Supporting Information

Two Co-based MOFs assembled from an amine-functionalized pyridine-carboxylate ligand: inorganic acid-directed structural variety and gas adsorption properties

Zhenzhen Jiang, Ping Zou, Tingting Xu, Lihui Fan, Simin Hu, Jingxian Chen 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

(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.

(2) IAST Calculations

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

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

In the equation above, q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculated the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

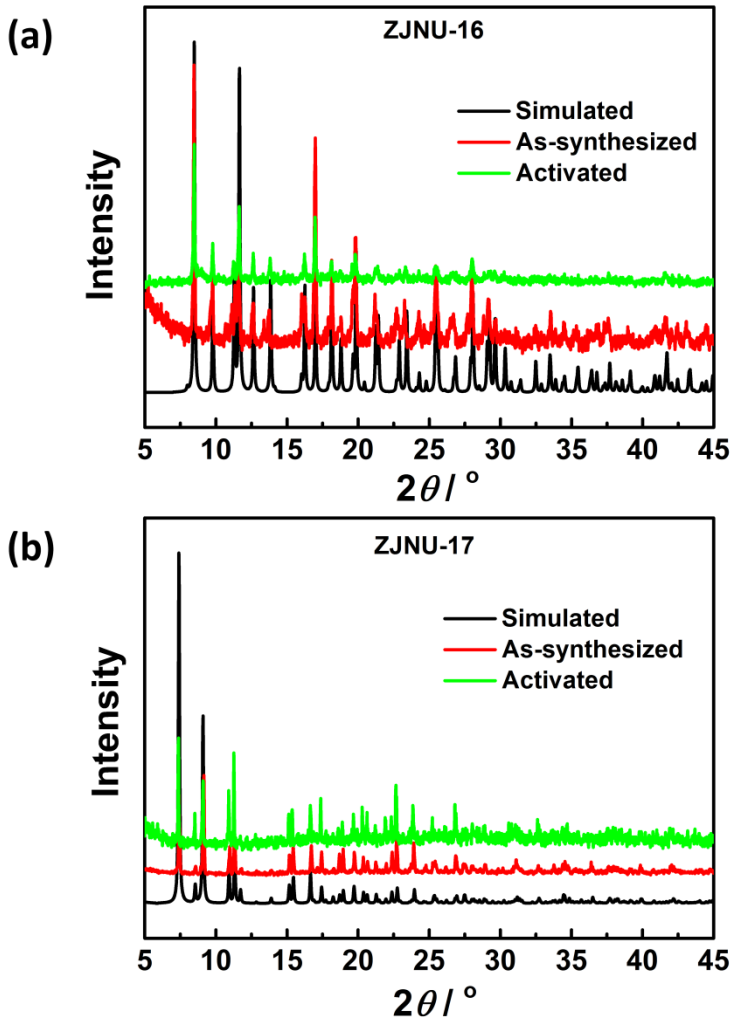


Fig. S1 Comparison of simulated and experimental PXRD patterns of (a) **ZJNU-16** and (b) **ZJNU-17**.

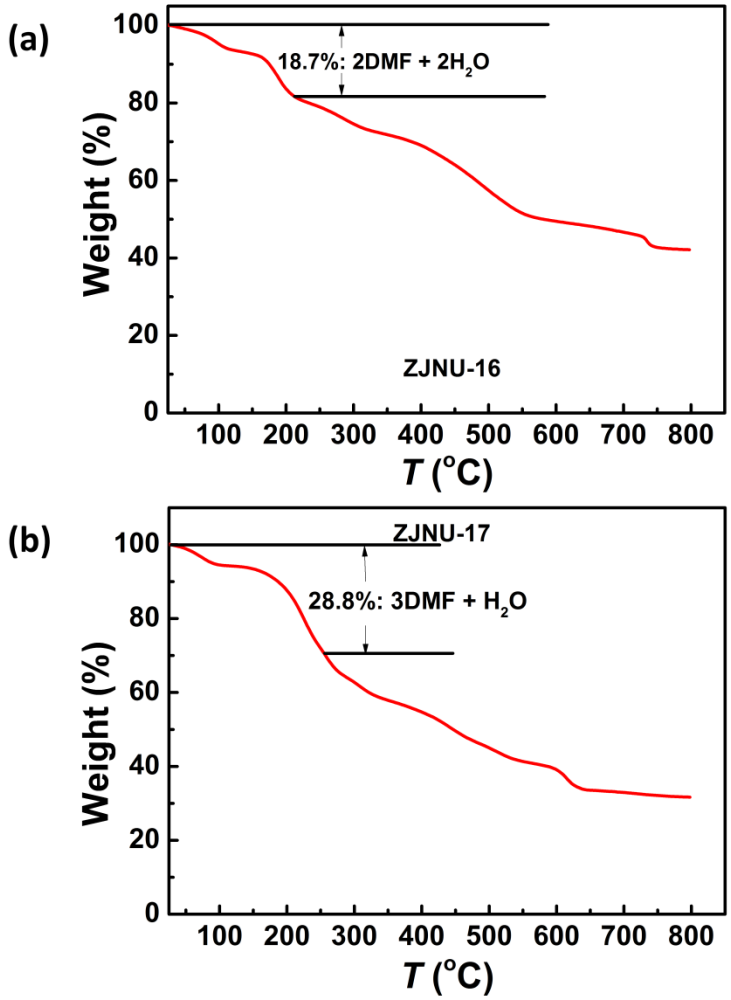


Fig. S2 TGA curves of as-synthesized (a) **ZJNU-16** and (b) **ZJNU-17** under N_2 atmosphere.

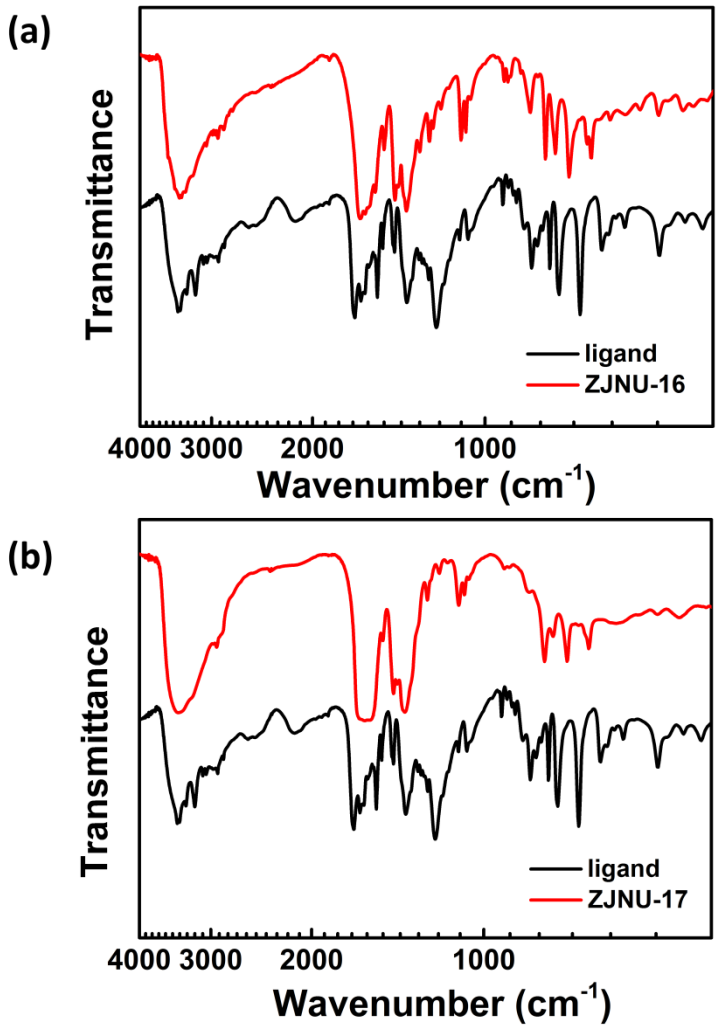


Fig. S3 Comparison of FTIR spectra of (a) as-synthesized **ZJNU-16** and its ligand H_2L, and (b) as-made **ZJNU-17** and its ligand H_2L.

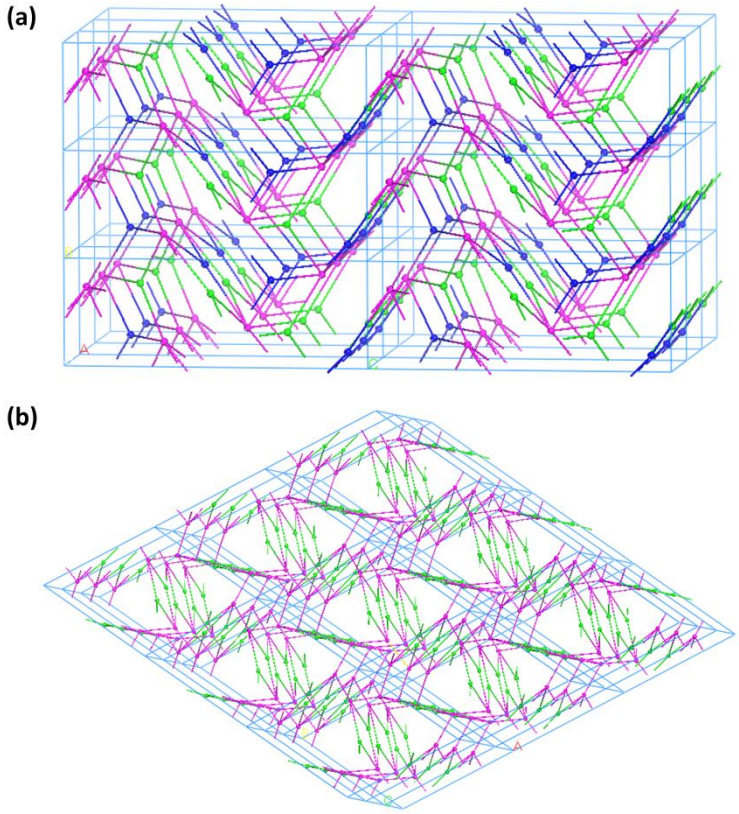
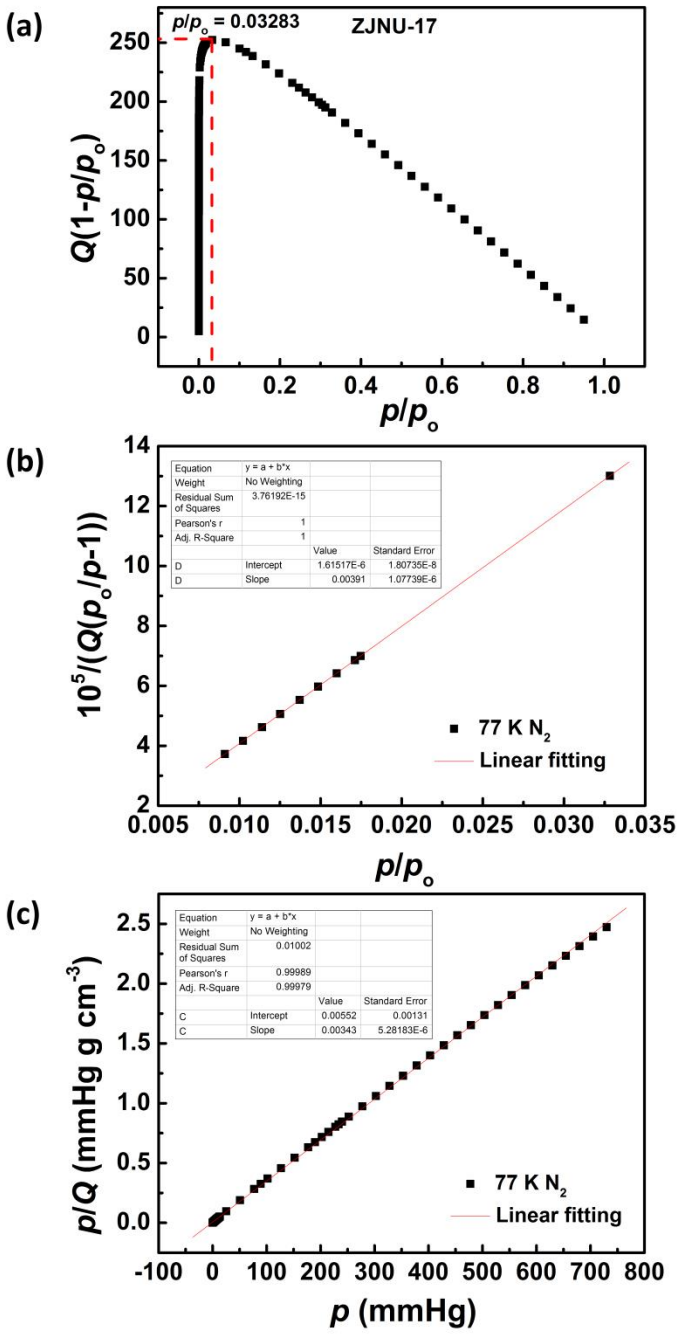


Fig. S4 The topological structures of (a) **ZJNU-16** and (b) **ZJNU-17**.



S_{BET} = 1/(1.61517×10^{-6} + 0.00391)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1113 m^2 g^{-1}

$S_{Langmuir}$ = (1/0.00343)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1269 m^2 g^{-1}

BET constant C = 1 + 0.00391/1.61517×10^{-6} = 2422

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.01992$$

Fig. S5 The consistency plot (a), BET surface area plot (b), and Langmuir surface area plot (c) for **ZJNU-17**.

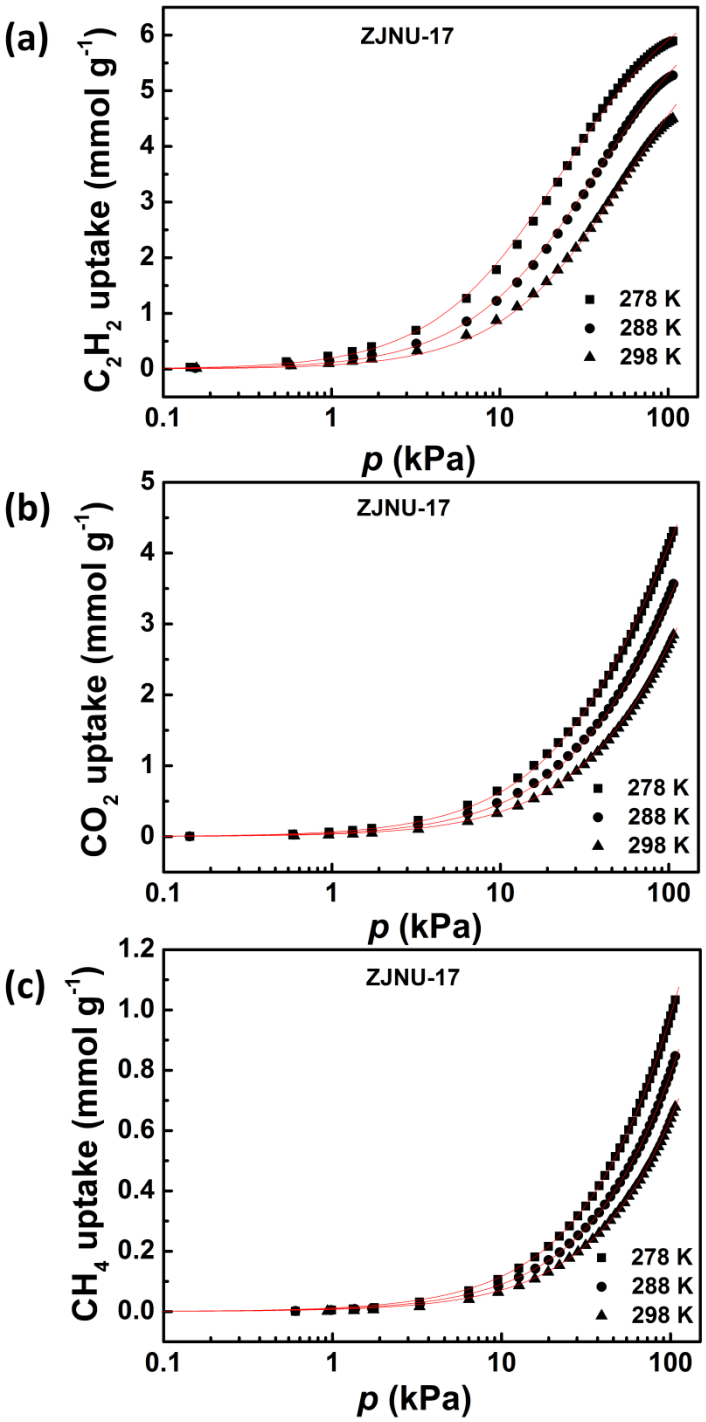
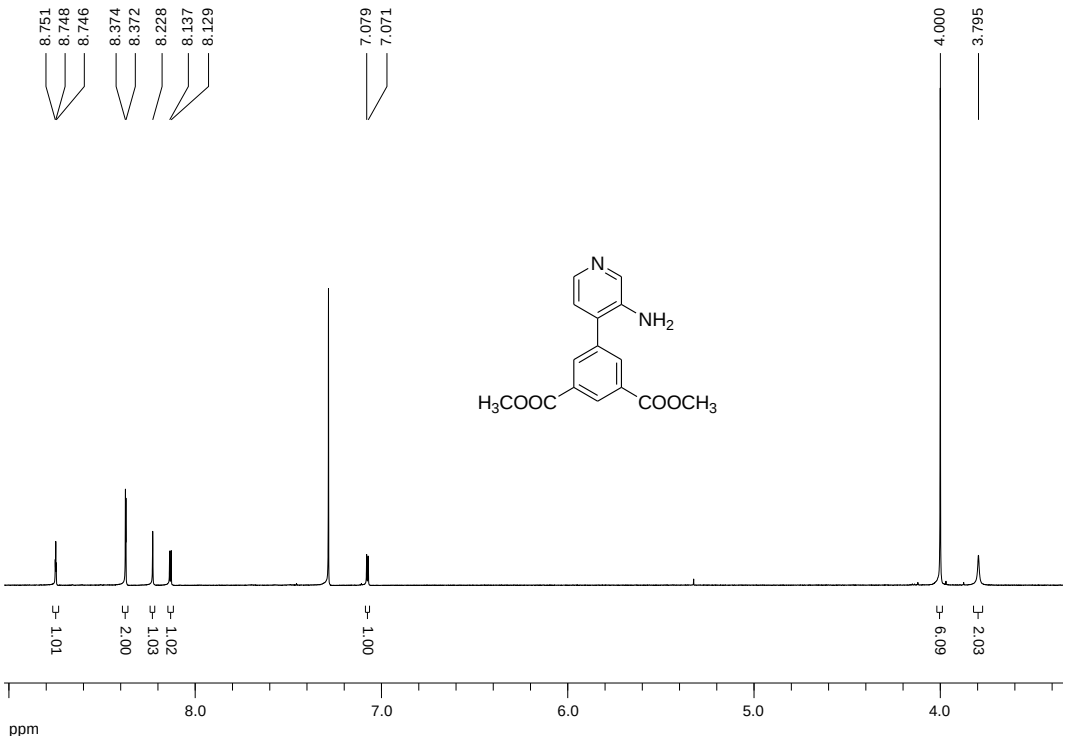
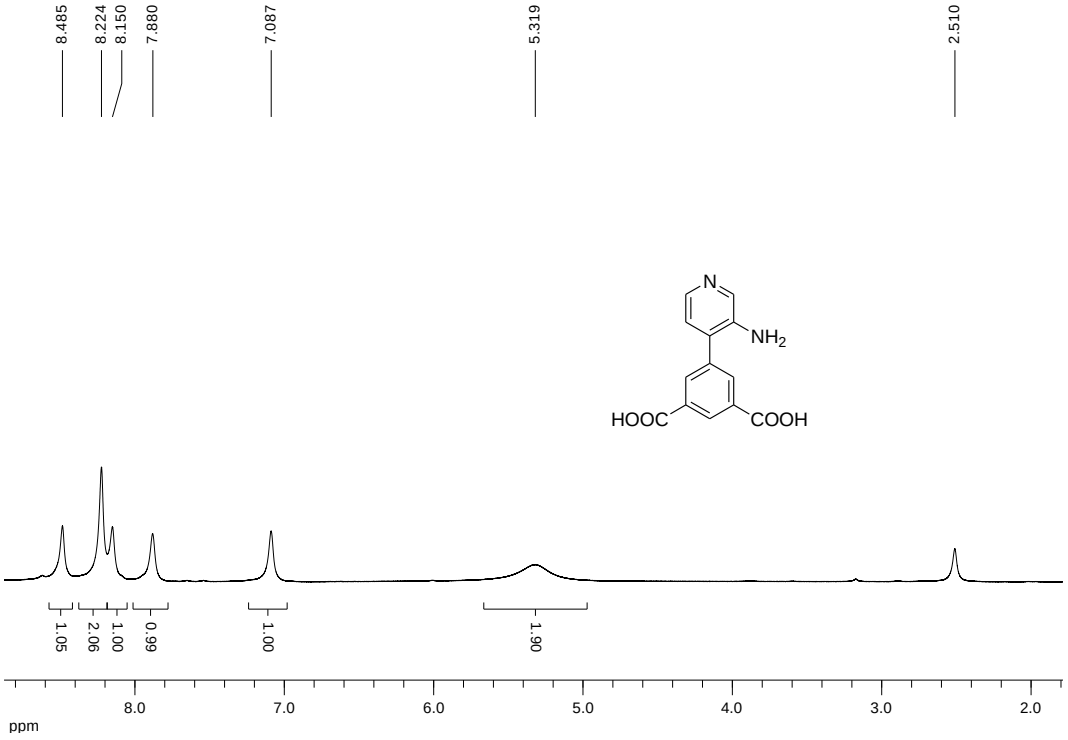


Fig. S6 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-17** with the fitted isotherms at 278 K, 288 K, and 298 K.


8.751
8.748
8.746
8.374
8.372
8.228
8.137
8.129
7.079
7.071
4.000
3.795
N
NH2
H3COOC
COOCH3
1.01
2.00
1.03
1.02
1.00
6.09
2.03
8.0
7.0
6.0
5.0
4.0
ppm


8.485
8.224
8.150
7.880
7.087
5.319
2.510
N
NH2
HOOC
COOH
1.05
2.06
1.00
0.99
1.00
1.90
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm

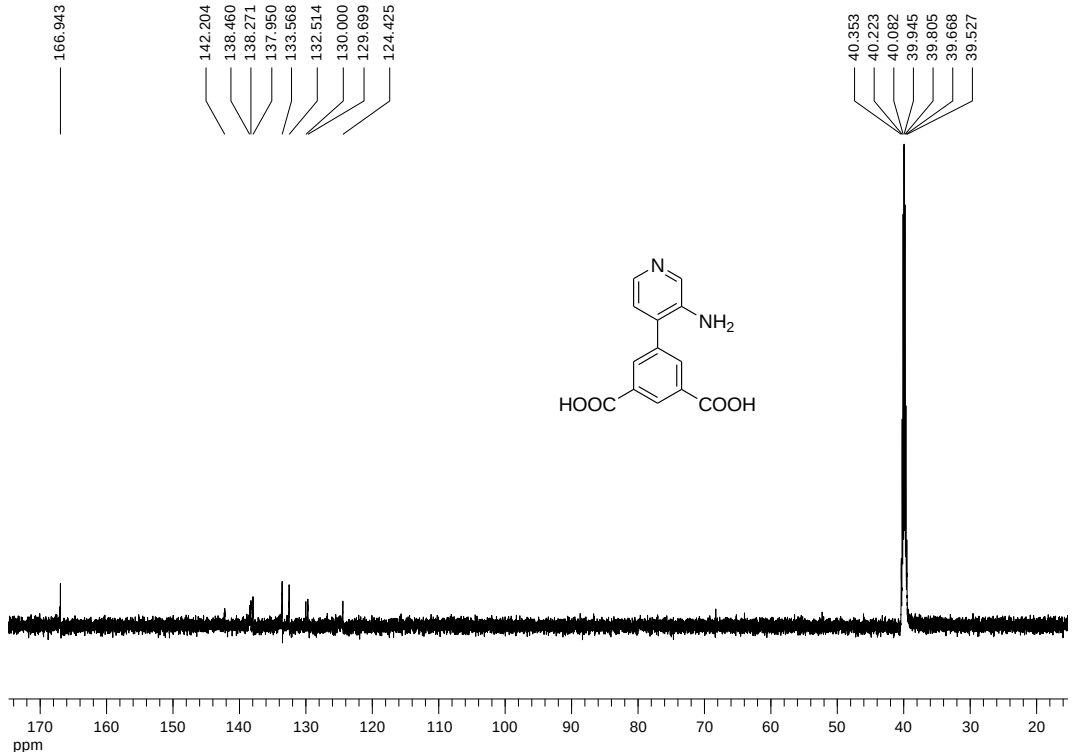


Fig. S7 ^{1}H and ^{13}C NMR spectra.

Table S1 Crystal data and structure refinement for **ZJNU-16** and **ZJNU-17**.

MOFs	**ZJNU-16**	**ZJNU-17**
Empirical formula	$C_{33}H_{40}N_6O_{17}Co_3$	$C_{25}H_{35}N_5O_{15}Co_3$
Formula weight	969.50	822.37
Temperature (K)	150(2)	150(2)
λ (Å)	0.71073	0.71073
Crystal system	Tetragonal	Hexagonal
Space group	$P4_1$	$P6_1$
Unit cell dimensions	a = 11.0533(6) Å b = 11.0533(6) Å c = 31.3156(16) Å α = 90° β = 90° γ = 90°	a = 23.8554(5) Å b = 23.8554(5) Å c = 11.0075(2) Å α = 90° β = 90° γ = 120°
V (Å^3)	3826.0(5)	5424.9(2)
Z	4	6
D_c (g cm^{-3})	1.683	1.510
μ (mm^{-1})	1.370	1.429
F(000)	1988	2526
θ range for data collection (°)	2.255 to 27.452	2.518 to 27.515
Limiting indices	$-13 \le h \le 14$ $-14 \le k \le 14$ $-35 \le l \le 40$	$-28 \le h \le 30$ $-31 \le k \le 28$ $-14 \le l \le 13$
Reflections collected / unique	31583 / 8352	45929 / 8245
R_{int}	0.0459	0.0622
Max. and min. transmission	0.860 and 0.825	0.867 and 0.717
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8352/572/584	8245/274/372
Goodness-of-fit on F^2	1.072	1.054
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0400 wR_2 = 0.0999	R_1 = 0.0370 wR_2 = 0.0937
R indices (all data)	R_1 = 0.0426 wR_2 = 0.1026	R_1 = 0.0412 wR_2 = 0.0974
Largest diff. peak and hole (e·Å^{-3})	0.785 and -0.850	0.359 and -0.381
CCDC	1992922	1992923

Table S2 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-17**.

Adsorbates	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	7.06906	5.70679×10^{-9}	35.688	1.1232	0.99908
CO_2	10.7707	7.14104×10^{-7}	20.950	1	0.99952
CH_4	5.55935	1.25292×10^{-6}	17.207	1	0.99982

Table S3 Summary of pore textural parameters and gas adsorption properties of **ZJNU-17**.

MOF		**ZJNU-16**	**ZJNU-17**
$S_{BET}/S_{Langmuir}$ (m^2 g^{-1})		5/10	1113/1269
V_p (cm^3 g^{-1})		0.005	0.4566
D_c (g cm^{-3})		1.304	1.2086
C_2H_2 uptake[a] (cm^3 g^{-1}, STP)	298 K	1.0	100.9
	288 K	NA	118.2
	278 K	NA	132.1
CO_2 uptake[a] (cm^3 g^{-1}, STP)	298 K	6.1	63.8
	288 K	NA	79.9
	278 K	NA	96.6
CH_4 uptake[a] (cm^3 g^{-1}, STP)	298 K	0.4	15.2
	288 K	NA	19.0
	278 K	NA	23.2
C_2H_2/CH_4 (v/v = 1/1) IAST adsorption selectivity[a]	298 K	NA	15.5
	288 K	NA	20.5
	278 K	NA	28.0
C_2H_2/CO_2 (v/v = 1/1) IAST adsorption selectivity[a]	298 K	NA	2.5
	288 K	NA	2.9
	278 K	NA	3.2

$S_{BET}/S_{Langmuir}$ = BET and Langmuir surface areas derived from 77 K N_2 adsorption isotherm data; V_p = total pore volumes derived from 77 K N_2 adsorption isotherm data; D_c = the framework densities calculated from single-crystal X-ray structures; STP = standard temperature and pressure; [a] at 1 atm. NA = not available

Table S4 Summarizes of physical parameters of C_2H_2, CO_2, and CH_4

Adsorbates	BP (K)	T_c (K)	p_c (bar)	Kinetic diameter (Å)	Molecular dimension (Å)	Polarizability ($\times10^{25}$ cm^3)	Dipole moment ($\times10^{18}$ esu cm)	Quadruple moment ($\times10^{26}$ esu cm^2)
C_2H_2	188.40	308.30	61.14	3.3	3.3×3.3×5.7	33.3-39.3	0	+7.5
CO_2	194.65	304.12	73.74	3.3	3.2×3.3×5.4	29.11	0	-4.3
CH_4	111.66	190.56	45.99	3.758	3.7×3.7×3.7	25.93	0	0

BP: normal boiling point; T_c: critical temperature; p_c: critical pressure