Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

A ligand conformation preorganization approach to construct a copper-hexacarboxylate framework with a novel topology for selective gas adsorption

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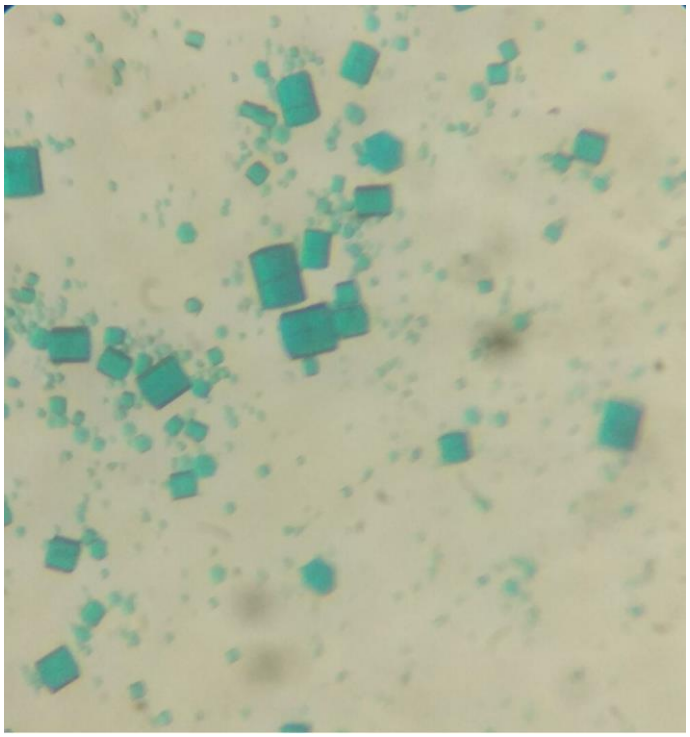


Fig. S1 The electronic photograph of the as-synthesized **ZJNU-100**.

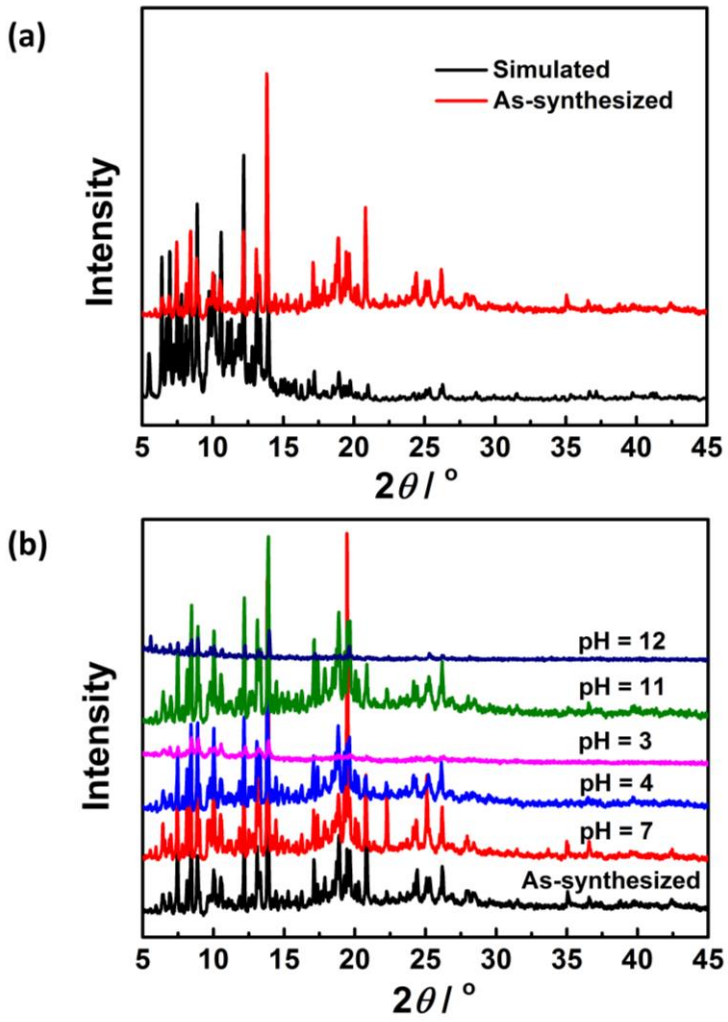


Fig. S2 (a) The simulated (black) and experimental (red) PXRD patterns of **ZJNU-100**; (b) the PXRD patterns of **ZJNU-100** after immersion in aqueous HCl/NaOH solutions with pH ranging from 3 to 12 for 24 h.

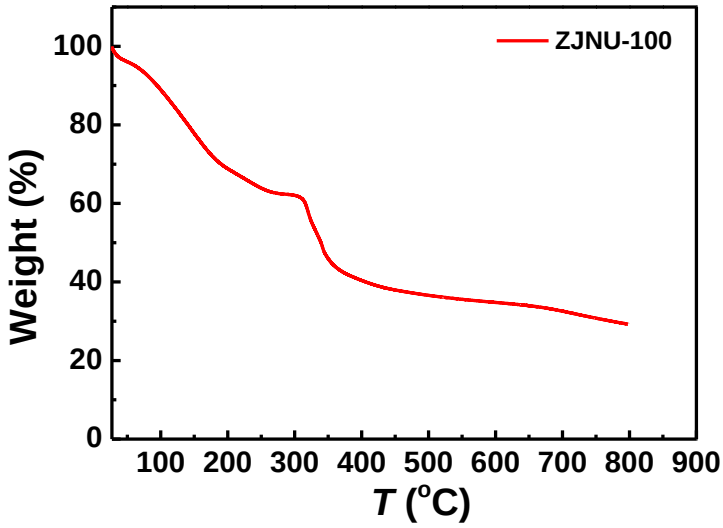


Fig. S3 The TGA curve of **ZJNU-100** under nitrogen atmosphere.

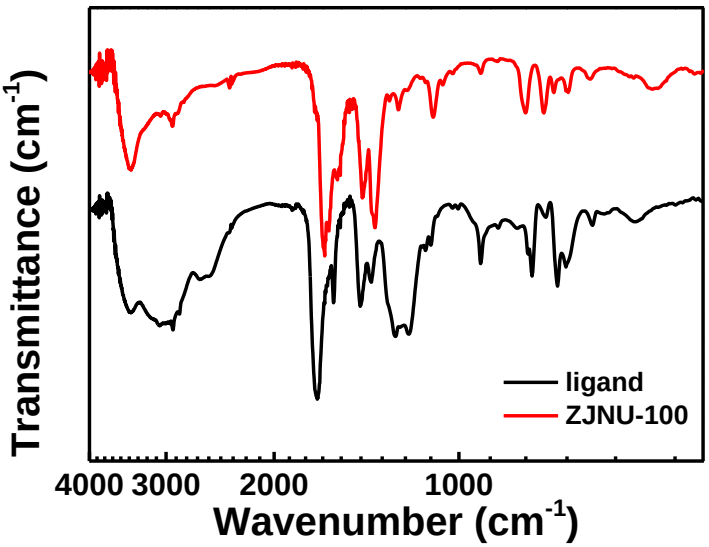
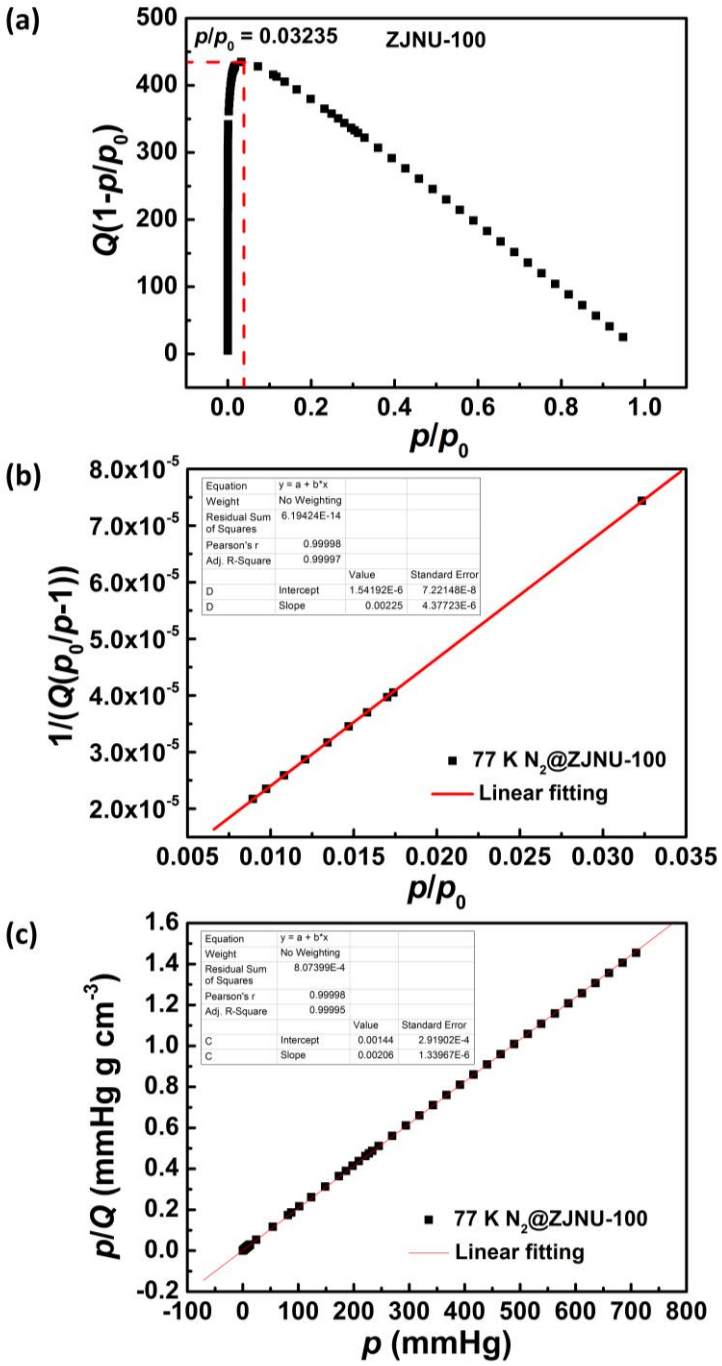


Fig. S4 Comparison of FTIR spectra of **ZJNU-100** and its corresponding ligand H_6L.



S_{BET} = 1/(1.54192 ×10^{-6}+ 0.00225)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1933 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00206)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2113 m^2 g^{-1}

BET constant C = 1 + 0.00225/1.54192 ×10^{-6} = 1460

$$(p/p_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.0255$$

Fig. S5 (a) The consistency, (b) BET surface area, and (c) Langmuir surface area plots for **ZJNU-100**.

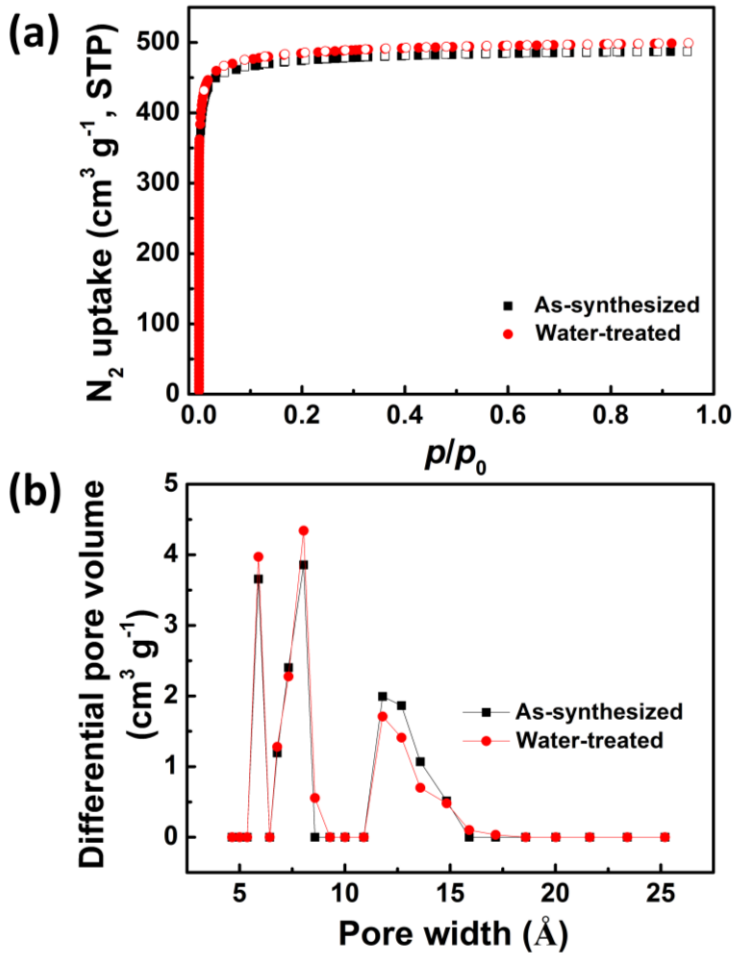


Fig. S6 (a) N_2 isotherms at 77 K and (b) DFT pore size distributions of **ZJNU-100** before and after immersion in water at room temperature for 24 h.

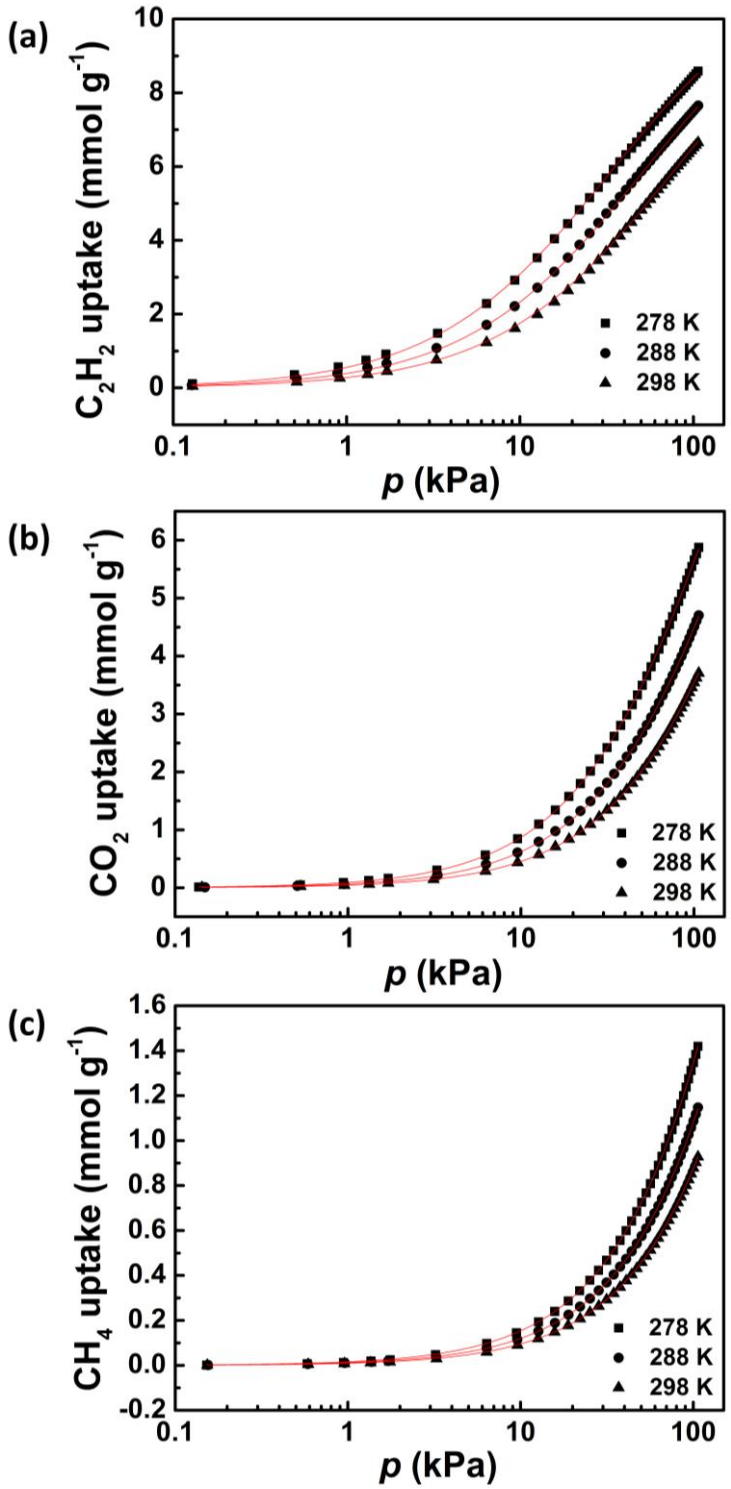
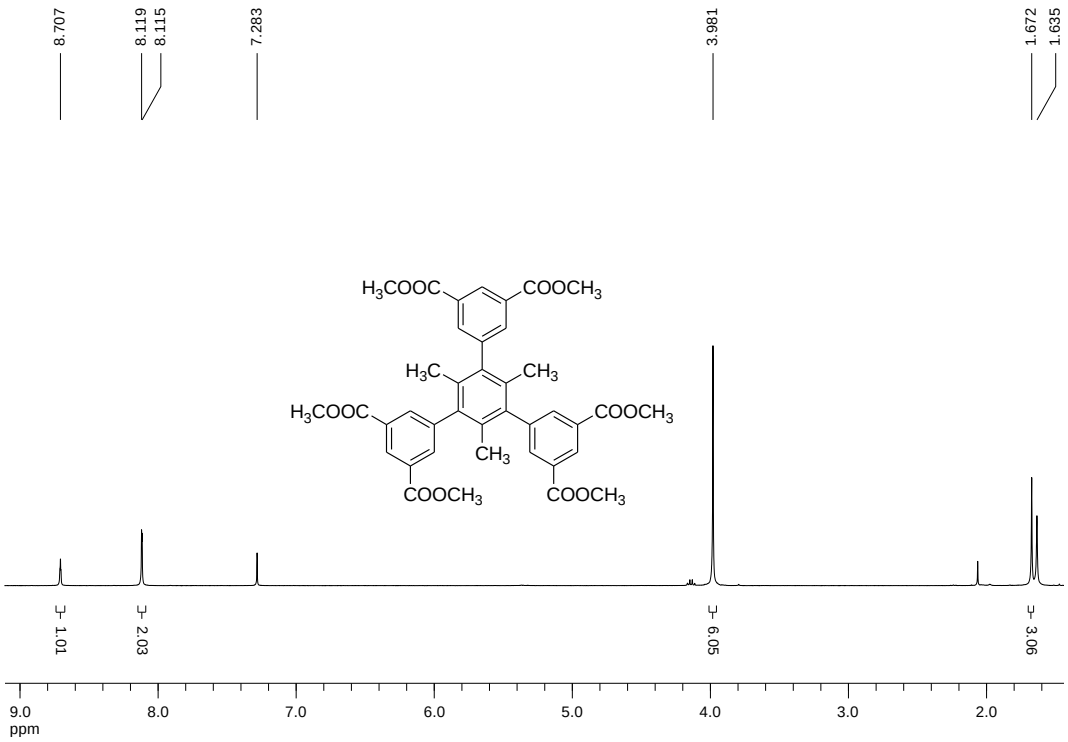
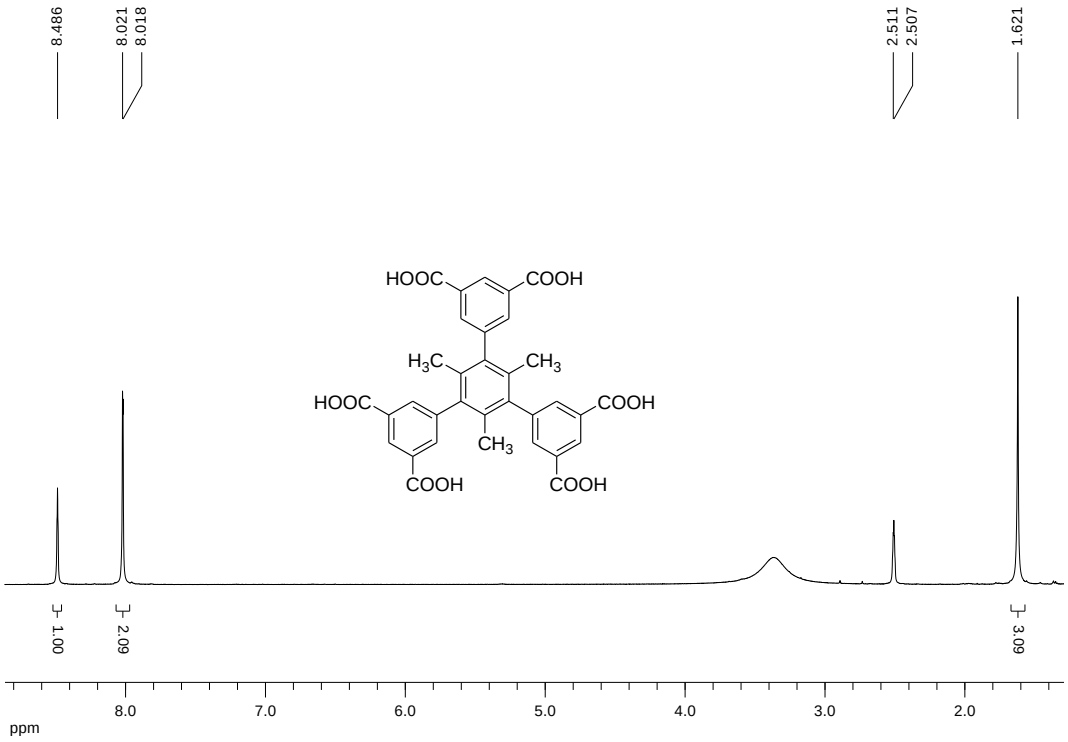


Fig. S7 Comparison of the pure-component isotherm data for (a) C_2H_2, (b) CO_2, and (c) CH_4 in **ZJNU-100** with the fitted isotherms at 278 K, 288 K, and 298 K.


8.707
8.119
8.115
7.283
3.981
1.672
1.635
H3COOC
COOCH3
H3C
CH3
H3COOC
COOCH3
CH3
COOCH3
COOCH3
1.01
2.03
6.05
3.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm


8.486
8.021
8.018
2.511
2.507
1.621
HOOC
COOH
H3C
CH3
HOOC
COOH
CH3
COOH
COOH
1.00
2.09
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm

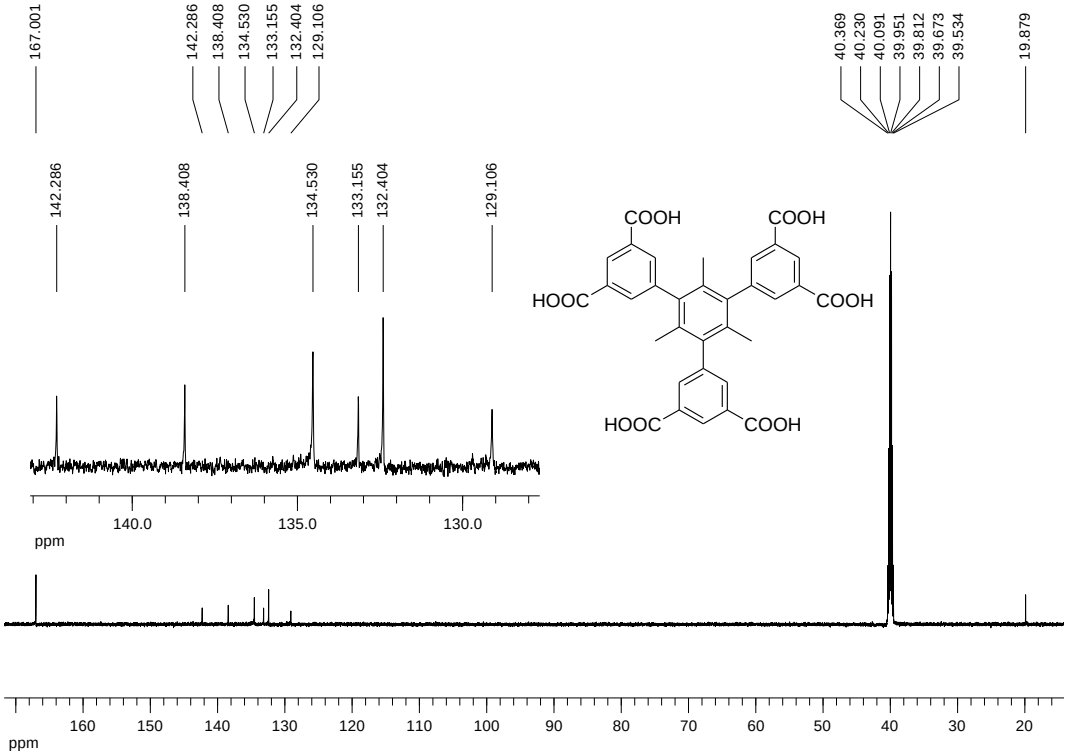
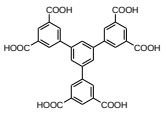
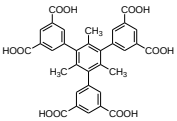
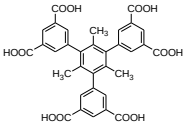
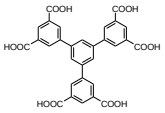
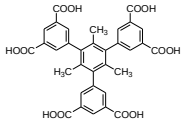
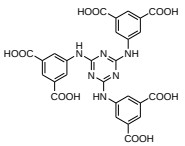
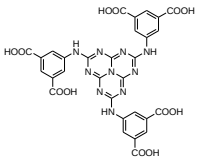
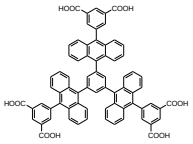
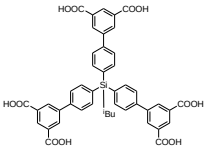
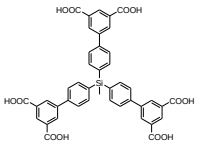
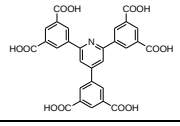


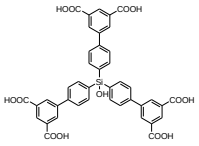
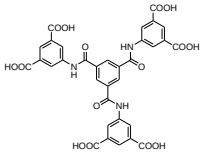
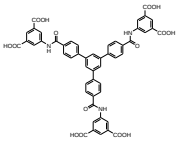
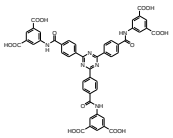
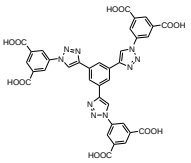
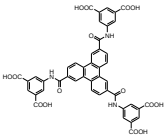
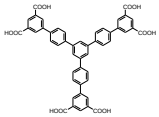
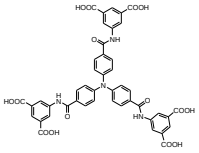
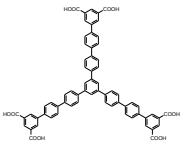
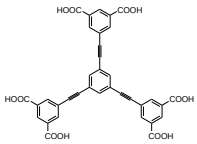
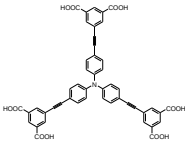
Fig. S8 ^{1}H and ^{13}C NMR spectra.

Table S1 Crystal data and structure refinement for **ZJNU-100**.

MOFs	**ZJNU-100**
Empirical formula	$C_{297}H_{162}Cu_{24}O_{132}$
Formula weight	7367.22
λ (Å)	1.54178
Crystal system	Hexagonal
Space group	*P6/mmm*
Unit cell dimensions	a = 63.7383(15) Å b = 63.7383(15) Å c = 25.3645(7) Å α = 90° β = 90° γ = 120°
V (Å^3)	89240(5)
Z	6
D_c (g cm^{-3})	0.823
μ (mm^{-1})	1.333
F(000)	22176
θ range for data collection (°)	1.917 to 68.338
Limiting indices	$-44 \le h \le 76$ $-76 \le k \le 59$ $-30 \le l \le 26$
Reflections collected / unique	352872 / 29233
R_{int}	0.1101
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	29233 / 3472 / 1204
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1174 wR_2 = 0.2795
R indices (all data)	R_1 = 0.1370 wR_2 = 0.2881
Largest diff. peak and hole (e·Å^{-3})	2.338 and -1.904
CCDC	1877489

Table S2 Summaries of gas adsorption properties and pore textural parameters of some reported MOFs based on triisophthalate ligands.

MOFs	Metal ion	Ligand structure	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	C_2H_2 uptake ($cm^3 g^{-1}$, STP)	CO_2 uptake ($cm^3 g^{-1}$, STP)	*Ref.*
Zn_4O(BHB)	Zn^{2+}		156	NA	NA	35 (273 K, 1 atm)	1
SDU-1	Zn^{2+}		779	0.353	NA	NA	2, 3
NPC-5	Co^{2+}		1140	0.496	NA	NA	2
UTSA-20	Cu^{2+}		1156	0.63	150.3 (296 K, 1 atm)	82.4 (296 K, 1 atm)	4, 5
ZJNU-100	Cu^{2+}		1933	0.754	149.1 (298 K, 1 atm)	83.1 (298 K, 1 atm)	This work
Cu-TDPAT	Cu^{2+}		1938	0.93	177.7 (298 K, 1 atm)	132 (298 K, 1 atm)	6, 7
Cu-TDPAH	Cu^{2+}		2171	0.91	155.7 (298 K, 1 atm)	116 (298 K, 1 atm)	8
MFM-132	Cu^{2+}		2466	1.06	NA	NA	9
SDU-8	Cu^{2+}		2516	1.02	NA	NA	10
SDU-7	Cu^{2+}		2713	1.10	NA	NA	10
GDMU-2	Cu^{2+}		2758	1.17	NA	74 (273 K, 1 bar)	11

SDU-6	Cu^{2+}		2826	1.17	NA	NA	[10]
Cu-TPBTM	Cu^{2+}		3160	1.268	NA	NA	[12]
$Cu_3(BTB^{6-})$	Cu^{2+}		3288	1.77	NA	NA	[13]
$Cu_3(TATB^{6-})$	Cu^{2+}		3360	1.91	NA	NA	[13]
NTU-105 (NU-125) (NOTT-122)	Cu^{2+}		3543	1.33	NA	187 (273 K, 1 atm)	[14-16]
HNUST-5	Cu^{2+}		3643	1.46	NA	56 (298 K, 1 bar)	[17]
NOTT-112	Cu^{2+}		3800	1.69	NA	NA	[18]
Cu-NTTA	Cu^{2+}		3931	1.27	NA	65.5 (298 K, 800 Tor)	[19]
NOTT-119 (PCN-69)	Cu^{2+}		4118	2.35	NA	NA	[20, 21]
PMOF-2 (PCN-61)	Cu^{2+}		4180	NA	NA	NA	[22, 23]
PCN-66	Cu^{2+}		4600	1.63	NA	NA	[22]

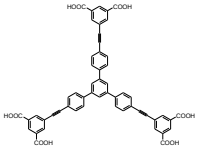
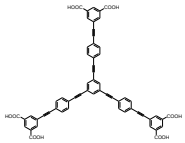
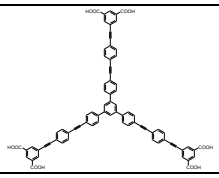
PCN-68	Cu^{2+}		6033	2.13	NA	NA	22
NU-100 (PCN-610)	Cu^{2+}		6143	2.82	NA	NA	22, 24
NU-110	Cu^{2+}		7140	4.4	NA	NA	25

Table S3 Langmuir-Freundlich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-100**.

Guest	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v	R^2
C_2H_2	11.66812	1.3048×10^{-6}	24.392	0.85623	0.99973
CO_2	14.38261	2.63295×10^{-7}	23.353	1	0.99996
CH_4	9.7708	1.1718×10^{-6}	16.680	1	0.99998

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