Electronic Supplementary Material (ESI) for Dalton Transactions.

A Comparative Study of C_2H_2 Adsorption Properties in Five Isomeric Copper-Based MOFs Based on Naphthalene-Derived Diisophthalates

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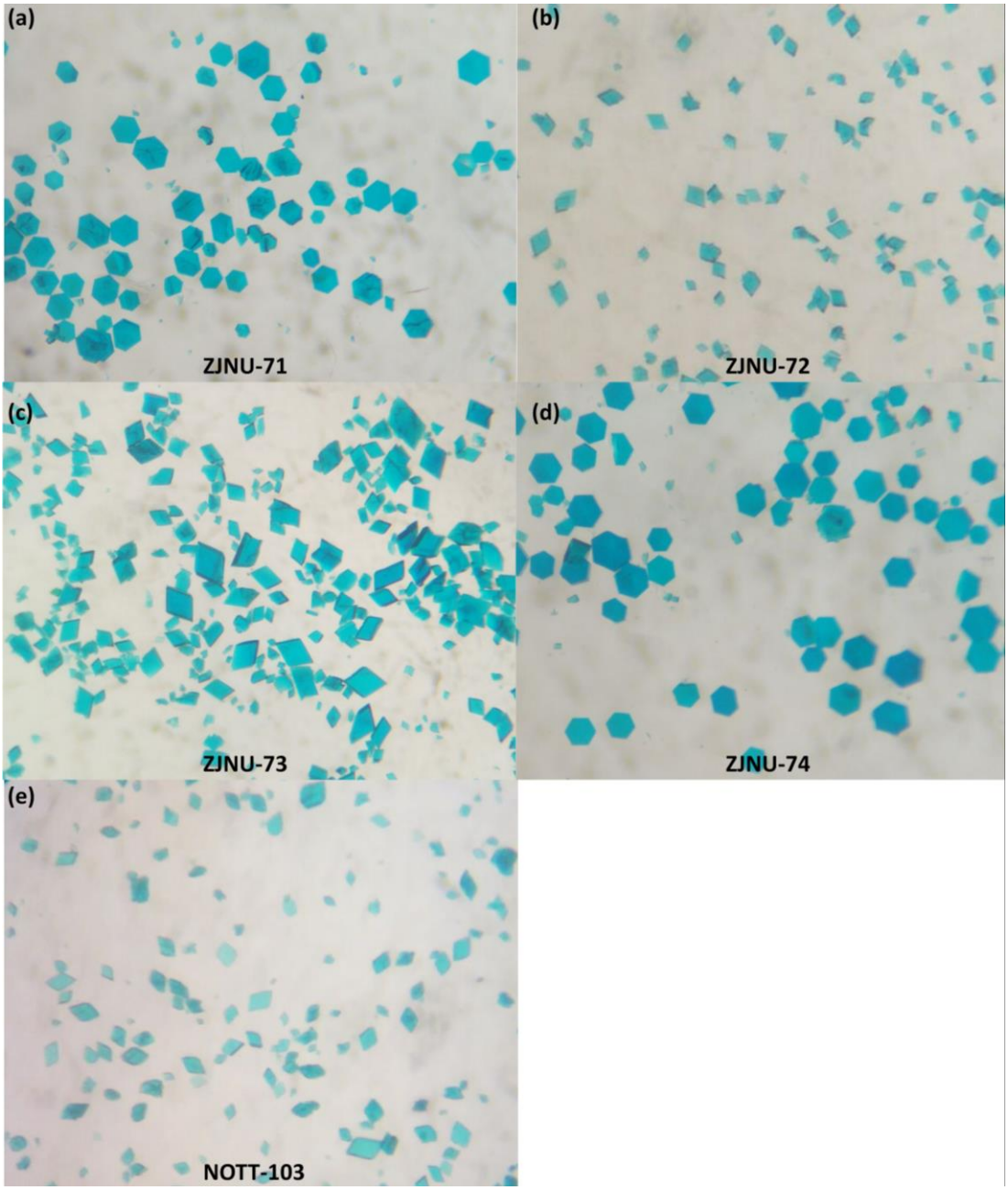


Fig. S1 The photographs of the as-synthesized (a) **ZJNU-71**, (b) **ZJNU-72**, (c) **ZJNU-73**, (d) **ZJNU-74** and (e) **NOTT-103**.

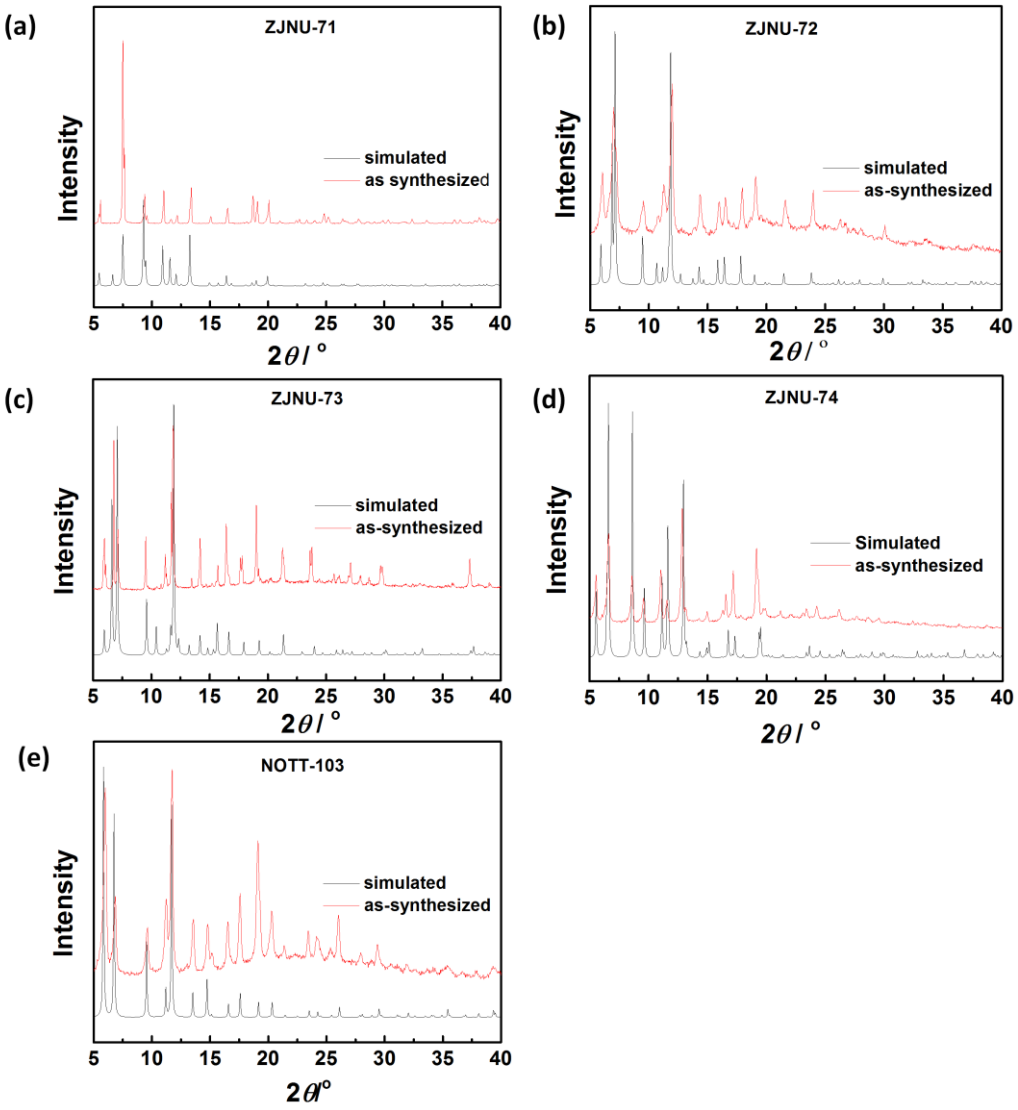


Fig. S2 Comparison of the experimental (red) and simulated (black) PXRD patterns of (a) **ZJNU-71**, (b) **ZJNU-72**, (c) **ZJNU-73**, (d) **ZJNU-74**, and (e) **NOTT-103**.

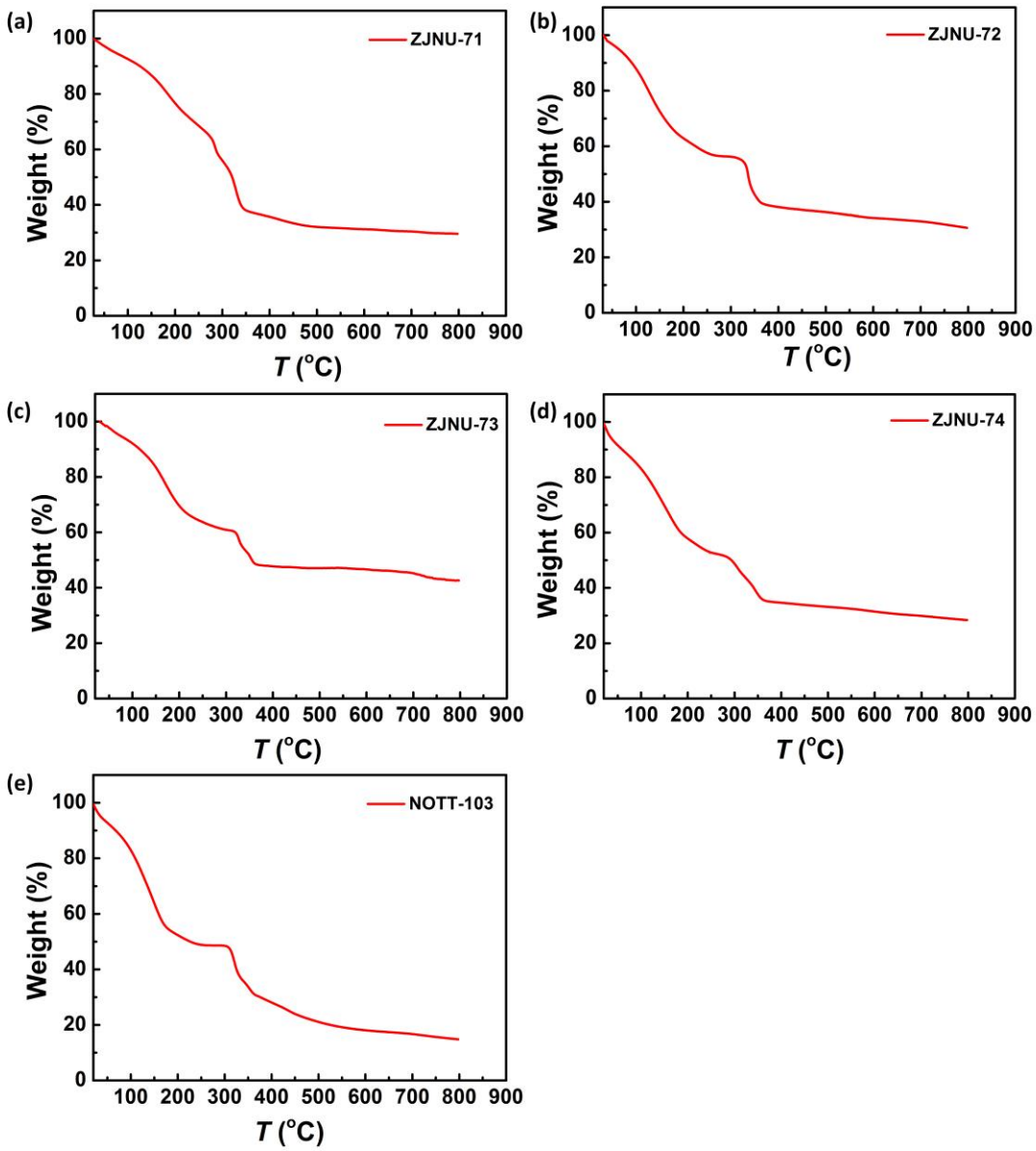


Fig. S3 TGA curves for the as-synthesized samples of (a) **ZJNU-71**, (b) **ZJNU-72**, (c) **ZJNU-73**, (d) **ZJNU-74**, and (e) **NOTT-103** under nitrogen atmosphere.

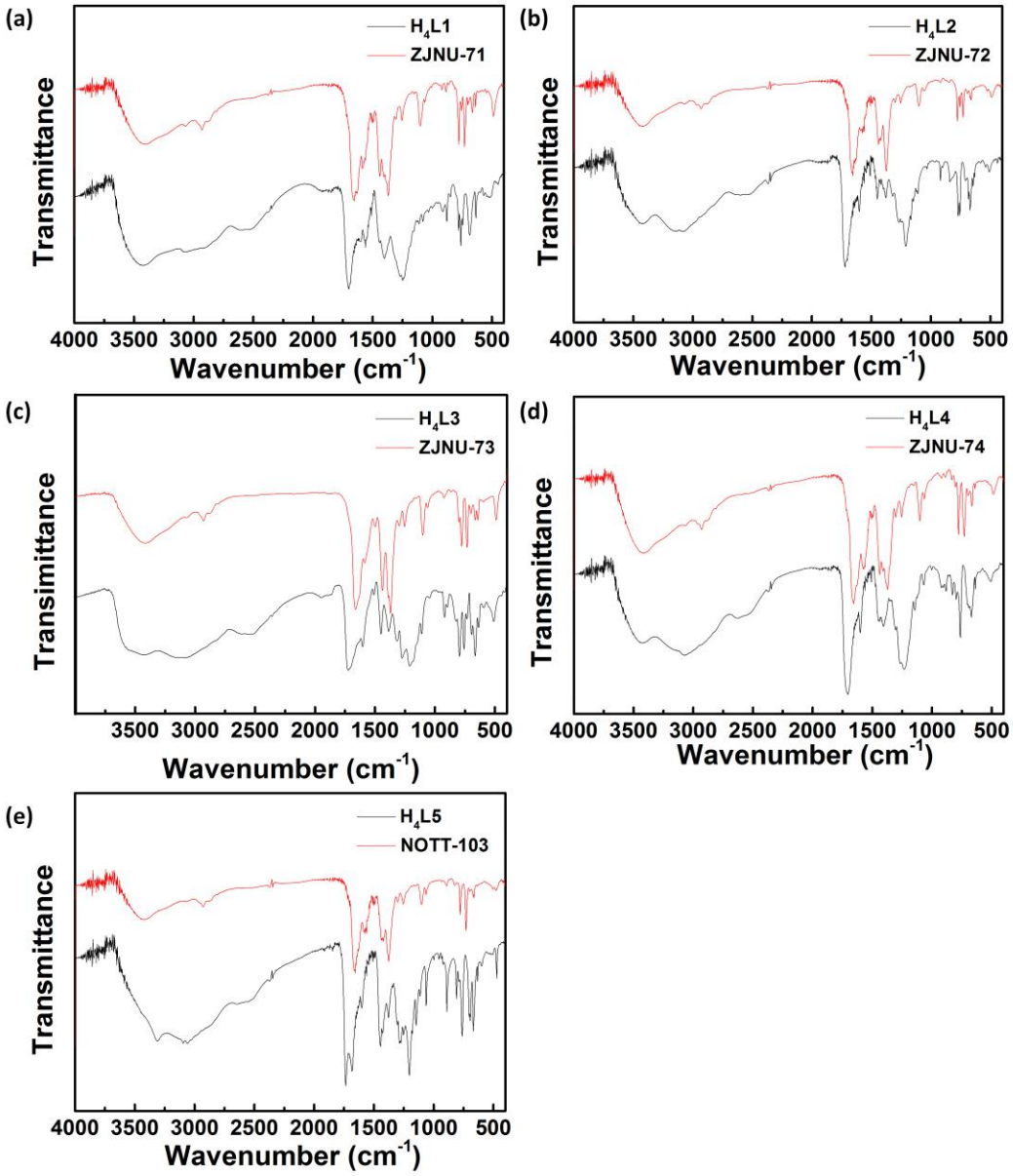


Fig. S4 Comparison of FTIR spectra of as-synthesized (a) **ZJNU-71**, (b) **ZJNU-72**, (c) **ZJNU-73**, (d) **ZJNU-74**, and (e) **NOTT-103** and their corresponding organic ligands.

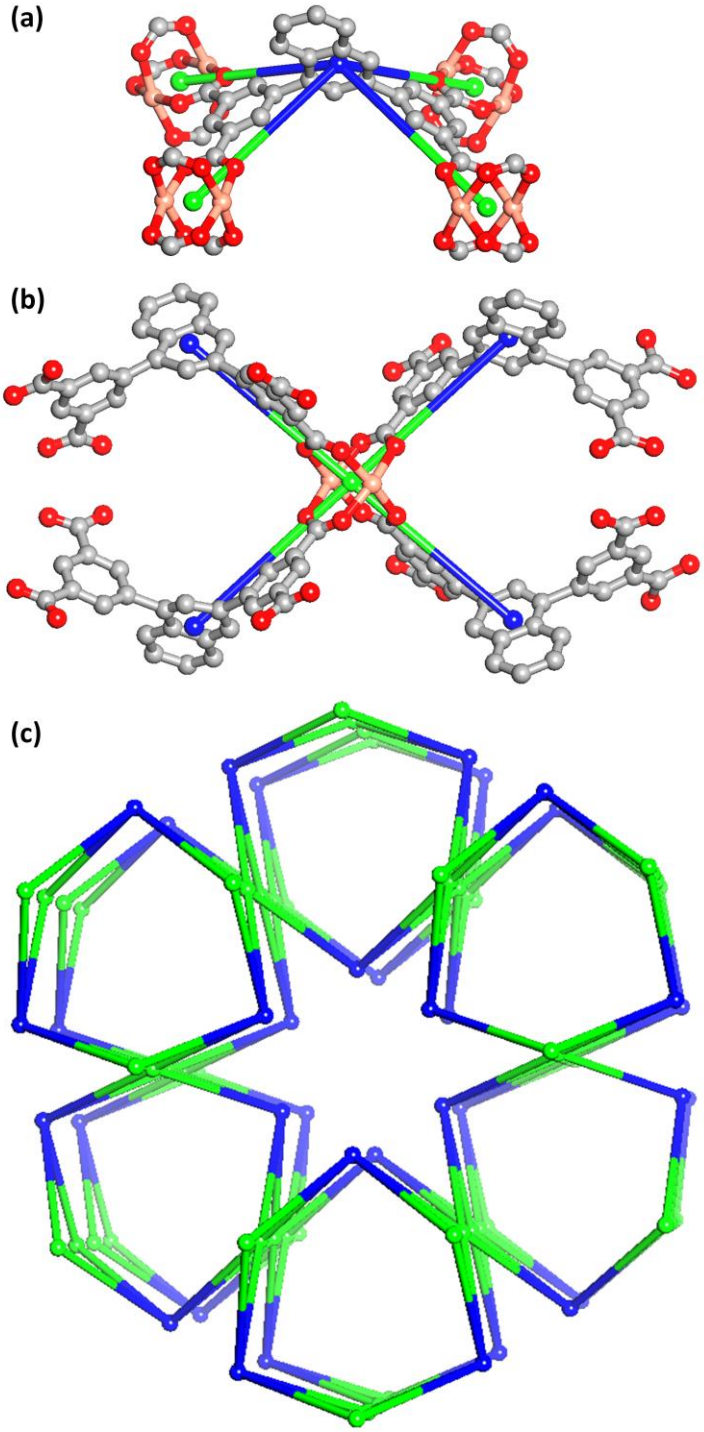


Fig. S5 Topological structure of **ZJNU-71**: views of (a) dinuclear [$Cu_2(COO)_4$] SBU and (b) the organic linker as 4-connected nodes; (c) the schematic representation of the *ssa* topology.

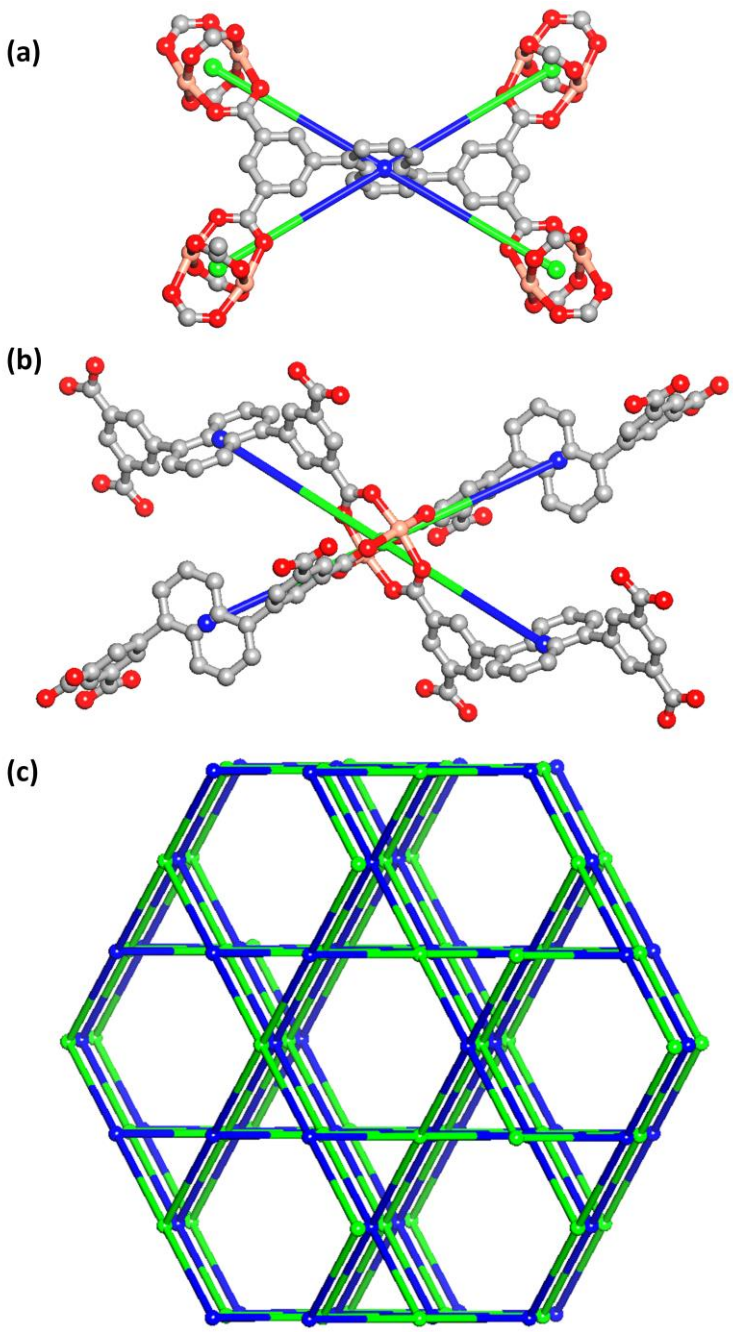
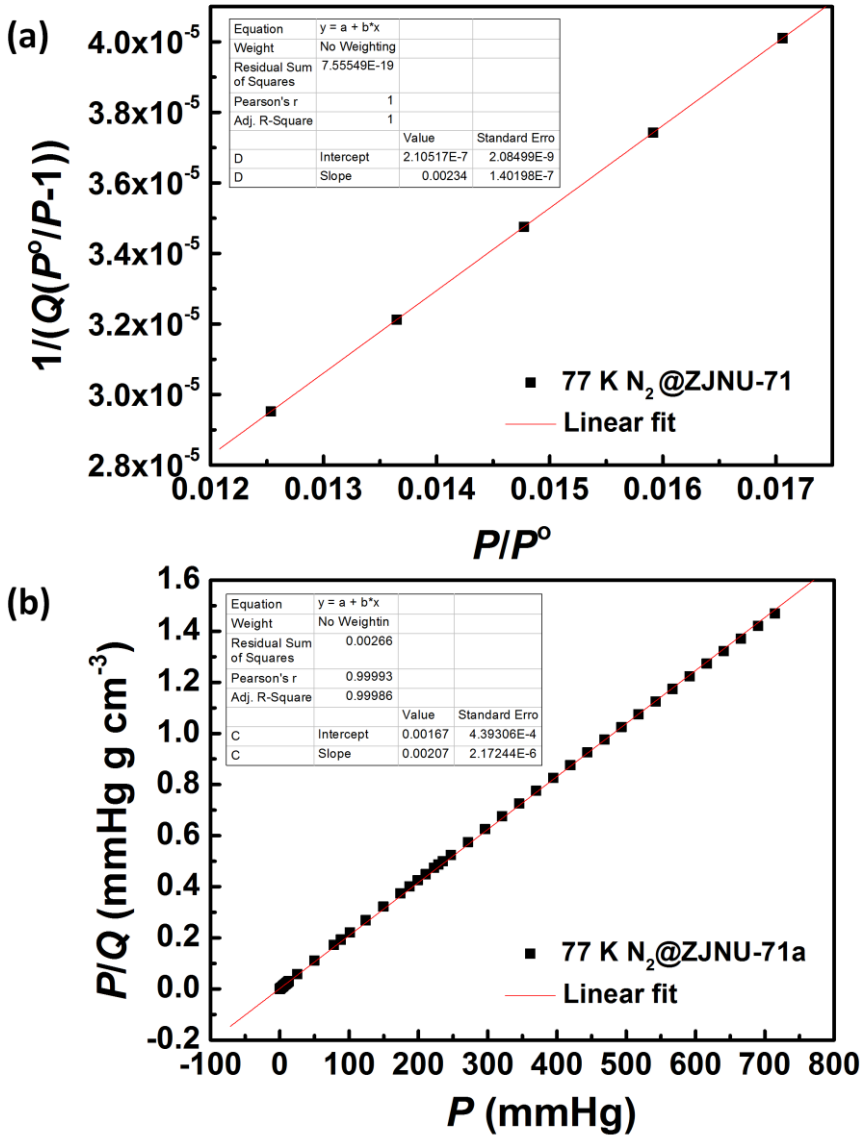


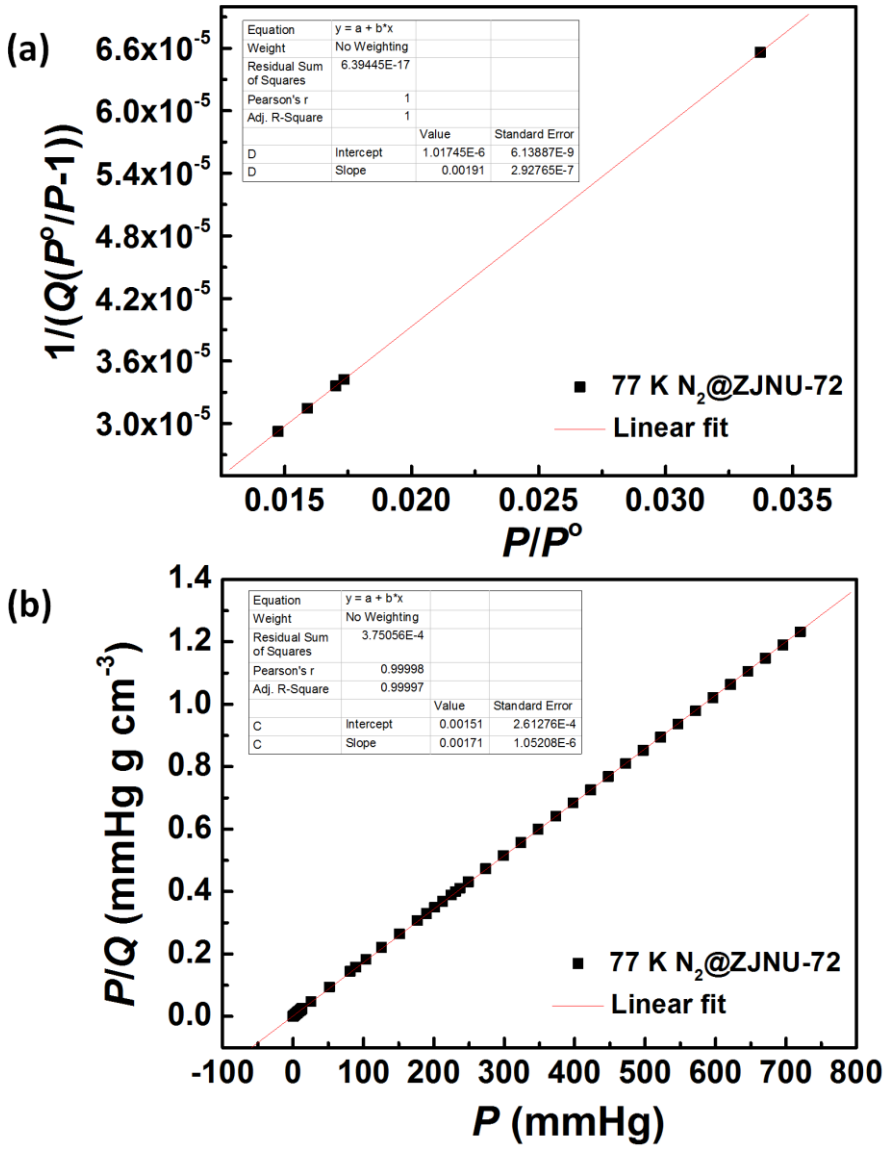
Fig. S6 Topological structure of **ZJNU-73**: views of (a) dinuclear $[Cu_2(COO)_4]$ SBU and (b) the organic linker as 4-connected nodes; (c) the schematic representation of the *nbo* topology.



S_{BET} = 1/(2.10517 ×10^{-7} + 0.00234)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1860 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00207)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2103 m^2 g^{-1}

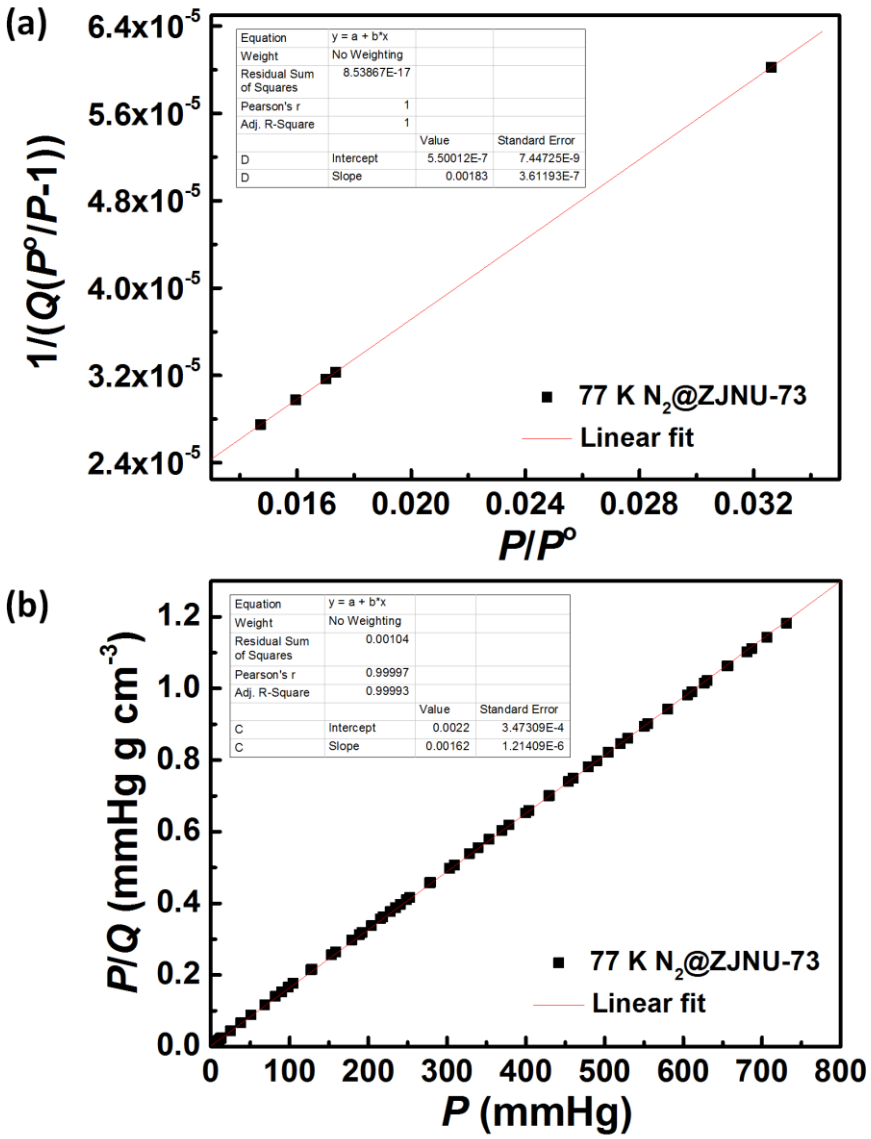
Fig. S7 (a) BET and (b) Langmuir plots for **ZJNU-71**.



S_{BET} = 1/(1.01745 ×10^{-6} + 0.00191)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2278 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00171)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2546 m^2 g^{-1}

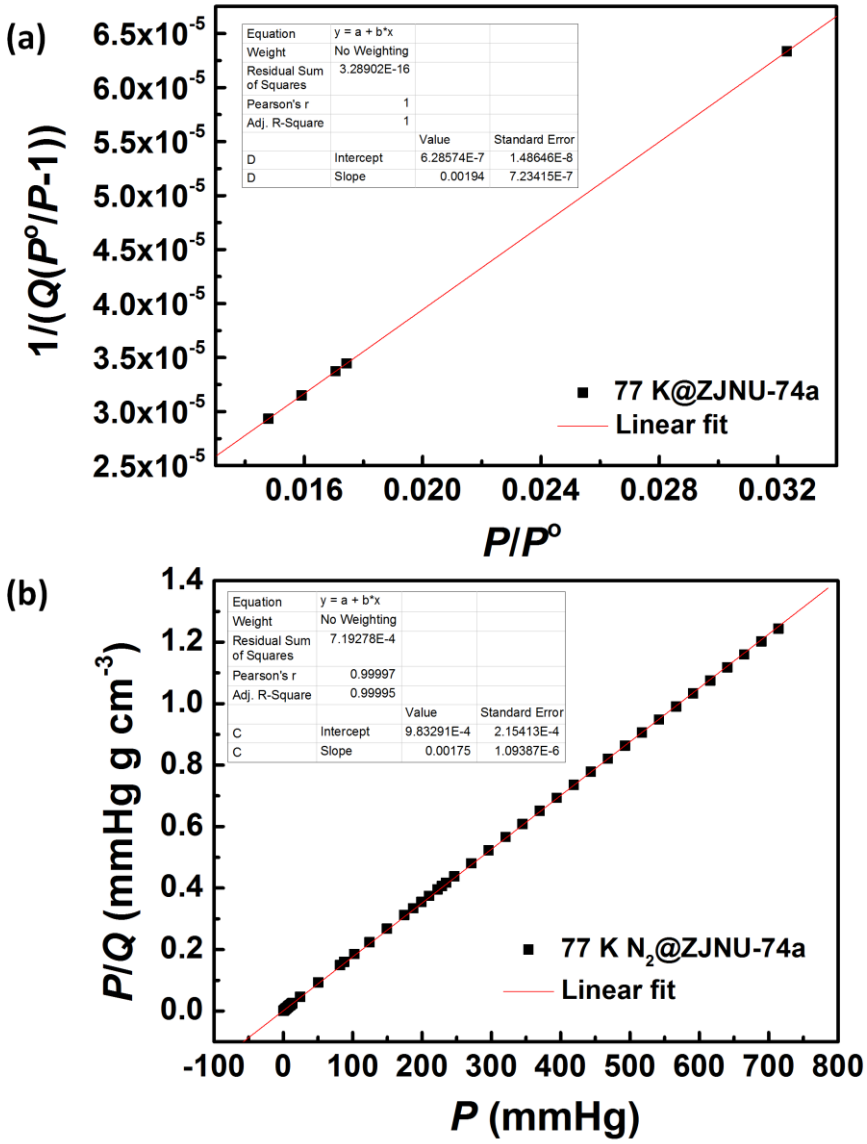
Fig. S8 (a) BET and (b) Langmuir plots for **ZJNU-72**.



S_{BET} = 1/(5.50012 ×10^{-7} + 0.00183)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2378 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00162)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2687 m^2 g^{-1}

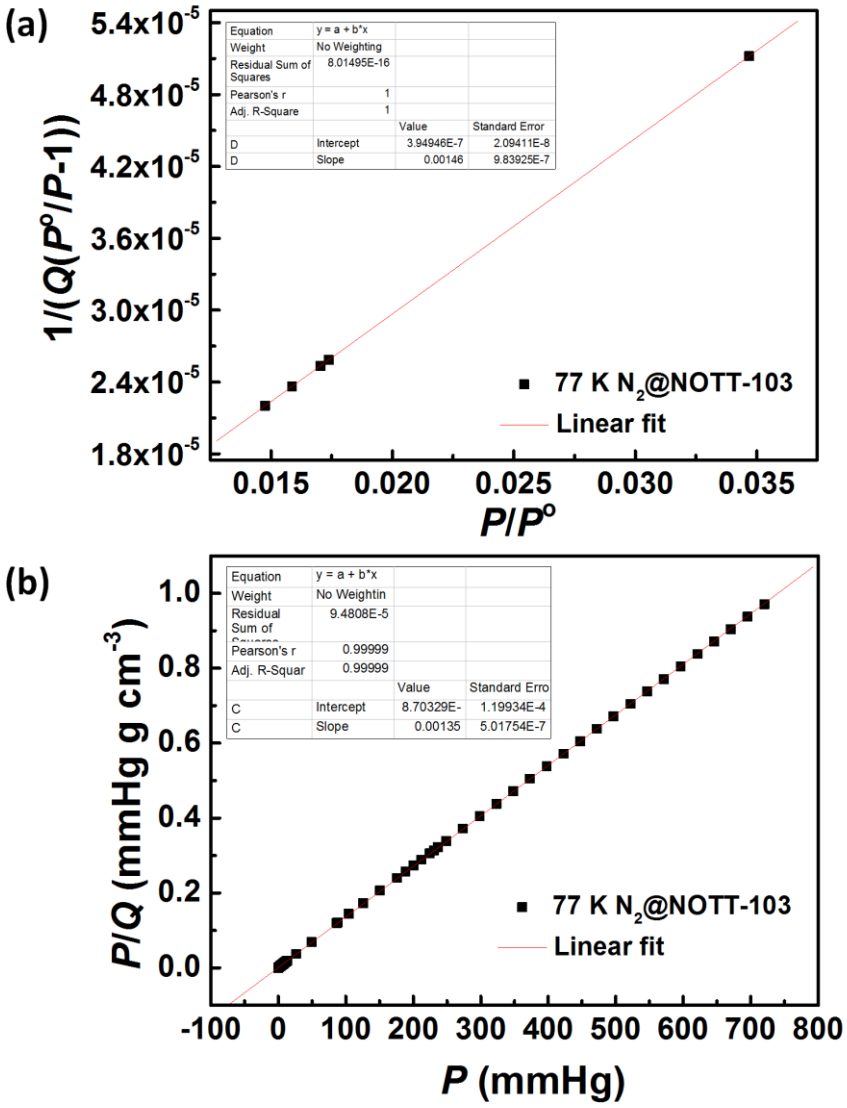
Fig. S9 (a) BET and (b) Langmuir plots for **ZJNU-73**.



S_{BET} = 1/(6.28574 ×10^{-7} + 0.00194)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2243 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00175)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2488 m^2 g^{-1}

Fig. S10 (a) BET and (b) Langmuir plots for **ZJNU-74**.



S_{BET} = 1/(3.94946 ×10^{-7} + 0.00146)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2981 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00135)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 3225 m^2 g^{-1}

Fig. S11 (a) BET and (b) Langmuir plots for **NOTT-103**.

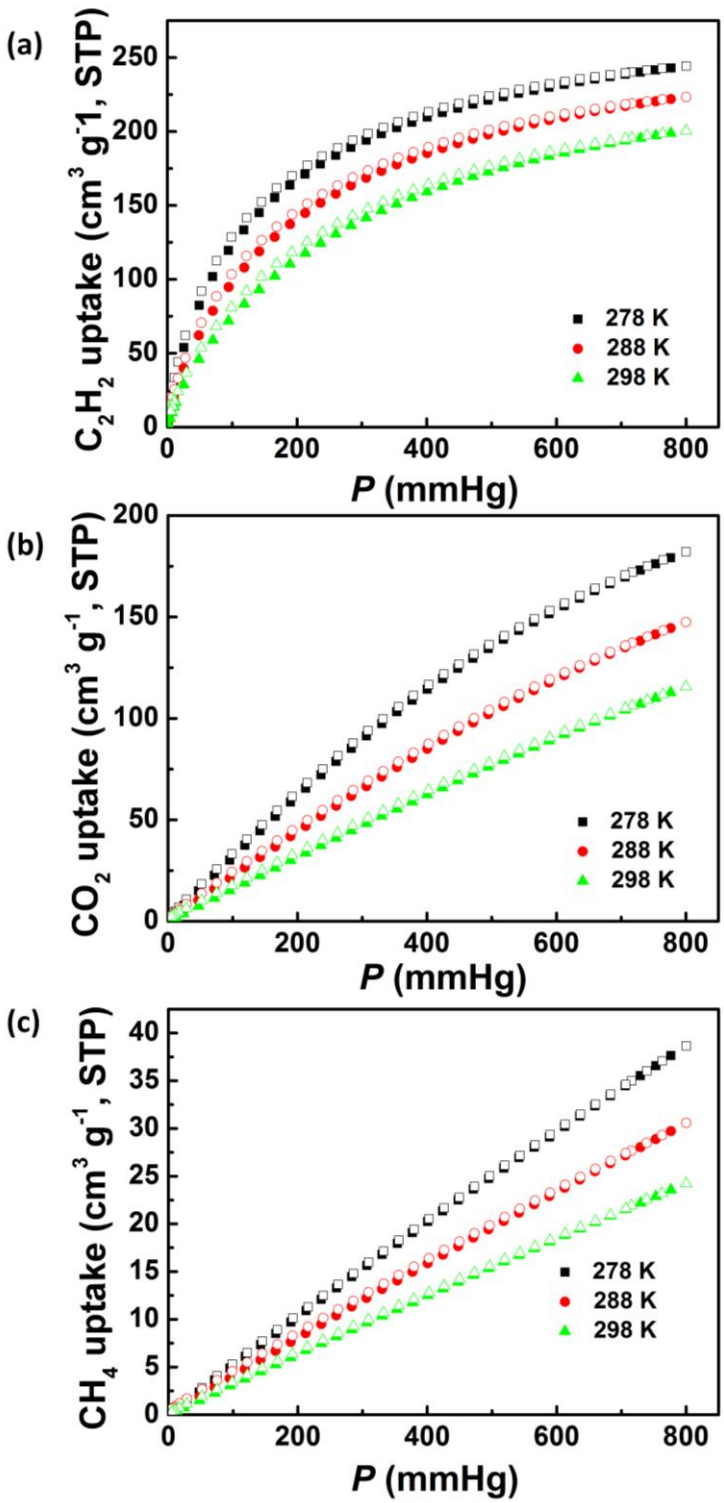


Fig. S12 (a) C_2H_2, (b) CO_2 and (c) CH_4 isotherms of **ZJNU-71** at three different temperatures of 278 K, 288 K and 298 K. The solid and open symbols represent adsorption and desorption, respectively.

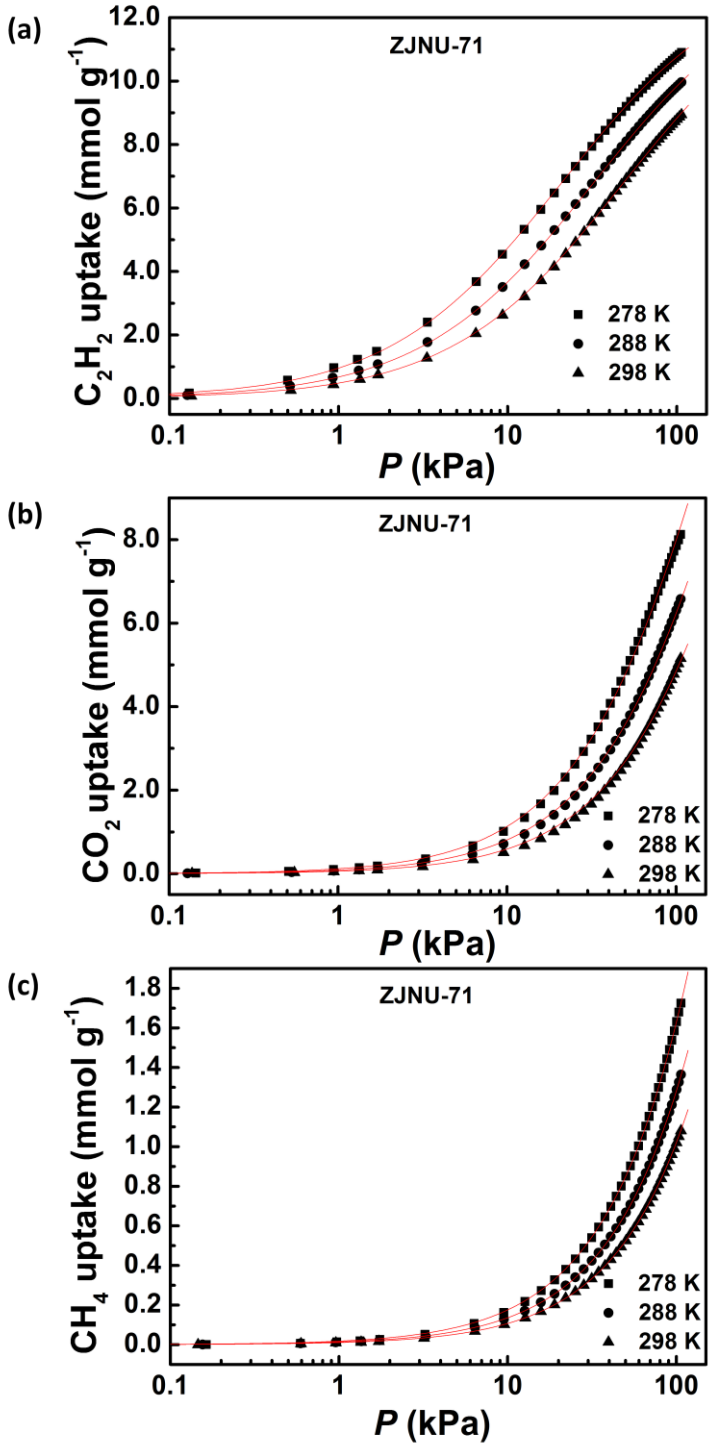


Fig. S13 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-71** with the fitted isotherms (shown by continuous solid lines) at 278 K, 288 K and 298 K.

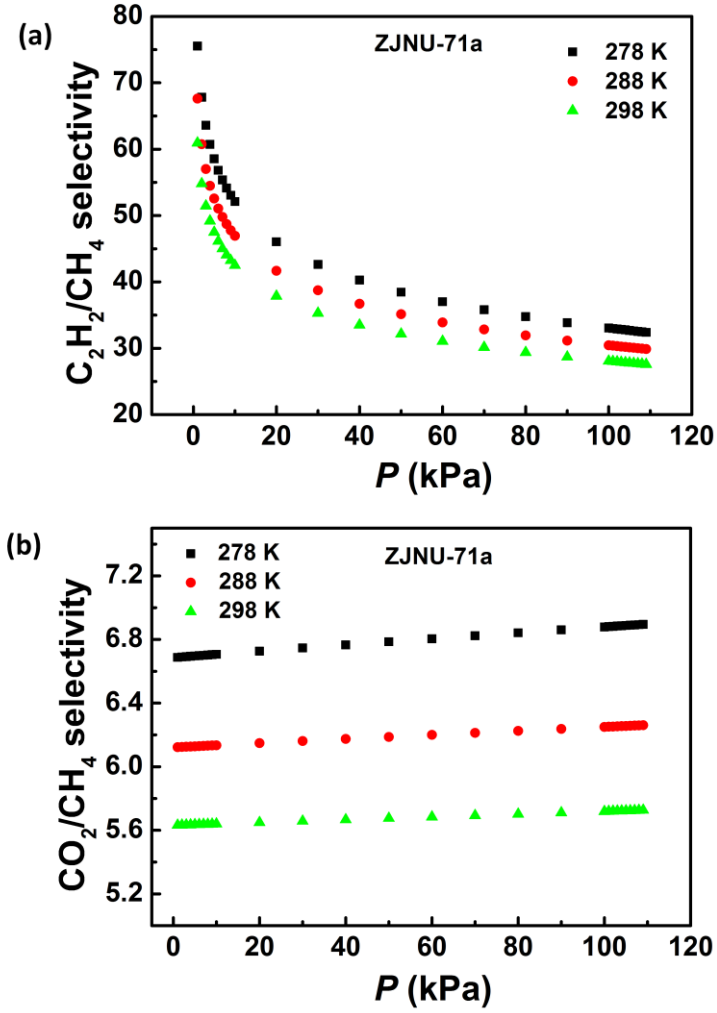
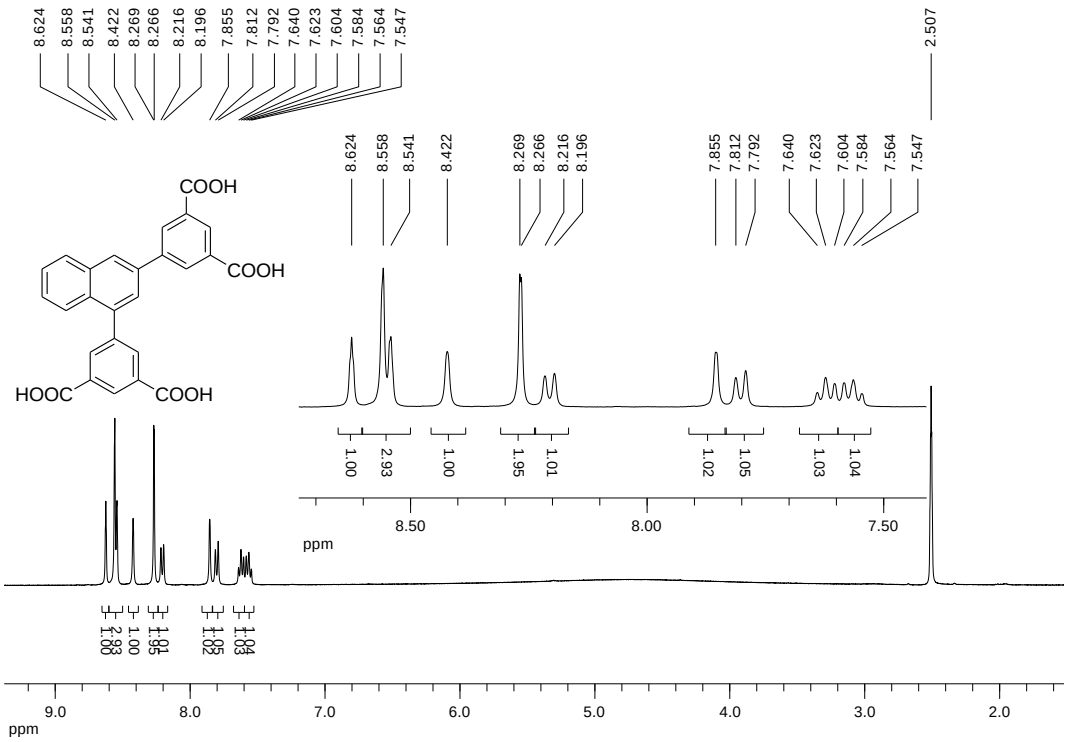


Fig. S14 IAST selectivities for the equimolar (a) C_2H_2/CH_4 and (b) CO_2/CH_4 gas mixtures in **ZJNU-71** at three different temperatures of 278 K, 288 K and 298 K.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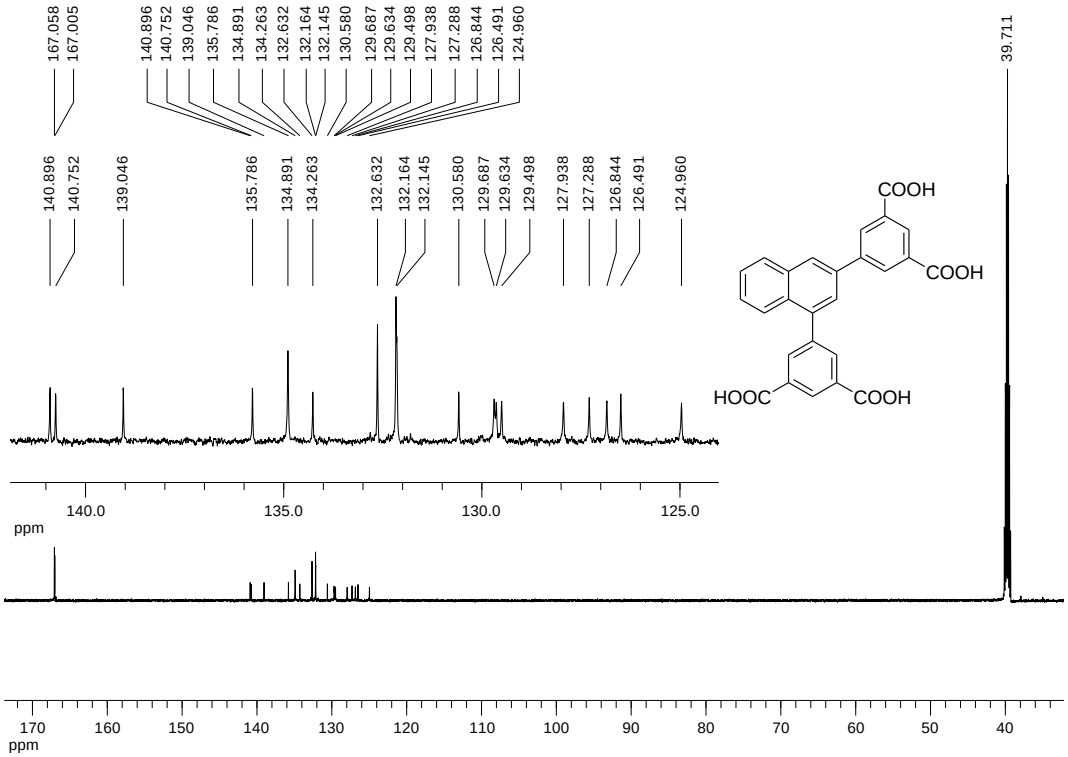
8.541
8.422
8.269
8.266
8.216
8.196
7.855
7.812
7.792
7.640
7.623
7.604
7.584
7.564
7.547
2.507
COOH
COOH
HOOC
COOH
1.00
2.83
1.00
1.96
1.01
1.02
1.05
1.03
1.04
8.50
8.00
7.50
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm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167.005
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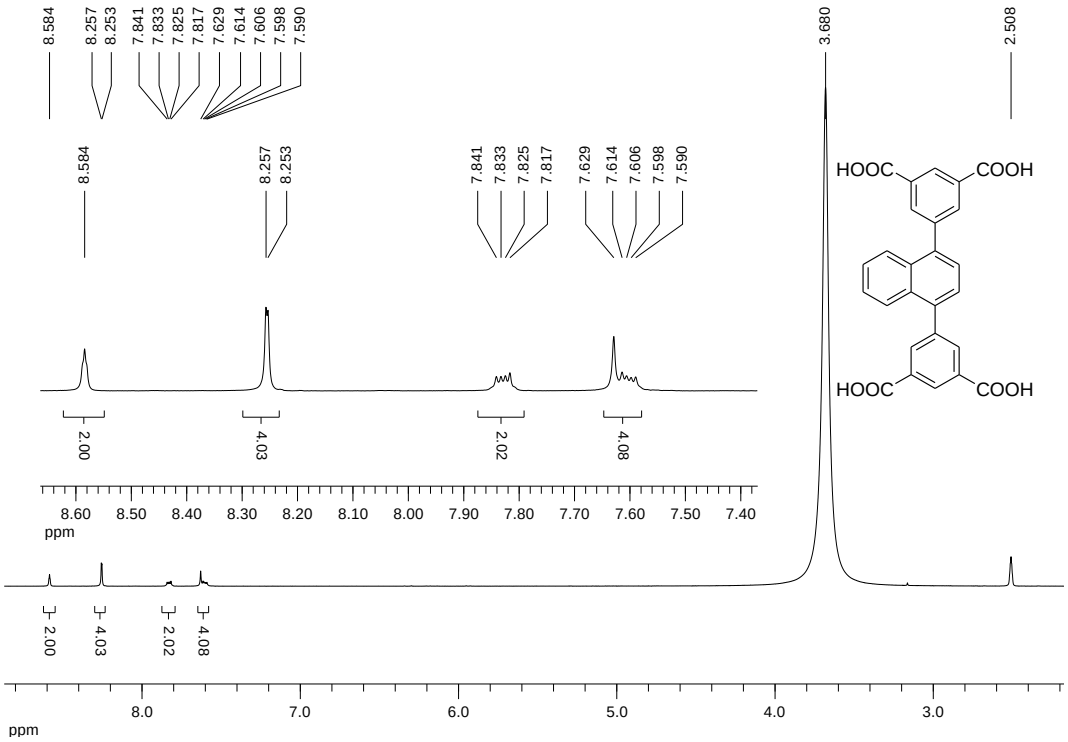
140.752
139.046
135.786
134.891
134.263
132.632
132.164
132.145
130.580
129.687
129.634
129.498
127.938
127.288
126.844
126.491
124.960
39.711
COOH
COOH
HOOC
COOH
140.0
135.0
130.0
125.0
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm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8.253
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7.614
7.606
7.598
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3.680
2.508
HOOC
COOH
HOOC
COOH
2.00
4.03
2.02
4.08
8.60 8.50 8.40 8.30 8.20 8.10 8.00 7.90 7.80 7.70 7.60 7.50 7.40
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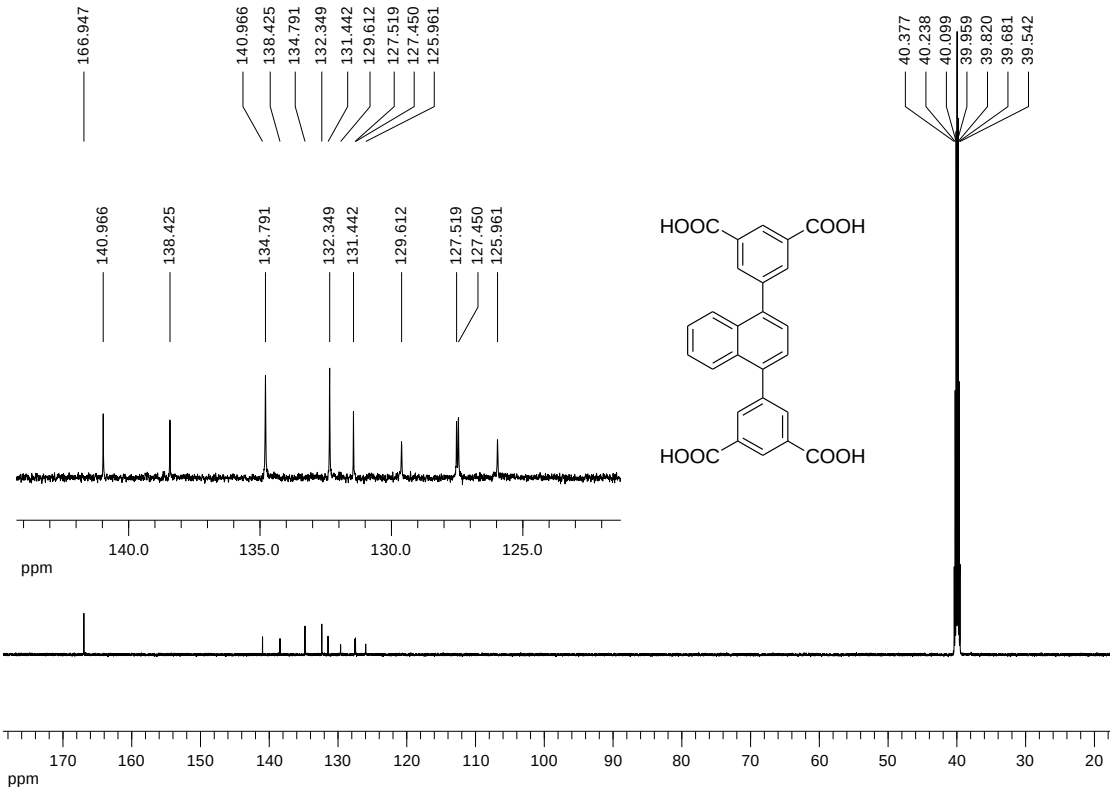
ppm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131.442
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127.519
127.450
125.961
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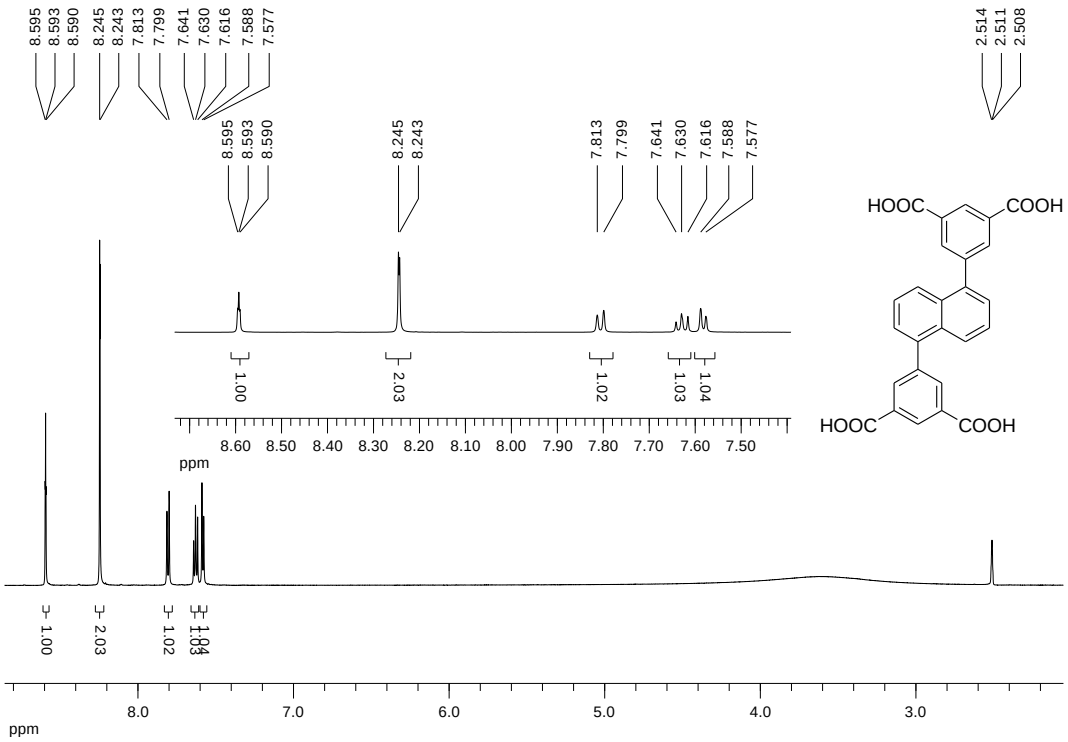
40.099
39.959
39.820
39.681
39.542
HOOC
COOH
HOOC
COOH
140.0 135.0 130.0 125.0
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm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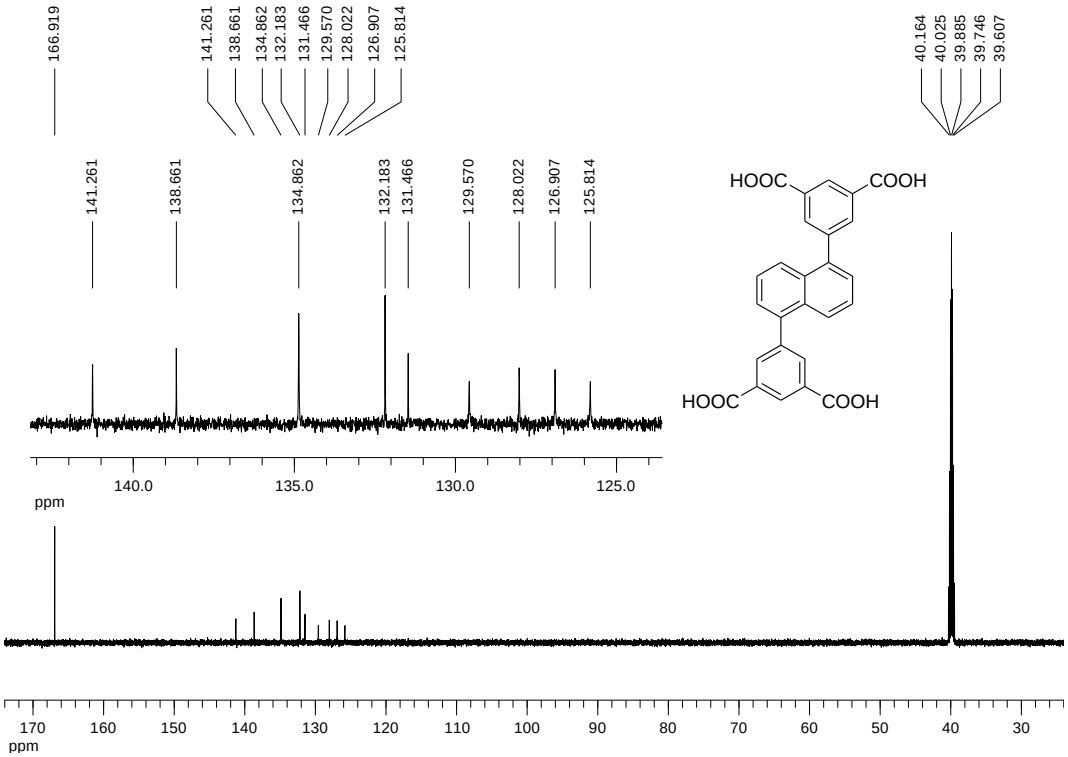
2.511
2.508
HOOC
COOH
HOOC
COOH
1.00
2.03
1.02
1.03
1.04
8.60 8.50 8.40 8.30 8.20 8.10 8.00 7.90 7.80 7.70 7.60 7.50
ppm
8.0 7.0 6.0 5.0 4.0 3.0
ppm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134.862
132.183
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129.570
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126.907
125.814
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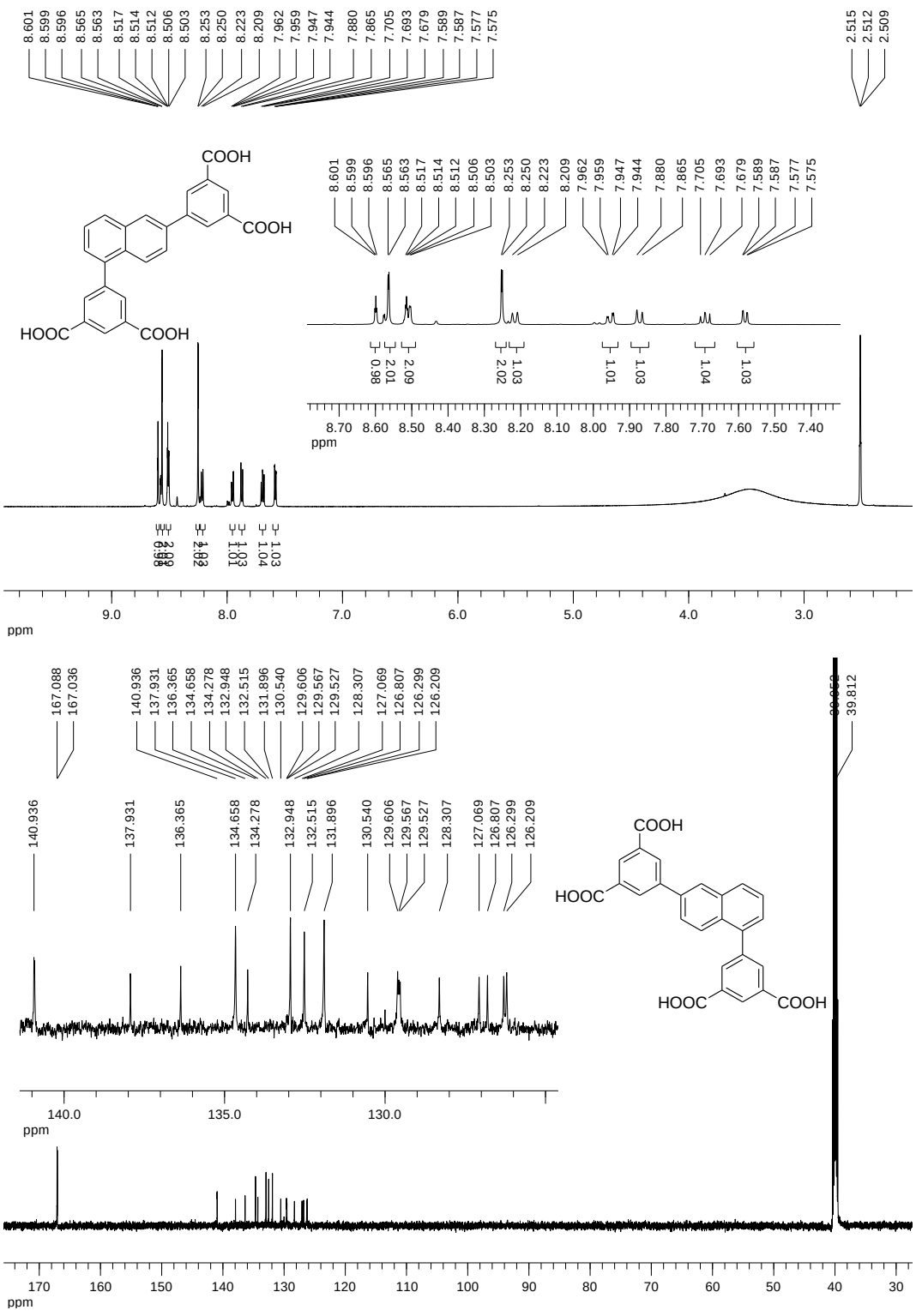
40.025
39.885
39.746
39.607
HOOC
COOH
HOOC
COOH
140.0 135.0 130.0 125.0
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
ppm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8.563
8.517
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8.503
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8.223
8.209
7.962
7.959
7.947
7.944
7.880
7.865
7.705
7.693
7.679
7.589
7.587
7.577
7.575
2.515
2.512
2.509
COOH
COOH
HOOC
COOH
0.98
1.01
2.09
2.02
1.03
1.01
1.03
1.04
1.03
8.70 8.60 8.50 8.40 8.30 8.20 8.10 8.00 7.90 7.80 7.70 7.60 7.50 7.40
ppm
9.0 8.0 7.0 6.0 5.0 4.0 3.0
ppm

167.088
167.036
140.936
137.931
136.365
134.658
134.278
132.948
132.515
131.896
130.540
129.606
129.567
129.527
128.307
127.069
126.807
126.299
126.209
39.812
COOH
HOOC
HOOC
COOH
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ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
ppm

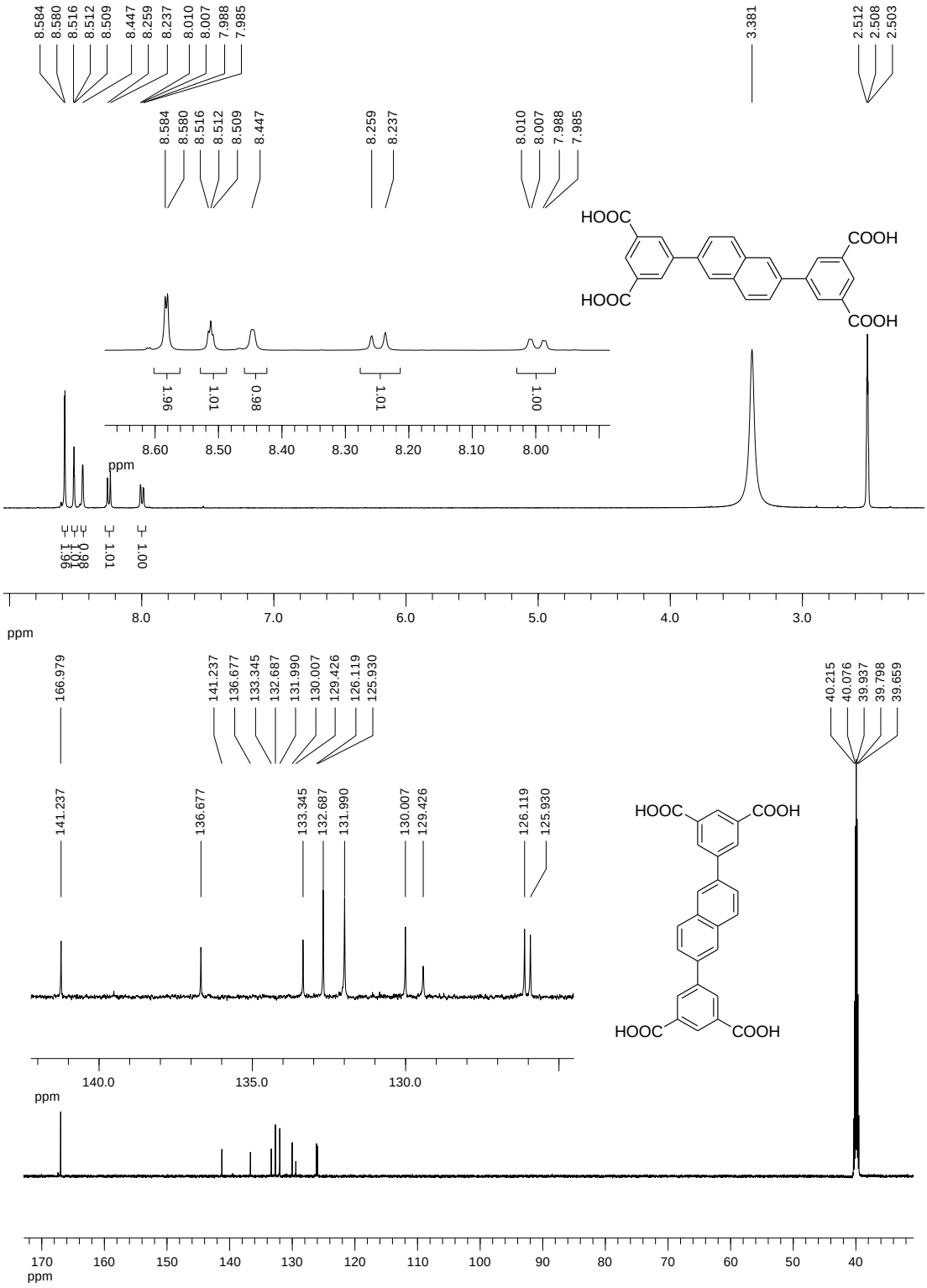

Fig. S15 ^{1}H and ^{13}C NMR spectra of the organic ligands.

Table S1 Crystal data and structure refinement for **ZJNU-71-74**.

MOFs	**ZJNU-71**	**ZJNU-72**	**ZJNU-73**	**ZJNU-74**
Empirical formula	$C_{38}H_{46}Cu_2N_4O_{15}$	$C_{39}H_{48}Cu_2N_4O_{15}$	$C_{44}H_{58}Cu_2N_6O_{16}$	$C_{38}H_{48}Cu_2N_4O_{16}$
Formula weight	925.87	939.89	1054.04	943.88
λ (Å)	0.71073	1.54184	0.71069	1.54184
Crystal system	Hexagonal	Trigonal	Trigonal	Hexagonal
Space group	$P6_3/mmc$	R-3m	R-3m	$P6_3/mmc$
Unit cell dimensions	a = 18.6937(6) Å b = 18.6937(6) Å c = 23.5643(14) Å α = 90° β = 90° γ = 120°	a = 18.5945(3) Å b = 18.5945(3) Å c = 38.5773(9) Å α = 90° β = 90° γ = 120°	a = 18.563(3) Å b = 18.563(3) Å c = 39.708(6) Å α = 90° β = 90° γ = 120°	a = 18.3150(7) Å b = 18.3150(7) Å c = 26.7665(14) Å α = 90° β = 90° γ = 120°
V (Å^3)	7131.4(5)	11551.3(4)	11850(3)	7775.6(6)
Z	6	9	9	6
D_c (g cm^{-3})	1.294	1.216	1.329	1.209
μ (mm^{-1})	0.958	1.537	0.877	1.539
F(000)	2880	4392	4950	2940
Crystal size (mm)	0.28 × 0.21 × 0.09	0.23 × 0.18 × 0.13	0.22 × 0.14 × 0.13	0.23 × 0.15 × 0.10
θ range for data collection (°)	1.258 to 27.544	3.437 to 74.661	1.367 to 27.586	4.322 to 74.004
Limiting indices	$-24 \le h \le 24$ $-24 \le k \le 24$ $-30 \le l \le 30$	$-20 \le h \le 23$ $-22 \le k \le 21$ $-47 \le l \le 45$	$-24 \le h \le 24$ $-24 \le k \le 24$ $-51 \le l \le 51$	$-20 \le h \le 13$ $-15 \le k \le 22$ $-32 \le l \le 27$
Reflections collected / unique	115435 / 3063	16158 / 2856	78489 / 3341	23236 / 2905
R_{int}	0.1228	0.0266	0.1116	0.0551
Max. and min. transmission	0.9214 and 0.7817	0.897 and 0.827	0.8992 and 0.8376	0.857 and 0.758
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3063 / 91 / 122	2856 / 109 / 122	3341 / 60 / 100	2905 / 103 / 119
Goodness-of-fit on F^2	1.059	1.006	1.090	1.103
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0602 wR_2 = 0.1749	R_1 = 0.0695 wR_2 = 0.2158	R_1 = 0.0756 wR_2 = 0.2082	R_1 = 0.1205 wR_2 = 0.3686
R indices (all data)	R_1 = 0.1153 wR_2 = 0.1971	R_1 = 0.0724 wR_2 = 0.2191	R_1 = 0.1075 wR_2 = 0.2271	R_1 = 0.1969 wR_2 = 0.4127
Largest diff. peak and hole (e.Å^{-3})	0.902 and -0.330	1.276 and -0.795	0.971 and -0.606	0.565 and -0.361
CCDC	1558046	1558047	1531020	1558048

Table S2 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-71**

	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	13.60272	1.77775×10^{-6}	24.6	0.84913
CO_2	24.42784	2.15324×10^{-7}	23.2	1
CH_4	19.9899	5.23044×10^{-7}	17.2	1

Calculation of Isosteric Heats of Adsorption

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 2020 HD88 surface-area-and-pore-size analyzer machine.

Fitting of Pure-Component Isotherms

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

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

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. Fig S13 provides a comparison of the experimental isotherm data for C_2H_2, CO_2 and CH_4 in **ZJNU-71** with the isotherm fits. The corresponding fitting parameters are provided in Table S2.