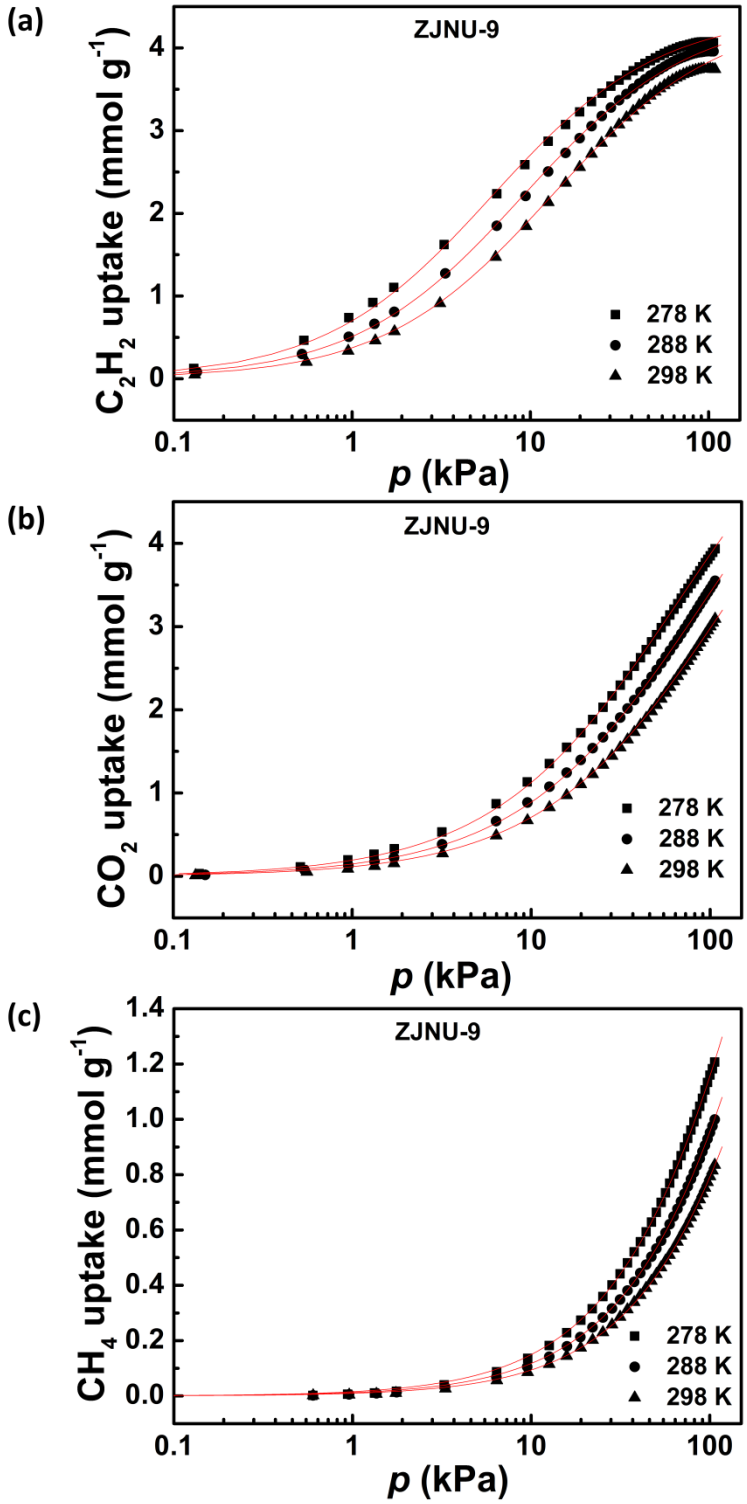


Fig. S6 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-9** with the fitted isotherms at 278 K, 288 K, and 298 K.

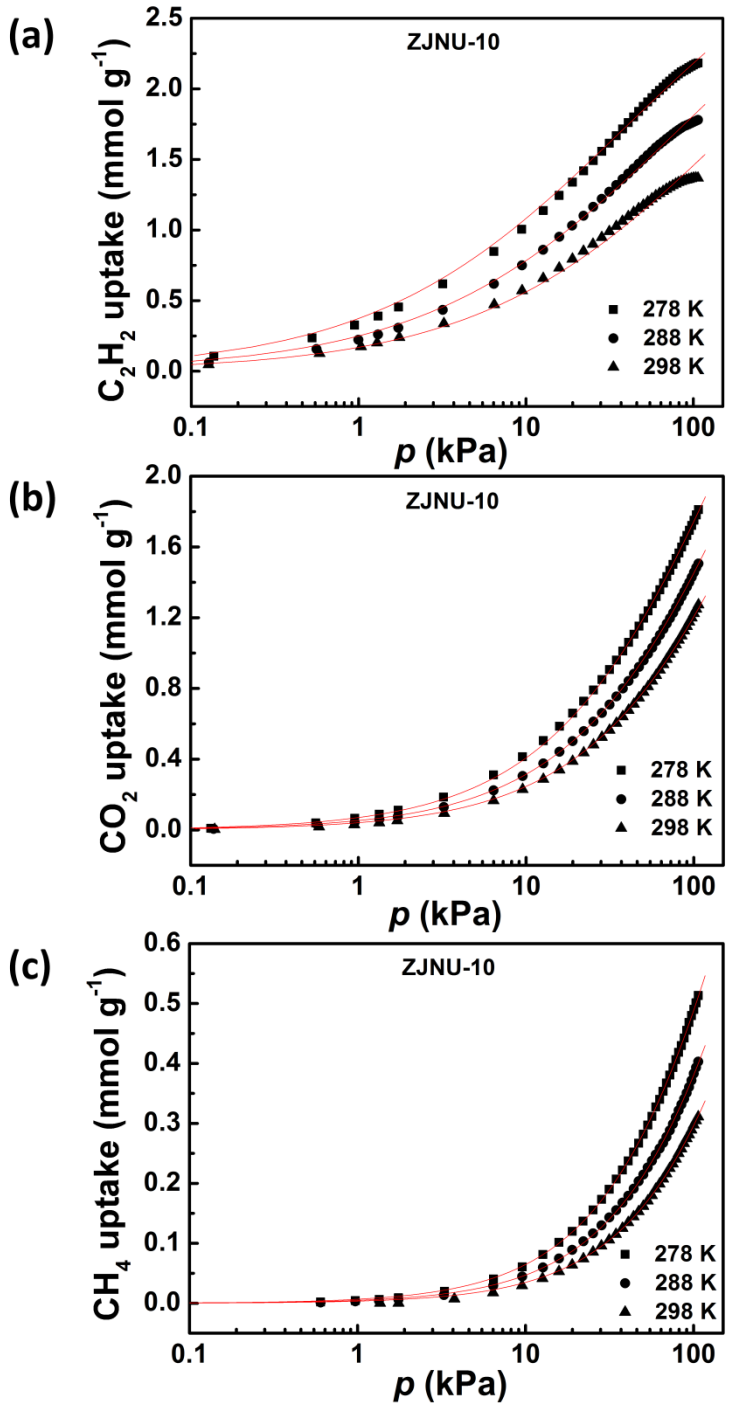


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-10** with the fitted isotherms at 278 K, 288 K, and 298 K.

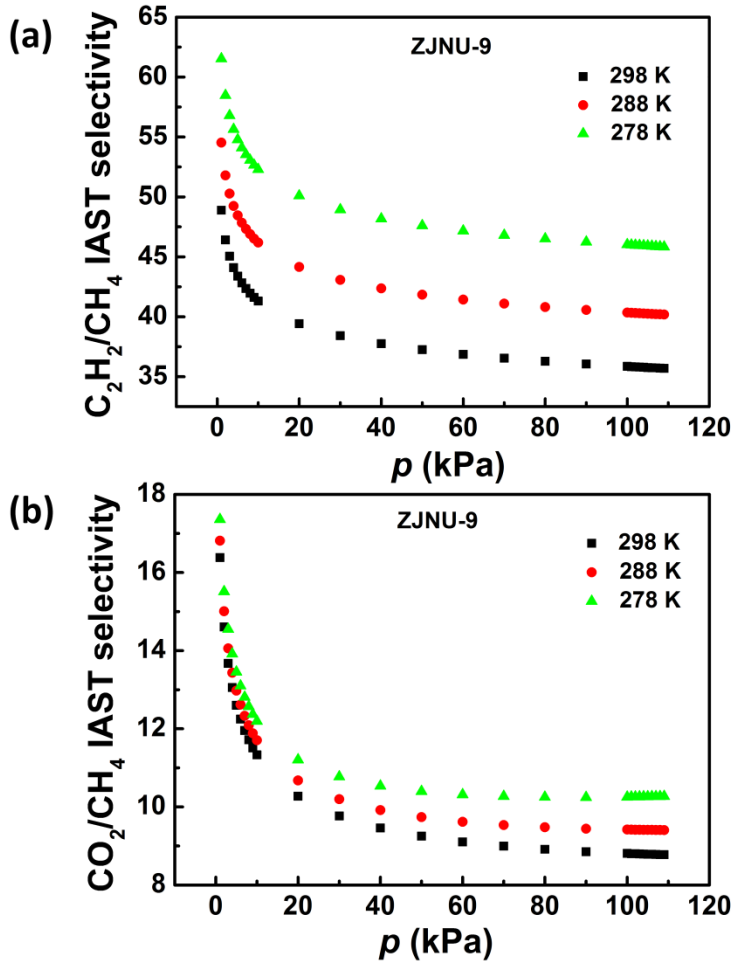


Fig. S8 IAST calculations of (a) C_2H_2/CH_4 and (b) CO_2/CH_4 adsorption selectivities of **ZJNU-9** for the equimolar binary gas mixtures at three different temperatures of 298 K, 288 K, and 278 K.

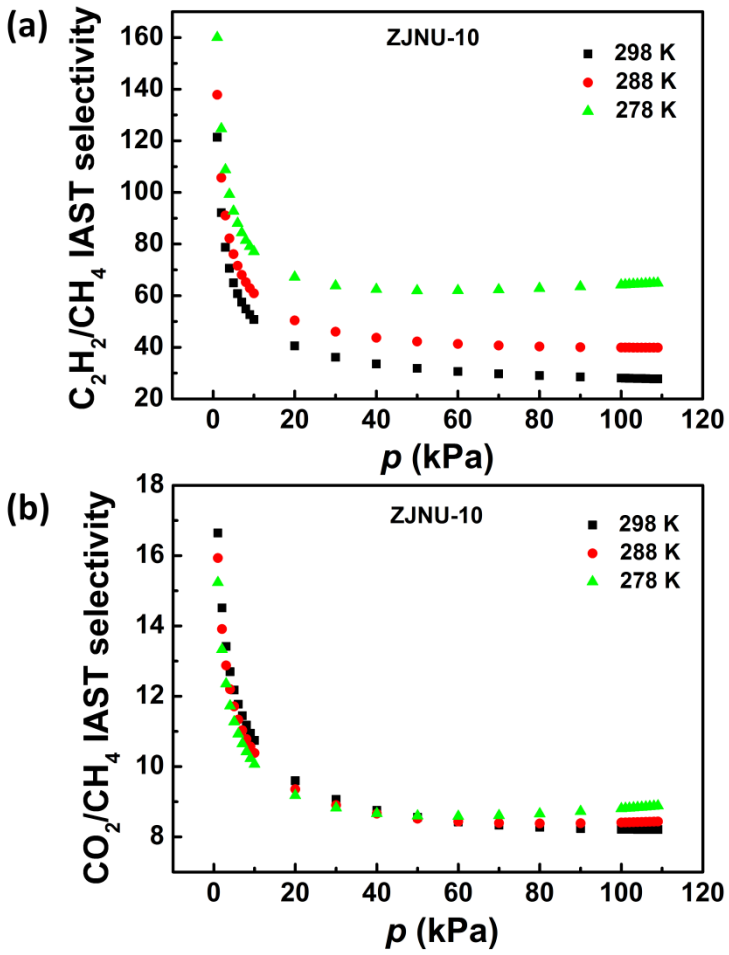
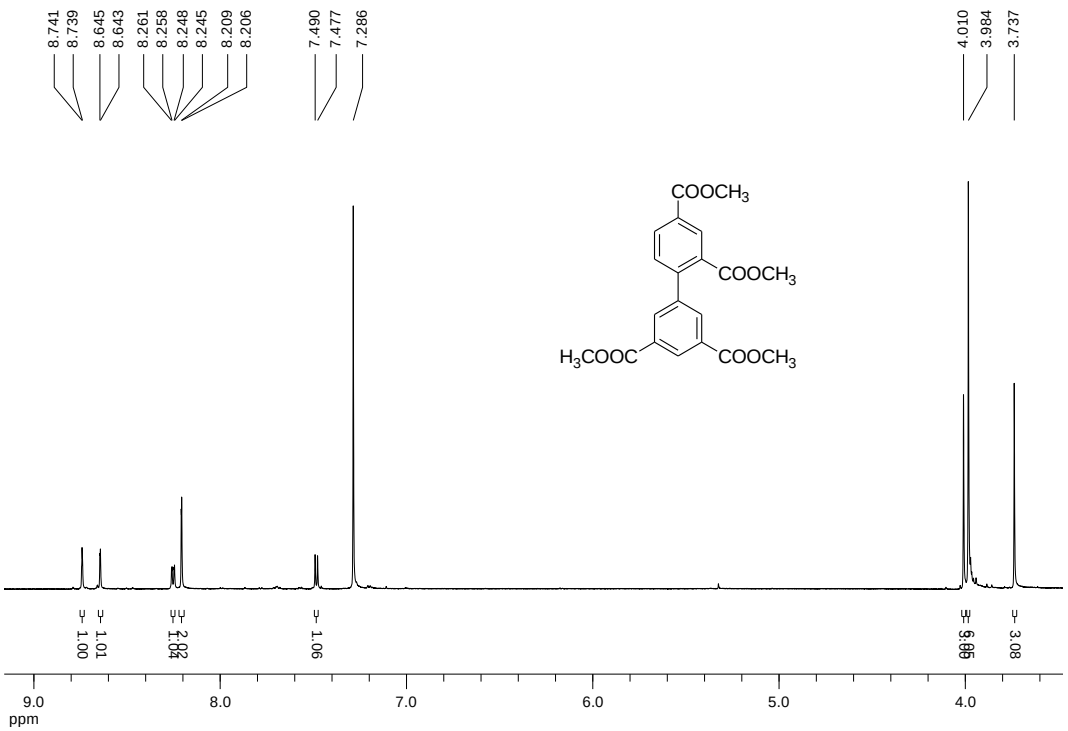


Fig. S9 IAST calculations of (a) C_2H_2/CH_4 and (b) CO_2/CH_4 adsorption selectivities of **ZJNU-10** for the equimolar binary gas mixtures at three different temperatures of 298 K, 288 K, and 278 K.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8.258
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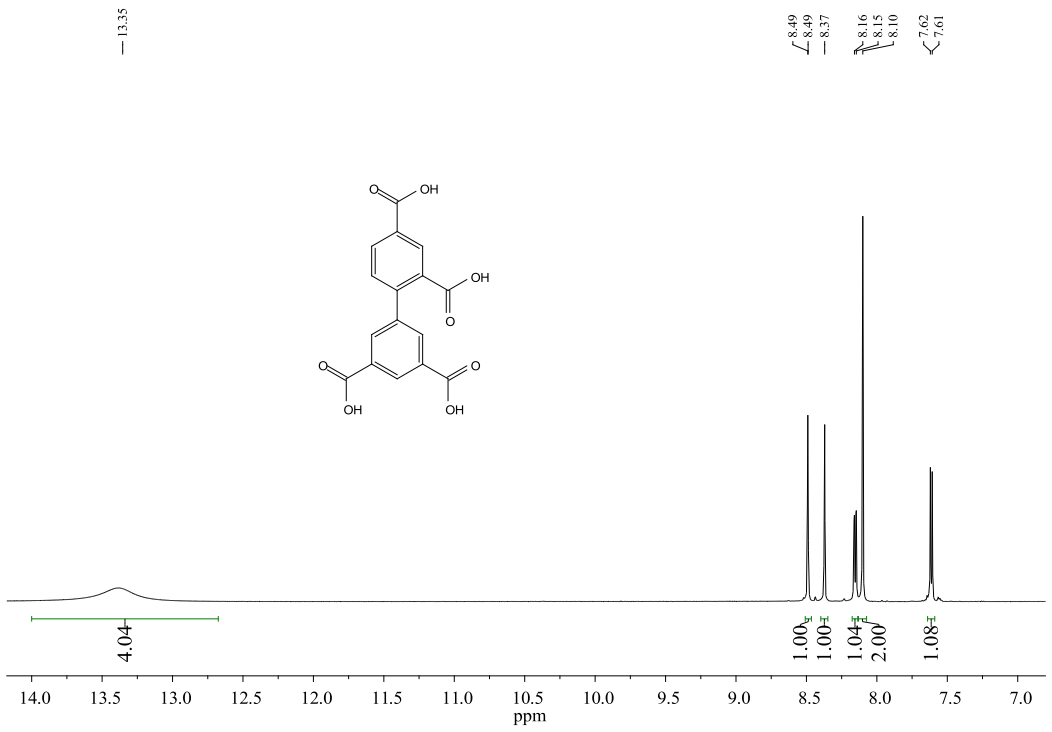
8.206
7.490
7.477
7.286
4.010
3.984
3.737
COOCH3
COOCH3
H3COOC
COOCH3
1.00
1.01
2.82
2.84
1.06
6.06
6.06
3.08
9.0
8.0
7.0
6.0
5.0
4.0
ppm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7.62
7.61
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4.04
1.00
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1.04
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13.0
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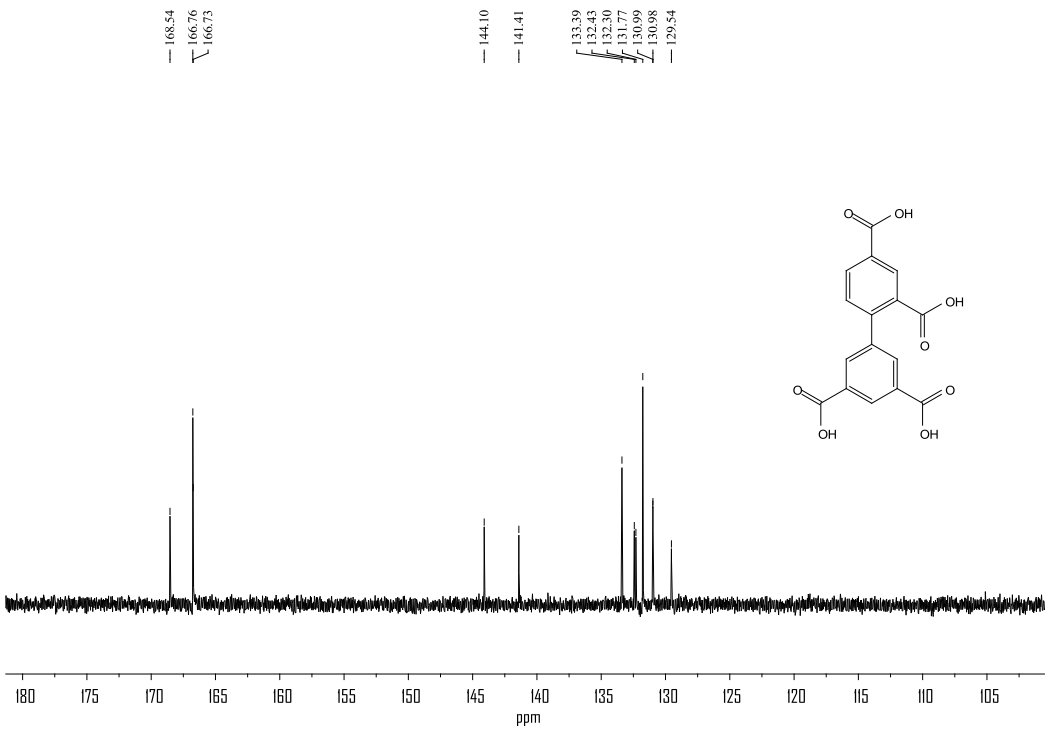
7.5
7.0
ppm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166.73
144.10
141.41
133.39
132.43
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131.77
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130.98
129.54
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OH
OH
OH
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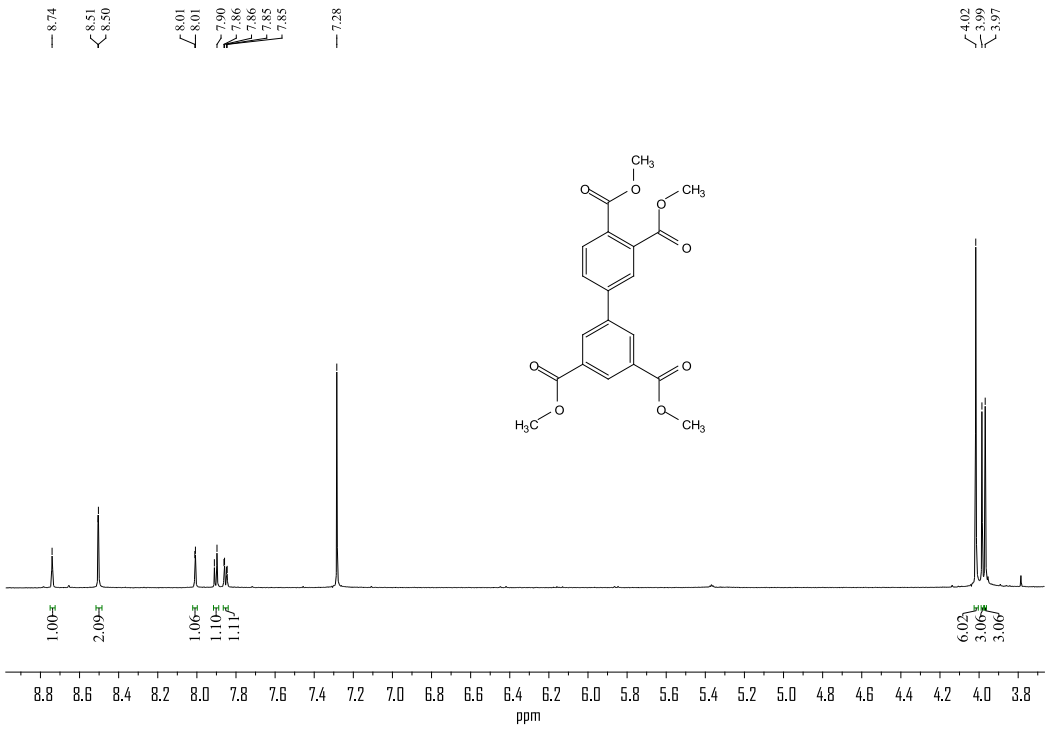
ppm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7.86
7.85
7.85
7.28
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3.97
CH3
CH3
CH3
1.00
2.09
1.06
1.10
1.11
6.02
3.06
3.06
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
ppm

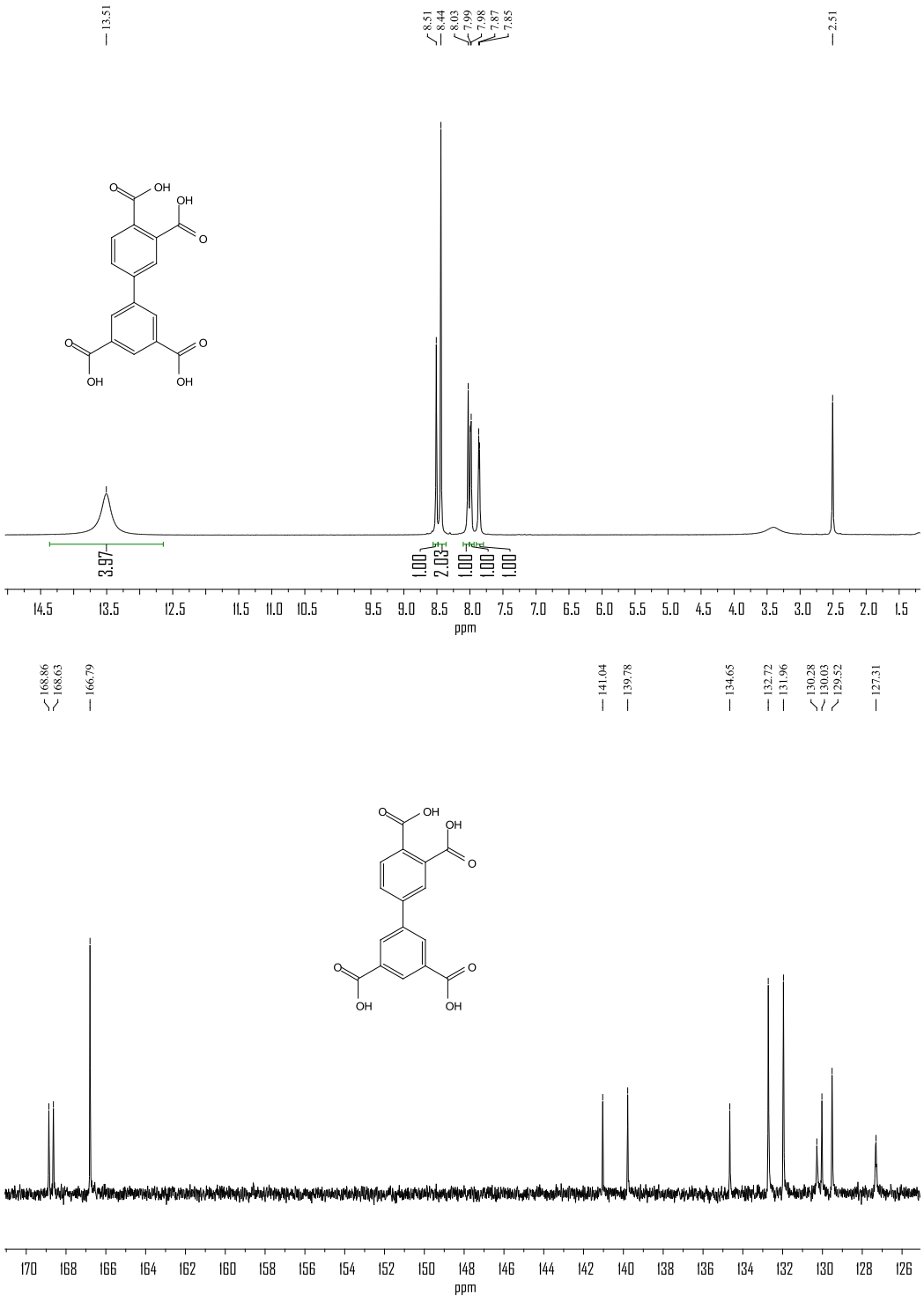

Fig. S10 ^{1}H and ^{13}C NMR spectra

Table S1 Crystal data and structure refinement for **ZJNU-9** and **ZJNU-10**.

MOFs	**ZJNU-9**	**ZJNU-10**
Empirical formula	$C_{51.5}H_{67.5}Cu_4N_{6.5}O_{27.5}$	$C_{108}H_{147}Cl_2Cu_{10}N_{11}O_{56}$
Formula weight	1471.78	3201.66
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	*C2/m*	*Cmmm*
Unit cell dimensions	a = 19.3334(10) Å b = 25.6921(12) Å c = 15.8595(13) Å α = 90° β = 123.080(2)° γ = 90°	a = 26.5456(16) Å b = 44.633(3) Å c = 26.5717(16) Å α = 90° β = 90° γ = 90°
V (Å^3)	6600.8(7)	31482(3)
Z	4	8
D_c (g cm^{-3})	1.481	1.351
μ (mm^{-1})	1.356	1.436
F(000)	3032	13152
θ range for data collection (°)	2.642 to 27.501	2.194 to 25.032
Limiting indices	$-25 \le h \le 25$ $-33 \le k \le 33$ $-17 \le l \le 20$	$-31 \le h \le 31$ $-53 \le k \le 53$ $-31 \le l \le 25$
Reflections collected / unique	28259 / 7683	82562 / 14419
R_{int}	0.0242	0.1045
Max. and min. transmission	0.875 and 0.836	0.866 and 0.866
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7683 / 7 / 312	14419 / 408 / 558
Goodness-of-fit on F^2	1.077	1.096
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0482 wR_2 = 0.2030	R_1 = 0.0660 wR_2 = 0.1571
R indices (all data)	R_1 = 0.0524 wR_2 = 0.2133	R_1 = 0.1389 wR_2 = 0.1891
Largest diff. peak and hole (e·Å^{-3})	2.588 and -4.979	1.368 and -1.116
CCDC	2016107	2016108

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-9**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	4.41547	4.84947×10^{-6}	24.426	0.92377	0.9991
CO_2	6.67589	1.02283×10^{-5}	18.441	0.8319	0.99964
CH_4	4.57312	2.66966×10^{-6}	16.510	1	0.99987

Table S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-10**

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	3.44993	3.57848×10^{-7}	29.434	0.57534	0.99647
CO_2	4.59353	4.81721×10^{-6}	18.662	0.79866	0.99973
CH_4	1.79571	2.87535×10^{-7}	21.890	1	0.99982

Table S4 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	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 S5 Summaries of gas adsorption properties of **ZJNU-9** and **ZJNU-10**

MOFs		**ZJNU-9**	**ZJNU-10**
$S_{BET}/S_{Langmuir}$ (m^2 g^{-1})		11/17	385/429
V_p (cm^3 g^{-1})		0.00154	0.153
C_2H_2 uptake[a] (cm^3 g^{-1}, STP)	298 K	83.9	30.7
	288 K	88.7	39.9
	278 K	91.1	48.9
CO_2 uptake[a] (cm^3 g^{-1}, STP)	298 K	69.3	28.5
	288 K	79.6	33.8
	278 K	88.2	40.6
CH_4 uptake[a] (cm^3 g^{-1}, STP)	298 K	18.7	7.0
	288 K	22.4	9.0
	278 K	27.1	11.5
C_2H_2/CH_4 IAST[a] (*v*/*v* = 1/1) selectivity	298 K	35.7	27.8
	288 K	40.2	39.8
	278 K	45.8	64.9
CO_2/CH_4 IAST[a] (*v*/*v* = 1/1) selectivity	298 K	8.8	8.2
	288 K	9.4	8.4
	278 K	10.3	8.9

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