The Accessibility of Nitrogen Sites Makes Difference to Selective CO_2 Adsorption in a Family of Isostructural Metal-Organic Frameworks

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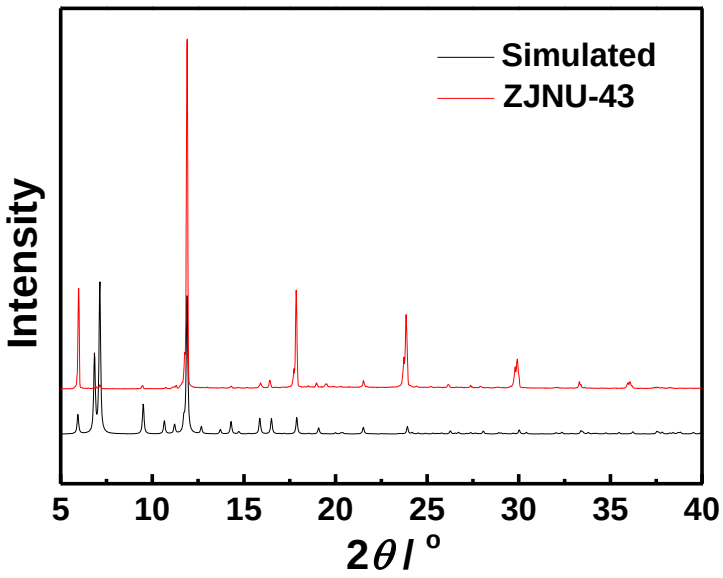


Figure S1. PXRD pattern of as-synthesized MOF **ZJNU-43** together with the one simulated from cif file. Calculated PXRD patterns were generated using Mercury 1.4.1.

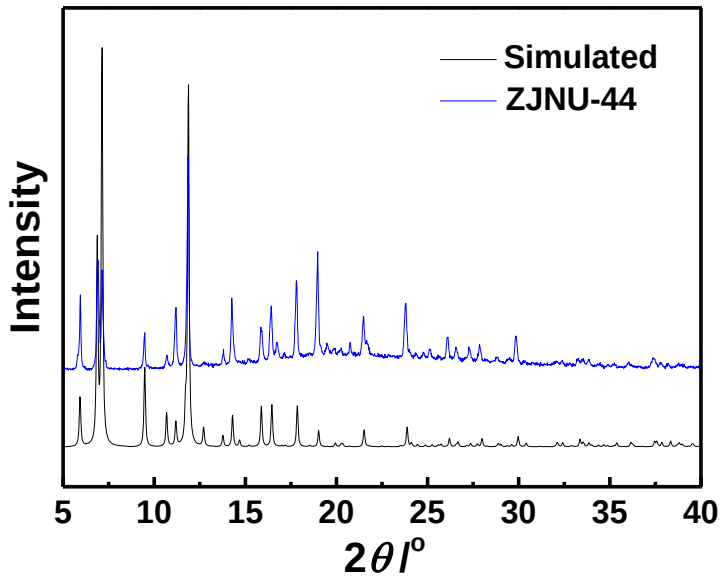


Figure S2. PXRD pattern of the as-synthesized MOF **ZJNU-44** together with the one simulated from its cif file. Calculated PXRD patterns were generated using Mercury 1.4.1.

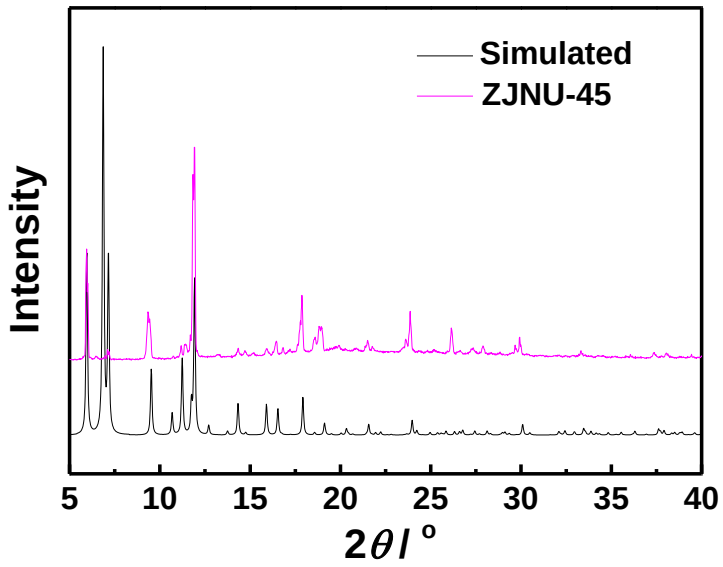


Figure S3. PXRD pattern of the as-synthesized MOF **ZJNU-45** together with the one simulated from its cif file. Calculated PXRD patterns were generated using Mercury 1.4.1.

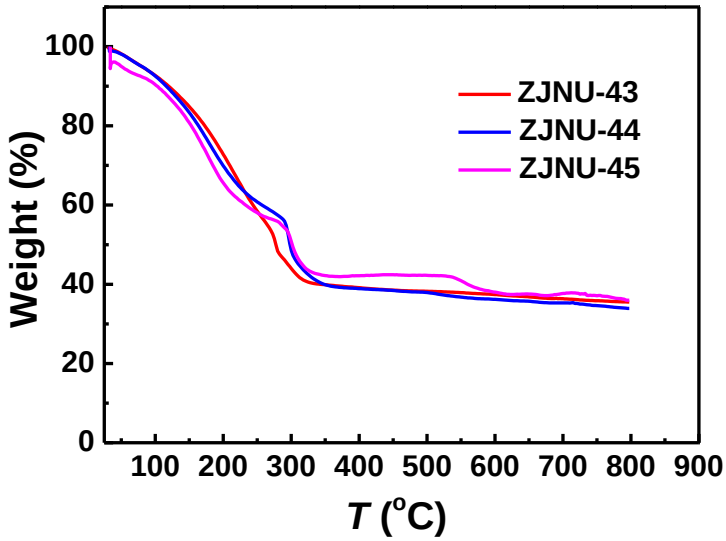


Figure S4. TGA curves of as-synthesized MOFs **ZJNU-43** (red)**, ZJNU-44** (blue) and **ZJNU-45** (magenta) under a nitrogen atmosphere with a heating rate of 5 ^{o}C min^{-1}.

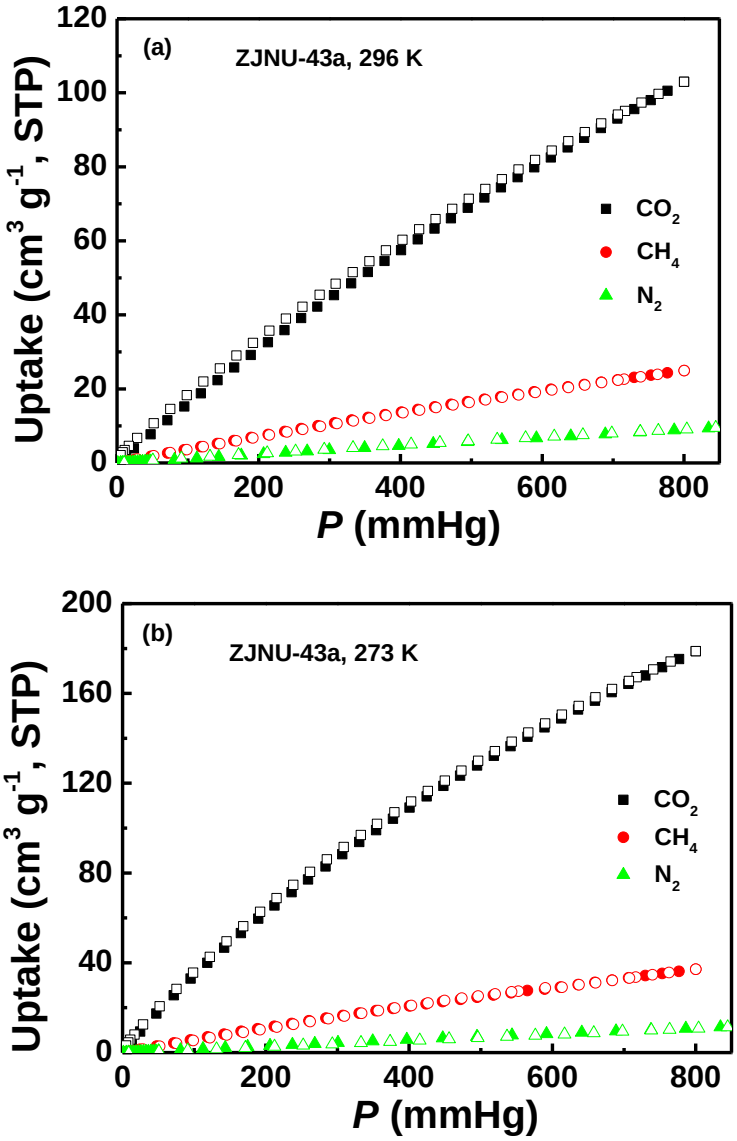


Figure S5. CO_2, CH_4 and N_2 sorption isotherms of **ZJNU-43a** at 296 K (a) and 273 K (b). Solid and open symbols represent adsorption and desorption, respectively.

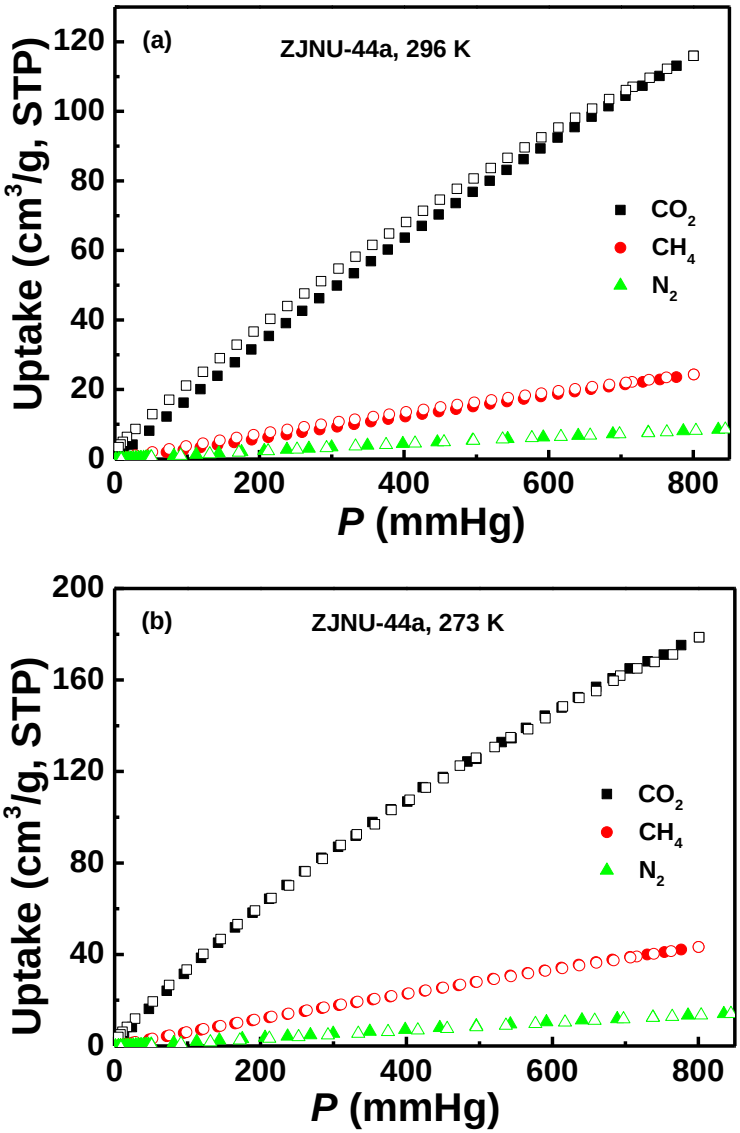


Figure S6. CO_2, CH_4 and N_2 sorption isotherms of **ZJNU-44a** at 296 K (a) and 273 K (b). solid and open symbols represent adsorption and desorption, respectively.

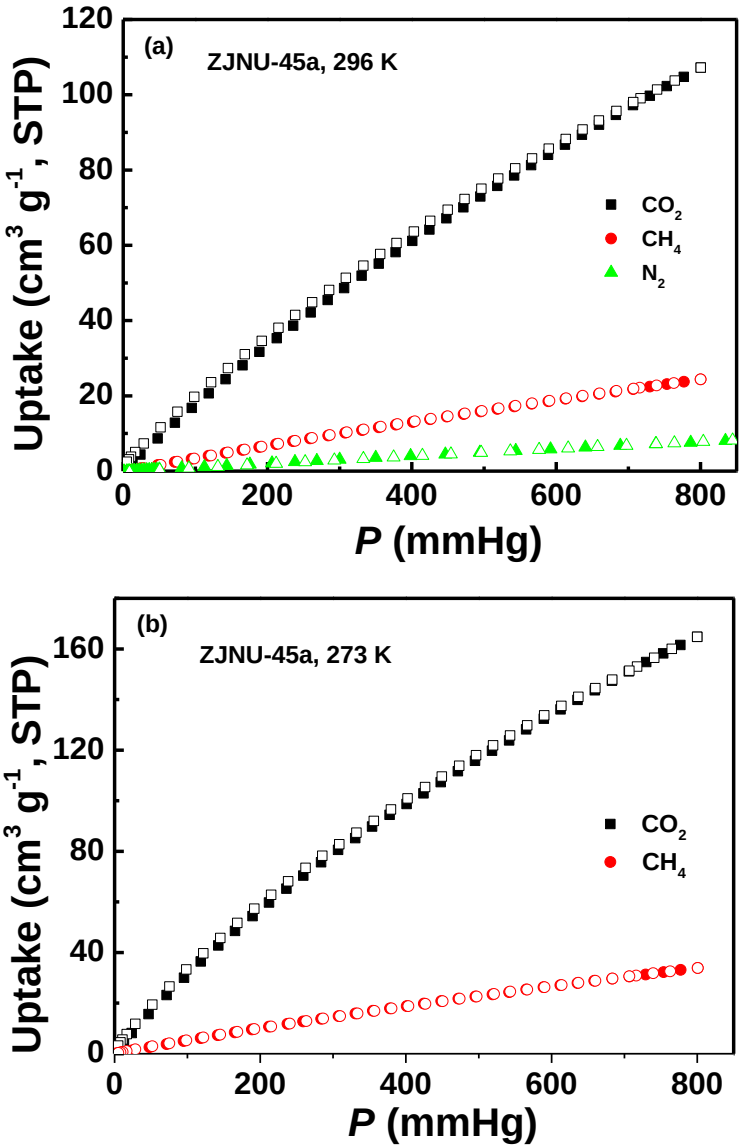


Figure S7. CO_2, CH_4 and N_2 sorption isotherms of **ZJNU-45a** at 296 K (a) and 273 K (b). Solid and open symbols represent adsorption and desorption, respectively.

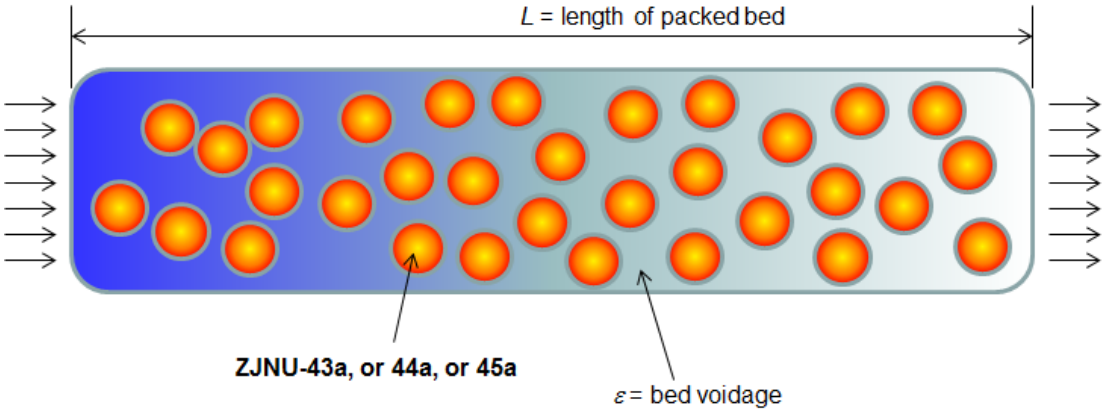


Figure S8. Schematic of the breakthrough apparatus. The length L = 0.3 m. The apparatus is operated at 296 K, and at a total gas pressure P = 200 kPa. The bed porosity, ε = 0.4. The interstitial gas velocity, u = 0.04 m s^{-1}.

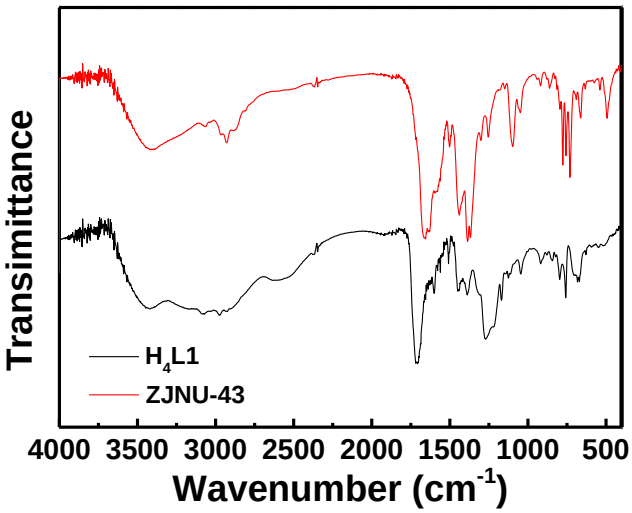


Figure S9. FTIR spectra of the organic linker H_4L1 and the as-synthesized MOF **ZJNU-43**.

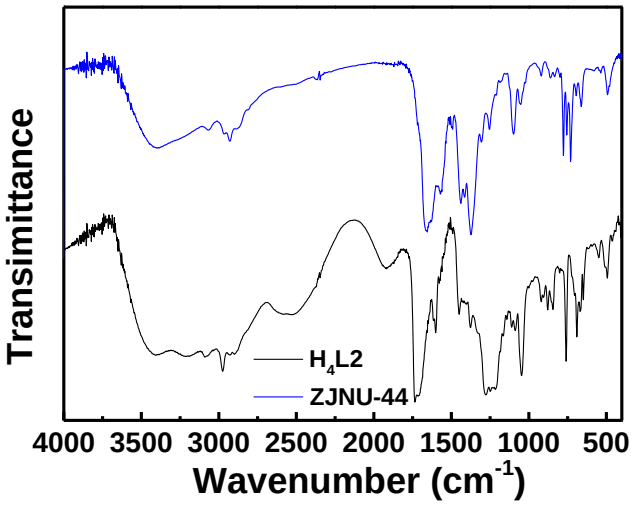


Figure S10. FTIR spectra of the organic linker H_4L2 and the as-synthesized MOF **ZJNU-44**.

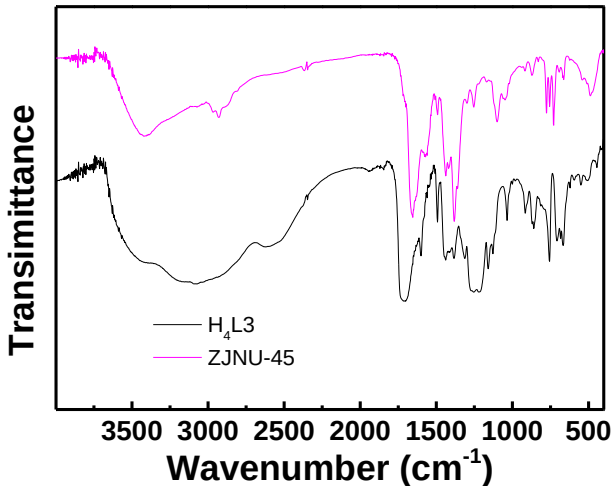
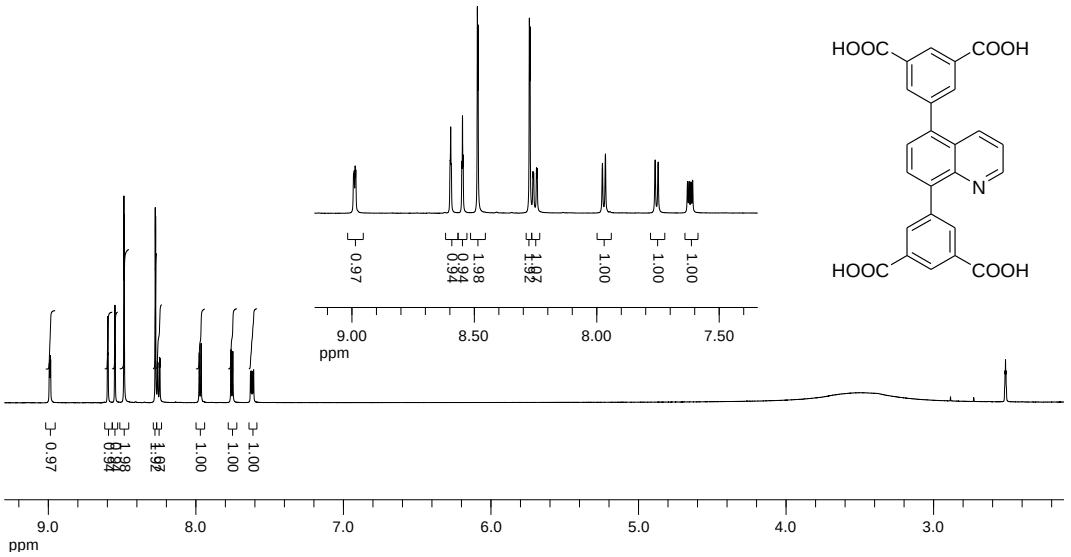


Figure S11. FTIR spectra of the organic linker H_4L3 and the as-synthesized MOF **ZJNU-45**.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COOH
N
HOOC
COOH
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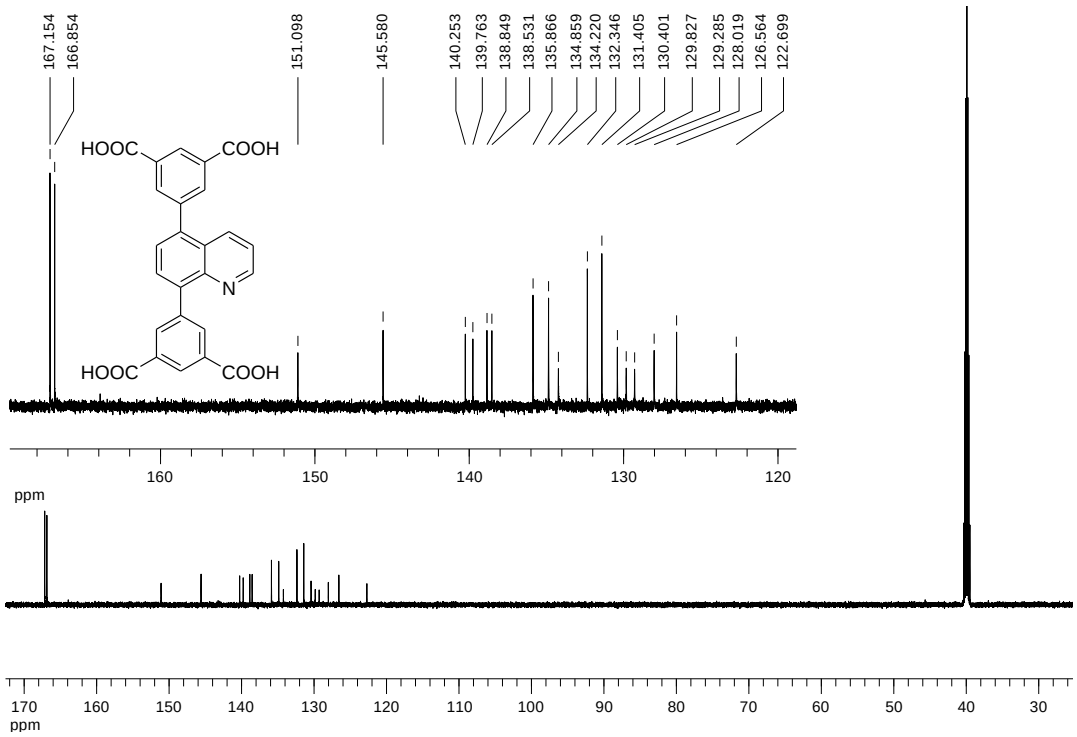
0.94
0.94
1.98
1.97
1.97
1.00
1.00
1.00
9.00
8.50
8.00
7.50
ppm
0.97
0.94
0.94
1.98
1.97
1.97
1.00
1.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm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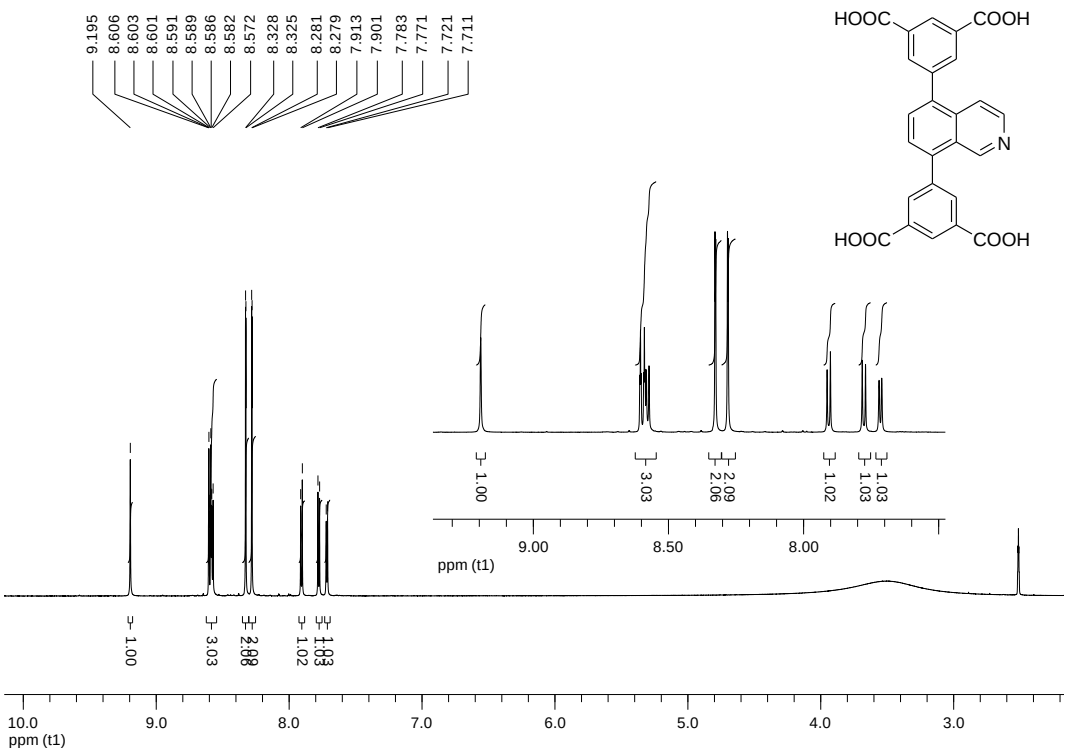
166.854
151.098
145.580
140.253
139.763
138.849
138.531
135.866
134.859
134.220
132.346
131.405
130.401
129.827
129.285
128.019
126.564
122.699
HOOC
COOH
N
HOOC
COOH
160
150
140
130
120
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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8.606
8.603
8.601
8.591
8.589
8.586
8.582
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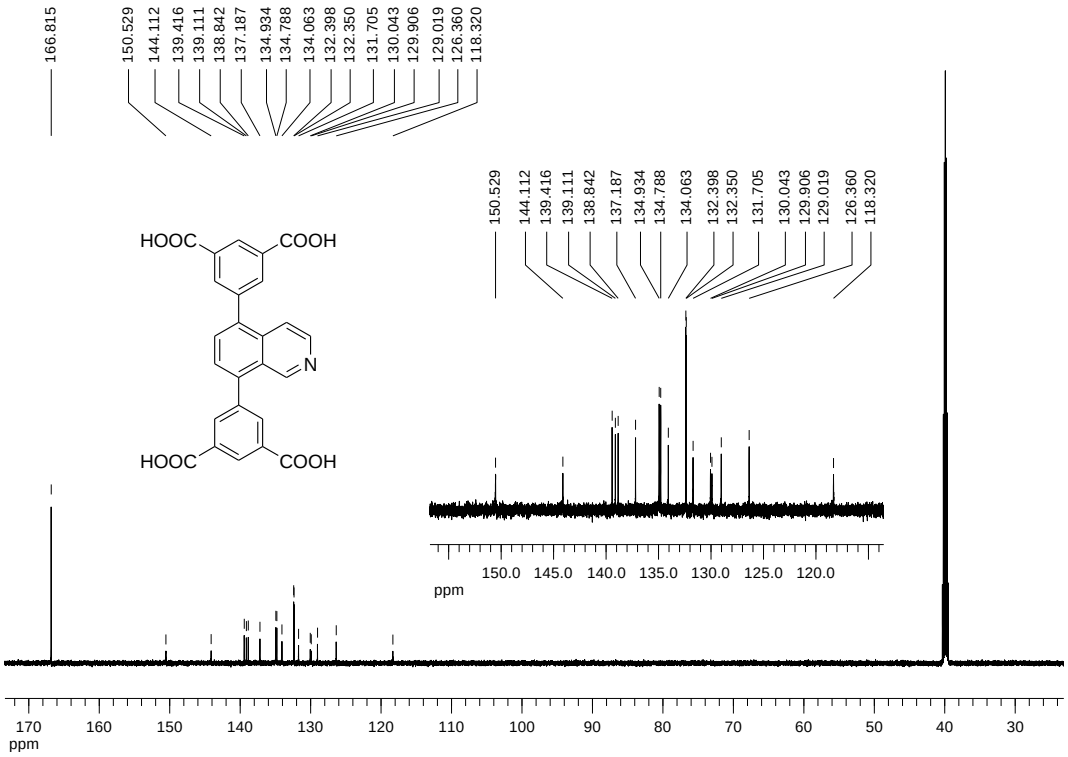
8.328
8.325
8.281
8.279
7.913
7.901
7.783
7.771
7.721
7.711
HOOC
COOH
N
HOOC
COOH
1.00
3.03
2.08
2.08
1.03
1.03
1.02
1.00
3.03
2.09
2.06
1.02
1.03
1.03
9.00
8.50
8.00
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm (t1)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150.529
144.112
139.416
139.111
138.842
137.187
134.934
134.788
134.063
132.398
132.350
131.705
130.043
129.906
129.019
126.360
118.320
HOOC
COOH
N
HOOC
COOH
150.0
145.0
140.0
135.0
130.0
125.0
120.0
ppm
170
160
150
140
130
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110
100
90
80
70
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50
40
30
ppm

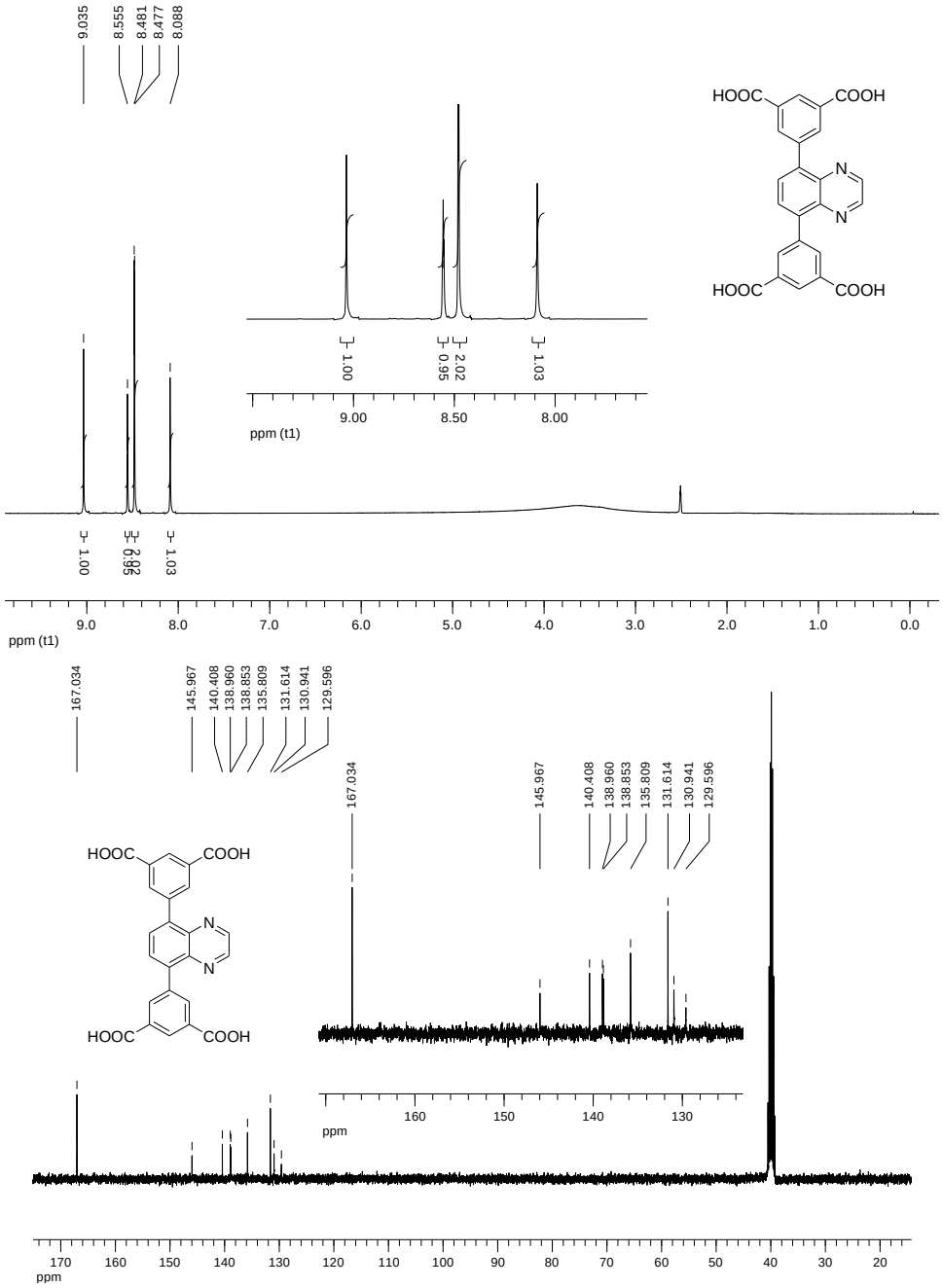

Figure S12. ^{1}H NMR and ^{13}C NMR spectra of the organic linkers in DMSO-d_6.

Table S1. Comparison of the textural properties of **ZJNU-43a**, **ZJNU-44a and ZJNU-45a**.

MOFs	S_{BET} ($m^2\ g^{-1}$)	$S_{Langmuir}$ ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	D_c ($g\ cm^{-3}$)
ZJNU-43a	2243	2516	0.8943	0.7483
ZJNU-44a	2314	2576	0.9158	0.7471
ZJNU-45a	2232	2473	0.8774	0.7544

Table S2. Langmuir parameters for adsorption of CO_2, CH_4, and N_2 in **ZJNU-43a**. These isotherm fits are based on data at 273 K and 296 K.

	q_{sat} ($mol\ kg^{-1}$)	b_0 (Pa^{-1})	E ($kJ\ mol^{-1}$)
CO_2	21	2.63×10^{-10}	22.7
CH_4	7.7	7.56×10^{-9}	13.3
N_2	6.9	5.63×10^{-8}	6

Table S3. Langmuir parameters for adsorption of CO_2, CH_4, and N_2 in **ZJNU-44a**. These isotherm fits are based on data at 273 K and 296 K.

	q_{sat} ($mol\ kg^{-1}$)	b_0 (Pa^{-1})	E ($kJ\ mol^{-1}$)
CO_2	24	1.77×10^{-9}	17.9
CH_4	22.5	2.91×10^{-10}	18.3
N_2	10	1.27×10^{-9}	14.2

Table S4. Langmuir parameters for adsorption of CO_2, and CH_4 in **ZJNU-45a**. These isotherm fits are based on data at 273 K and 296 K.

	q_{sat} ($mol\ kg^{-1}$)	b_0 (Pa^{-1})	E ($kJ\ mol^{-1}$)
CO_2	19	2.42×10^{-9}	17.7
CH_4	7.8	1.48×10^{-8}	11.5

Table S5. Langmuir parameters for adsorption of N_2 in **ZJNU-45a**. These isotherm fits are based on data at 296 K.

	q_{sat} (mol kg^{-1})	b (Pa^{-1})
N_2	10	3.8×10^{-7}

Table S6. Crystal data and structure refinement for **ZJNU-43, ZJNU-44** and **ZJNU-45.**

MOFs	**ZJNU-43**	**ZJNU-44**	**ZJNU-45**
Empirical formula	$C_{25}H_{15}NO_{10}Cu_2$	$C_{25}H_{15}NO_{10}Cu_2$	$C_{24}H_{14}N_2O_{10}Cu_2$
Formula weight	616.48	616.48	617.47
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54184	1.54184	1.54184
Crystal system	Trigonal	Trigonal	Trigonal
Space group	*R*-3m	*R*-3m	*R*-3m
Unit cell dimensions	a = 18.5943(3) b = 18.5943(3) c = 38.7113(6) α = 90° β = 90° γ = 120°	a = 18.6463(4) b = 18.6463(4) c = 38.5563(11) α = 90° β = 90° γ = 120°	a = 18.5565(4) b = 18.5565(4) c = 38.6189(8) α = 90° β = 90° γ = 120°
Volume (Å^3)	11591.2(3)	11609.4(5)	11516.6(4)
Z	9	9	9
Calculated density (g cm^{-3})	0.7947	0.7935	0.8012
Absorption coefficient (mm^{-1})	1.225	1.272	1.320
F(000)	2322	8262	2934
θ range for data collection (°)	2.97 to 73.93	2.97 to 74.29	2.98 to 73.88
Limiting indices	-23≤h≤21, -22≤k≤23, -41≤l≤47	-22≤h≤14, -20≤k≤23, -43≤l≤47	-15≤h≤22, -16≤k≤20, -42≤l≤47
Reflections collected / unique	19641 / 2856 [R_{int} = 0.0364]	14539 / 2856 [R_{int} = 0.0450]	14548 / 2821 [R_{int} = 0.0305]
Completeness to θ	θ = 73.93, 99.5 %	θ = 74.29, 98.7 %	θ = 73.88, 98.6 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2856 / 41 / 148	2856 / 36 / 154	2821 / 51 / 155
Goodness-of-fit on F^2	1.239	1.299	1.059
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0889, wR_2 = 0.2590	R_1 = 0.0944, wR_2 = 0.2761	R_1 = 0.0578, wR_2 = 0.1788
R indices (all data)	R_1 = 0.0969, wR_2 = 0.2763	R_1 = 0.1032, wR_2 = 0.2937	R_1 = 0.0621, wR_2 = 0.1864
Largest diff. peak and hole (e.Å^{-3})	1.475 and -0.661	1.520 and -0.616	0.743 and -0.483
CCDC	1052691	1052692	1055566