Electronic Supplementary Information (ESI)

Assembly of a unique octa-nuclear copper cluster-based metal-organic framework with highly selective CO_2 adsorption over N_2 and CH_4

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Materials and Methods

The ligand was prepared according to the literature.[1] All the other reagents were obtained from commercial sources and used without further purification.

Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2550 diffractometer with CuKα radiation (λ = 1.5418 Å). The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The infrared (IR) spectra were recorded within the 4000-400 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer with KBr pellets. Thermogravimetric (TG) analyses were performed on TGA Q500 V20.10 Build 36 thermogravimetric analyzer in the temperature range 35-800 °C under air flow with the heating rate of 10 ^oC min^{-1}. N_2, CH_4 and CO_2 sorption isotherm measurements of **JLU-Liu1** were carried out on a Micromeritics ASAP 2020 instrument.

Single Crystal X-ray Structure Determination

Data were collected on a Bruker Apex II CCD diffractometer at 293(2) K for **JLU-Liu1**, with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELXTL.[2] All non-hydrogen atoms were easily found from the difference Fourier map. All non-hydrogen atoms were refined anisotropically. PLATON/SQUEEZE[3] was employed to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the generated data. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1.

Table S1. Crystal data and structure refinement for compound **JLU-Liu1**.

Name	**JLU-Liu1**
Empirical formula	$C_{15.5}H_{24.5}Cu_4N_{3.5}O_{19.5}S_3$
Formula weight	922.23
Temperature (K)	293(2)
Wave length (Å)	0.71073
Crystal system	Tetragonal
Space group	$P4_32_12$
a (Å)	13.6542(9)
b (Å)	13.6542(9)
c (Å)	42.160(4)
Volume (Å^3)	7860.1(10)
Z, D_{calc} (Mg/m^3)	8, 1.559
Absorption coefficient (mm^{-1})	2.362
F (000)	3696
θ range (deg)	1.57 to 28.4
Limiting indices	-13≤h≤18
	-17≤k≤18
	-56≤l≤52
reflections collected/	49638/9858
unique (Rint)	[R(int)= 0.0494]
Crystal size (mm^3)	0.27×0.24×0.21
Data/restraints/parameters	9802/108/389
Goodness-of-fit on F^2	99.8 %
R_1, wR_2 ($I>2\sigma(I)$)	0.0349, 0.0931
R_1, wR_2 (all data))	0.0384, 0.0943
largest difference in peak and hole (e Å^{-3})	0.907, -0.692

$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[\ w\ (F_o^2-F_c^2)^2]\ /\ \sum[\ w\ (F_o^2)^2]]^{1/2}$

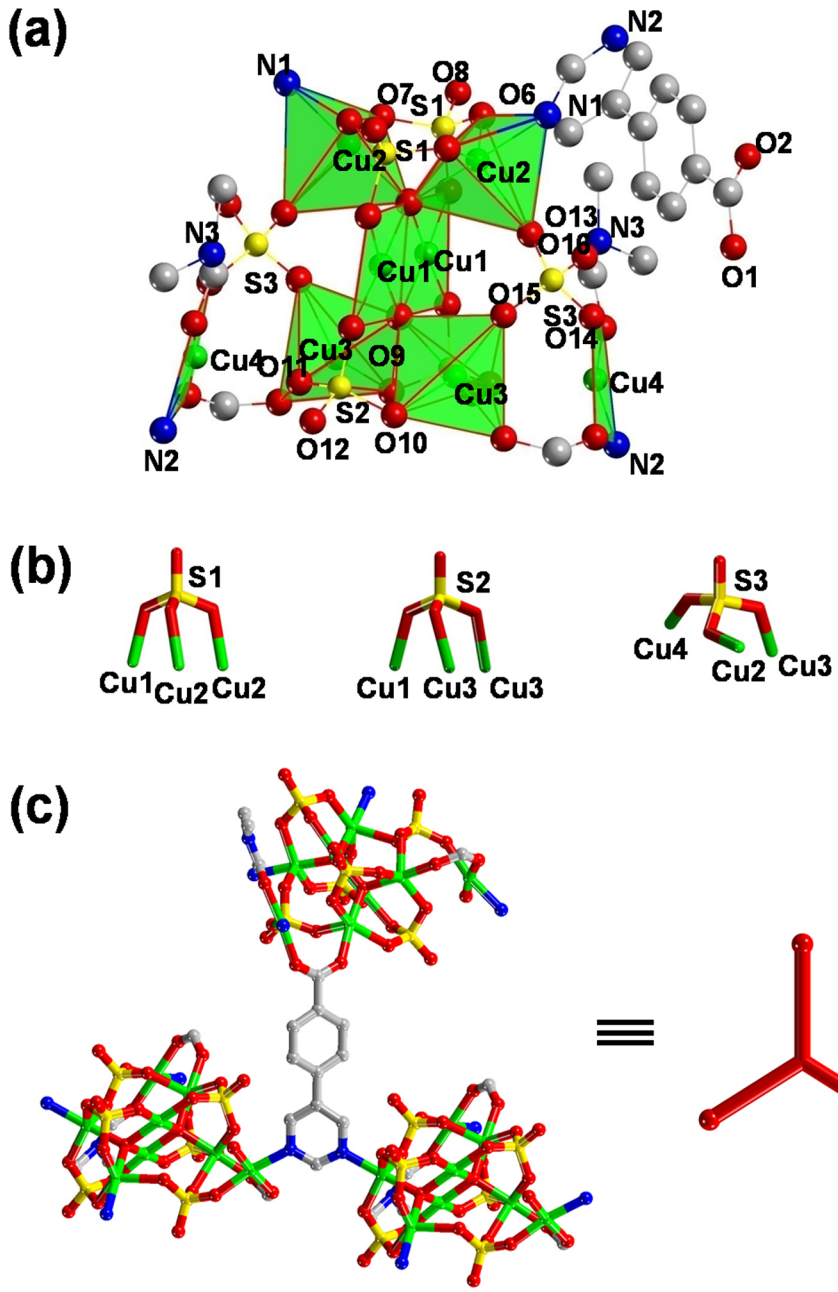

Figure S1. Coordination states in the crystal structure of **JLU-Liu1:** (a) coordinated mode of the octa-nuclear copper SBU; (b) coordination modes of the three sulfate ions; (c) the 4-PmBC^{-} ligand linked to three octa-nuclear copper SBU, which can be viewed as a 3-connected node. Color scheme: copper: green; carbon: grey; oxygen: red, nitrogen, blue, sulfur yellow. H atoms are omitted for clarity.

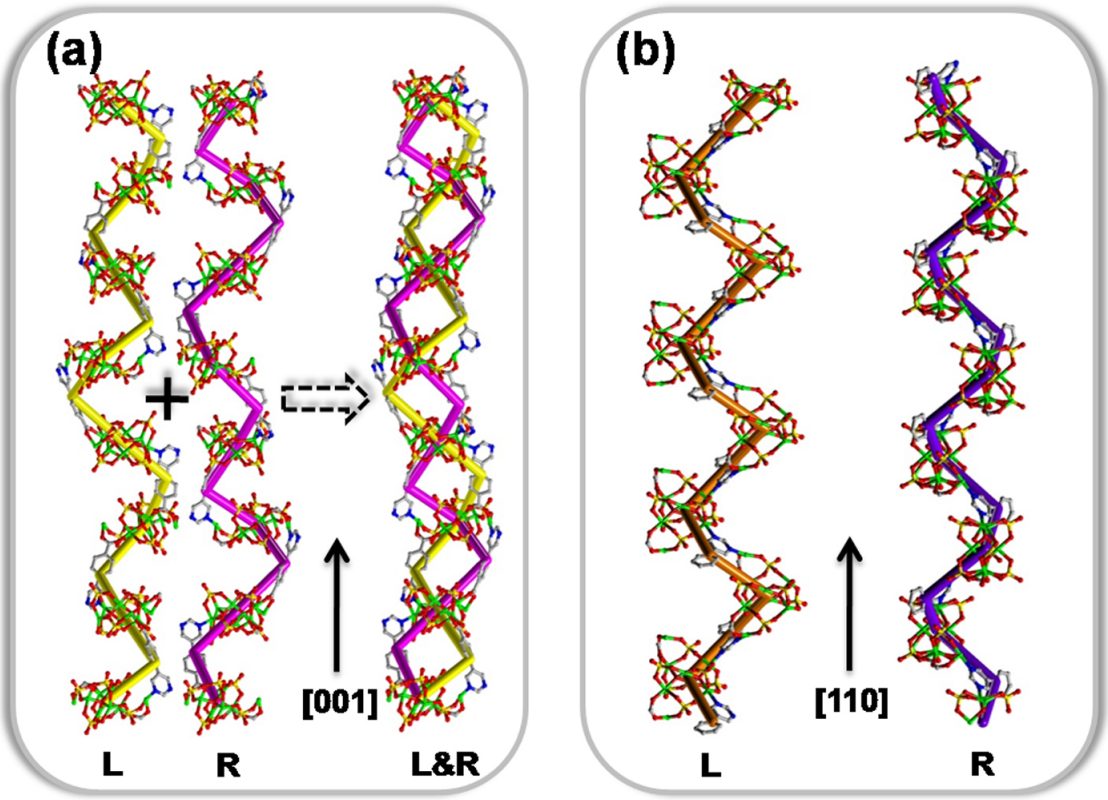

Figure S2. The exhibition of the helical chains in the framework of **JLU-Liu1**: (a) a left-handed (L) and a right-handed (R) helix intersect at the copper clusters to form a double helical chain along [001] direction; (b) a left-handed (L) and a right-handed (R) helix along [110] direction.

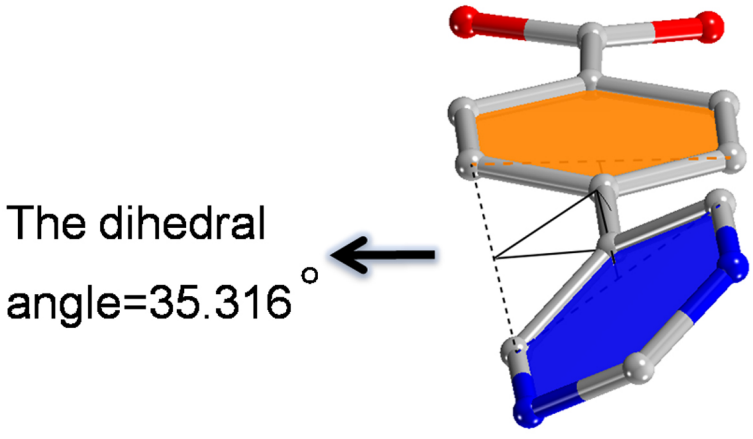

Figure S3. The dihedral angle between two aromatic rings.

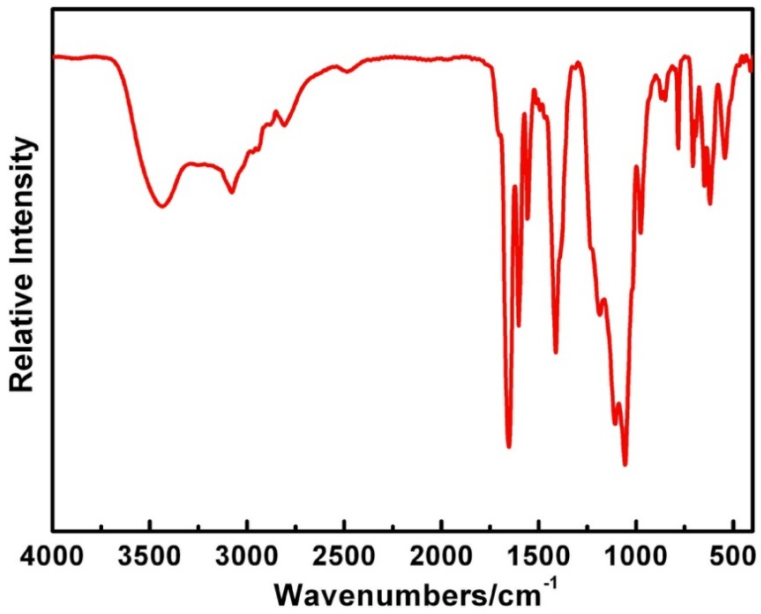

Figure S4. Infrared spectra for **JLU-Liu1** (KBr, cm^{-1}): 3027br, 2930br, 1661s, 1584s, 1433s, 1311w, 1259w, 1104m, 1059w, 923w, 785m, 729m, 673w, 537w, 451w.

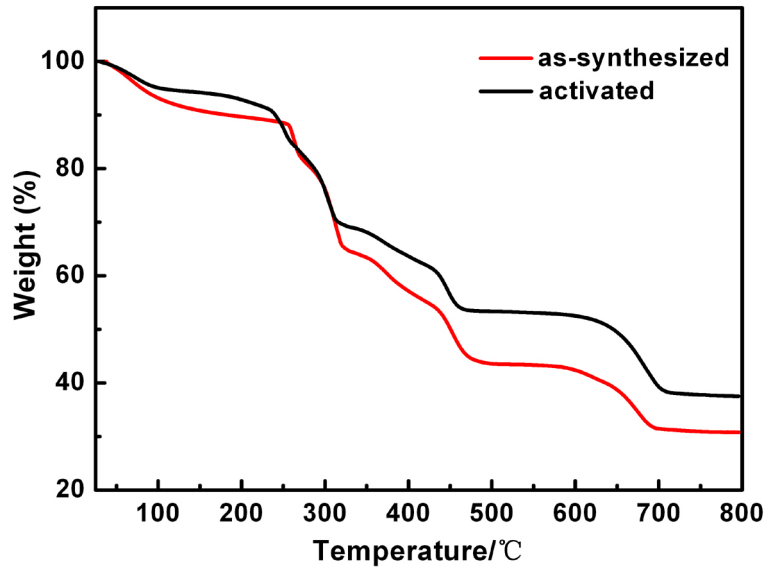

Figure S5. The TGA curve of as-synthesized and activated **JLU-Liu1**.

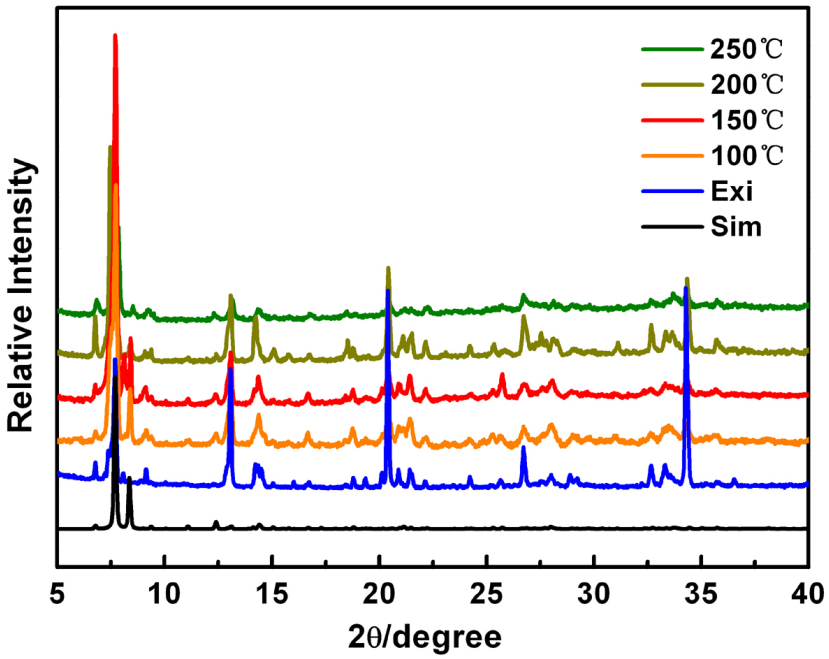

Figure S6. Variable-temperature powder XRD patterns of **JLU-Liu1**.

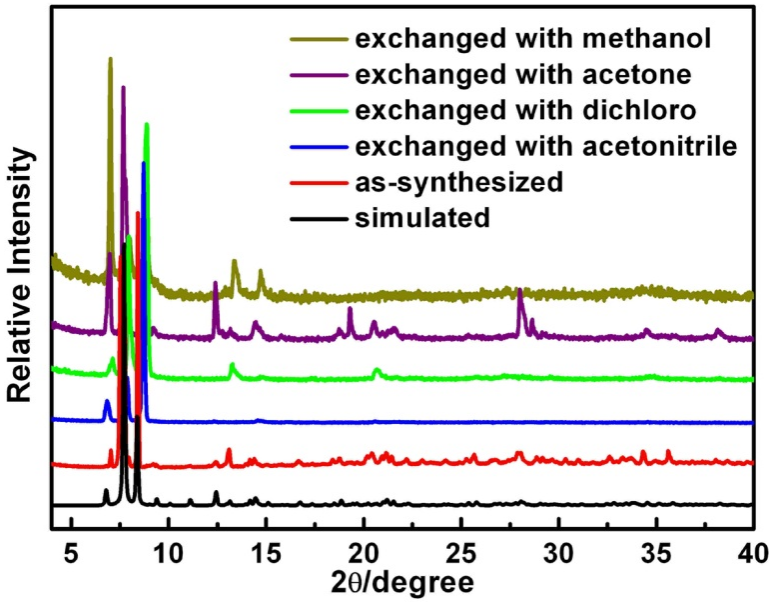

Figure S7. The XRD patterns of **JLU-Liu1** after immersed in different solvents.

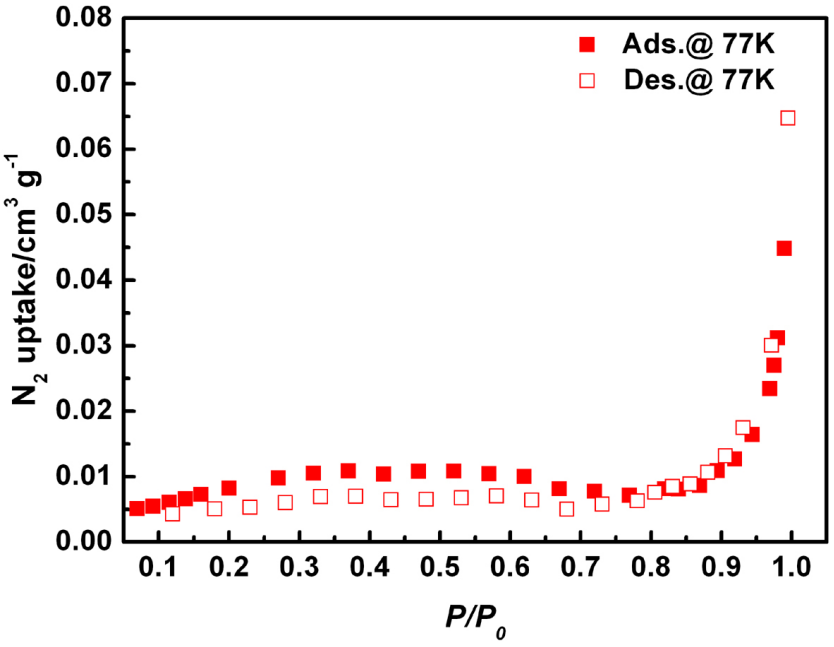

Figure S8. The N_2 sorption isotherm of activated **JLU-Liu1** at 77K.

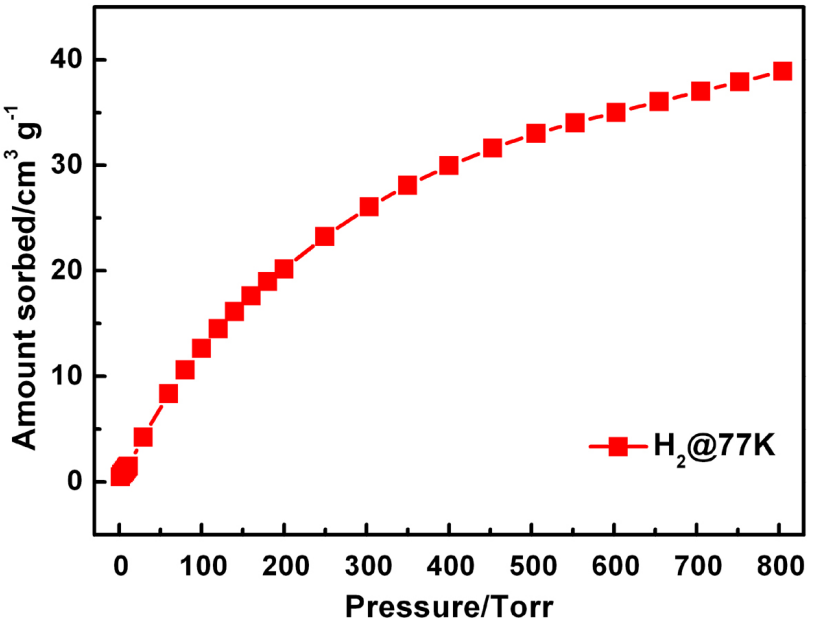

Figure S9. The H_2 sorption isotherm of activated **JLU-Liu1** at 77K.

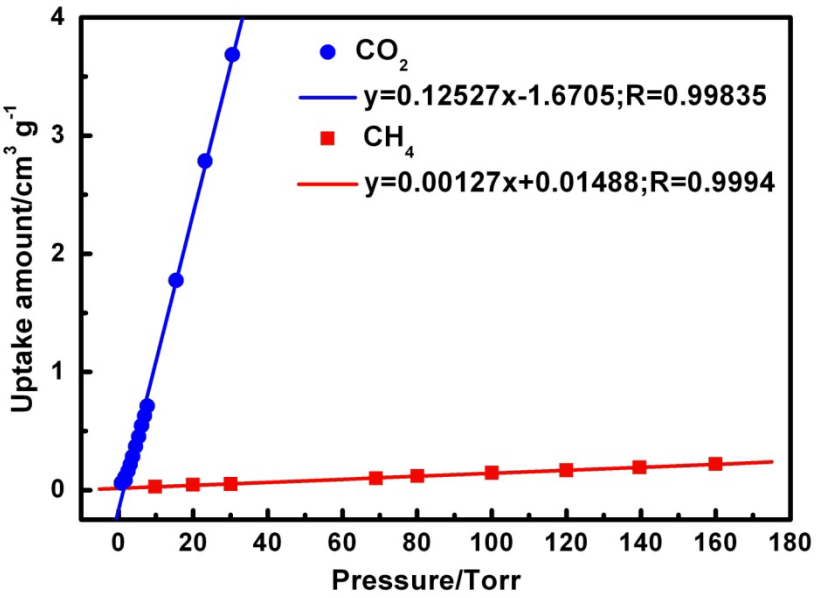

Figure S10. Calculation of CO_2:CH_4 selectivity by initial slope of the gas uptake on **JLU-Liu1**. (Blue dot and solid line: uptake of CO_2, red square and line: uptake of CH_4.)

References

1. Y. Gong and H. W. Pauls, *Synlett.* **2000**, 6, 829-831.

2. G. M. Sheldrick, SHELXTL-97, Program for Crystal Structure Refinement, University of Gottingen, 1997

3. A. L. Spek, *J. Appl. Crystallogr.* **2003**, 36, 7.