Electronic Supplementary Material (ESI) for CrystEngComm.


# Two copper-based MOFs constructed from a linear diisophthalate linker: supramolecular isomerism and gas adsorption properties

Minghui He, Tingting Xu, Zhenzhen Jiang, Xinjian Yu, Ying Zou, Luyao Yang, Xiaojuan Wang, Xia Wang and Yabing He*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: heyabing@zjnu.cn

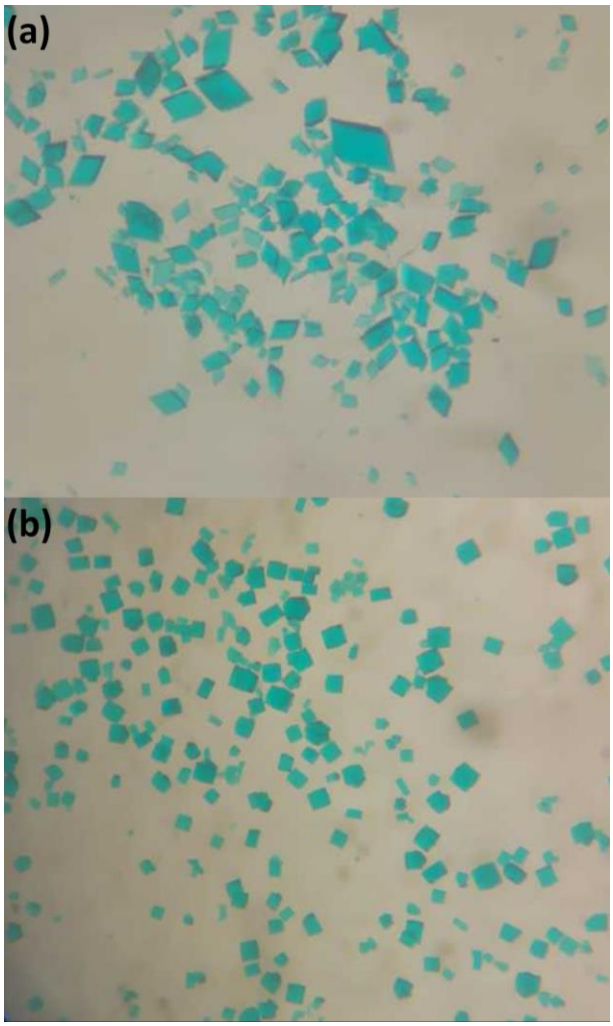



**Fig. S1** Electronic photographs of the as-synthesized (a) **ZJNU-96** and (b) **ZJNU-97**.

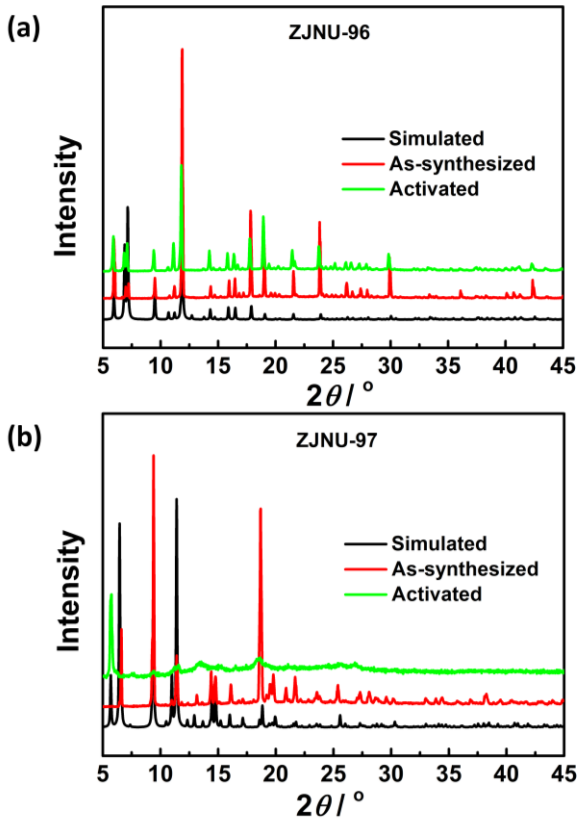



**Fig. S2** Experimental and simulated PXRD patterns for (a) **ZJNU-96** and (b) **ZJNU-97**.

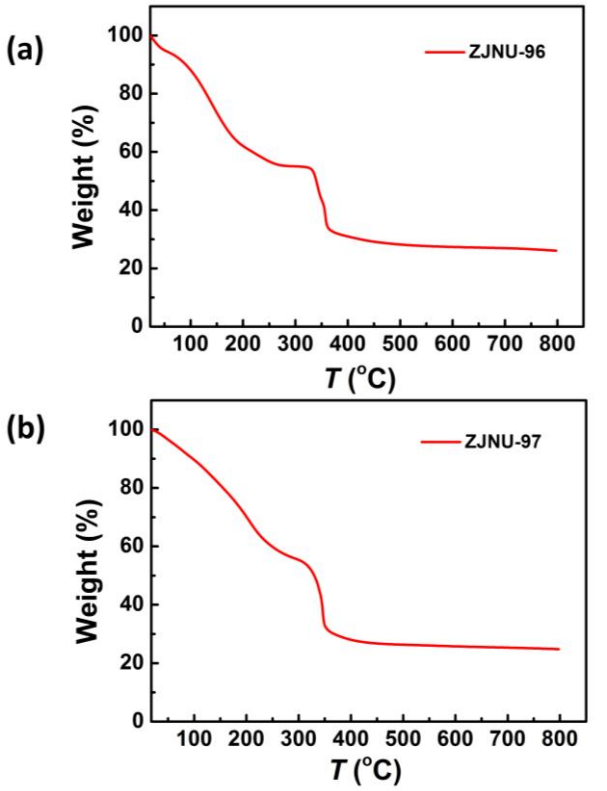



**Fig. S3** TGA curves of the as-synthesized (a) **ZJNU-96** and (b) **ZJNU-97** under $N_2$ atmosphere.

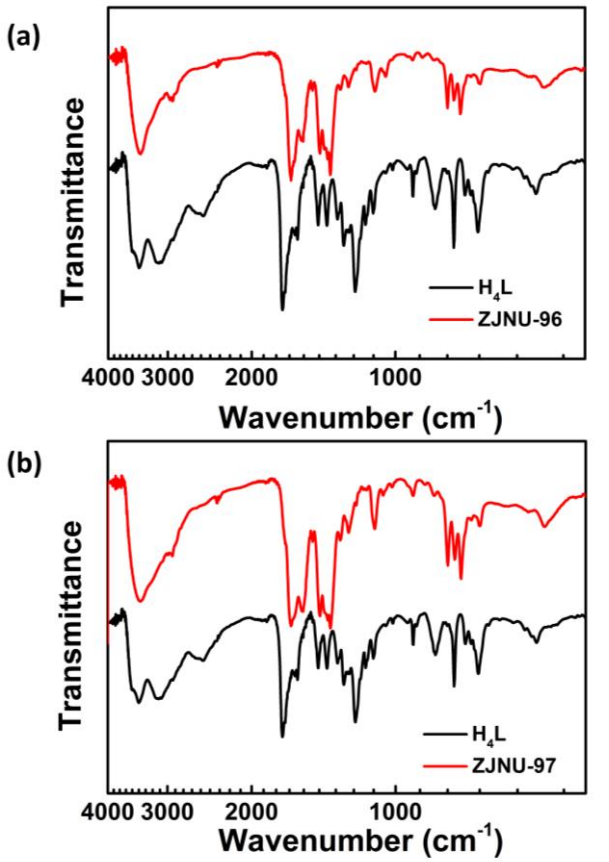



**Fig. S4** Comparison of FTIR spectra of the as-synthesized MOFs and their corresponding ligands.

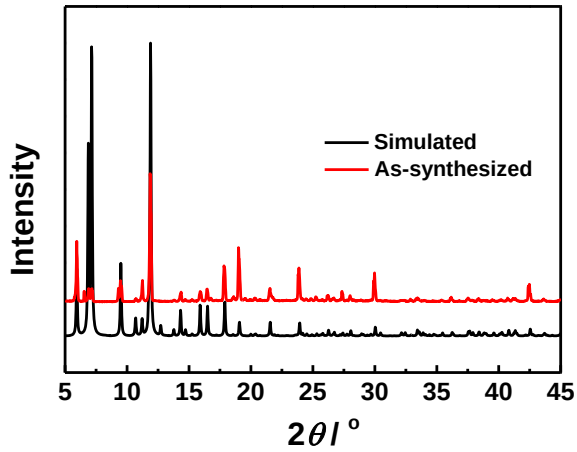



**Fig. S5**. The simulated PXRD pattern (black) of **ZJNU-96**, and the experimental PXRD pattern (red) of the as-synthesized solids obtained under the same solvothermal conditions as **ZJNU-97** except that HCl is replaced by $HBF_4$. The results indicate that the acid additive has an important effect on the final product.

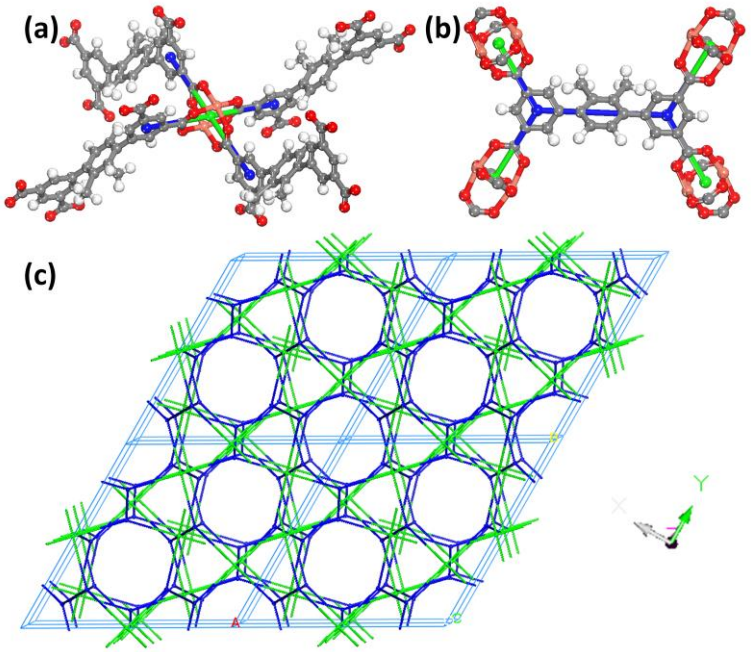



**Fig. S6** Topological analyses of **ZJNU-96**. (a) The dicopper paddlewheel SBU is simplified as a 4-connected node; (b) the ligand is viewed as a pair of 3-connected nodes; (c) the simplified topological network.

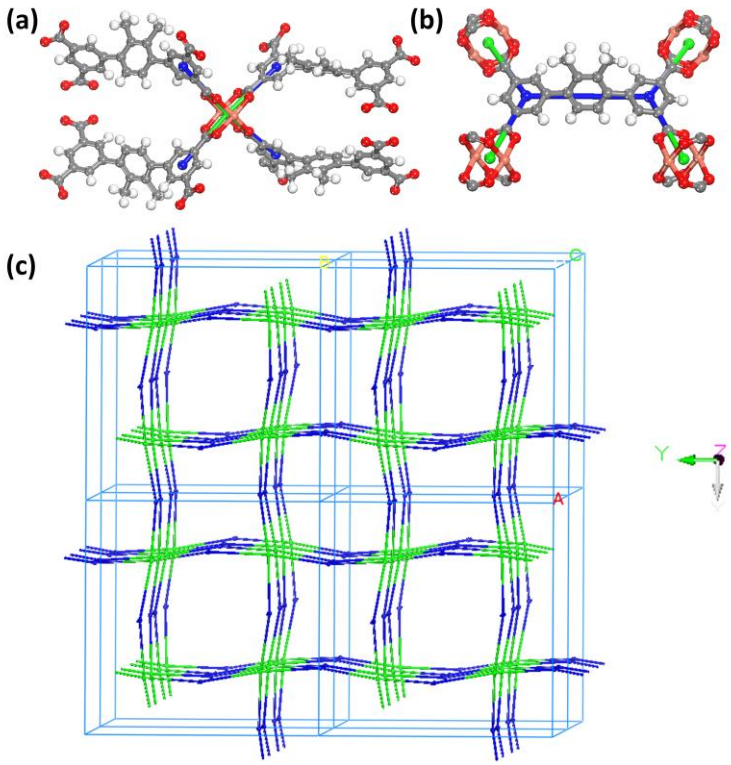
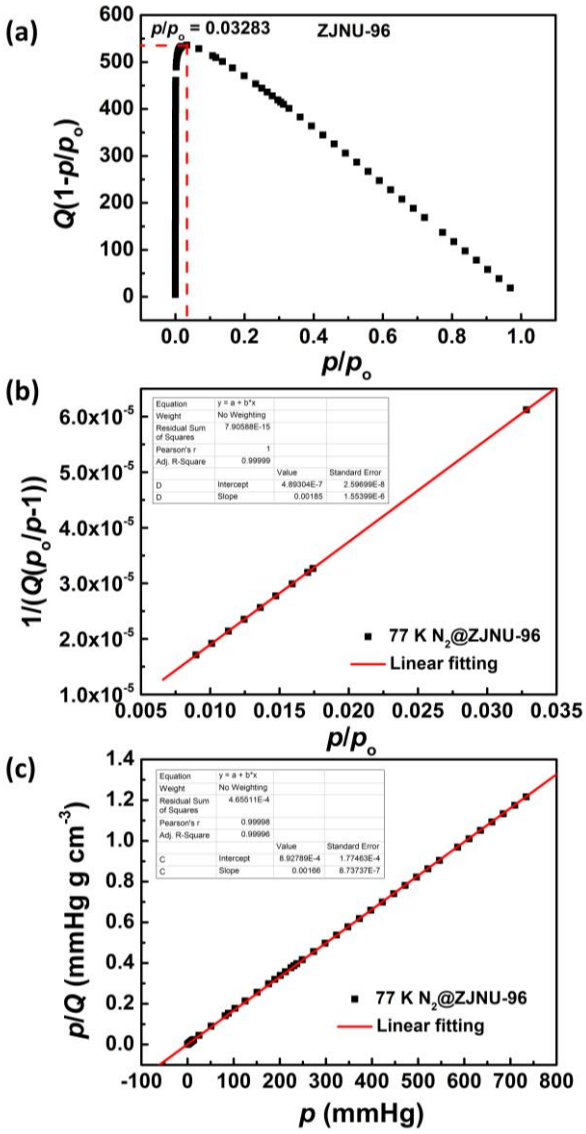



**Fig. S7** Topological analyses of **ZJNU-97**. (a) The dicopper paddlewheel SBU is simplified as a 4-connected node; (b) the ligand is viewed as a pair of 3-connected nodes; (c) the simplified topological network.



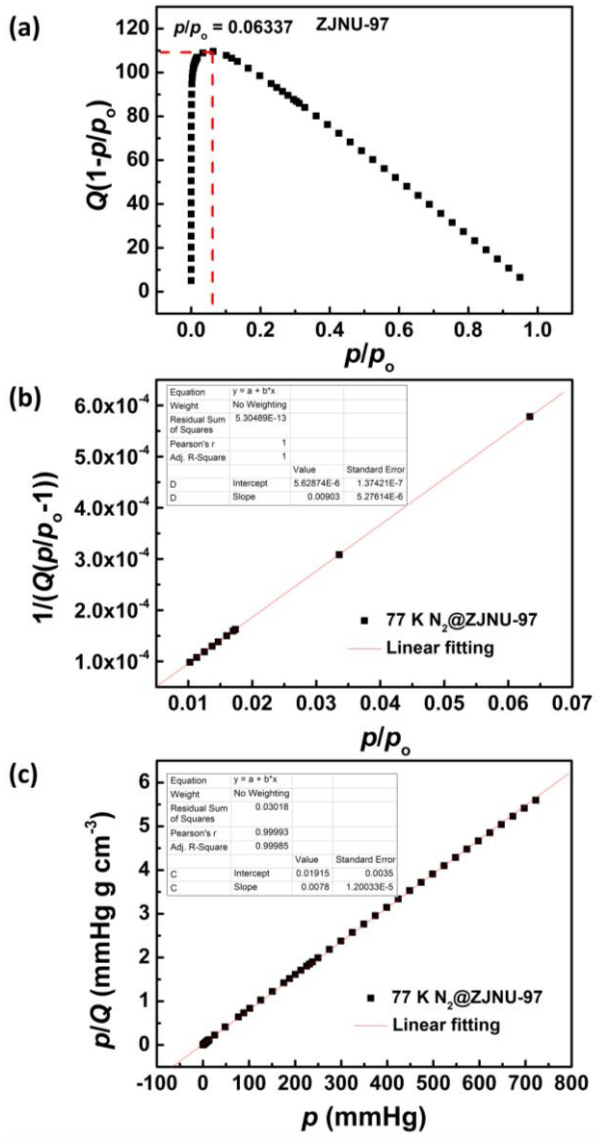

$S_{BET}$ = 1/(4.89304 ×10$^{-7}$+ 0.00185)/22414 × 6.023 × 10$^{23}$ × 0.162 × 10$^{-18}$ = 2352 m$^2$ g$^{-1}$

$S_{Langmuir}$ = (1/0.00166)/22414 × 6.023 × 10$^{23}$ × 0.162 × 10$^{-18}$ = 2622 m$^2$ g$^{-1}$

BET constant $C$ = 1 + 0.00185/4.89304×10$^{-7}$ = 3782

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01600$$

**Fig. S8** The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-96**.




$S_{BET}$ = 1/(5.62874 ×10$^{-6}$ + 0.00903)/22414 × 6.023 × 10$^{23}$ × 0.162 × 10$^{-18}$ = 482 m$^2$ g$^{-1}$

$S_{Langmuir}$ = (1/0.0078)/22414 × 6.023 × 10$^{23}$ × 0.162 × 10$^{-18}$ = 558 m$^2$ g$^{-1}$

BET constant $C$ = 1 + 0.00903/5.62874 ×10$^{-6}$ = 1605

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.02435$$

**Fig. S9** The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-97**.

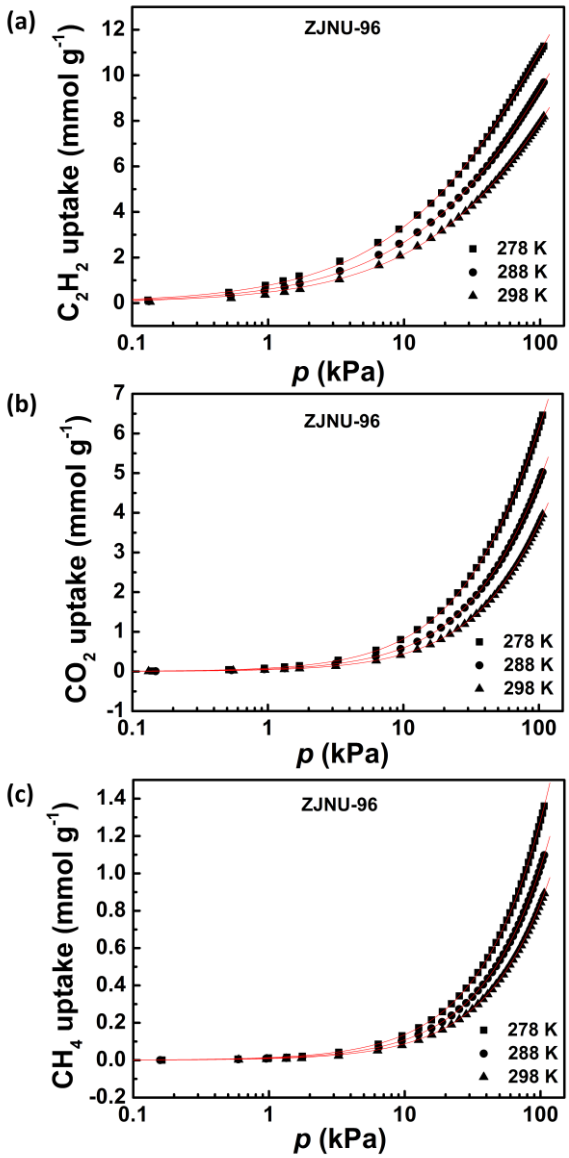
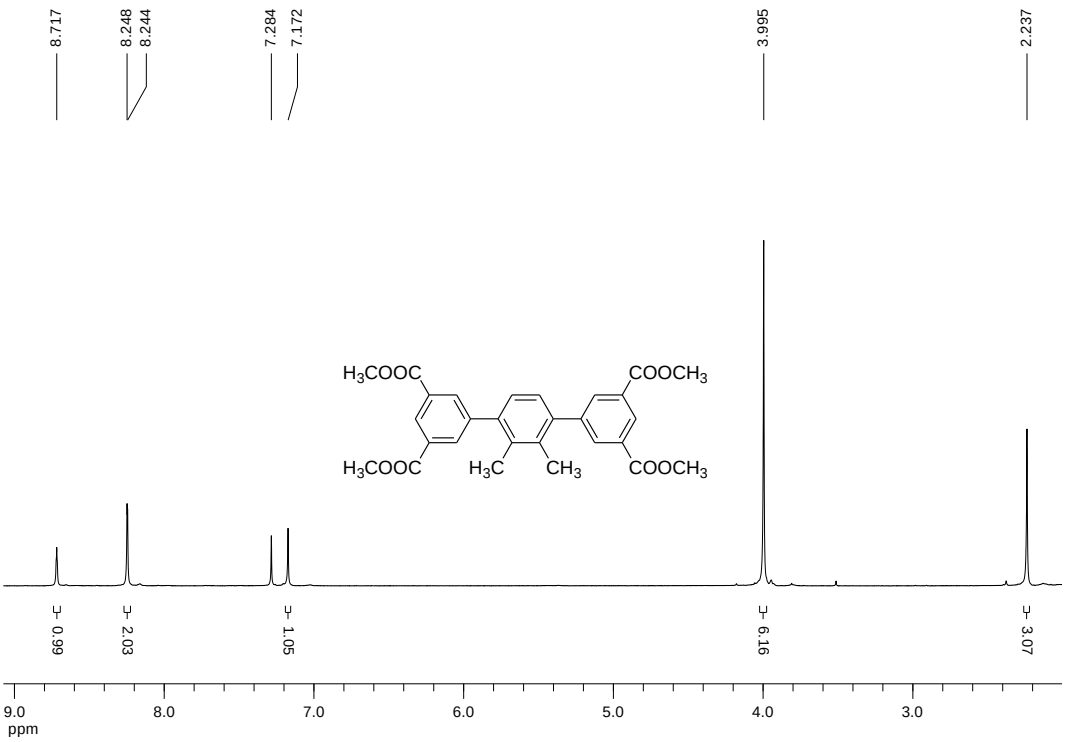
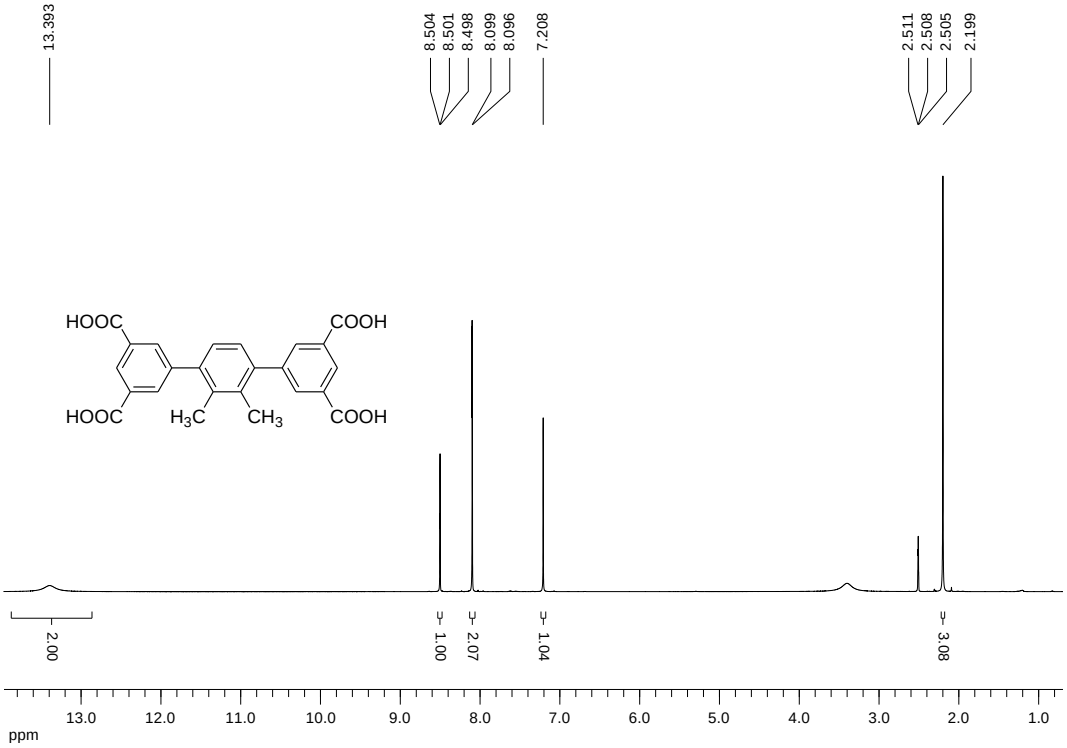



**Fig. S10** Comparison of the pure-component isotherm data for (a) $C_2H_2$, (b) $CO_2$, and (c) $CH_4$ in **ZJNU-96** with the fitted isotherms at 278 K, 288 K, and 298 K.


8.717
8.248
8.244
7.284
7.172
3.995
2.237
H3COOC
COOCH3
H3COOC
H3C
CH3
COOCH3
0.99
2.03
1.05
6.16
3.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
ppm


13.393
8.504
8.501
8.498
8.099
8.096
7.208
2.511
2.508
2.505
2.199
HOOC
COOH
HOOC
H3C
CH3
COOH
2.00
1.00
2.07
1.04
3.08
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm

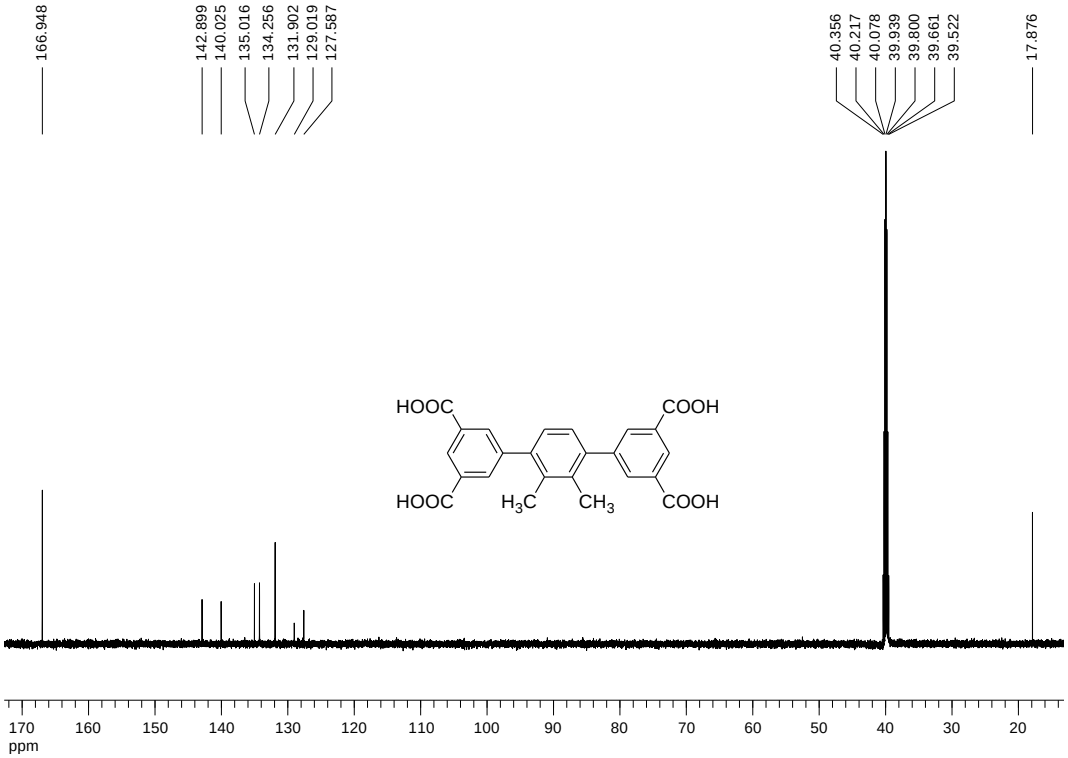



**Fig. S11** $^{1}$H and $^{13}$C NMR spectra.

**Table S1** Crystal data and structure refinement for **ZJNU-96** and **ZJNU-97**.

| MOFs | **ZJNU-96** | **ZJNU-97** |
|---|---|---|
| Empirical formula | $C_{24}H_{18}Cu_2O_{10}$ | $C_{24}H_{18}Cu_2O_{10}$ |
| Formula weight | 593.46 | 593.46 |
| $\lambda$ (Å) | 0.71073 | 0.71073 |
| Crystal system | Trigonal | Tetragonal |
| Space group | *R*-3*m* | $P4_2$/mnm |
| Unit cell dimensions | *a* = 18.5984(9) Å<br>*b* = 18.5984(9) Å<br>*c* = 38.5338(18) Å<br>$\alpha = 90^o$<br>$\beta = 90^o$<br>$\gamma = 120^o$ | *a* = 18.8260(8) Å<br>*b* = 18.8260(8) Å<br>c = 27.3427(12) Å<br>$\alpha = 90^o$<br>$\beta = 90^o$<br>$\gamma = 90^o$ |
| *V* (Å$^3$) | 11543.1(12) | 9690.8(9) |
| *Z* | 9 | 8 |
| $D_c$ (g cm$^{-3}$) | 0.768 | 0.814 |
| $\mu$ (mm$^{-1}$) | 0.855 | 0.906 |
| *F*(000) | 2700 | 2400 |
| Crystal size (mm) | 0.150 × 0.120 × 0.100 | 0.160 × 0.120 × 0.110 |
| $\theta$ range for data collection ($^o$) | 2.190 to 26.408 | 2.135 to 26.427 |
| Limiting indices | $-23 \le h \le 23$<br>$-23 \le k \le 19$<br>$-48 \le l \le 48$ | $-23 \le h \le 23$<br>$-23 \le k \le 23$<br>$-34 \le l \le 34$ |
| Reflections collected / unique | 34508 / 2890 | 119462 / 5310 |
| $R_{int}$ | 0.0480 | 0.0715 |
| Max. and min. transmission | 0.918 and 0.884 | 0.905 and 0.878 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2890 / 0 / 112 | 5310 / 1 / 151 |
| Goodness-of-fit on $F^2$ | 1.034 | 1.075 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.051<br>$wR_2$ = 0.1733 | $R_1$ = 0.0726<br>$wR_2$ = 0.3080 |
| *R* indices (all data) | $R_1$ = 0.0634<br>$wR_2$ = 0.1868 | $R_1$ = 0.0843<br>$wR_2$ = 0.3394 |
| Largest diff. peak and hole (e·Å$^{-3}$) | 1.375 and -0.525 | 1.799 and -0.972 |
| CCDC | 1878724 | 1902428 |

**Table S2** Langmuir-Freundlich parameters for adsorption of $C_2H_2$, $CO_2$, and $CH_4$ in **ZJNU-96**.

| Guest | $q_{sat}$ (mmol $g^{-1}$) | $b_0$ $(kPa)^{-v}$ | $E$ (kJ $mol^{-1}$) | $v$ | $R^2$ |
|---|---|---|---|---|---|
| $C_2H_2$ | 28.05037 | $1.75667\times10^{-5}$ | 17.084 | 0.6791 | 0.99985 |
| $CO_2$ | 22.02122 | $2.86031\times10^{-7}$ | 21.980 | 1 | 0.99995 |
| $CH_4$ | 17.1598 | $9.99996\times10^{-7}$ | 15.471 | 1 | 0.99998 |