Electronic Supplementary Material (ESI) for Dalton Transactions.

Rational Construction of an *ssa*-Type of MOF through Preorganizing the Ligand's Conformation and Its Exceptional Gas Adsorption Properties

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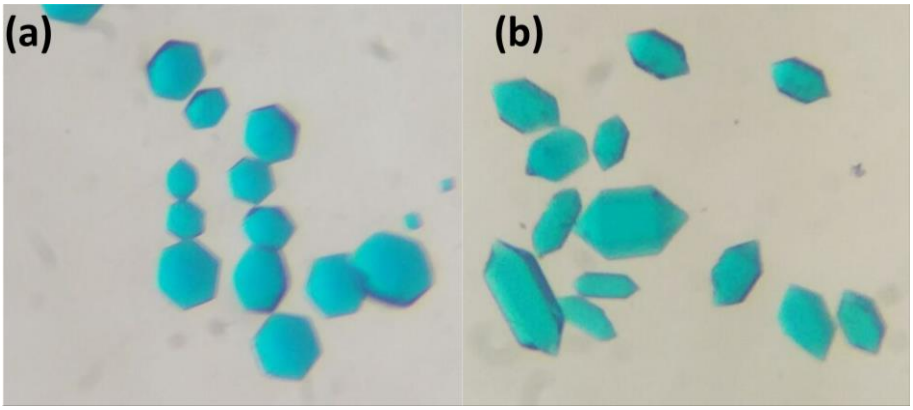


Fig. S1 The digital photographs of as-synthesized (a) **ZJNU-57a** and (b) **ZJNU-57b**.

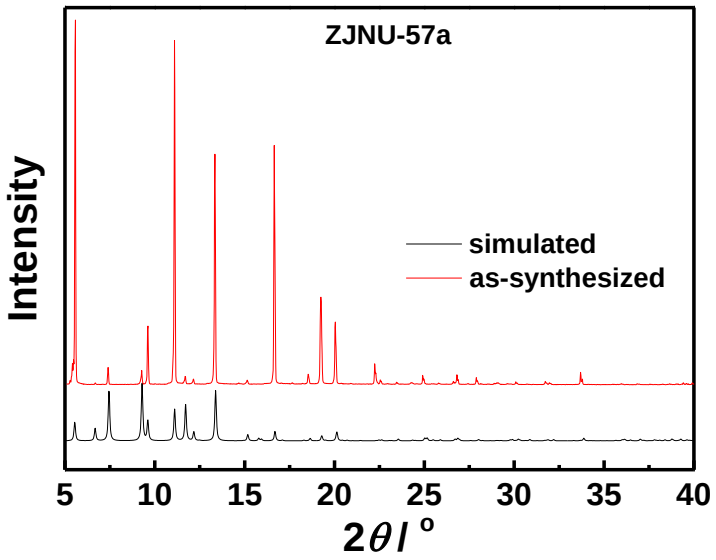


Fig. S2 The experimental (red) and simulated (black) PXRD patterns for **ZJNU-57a**.

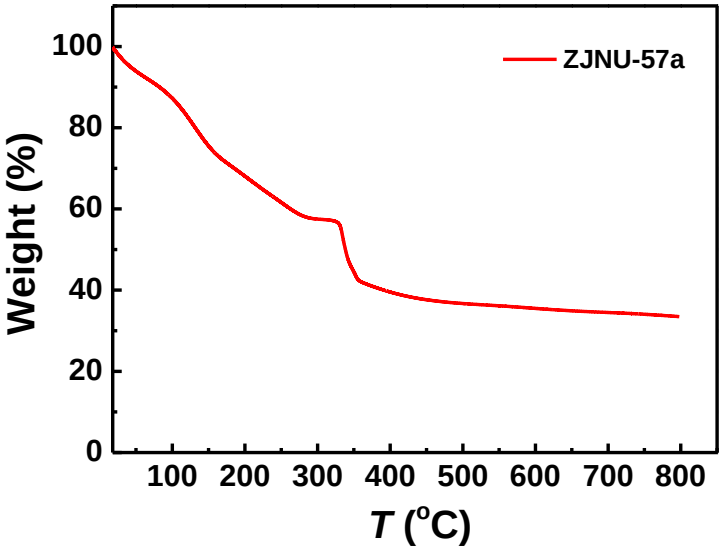


Fig. S3 TGA curve of the as-synthesized **ZJNU-57a** at nitrogen atmosphere.

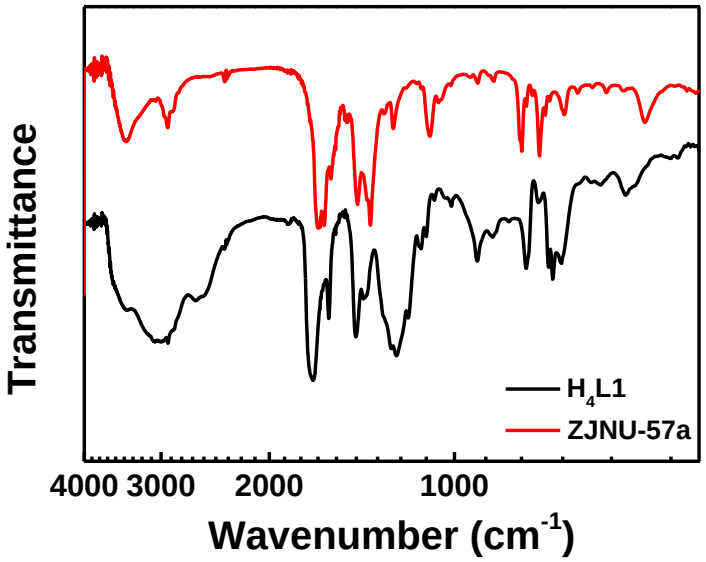
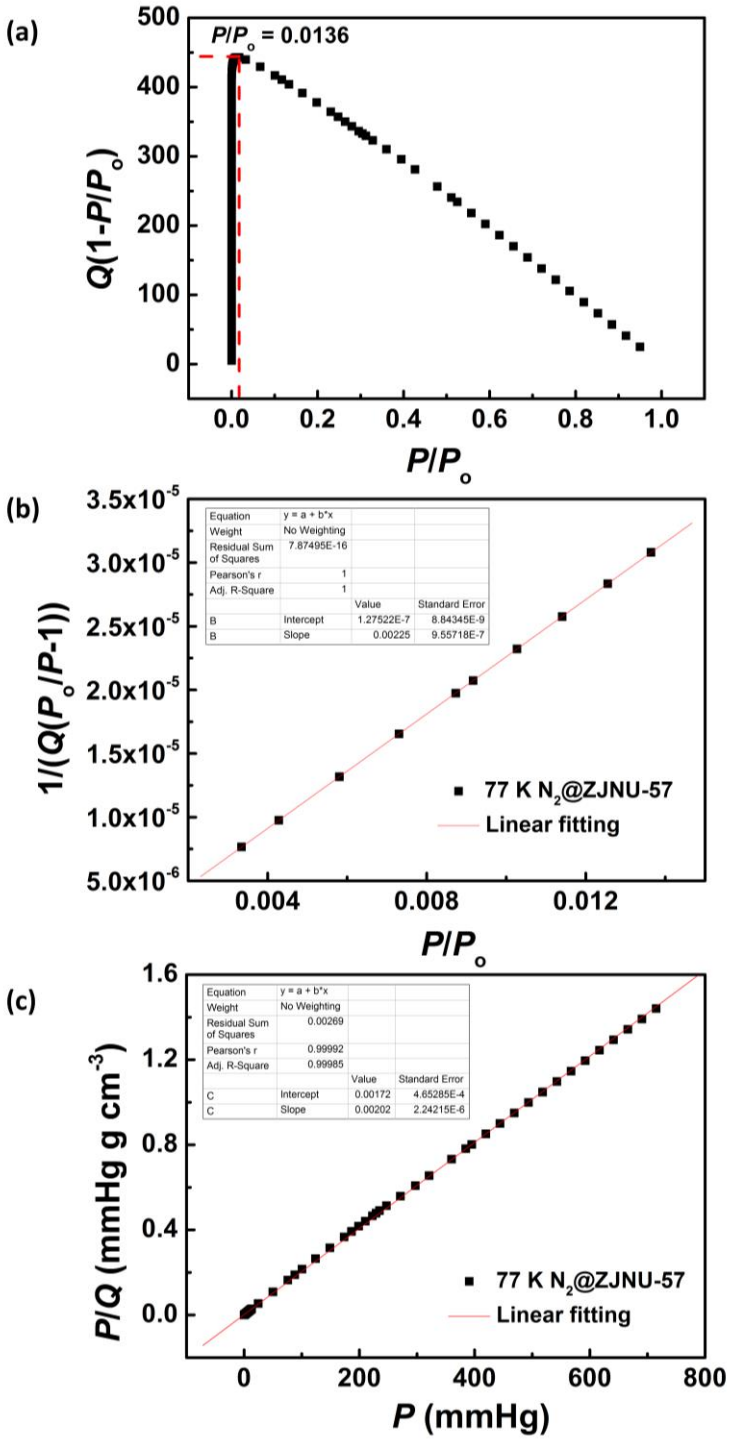


Fig. S4 FTIR spectra of the organic ligand H_4L (black) and the as-syntheiszed **ZJNU-57a** (red).



S_{BET} = 1/(1.27522 ×10^{-7}+ 0.00225)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1935 m^2 g^{-1}

$S_{Langmuir}$= (1/0.00202)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2155 m^2 g^{-1}

BET constant C = 1 + 0.00225/1.27522 ×10^{-7} = 17645

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.007472$$

Fig. S5 (a) The consistency, (b) BET and (c) Langmuir plots for **ZJNU-57**.

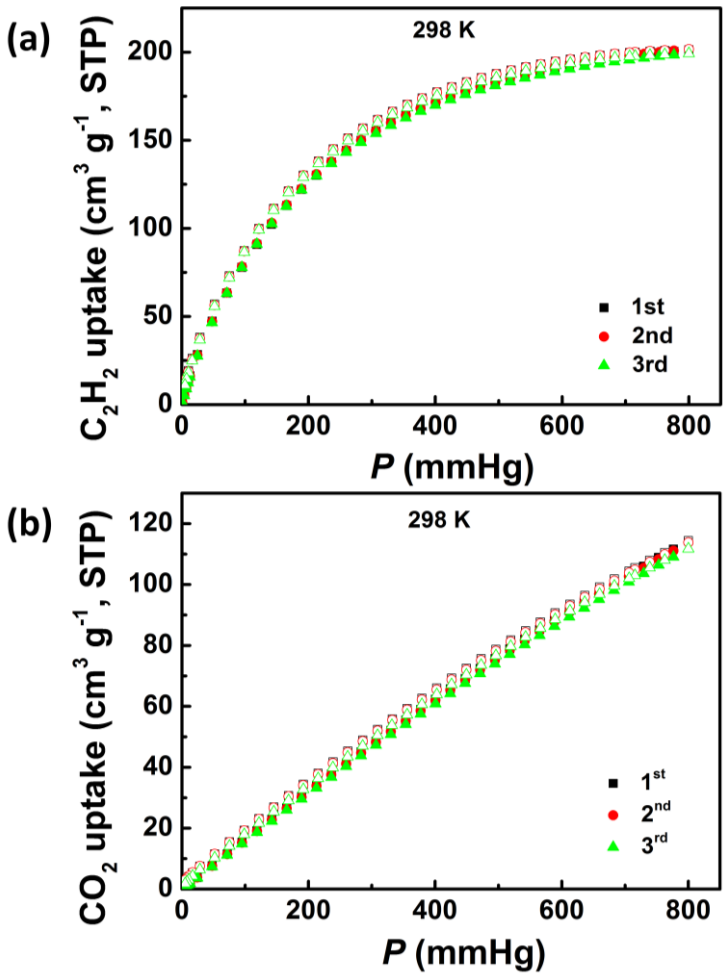


Fig. S6 Three adsorption-desorption cycles for (a) C_2H_2 and (b) CO_2 in **ZJNU-57** without reactivation between two consecutive cycles

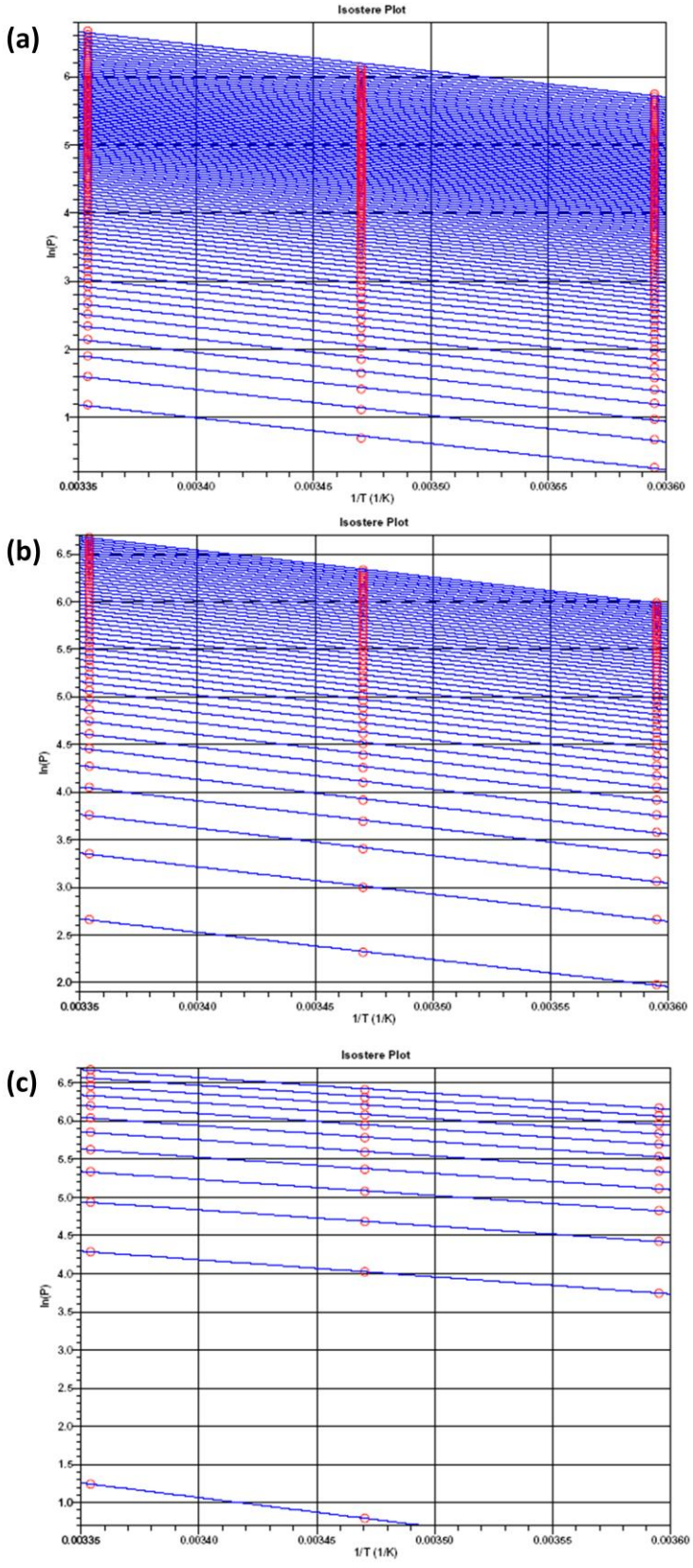


Fig. S7 Isostere plots for (a) C_2H_2, (b) CO_2 and (c) CH_4 adsorption in **ZJNU-57**

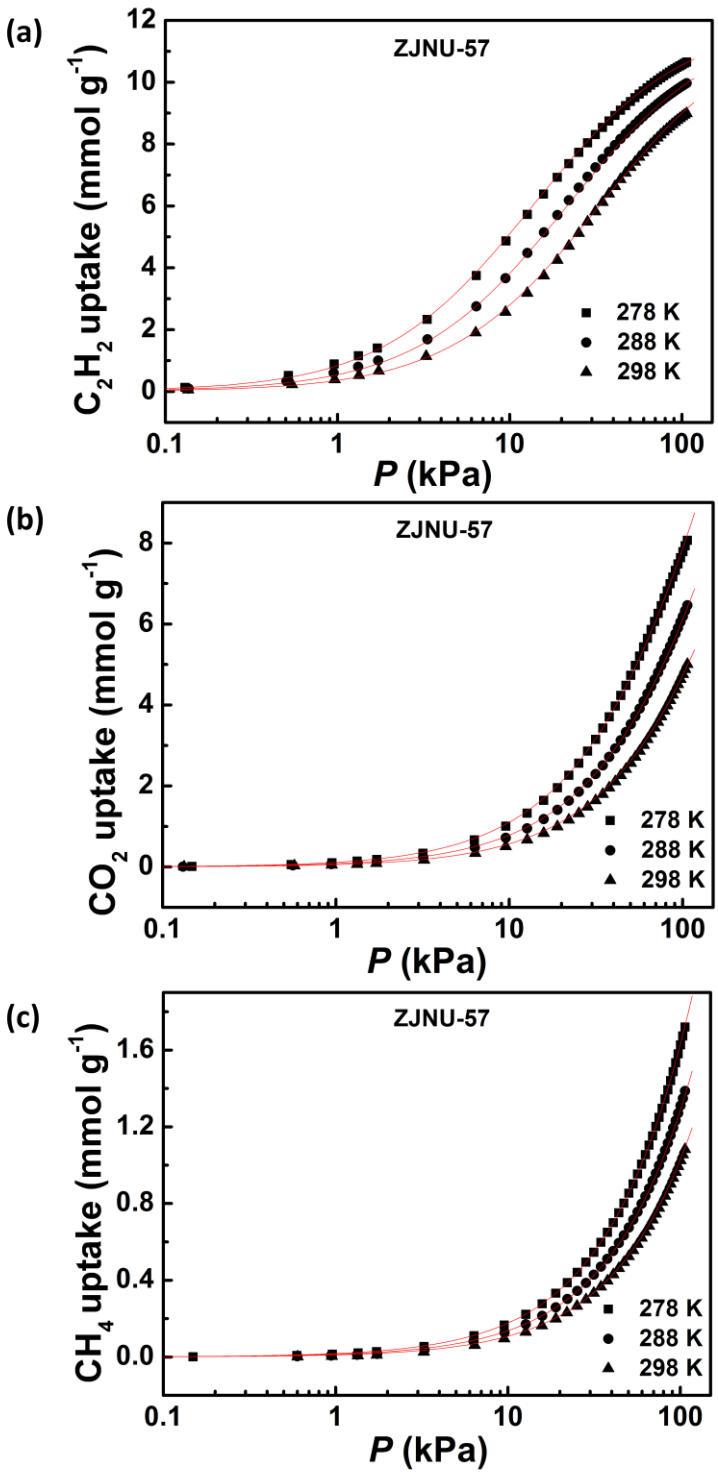


Fig. S8 Comparison of the pure-component isotherm data for C_2H_2, CO_2, and CH_4 in **ZJNU-57** with the fitted isotherms at 278 K, 288 K and 298 K

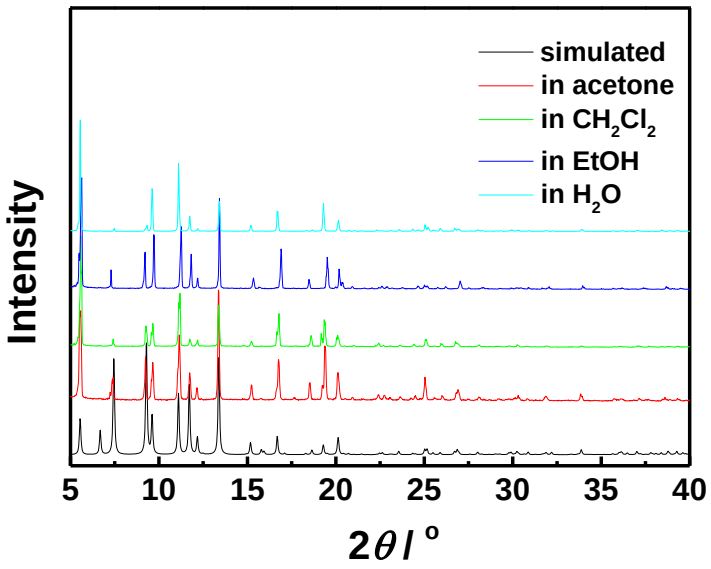


Fig. S9 PXRD patterns for those treated samples. The as-synthesized sample was soaked in acetone, dichloromethane, ethanol and water for 36 h at ambient conditions, and then collected for PXRD measurements.

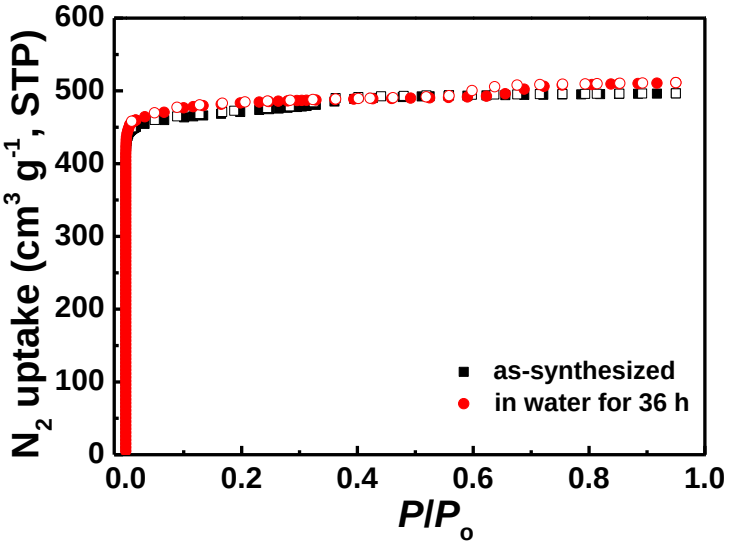
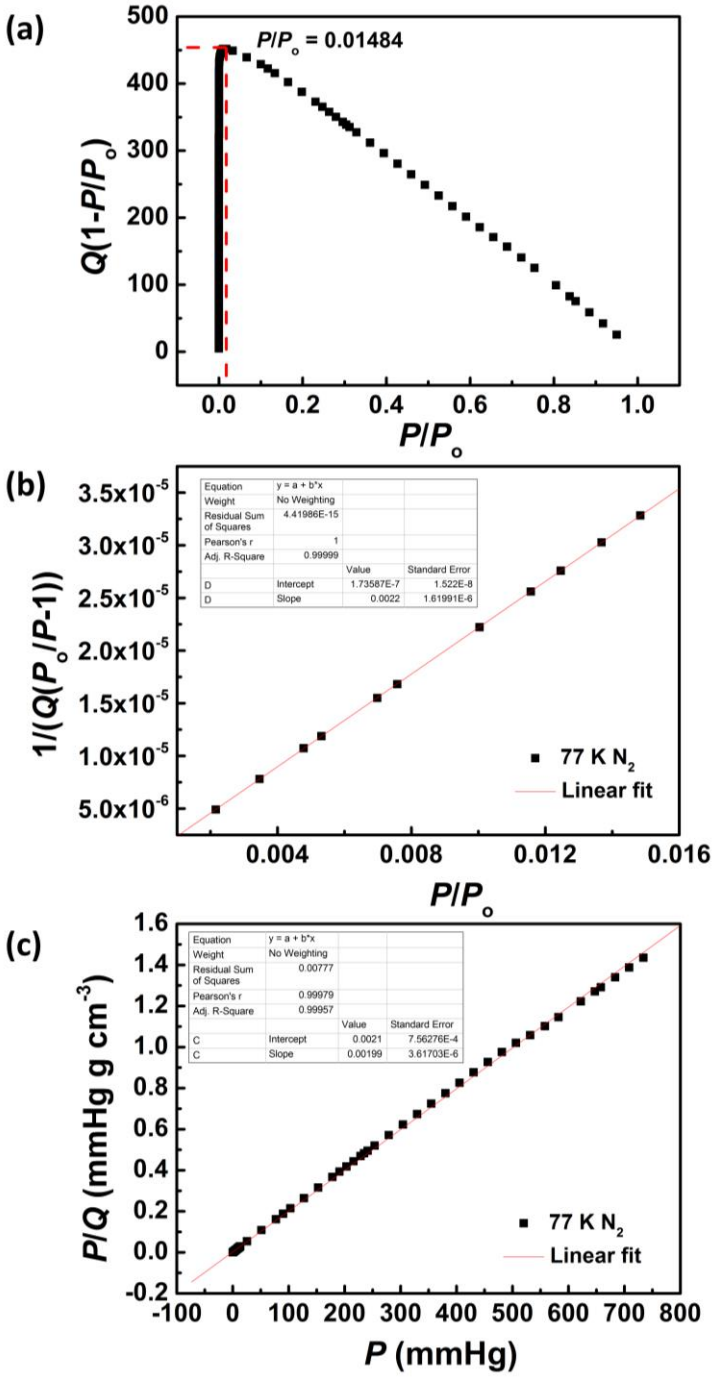


Fig. S10 Comparison of N_2 isotherms at 77 K of **ZJNU-57** before and after immersion in water for 36 h. The solid and open symbols represent adsorption and desorption, respectively. STP = standard temperature and pressure.



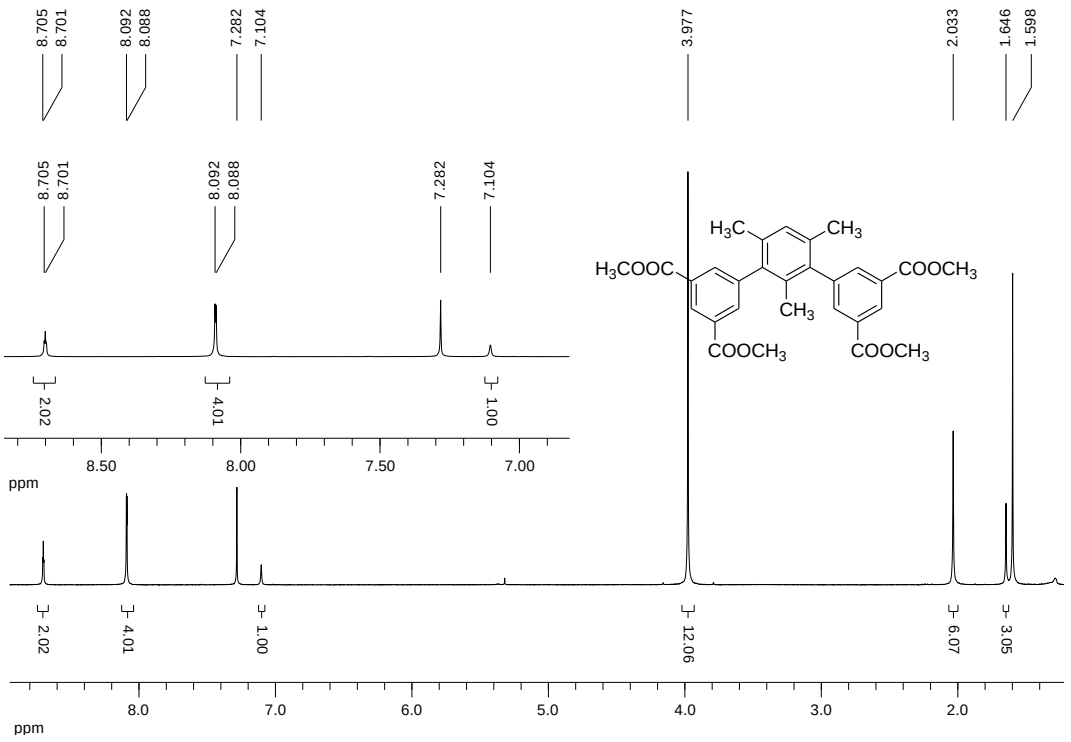
S_{BET} = 1/(1.73587 ×10^{-7}+ 0.0022)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 1978 m^2 g^{-1}

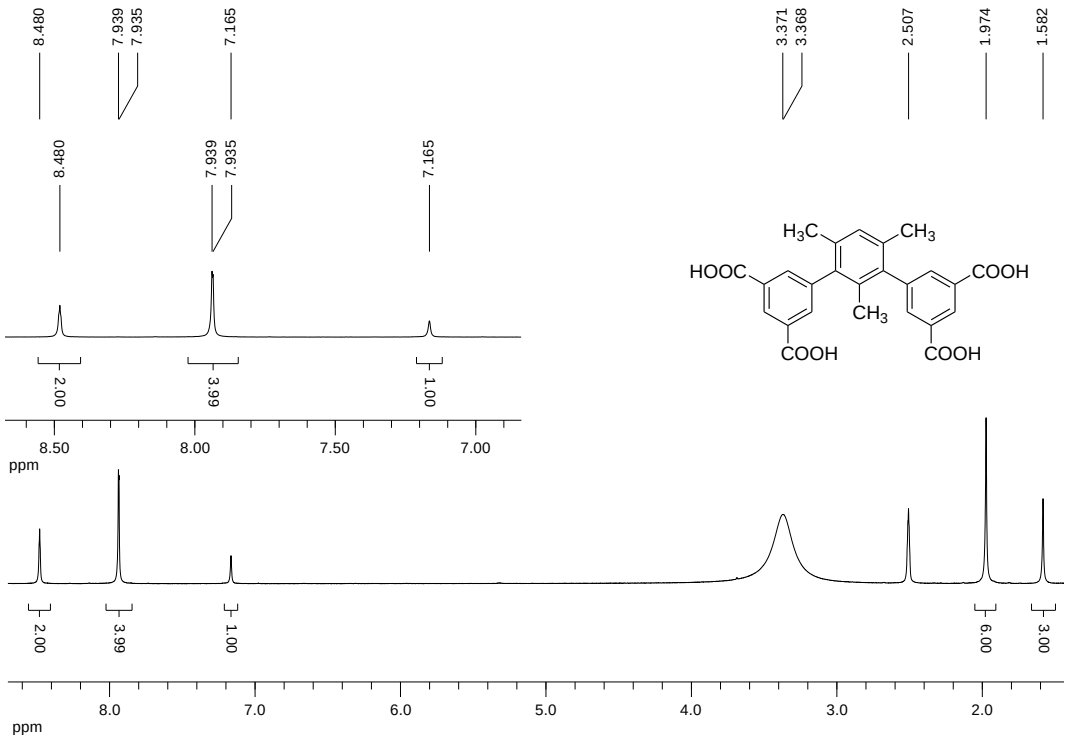
$S_{Langmuir}$= (1/0.00199)/22414 × 6.023 × 10^{23} × 0.162 × 10^{-18} = 2187 m^2 g^{-1}

BET constant C = 1 + 0.0022/1.73587 ×10^{-7} = 12675

$$(P/P_o)_{n_m} = \frac{1}{\sqrt{C}+1} = 0.008804$$

Fig. S11 (a) The consistency, (b) BET and (c) Langmuir plots for **ZJNU-57** which is immersed in water for 36 h .


8.705
8.701
8.092
8.088
7.282
7.104
3.977
2.033
1.646
1.598
H3C
CH3
H3COOC
COOCH3
CH3
COOCH3
COOCH3
2.02
4.01
1.00
12.06
6.07
3.05
8.50
8.00
7.50
7.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm


8.480
7.939
7.935
7.165
3.371
3.368
2.507
1.974
1.582
H3C
CH3
HOOC
COOH
CH3
COOH
COOH
2.00
3.99
1.00
9.00
3.00
8.50
8.00
7.50
7.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm

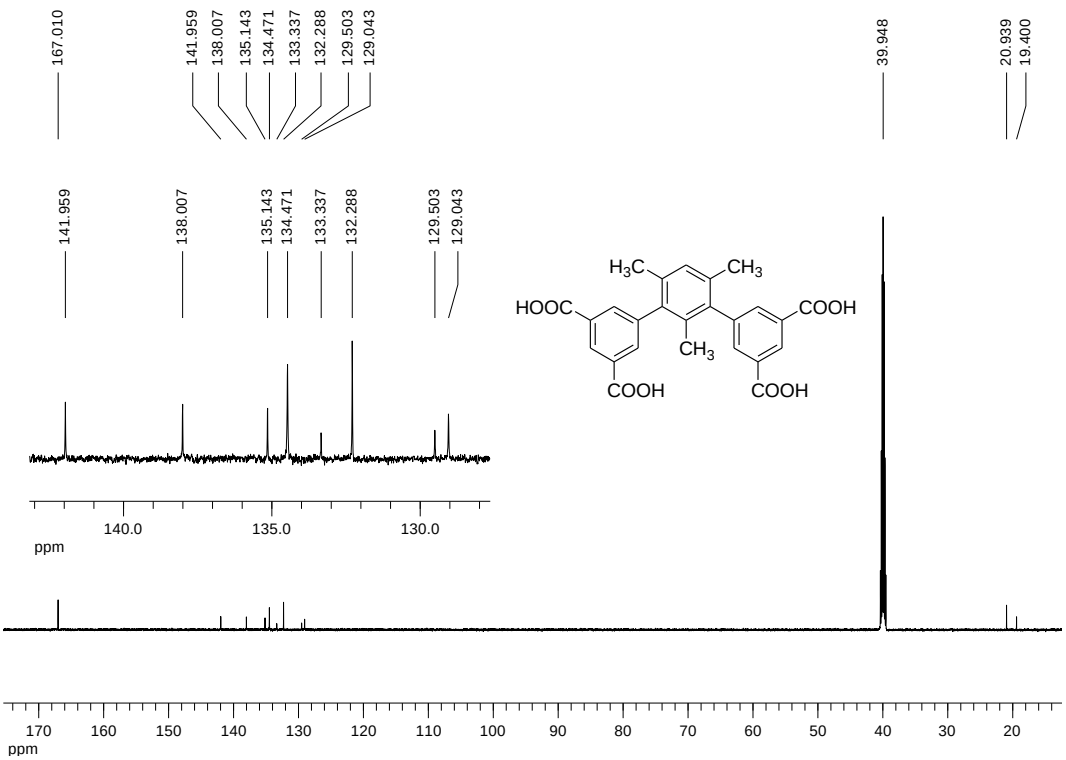


Fig. S11 ^{1}H and ^{13}C NMR spectra

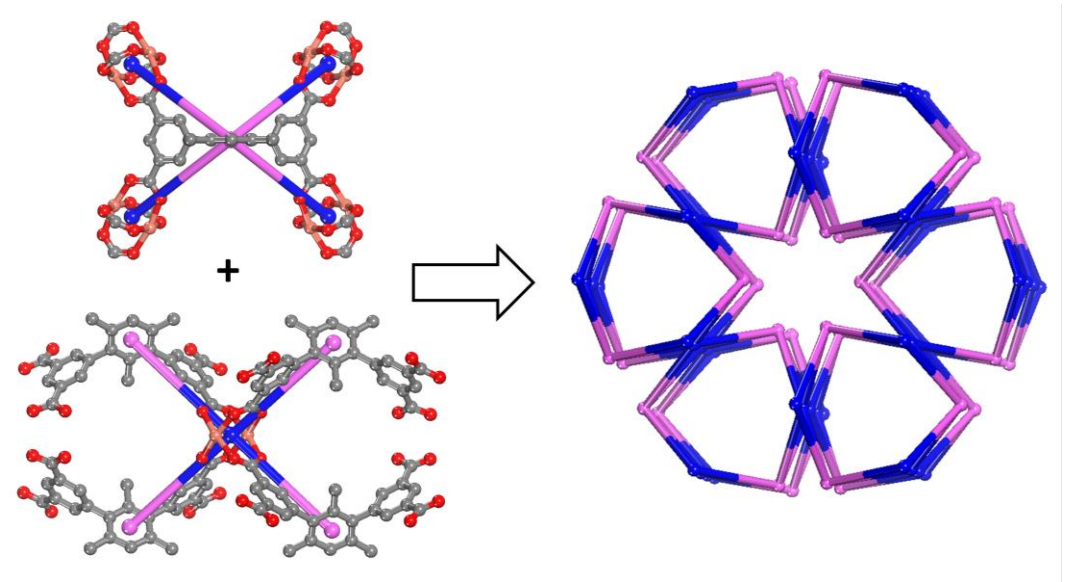


Fig. S12 Topological analyses for **ZJNU-57**. **ZJNU-57** can be rationalized as a (4,4)-connected *ssa*-type network with the point symbol of $(4^2\cdot6^4)(4^2\cdot8^4)$, which is based on the following simplifications. The dicopper paddlewheel unit is connected to four organic ligands and therefore can be regarded as four-connected nodes. Also, the organic ligand is connected to four dicopper paddlewheel units and therefore can be considered as 4-connected nodes.

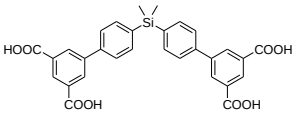
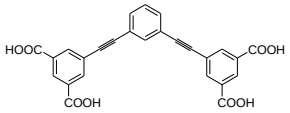
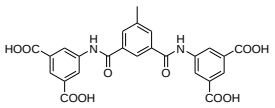
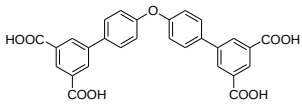
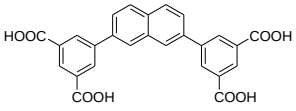
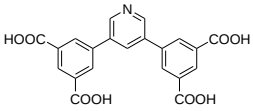
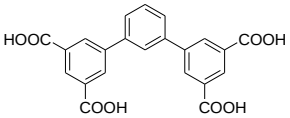
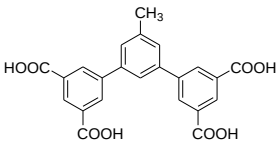
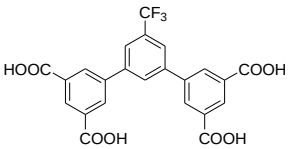
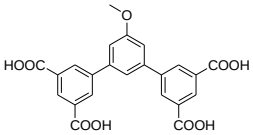
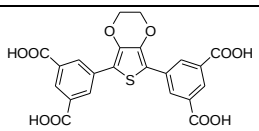
Table S1 Langmuir-Freundich parameters for adsorption of C_2H_2, CO_2, and CH_4 in **ZJNU-57**.

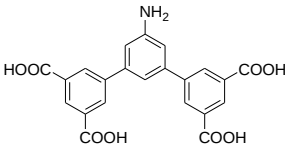
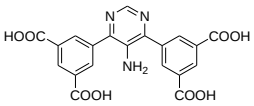
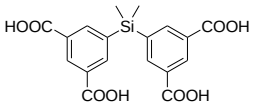
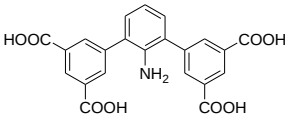
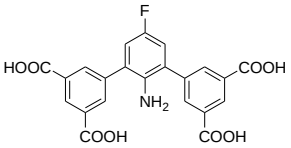
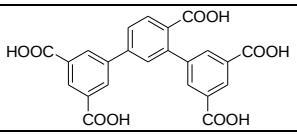
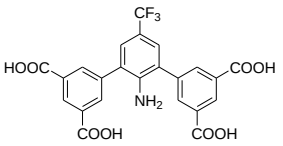
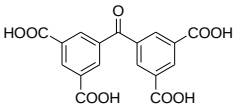
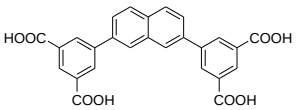
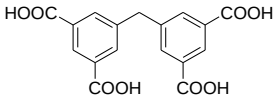
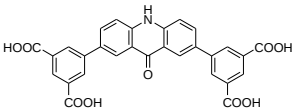
	q_{sat} (mmol g^{-1})	b_0 $(kPa)^{-v}$	E (kJ mol^{-1})	v
C_2H_2	12.00438	1.34133×10^{-7}	30.587	0.99312
CO_2	24.70544	1.86966×10^{-7}	23.403	1
CH_4	19.00656	5.96455×10^{-7}	17.011	1

Table S2 Crystal data and structure refinement for **ZJNU-57a** and **ZJNU-57b**.

MOFs	**ZJNU-57a**	**ZJNU-57b**
Empirical formula	$C_{25}H_{20}Cu_2O_{10}$	$C_{25}H_{20}Cu_2O_{10}$
Formula weight	607.49	607.49
λ (Å)	0.71073	1.34139
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3/mmc$	$P6_3/mmc$
Unit cell dimensions	a = 18.3886(3) Å b = 18.3886(3) Å c = 23.7146(9) Å α = 90° β = 90° γ = 120°	a = 18.4124(3) Å b = 18.4124(3) Å c = 23.7198(9) Å α = 90° β = 90° γ = 120°
V (Å^3)	6944.5(3)	6964.1(3)
Z	6	6
D_c (g cm^{-3})	0.872	0.869
μ (mm^{-1})	0.949	1.399
F(000)	1848	1848
θ range for data collection (°)	2.14 to 25.35	4.04 to 53.96
Limiting indices	$-19 \le h \le 14$ $-22 \le k \le 13$ $-28 \le l \le 24$	$-22 \le h \le 13$ $-13 \le k \le 17$ $-26 \le l \le 17$
Reflections collected / unique	22928 / 2402	14401 / 2353
R_{int}	0.0546	0.0602
Max. and min. transmission	0.9028 and 0.8113	0.8613 and 0.7391
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2402 / 0 / 97	2353 / 0 / 97
Goodness-of-fit on F^2	1.015	1.026
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0597 wR_2 = 0.1854	R_1 = 0.0577 wR_2 = 0.1869
R indices (all data)	R_1 = 0.0818 wR_2 = 0.1973	R_1 = 0.0830 wR_2 = 0.1967
Largest diff. peak and hole (e·Å^{-3})	0.519 and -0.694	0.381 and -0.549
CCDC	1587922	1587923

Table S3 Summary of the topological structures of copper-based MOFs derived from bent diisophthalate ligands

Topology Type	MOF	Ligand structure	Point symbol for metal nodes	Point symbol for Ligand nodes	Point symbol for the overall network	Ref
Type-I	UHM-6		{4·6²·8³} {4⁶}	{4·6⁴·8} {4²·6²·8²}	{4·6²·8³}₂{4·6⁴·8}₂{4²·6²·8²}{4⁶}	[1]
	PMOF-3		{4·6²·8³} {4⁶}	{4·6⁴·8} {4²·6²·8²}	{4·6²·8³}₂{4·6⁴·8}₂{4²·6²·8²}{4⁶}	[2]
	HNUST-4		{4·6²·8³} {4⁶}	{4·6⁴·8} {4²·6²·8²}	{4·6²·8³}₂{4·6⁴·8}₂{4²·6²·8²}{4⁶}	[3]
	FJI-H5		{4·6²·8³} {4⁶}	{4·6⁴·8} {4²·6²·8²}	{4·6²·8³}₂{4·6⁴·8}₂{4²·6²·8²}{4⁶}	[4]
	ZJNU-78		{4·6²·8³} {4⁶}	{4·6⁴·8} {4²·6²·8²}	{4·6²·8³}₂{4·6⁴·8}₂{4²·6²·8²}{4⁶}	[5]
Type-II	PCN-305		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[6]
	PCN-306		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[6]
	PCN-307		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[6]
	PCN-308		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[6]
	NJFU-3		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[7]
	Cu-DDC		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[8]

	ZJU-195		{4²·6⁴} {6⁴·8²}	{4·6⁴·8} {6⁶}	{4·6⁴·8}₂{4²·6⁴}{6⁴·8²}₂{6⁶}	[9]
Type-III	ZJNU-54		{4²·6⁴}	{4²·8⁴}	{4²·6⁴}{4²·8⁴}	[10]
	Cu_2L		{4²·6⁴}	{4²·8⁴}	{4²·6⁴}{4²·8⁴}	[11]
	Cu_2L		{4²·6⁴}	{4²·8⁴}	{4²·6⁴}{4²·8⁴}	[12]
	Cu_2L		{4²·6⁴}	{4²·8⁴}	{4²·6⁴}{4²·8⁴}	[13]
	Cu_2L		{4²·6⁴}	{4²·8⁴}	{4²·6⁴}{4²·8⁴}	[14]
	Cu_2L		{4²·6⁴}	{4²·8⁴}	{4²·6⁴}{4²·8⁴}	[15]
Type-IV	Cu_2(cdip)		{6⁴·8²} {4²·6⁴}	{4·6⁴·8} {4²·6²·8²}	{4·6⁴·8}₂{4²·6²·8²}{4²·6⁴}₂{6⁴·8²}	[16]
Type-V	PCN-88		{4⁶} {6⁴·8·10}	{4·6⁴·8} {6⁴·8²}	{4·6⁴·8}₂{4⁶}{6⁴·8·10}₂{6⁴·8²}	[17]
Type VI	PCN-12		{4·6²·8³} {4⁴·6²} {4²·6²·8²}	{4²·6³·8} {4²·6²·8²}	{4·6²·8³}₂{4²·6²·8²}₅{4²·6³·8}₄{4⁴·6²}	[18]
Type VII	Cu_2L		{4·6⁵} {4·6²·8³}	{4·6⁵} {4·6⁴·8}	{4·6²·8³}{4·6⁴·8}{4·6⁵}₄	[19]

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