C_2H_2 Adsorption in Three Isostructural Metal-Organic Frameworks: Boosting C_2H_2 Uptake by Rational Arrangement of Nitrogen Sites

Chengling Song, Jingjing Jiao, Qiyi Lin, Huimin Liu, and Yabing He*

College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: heyabing@zjnu.cn

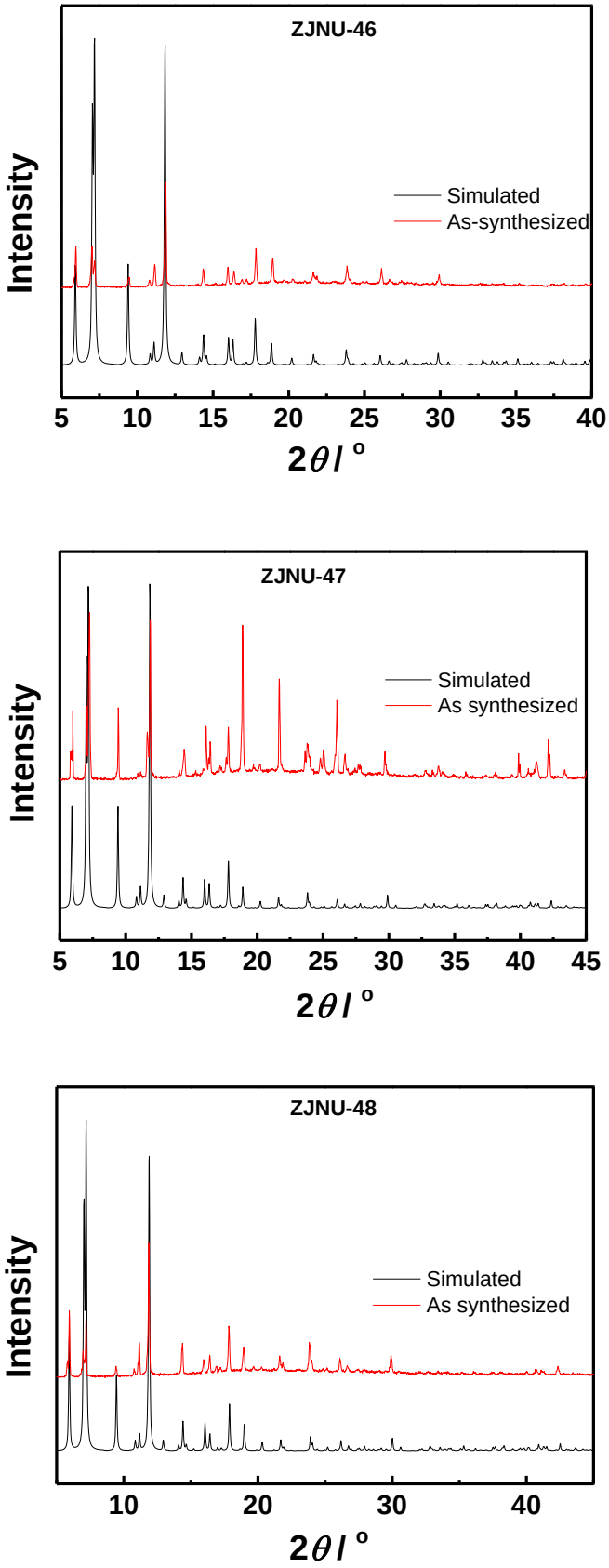


Fig. S1 PXRD patterns of the as-synthesized samples along with the simulated ones.

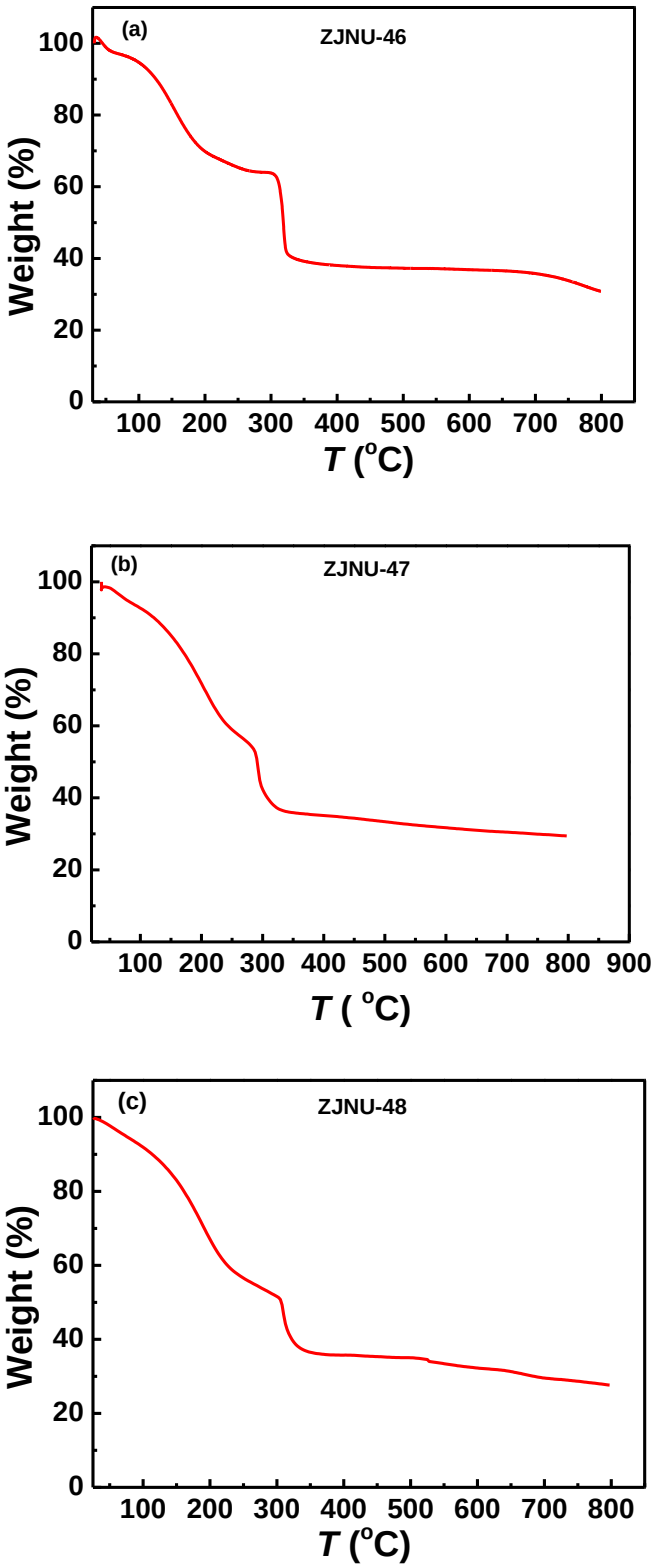
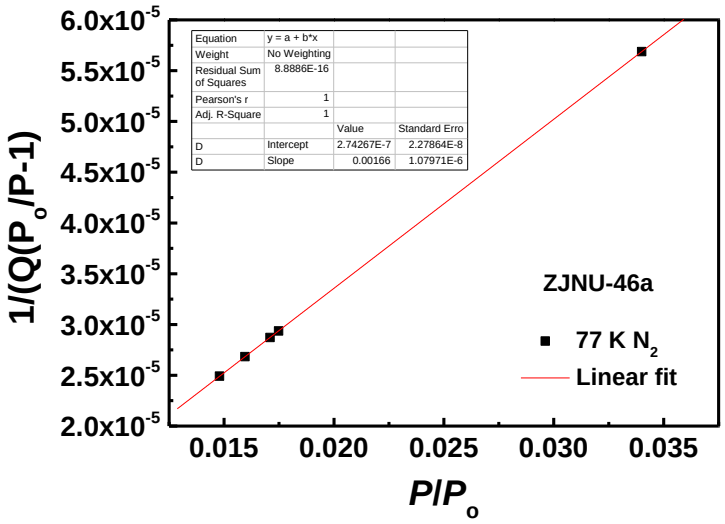
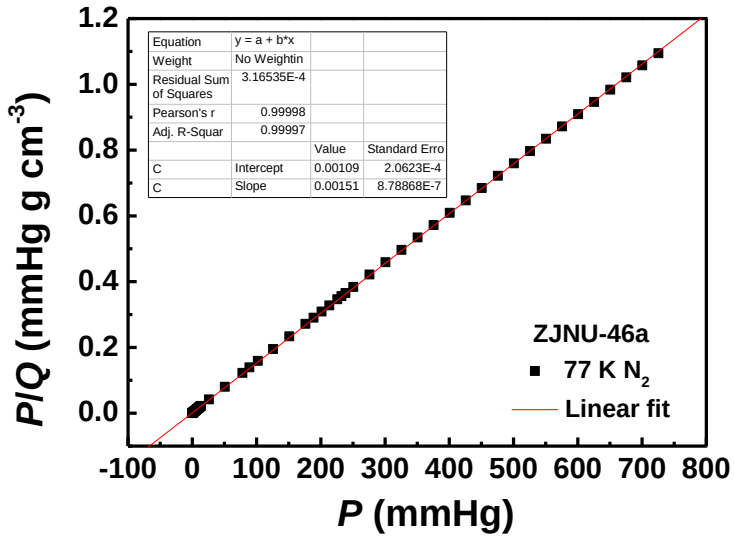


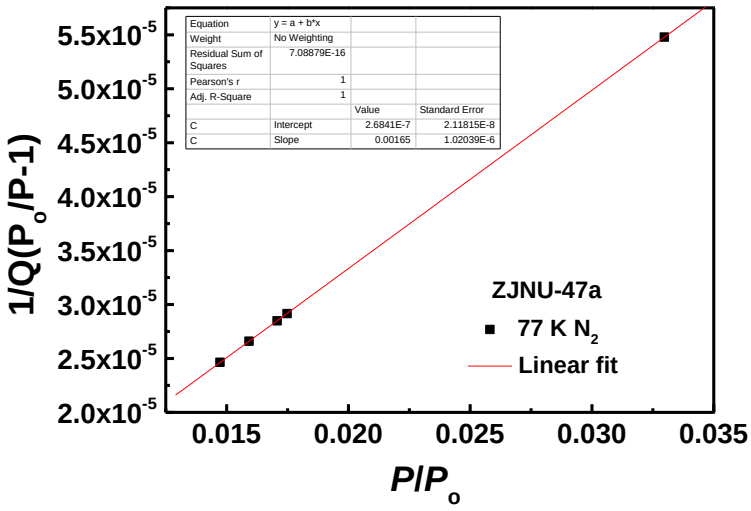
Fig. S2 TGA curves of as-synthesized **ZJNU-46** (a), **ZJNU-47** (b) and **ZJNU-48** (c).

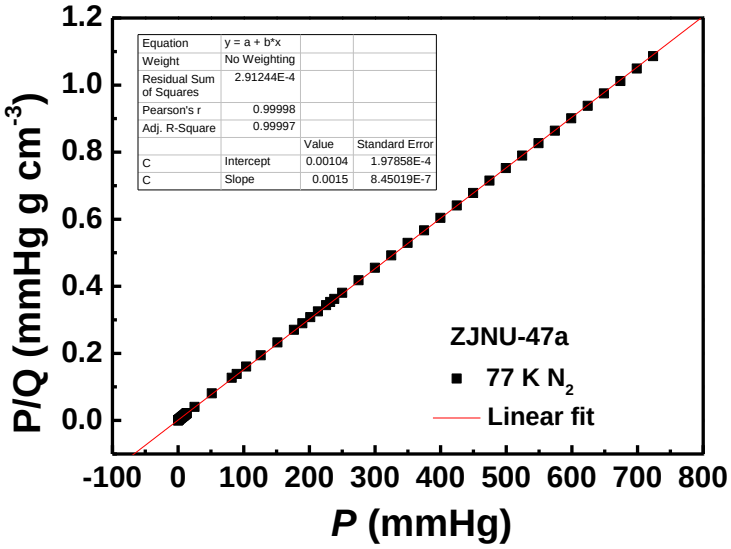




$S_{BET} = (1/(2.74267\times10^{-7}+0.00166))/22414\times6.023\times10^{23}\times0.162\times10^{-18} = 2622\ m^2\ g^{-1}$

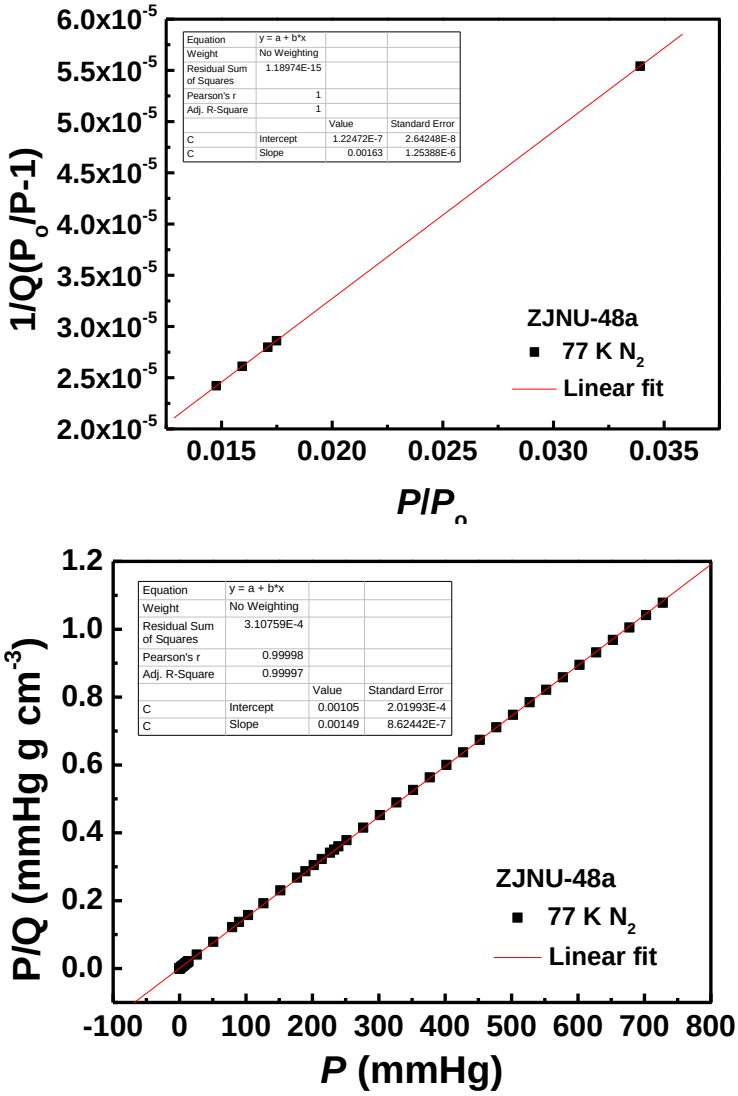
$S_{Langmuir} = (1/0.00151)/22414\times6.023\times10^{23}\times0.162\times10^{-18} = 2883\ m^2\ g^{-1}$





$S_{BET} = 1/(0.00165 + 2.6841 \times 10^{-7})/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 2638\ m^2\ g^{-1}$

$S_{Langmuir} = (1/0.0015)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 2902\ m^2\ g^{-1}$



S_{BET} = 1/(0.00163+1.22472×10^{-7})/22414×6.023×10^{23}×0.162×10^{-18} = 2670 m^2 g^{-1}

$S_{Langmuir}$ = 1/(0.00149)/22414×6.023×10^{23}×0.162×10^{-18} = 2922 m^2 g^{-1}

Fig. S3 BET and Langmuir plots for **ZJNU-46a**, **ZJNU-47a** and **ZJNU-48a**.

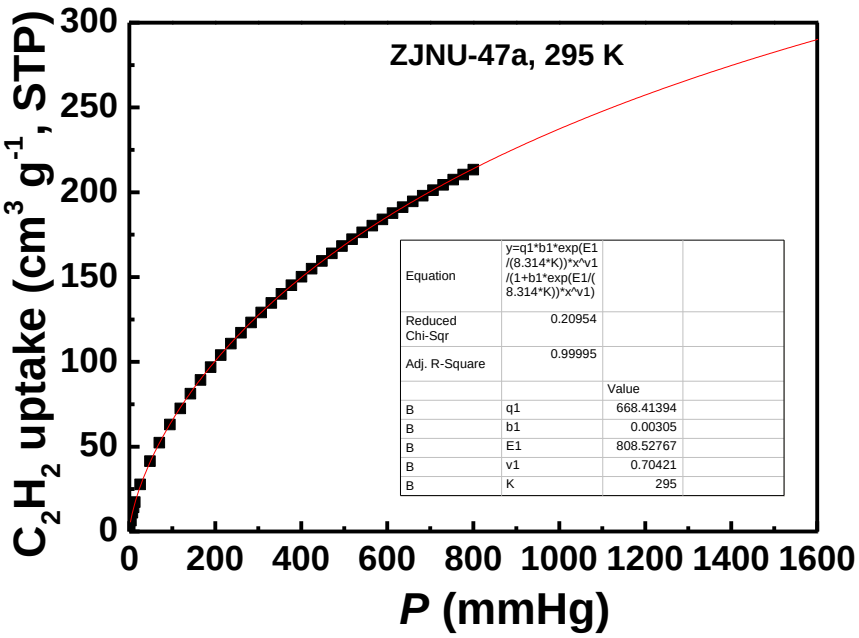


Fig. S4 Fitting the acetylene adsorption data of **ZJNU-47a** at 295 K with Langmuir-Freundlium model.

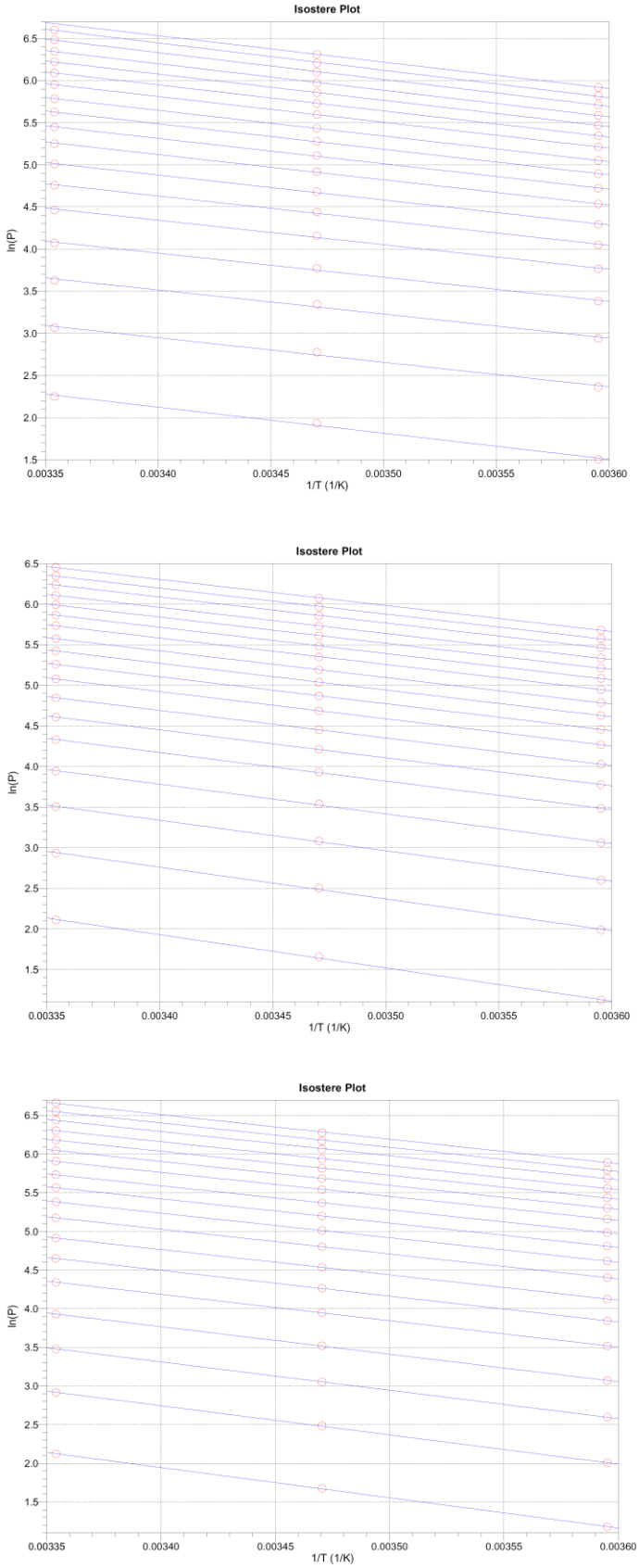


Fig. S5 Vant' Hoff isochores for C_2H_2 adsorption on **ZJNU-46a** (top), **ZJNU-47a** (middle) and **ZJNU-48a** (bottom)

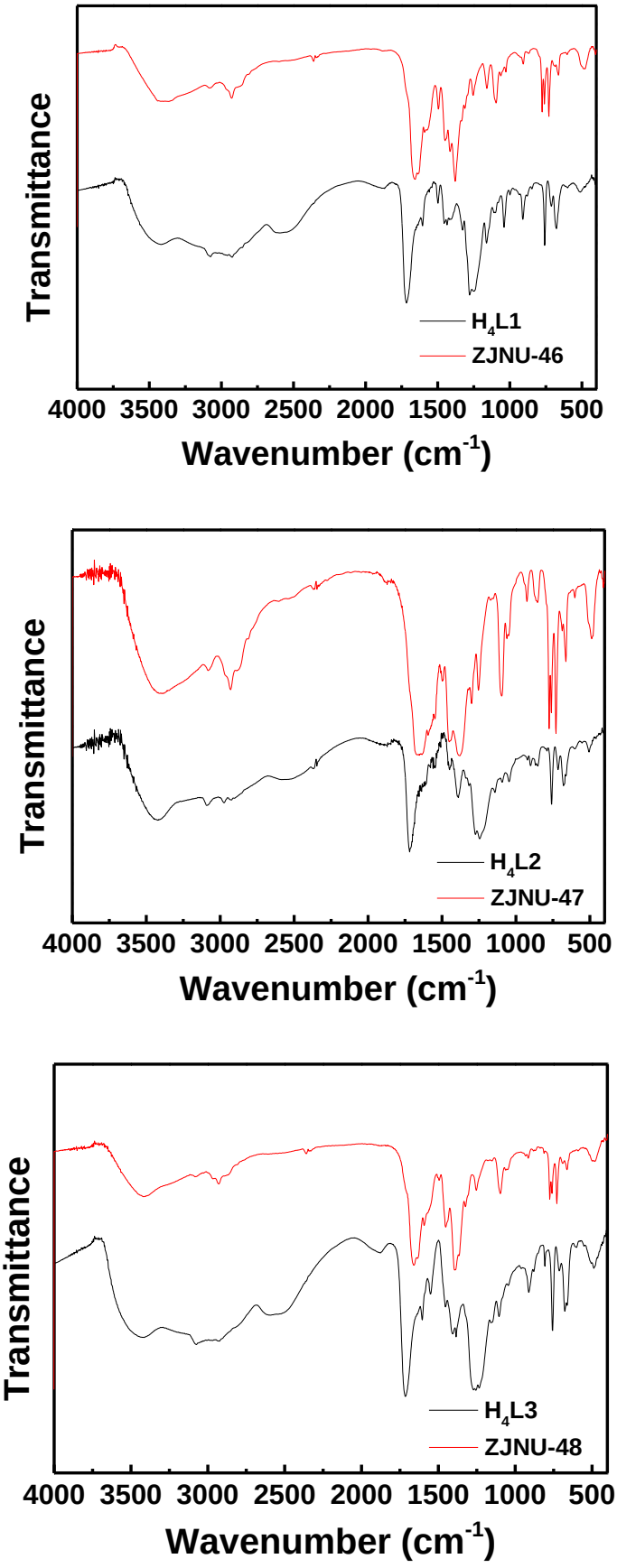
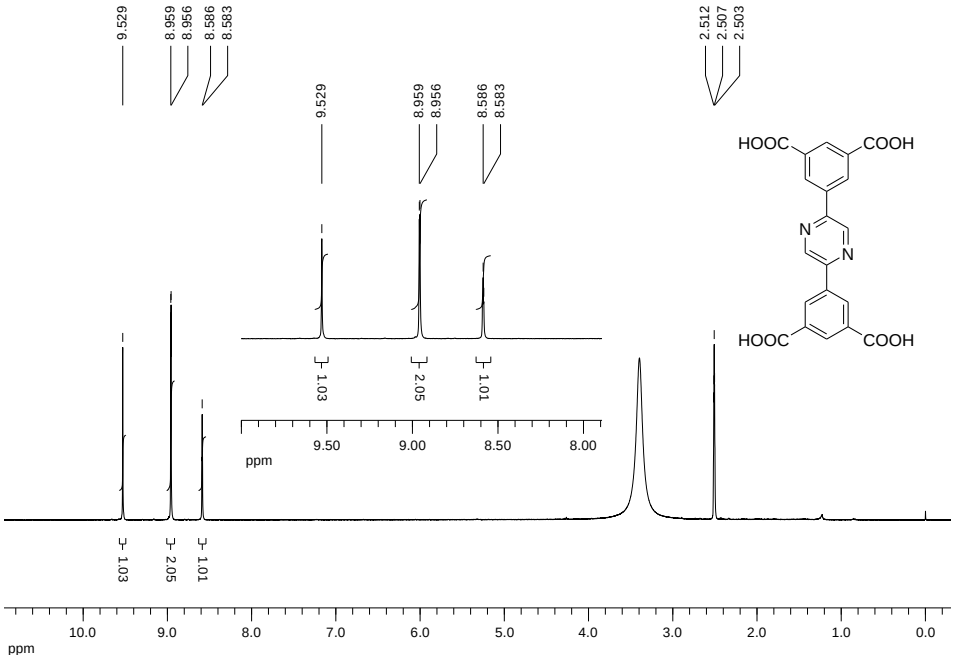
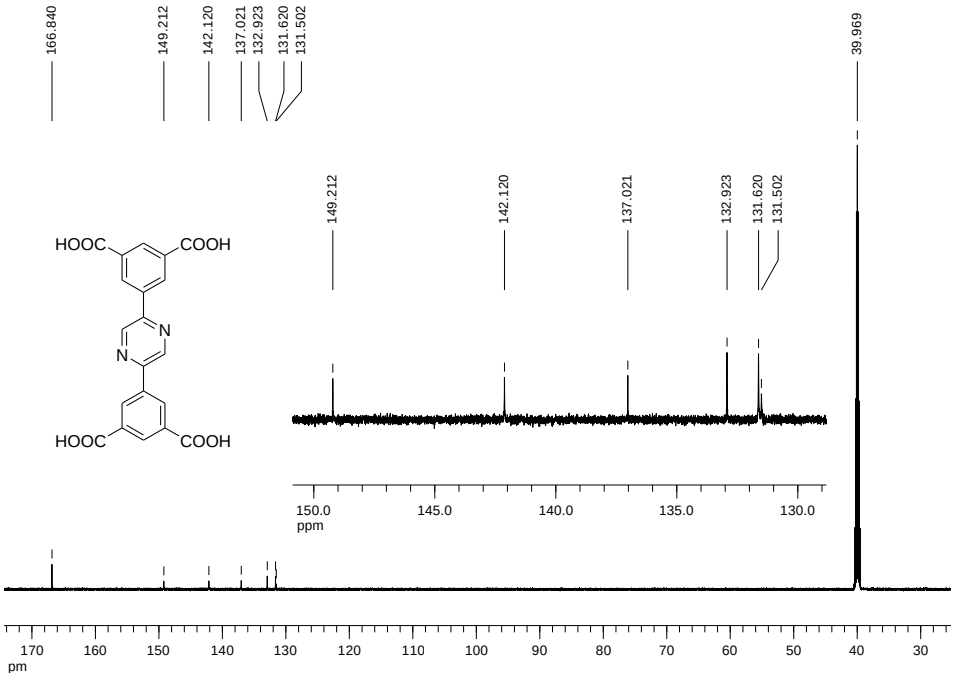
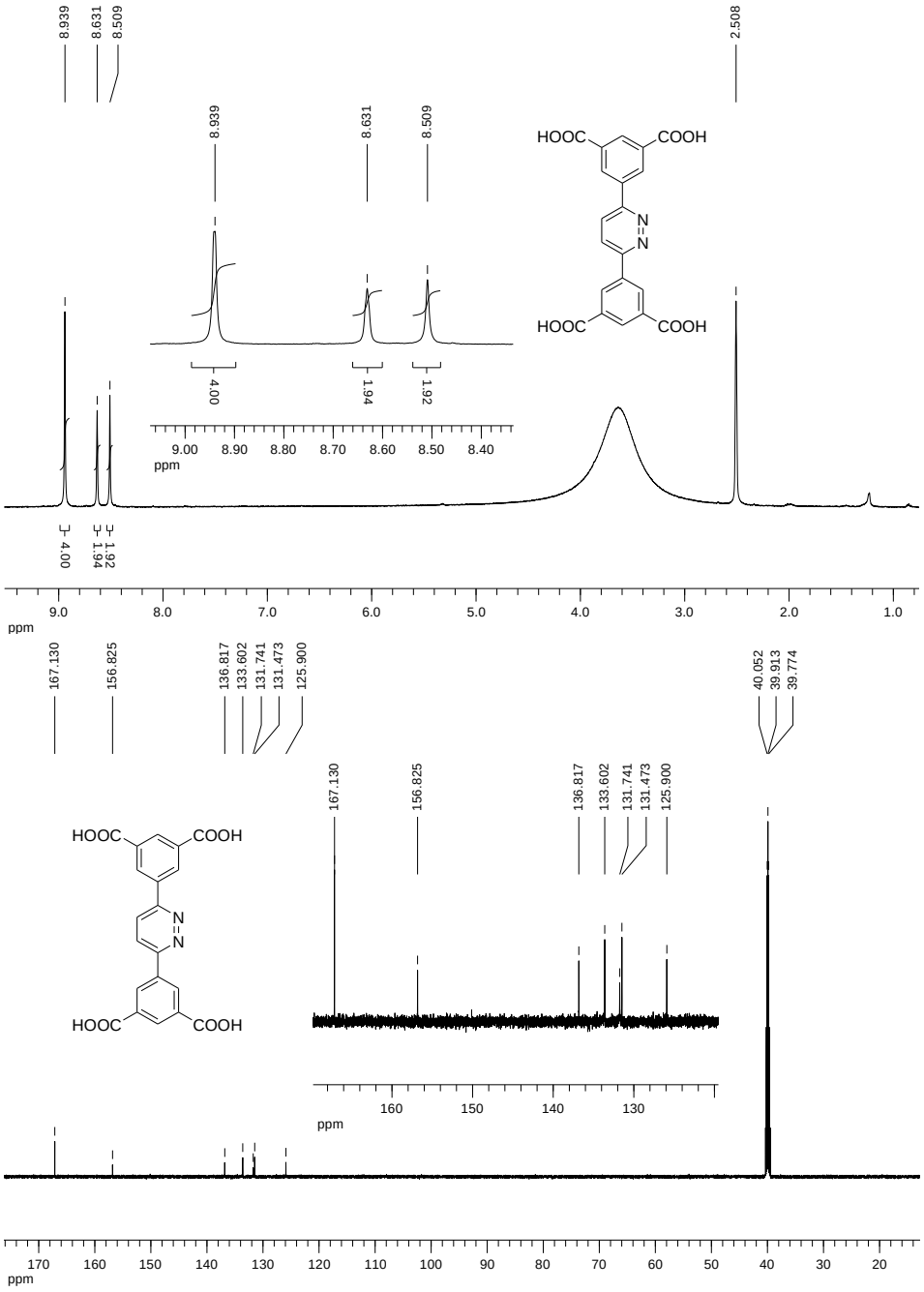


Fig. S6 FTIR spectra of the organic ligands and as-synthesized MOFs.


9.529
8.959
8.956
8.586
8.583
2.512
2.507
2.503
HOOC
COOH
N
N
HOOC
COOH
1.03
2.05
1.01
9.50
9.00
8.50
8.00
ppm
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


166.840
149.212
142.120
137.021
132.923
131.620
131.502
39.969
HOOC
COOH
N
N
HOOC
COOH
150.0
145.0
140.0
135.0
130.0
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
pm


8.939
8.631
8.509
2.508
HOOC
COOH
N
N
HOOC
COOH
4.00
1.94
1.92
9.00 8.90 8.80 8.70 8.60 8.50 8.40
ppm
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm
167.130
156.825
136.817
133.602
131.741
131.473
125.900
40.052
39.913
39.774
160 150 140 130
ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

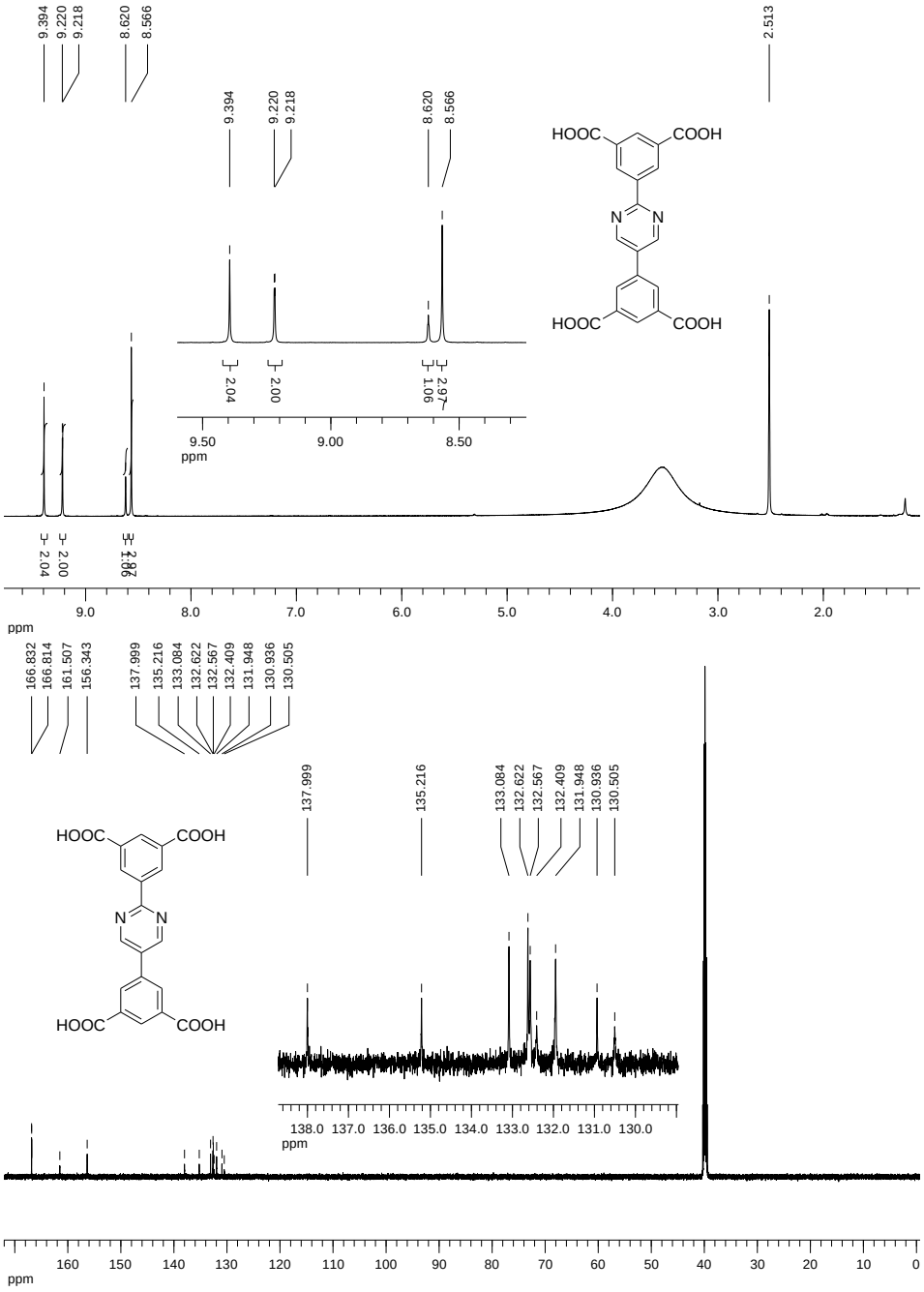


Fig. S7 ^{1}H NMR and ^{13}C NMR spectra

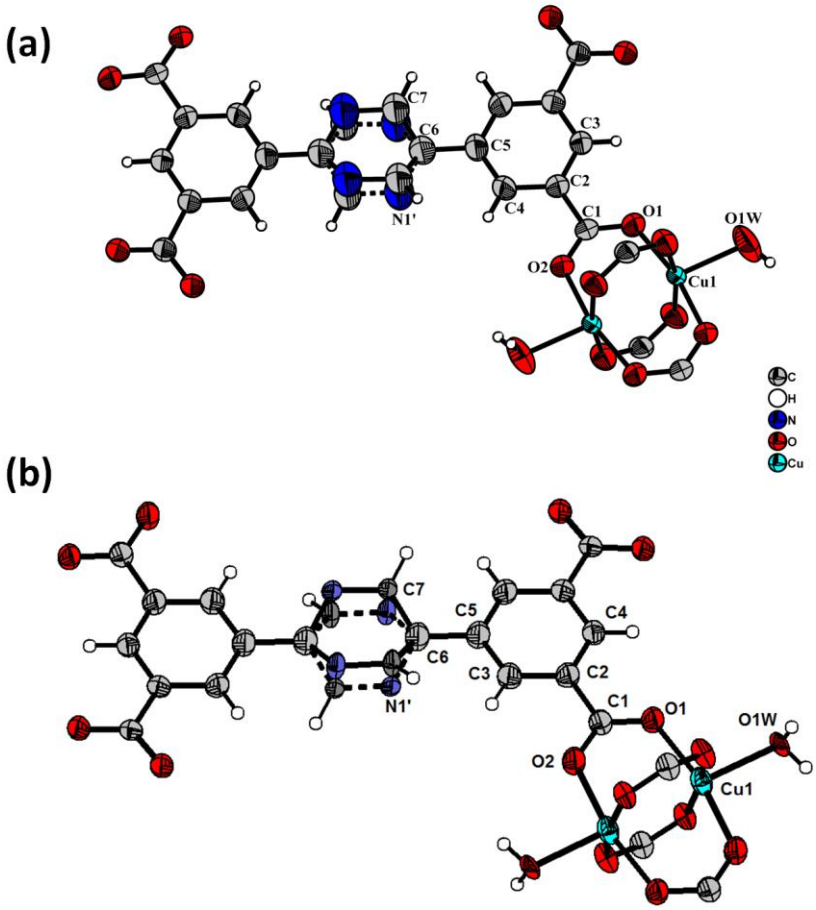


Fig. S8 ORTEP plots showing the asymmetric unit of (a) **ZJNU-46** and (b) **ZJNU-48**

Table S1 Crystal data and structure refinement for **ZJNU-46** and **ZJNU-48**.

Compounds	**ZJNU-46**	**ZJNU-48**
Empirical formula	$C_{20}H_{12}Cu_2N_2O_{10}$	$C_{10}H_6CuNO_5$
Formula weight	567.41	283.71
Wavelength (Å)	0.71073	0.71073
Crystal system	Trigonal	Trigonal
Space group	*R*-3m	*R*-3m
Unit cell dimensions	*a* = 18.8059(3) Å *b* = 18.8059(3) Å *c* = 37.6262(15) Å $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$	*a* = 18.65700(10) Å *b* = 18.65700(10) Å *c* = 38.0533(6) Å $\alpha = 90^o$ $\beta = 90^o$ $\gamma = 120^o$
Volume ($Å^3$)	11524.2(5)	11471.1(2)
Z	9	18
Calculated density (g cm^{-3})	0.733	0.737
Absorption coefficient (mm^{-1})	0.856	0.860
F(000)	2538	2538
Crystal size (mm)	0.33 × 0.21 × 0.16	0.31 × 0.24 × 0.10
θ range for data collection (^{o})	1.36 to 27.56	2.484 to 27.495
Limiting indices	$-24 \le h \le 24$, $-23 \le k \le 24$ $-48 \le l \le 39$	$-24 \le h \le 23$, $-24 \le k \le 24$, $-49 \le l \le 49$
Reflections collected / unique	32890 / 3249	41155 / 3211
R_{int}	0.1733	0.0650
Completeness to $\theta = 25.02$	99.9%	99.9%
Max. and min. transmission	0.8752 and 0.7654	0.9189 and 0.7764
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3249 / 19 / 95	3211 / 0 / 96
Goodness-of-fit on F^2	1.088	1.066
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0787$, $wR_2 = 0.2415$	$R_1 = 0.0310$, $wR_2 = 0.0981$
R indices (all data)	$R_1 = 0.0962$, $wR_2 = 0.2567$	$R_1 = 0.0360$, $wR_2 = 0.0992$
Largest diff. peak and hole (e.A^{-3})	1.525 and -0.473	0.746 and -0.483
CCDC	1056732	1441682