Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Two NbO-Type MOF Isomers Based on Linear and Zigzag Diisophthalate Ligands: Exploring the Effect of Ligand-Originated MOF Isomerization on Gas Adsorption Properties

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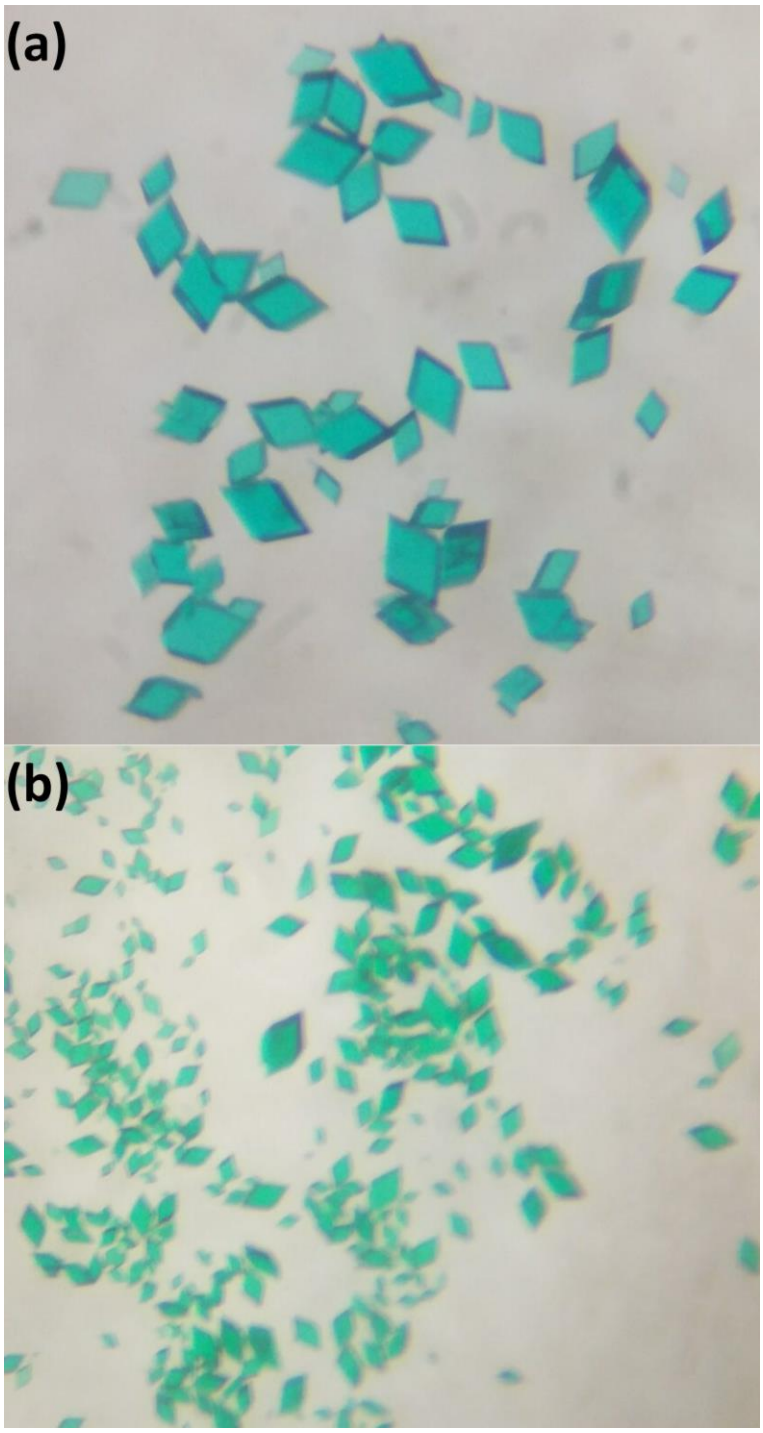


Fig. S1 The electronic photographs of the as-synthesized (a) **ZJNU-91** and (b) **ZJNU-92**.

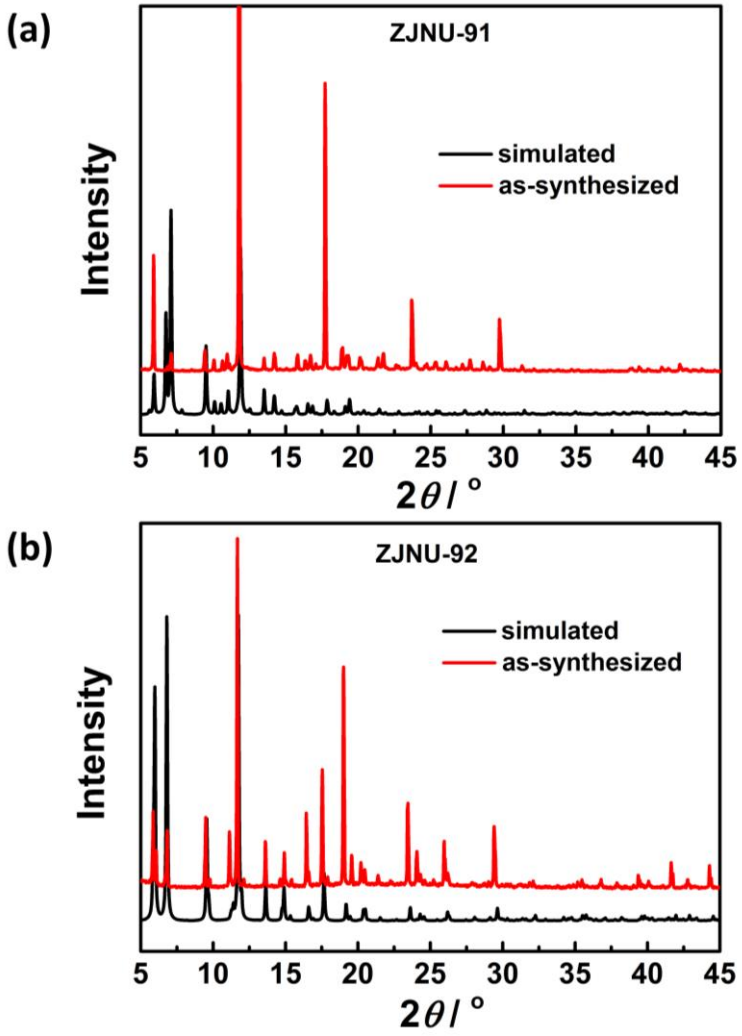


Fig. S2 Comparison of the simulated (black) and experimental (red) PXRD patterns of (a) **ZJNU-91** and (b) **ZJNU-92**.

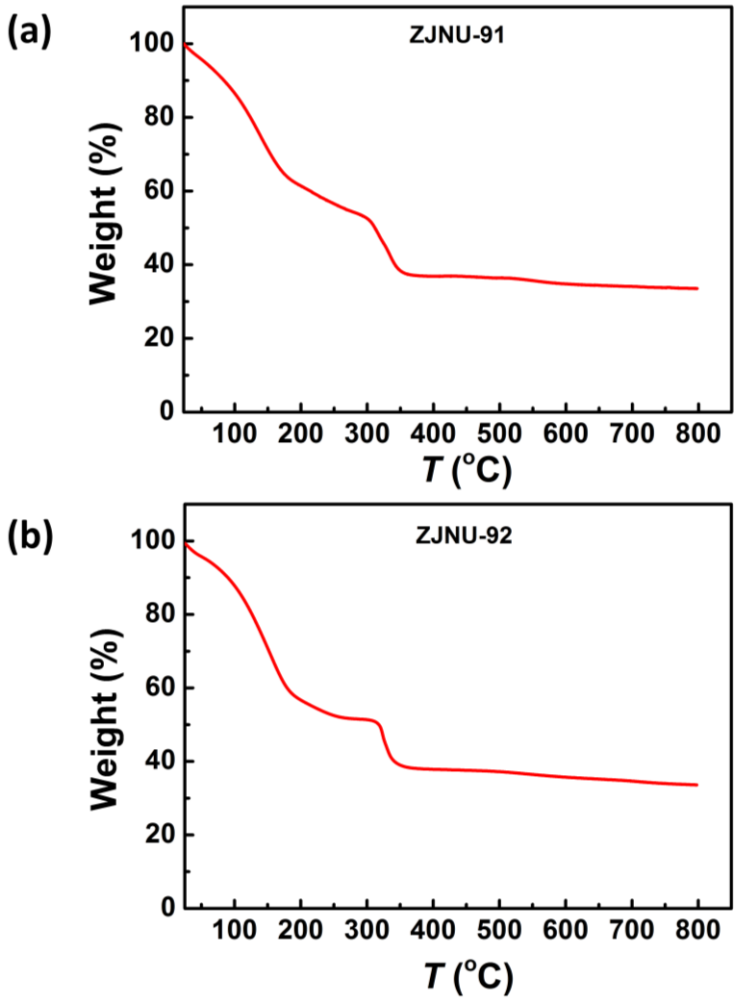


Fig. S3 TGA curves of (a) **ZJNU-91** and (b) **ZJNU-92** under nitrogen atmosphere.

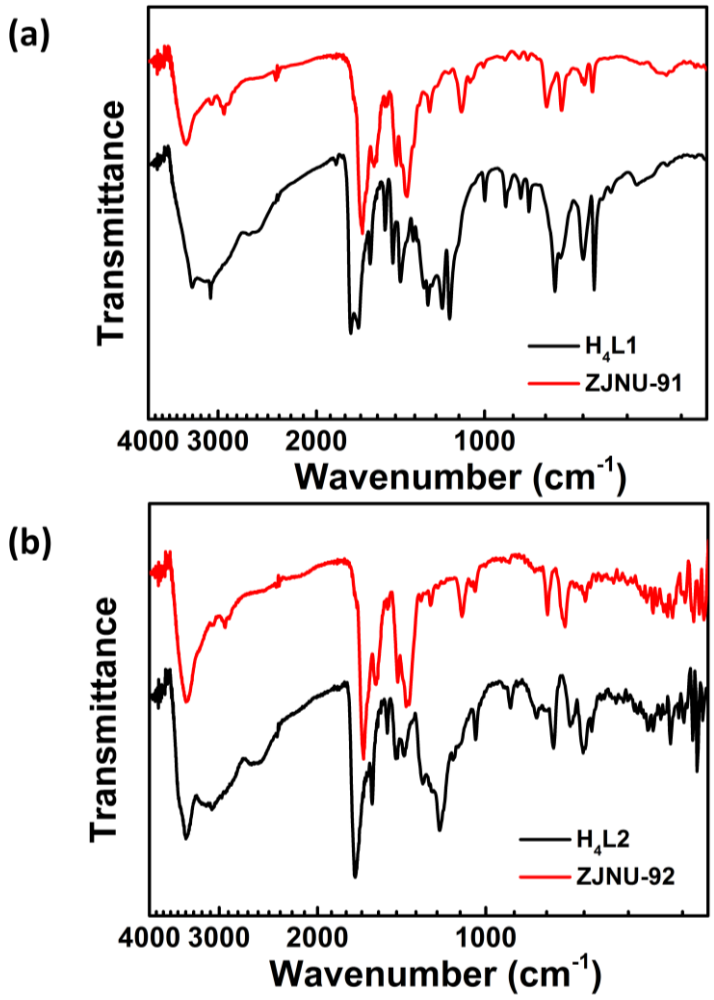
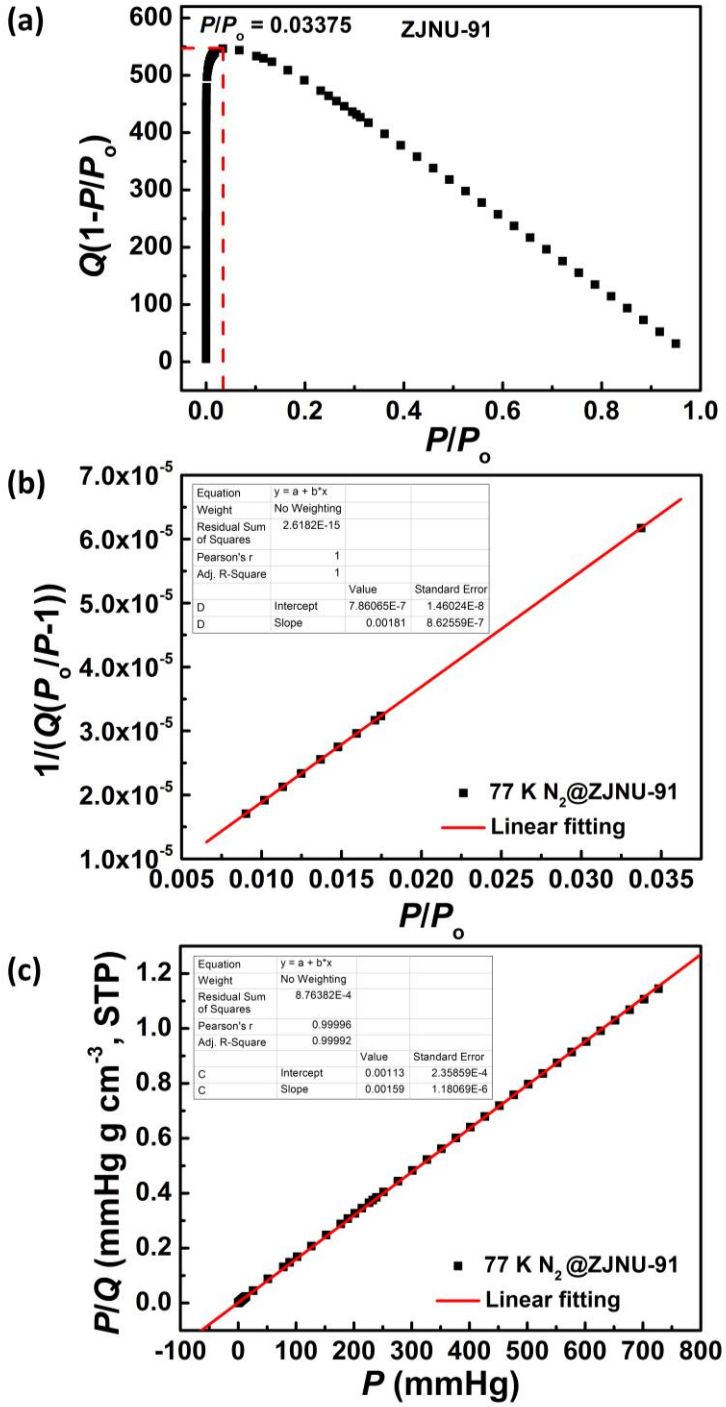


Fig. S4 Comparison of FTIR spectra of **ZJNU-91** and **ZJNU-9**2 and their corresponding ligands.



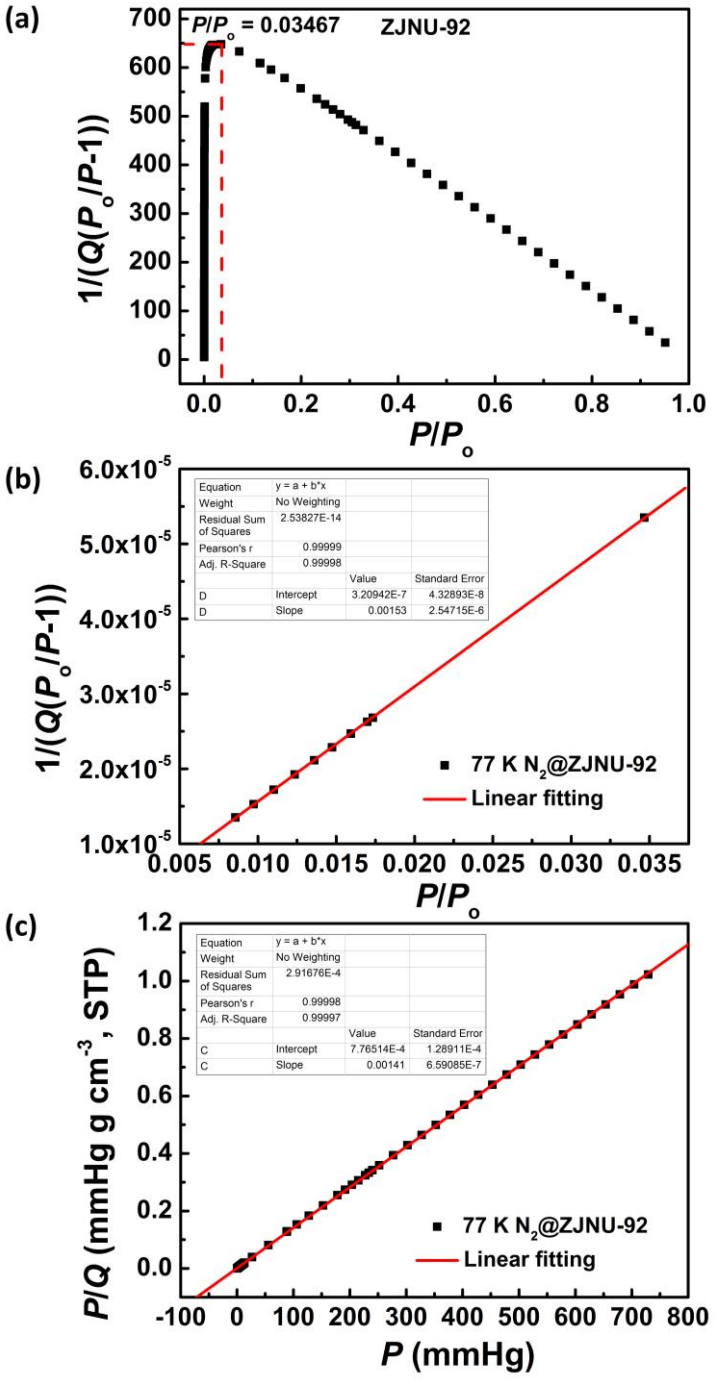
S_{BET} = 1/(7.86065 ×10^{-7}+ 0.00181)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2404 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00159)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2738 m^2 g^{-1}

BET constant C = 1 + 0.00181/7.86065 ×10^{-7} = 2304

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.02041$$

Fig. S5 The consistency (a), BET (b), and Langmuir (c) plots for **ZJNU-91**.



S_{BET} = 1/(3.20942 ×10^{-7}+0.00153)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2845 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00141)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 3087 m^2 g^{-1}

BET constant C = 1 + 0.00153/3.20942 ×10^{-7} = 4768

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.014275$$

Fig. S6 The consistency (a), BET (b), and Langmuir (c) plots for **ZJNU-92**.

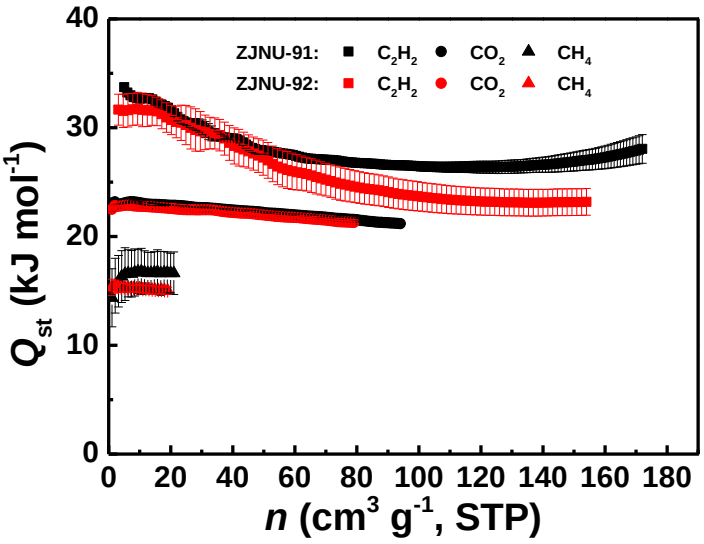


Fig. S7 Comparison of the isosteric heat of C_2H_2, CO_2 and CH_4 adsorption in **ZJNU-91** and **ZJNU-92**.

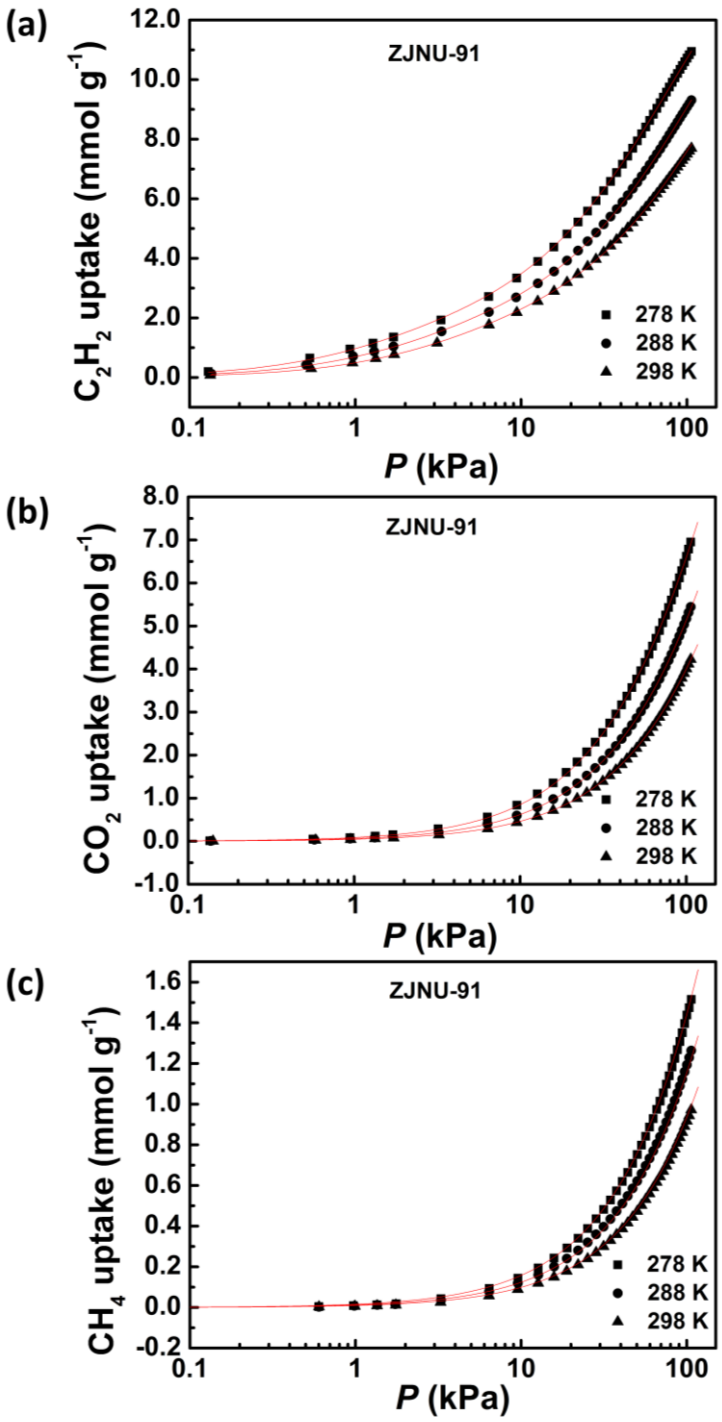


Fig. S8 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-91** with the fitted isotherms at 278 K, 288 K, and 298 K.

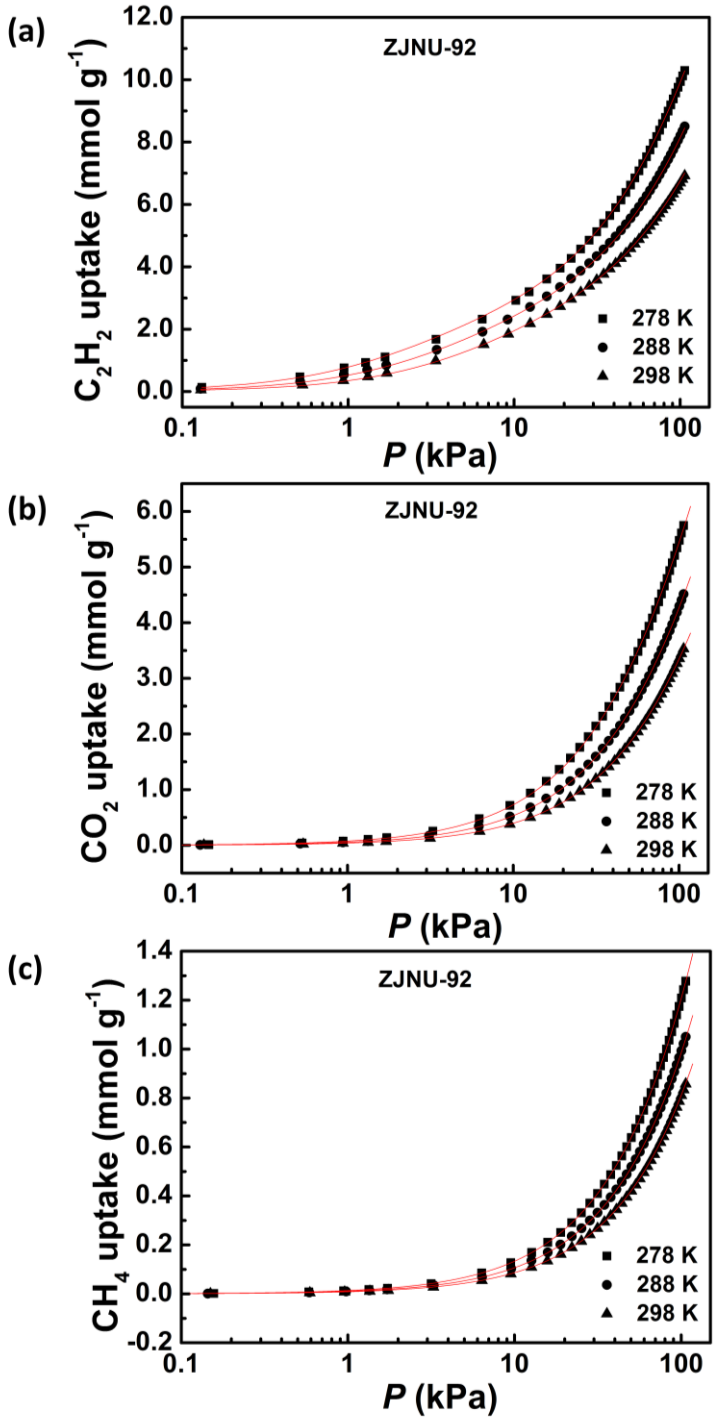


Fig. S9 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-92** with the fitted isotherms at 278 K, 288 K, and 298 K.

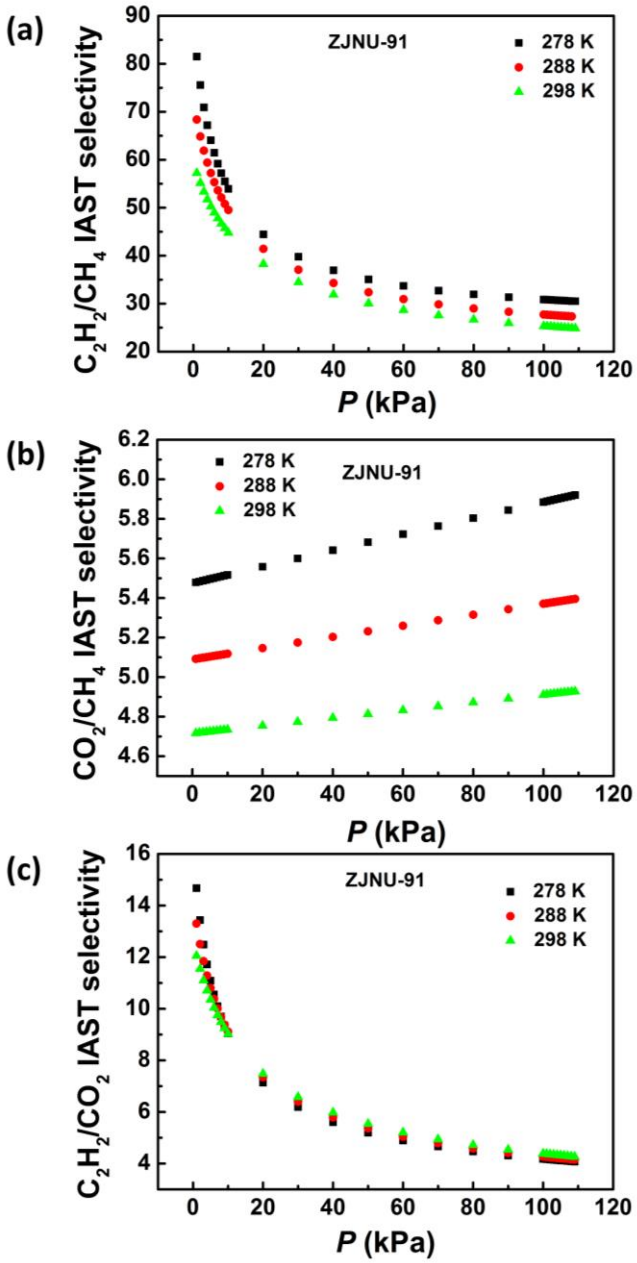


Fig. S10 IAST selectivities for the equimolar (a) C_2H_2-CH_4, (b) CO_2-CH_4 and (c) C_2H_2-CO_2 gas mixtures in **ZJNU-91** at three different temperatures of 278 K, 288 K, and 298 K.

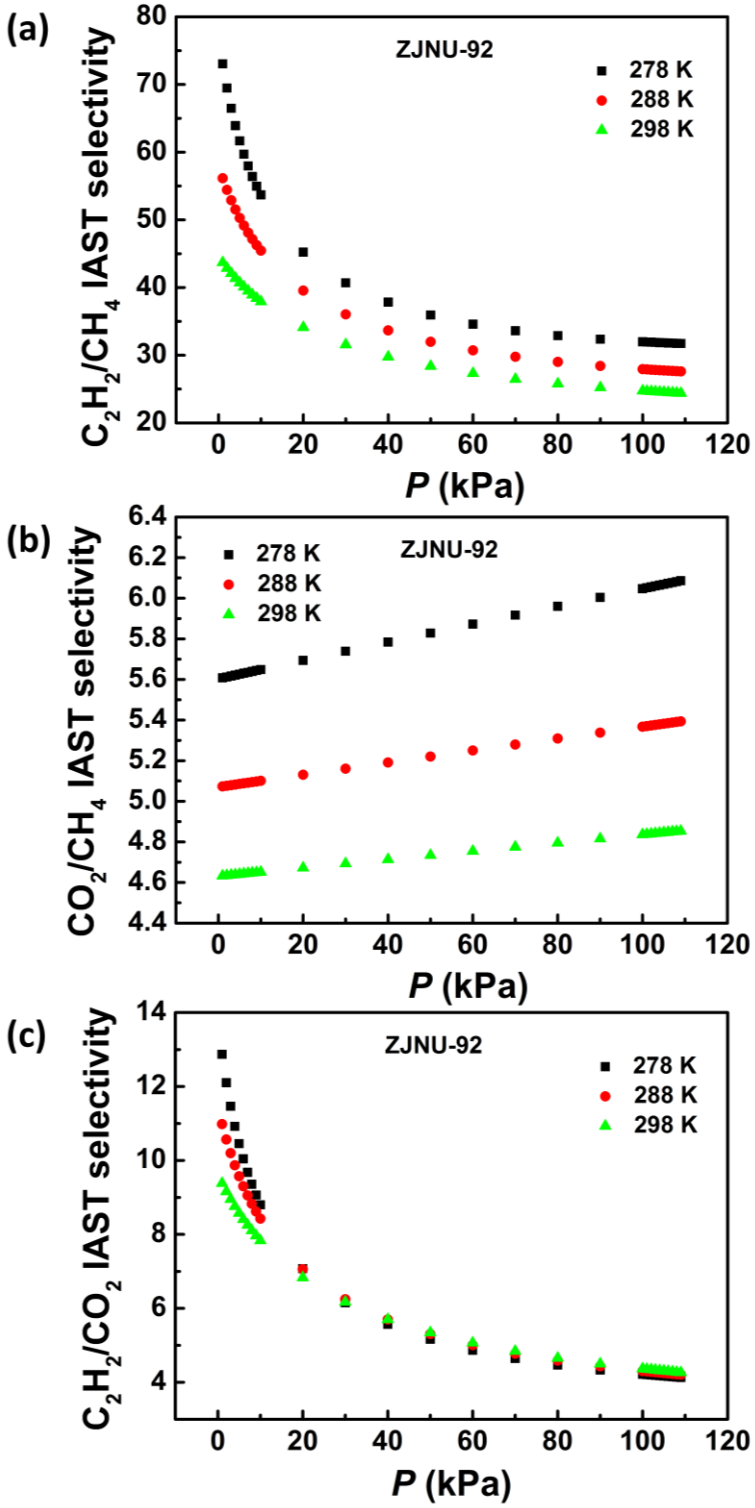
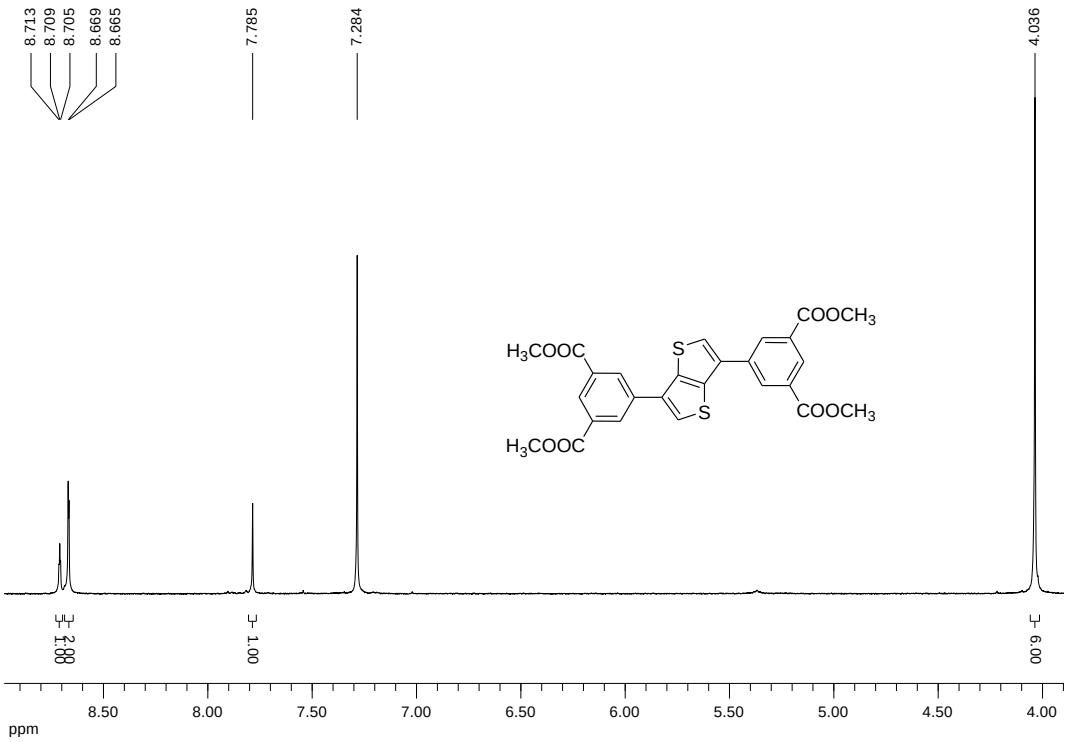


Fig. S11 IAST selectivities for the equimolar (a) C_2H_2-CH_4, (b) CO_2-CH_4 and (c) C_2H_2-CO_2 gas mixtures in **ZJNU-92** at three different temperatures of 278 K, 288 K, and 298 K.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8.669
8.665
7.785
7.284
4.036
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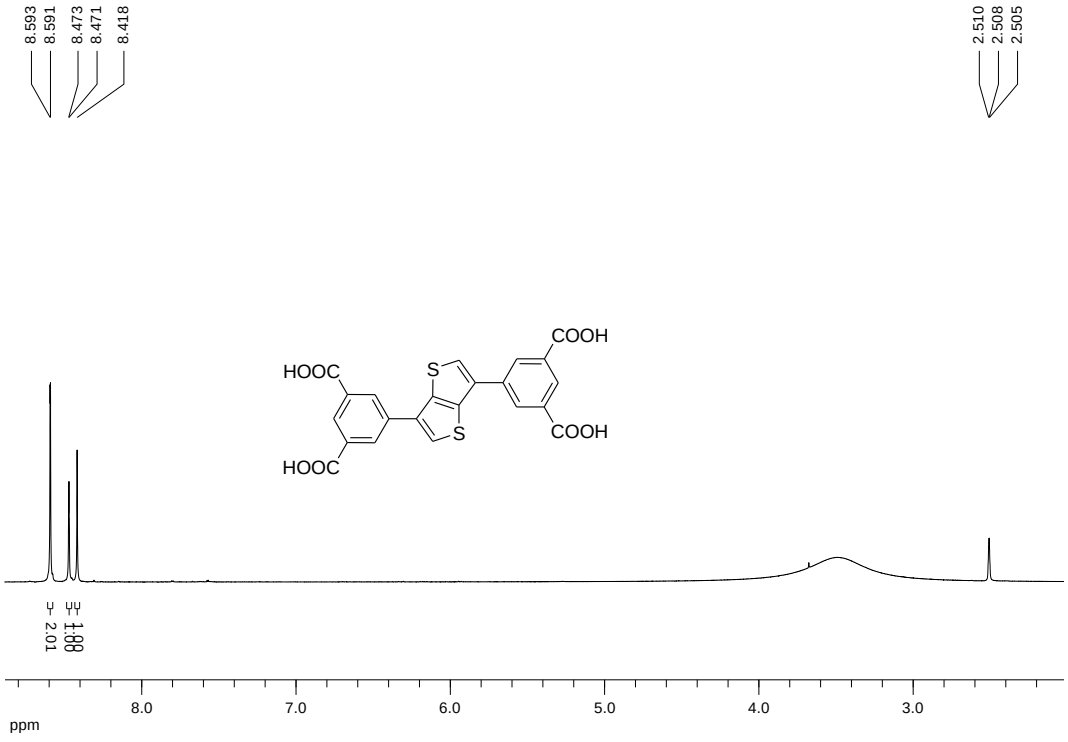
H3COOC
S
S
COOCH3
H3COOC
2.00
1.00
6.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
ppm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8.591
8.473
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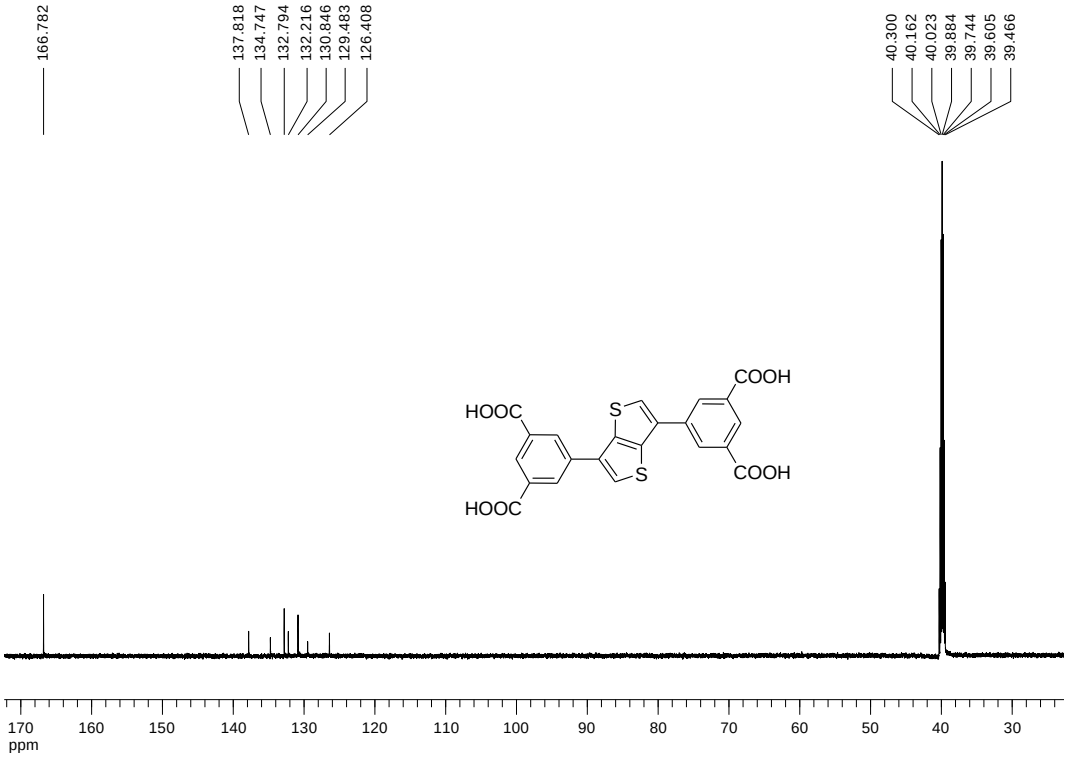
2.510
2.508
2.505
COOH
HOOC
S
S
COOH
HOOC
2.01
1.88
8.0
7.0
6.0
5.0
4.0
3.0
ppm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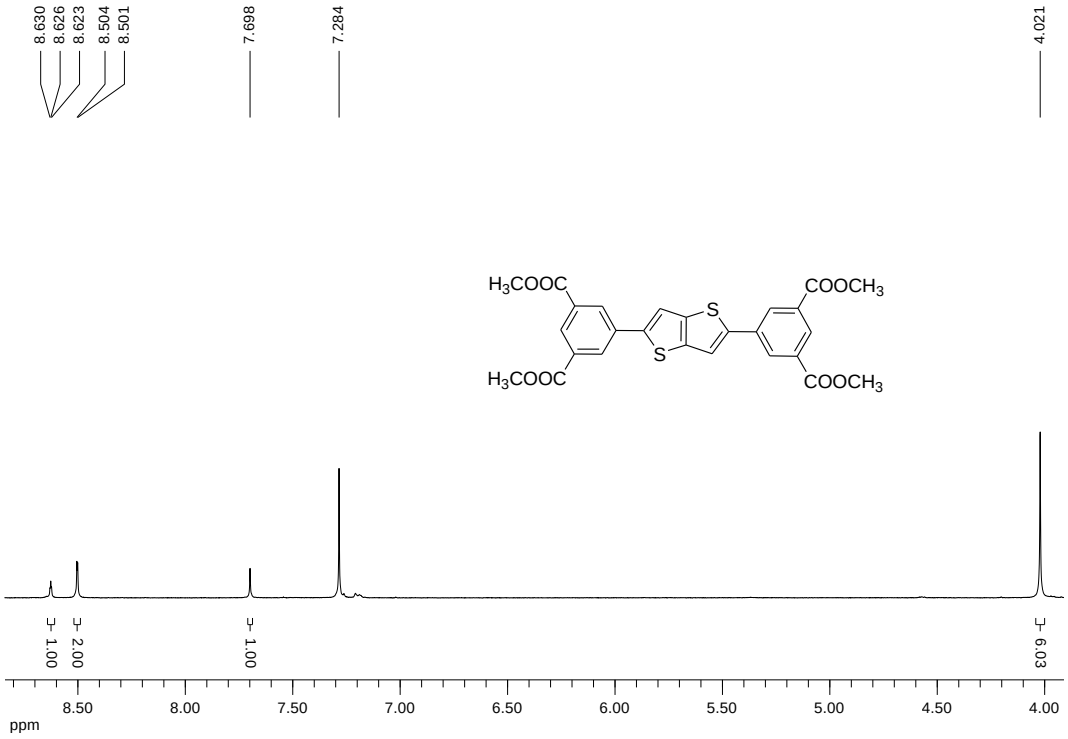
137.818
134.747
132.794
132.216
130.846
129.483
126.408
40.300
40.162
40.023
39.884
39.744
39.605
39.466
HOOC
HOOC
COOH
COOH
S
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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8.501
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COOCH3
S
S
1.00
2.00
1.00
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6.00
5.50
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4.50
4.00
ppm

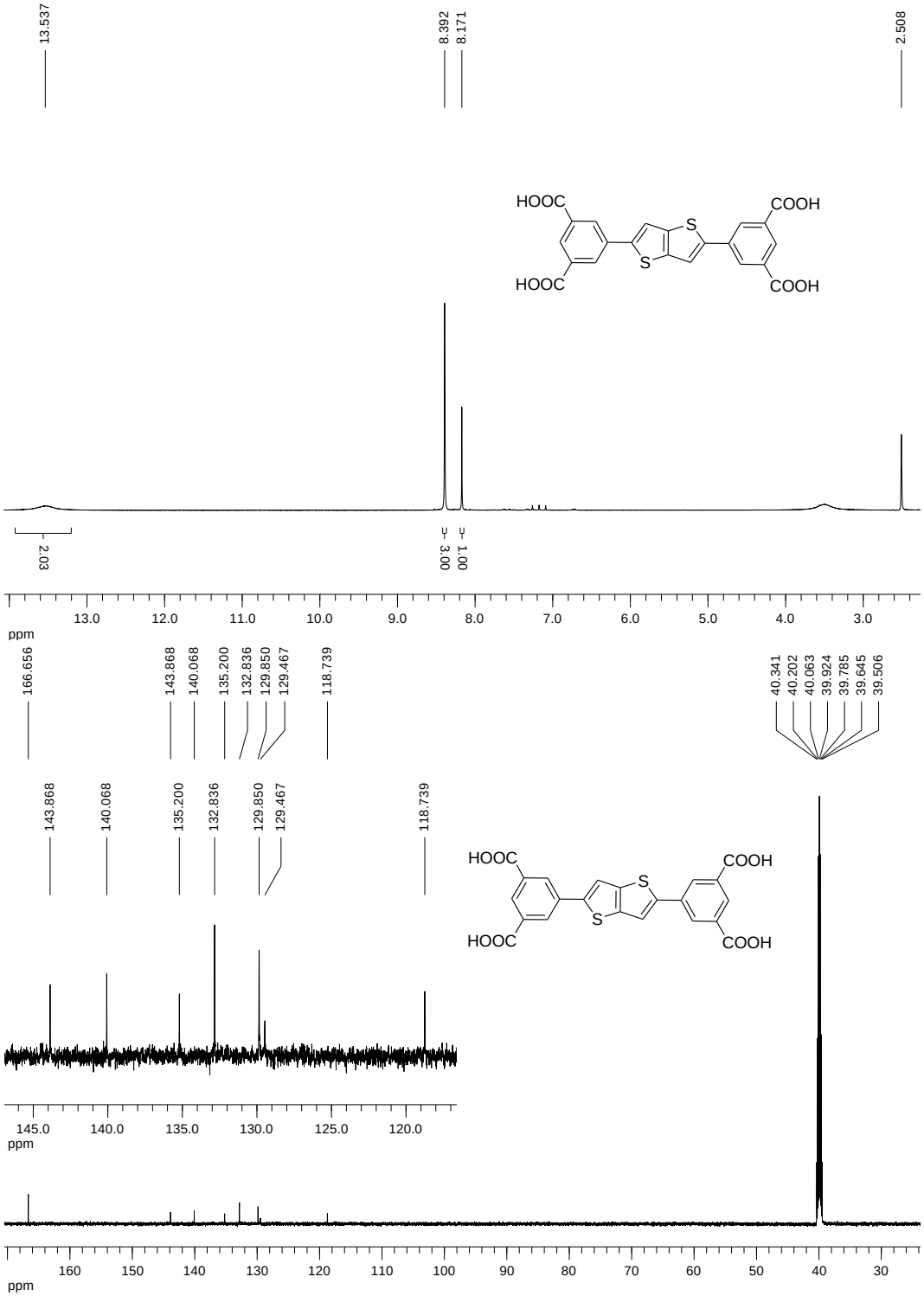

Fig. S12 NMR spectra

(1) **Q_{st} calculations**

The isosteric heats of adsorption (Q_{st}) were calculated using the Clausius-Clapeyron equation based on pure-component isotherms collected at three different temperatures of 278 K, 288 K and 298 K. The Q_{st} was defined as

$$Q_{st} = -R\left(\frac{\partial Inp}{\partial(1/T)}\right)_q$$

where p is the pressure, T is the temperature, R is the gas constant, and q is the adsorption amount. These calculations were done through the "Heat of Adsorption" function embedded in the software supplied by Micromeritics ASAP 2020HD88 surface-area-and-pore-size analyzer machine.

(2) IAST calculations

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2 can be formally defined as

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

where q_1 and q_2 are the component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz (*Ref.* Myers, A. L.; Prausnitz, J. M., Thermodynamics of Mixed-Gas Adsorption. *A.I.Ch.E.J.* **1965**, *11*, 121-127.).

Table S1 Crystal data and structure refinement for **ZJNU-91**, and **ZJNU-92**.

MOFs	**ZJNU-91**	**ZJNU-92**
Empirical formula	$C_{66}H_{42}Cu_6O_{30}S_6$	$C_{22}H_{12}Cu_2O_{10}S_2$
Formula weight	1888.72	627.52
λ (Å)	0.71073	1.54184
Crystal system	Monoclinic	Trigonal
Space group	*C2/c*	*R-3m*
Unit cell dimensions	a = 32.1419(9) Å b = 18.5746(2) Å c = 28.3151(6) Å α = 90° β = 112.511(3)° γ = 90°	a = 18.4854(3) Å b = 18.4854(3) Å c = 44.3369(10) Å α = 90° β = 90° γ = 120°
V (Å^3)	15616.7(6)	13120.6(4)
Z	4	9
D_c (g cm^{-3})	0.803	0.715
μ (mm^{-1})	0.923	1.777
F(000)	3792	2826
Crystal size (mm)	0.14 × 0.14 × 0.10	0.19 × 0.12 × 0.10
θ range for data collection (°)	1.63 to 26.37	2.99 to 74.16
Limiting indices	$-40 \le h \le 40$ $-23 \le k \le 21$ $-35 \le l \le 26$	$-11 \le h \le 23$ $-23 \le k \le 13$ $-50 \le l \le 54$
Reflections collected / unique	90048 / 15697	12519 / 3189
R_{int}	0.0950	0.0242
Max. and min. transmission	0.9134 and 0.8817	0.8423 and 0.7289
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	15697 / 0 / 454	3189 / 16 / 92
Goodness-of-fit on F^2	1.060	1.393
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1017 wR_2 = 0.2934	R_1 = 0.0698 wR_2 = 0.2844
R indices (all data)	R_1 = 0.1113 wR_2 = 0.3042	R_1 = 0.0737 wR_2 = 0.2959
Largest diff. peak and hole (e·Å^{-3})	1.351 and -1.072	1.641 and -0.963
CCDC	1865521	1865522

Table S2 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-91**.

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	15.95785	9.45447×10^{-8}	27.123	1	2.09813	9.4109×10^{-7}	30.869	1
CO_2	26.42044	3.10059×10^{-7}	21.447	1				
CH_4	14.83517	9.84928×10^{-7}	16.168	1				

Table S3 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-92**.

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	30.61154	2.00031×10^{-7}	22.385	1	2.52956	8.14405×10^{-8}	35.455	1
CO_2	19.43744	3.48269×10^{-7}	21.543	1				
CH_4	11.34026	1.80991×10^{-6}	14.997	1				

Table S4 Summary of the pore textural properties and adsorption data of the two MOFs investigated in this work

MOFs	S_{BET} ($S_{Langmuir}$) ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	D_c ($g\ cm^{-3}$)	C_2H_2 uptake at 1.05 atm [cm^3 (STP) g^{-1}]			CO_2 uptake at 1.05 atm [cm^3 (STP) g^{-1}]			$S_{C_2H_2/CH_4}$ [a]			S_{CO_2/CH_4} [a]		
				278 K	288 K	298 K	278 K	288 K	298 K	278 K	288 K	298 K	278 K	288 K	298 K
ZJNU-91	2404 (2738)	0.9824	0.7547	245.4	208.6	172.5	155.8	122.0	94.8	30.5	27.3	24.9	5.92	5.40	4.93
ZJNU-92	2845 (3087)	1.1026	0.6737	230.8	190.6	155.1	128.8	101.2	79.2	31.7	27.6	24.4	6.09	5.39	4.85

S_{BET}/$S_{Langgmuir}$: BET/Langmuir specific surface area; V_p: experimental pore volume determined by 77 K N_2 adsorption; D_c: framework density without guest molecules and terminal water molecules; [a] at 110 kPa.