

Supplementary Information

Synthesis, Structure and Highly Selective C₃H₈/CH₄ and C₂H₆/CH₄ Adsorptions of a (4,8)-c Ternary *flu*-Metal-organic Framework based upon both [Sc₄O₂(COO)₈] and [Cu₄OCl₆] Clusters

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General procedures. All reagents were obtained from commercial vendors and, unless otherwise noted, were used without further purification. Elemental analysis (C, H, N) were carried out with an Elementar Vario EL III. The IR spectra were obtained in the 4000~400 cm⁻¹ on a Bruker Tensor27 spectrometer using KBr pellets. Thermal gravimetric analyses (TGA) were performed under N₂ atmosphere (100 ml/min) with a heating rate of 5 °C/min using a Beijing Henven HTG-1 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu K α radiation. The content of metal ions in MOF sample were carried out with Optima 5300 DV ICP.

Synthesis of [Sc₄O₂(Cu₄Cl₆O)₂(L)₈·5H₂O]·xGuest (SNNU-Bai69). A solution of ScCl₃·6H₂O (10.0 mg, 0.04 mmol) and Cu(NO₃)₂·3H₂O (18.0 mg, 0.07 mmol) in 2.0 mL of acetonitrile was added in the solution of isonicotinic acid (HL, 5.0 mg, 0.04 mmol) in 1.2 mL of N,N'-dimethylformamide with stirring. The mixture was sealed in a Pyrex tube and heated to 120 °C for 24h. The yellow block crystals obtained were filtered and washed with DMF. Yield (based on HL) = 68%.

Sample activation. The as-synthesized sample of SNNU-Bai69 was soaked in CH₂Cl₂ for 3 days with CH₂Cl₂ refreshing every 8 hours. Then, the CH₂Cl₂-exchanged sample was activated at 30 °C for 2h, 50 °C for 0.5 h and 65 °C for 8 hours under vacuum to give the yellow block activated SNNU-Bai69, [Sc₄O₂(Cu₄Cl₆O)₂(L)₈·5H₂O]. Elemental analysis (%) calcd. for C₄₈H₄₂Cl₁₂Cu₈N₈O₂₅Sc₄ (activated

SNNU-Bai69): C 25.69, H 1.89, N 4.99; found: C 25.36, H 3.84, N 5.21. ICP (ppm): Sc, 6.813; Cu, 19.342.

X-ray crystallography. Single-crystal X-ray diffraction data were measured on a Bruker D8 Venture at 153 K using graphite monochromated Cu/K α radiation ($\lambda = 1.54178 \text{ \AA}$). Data reduction was made with the Bruker SAINT program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package^[1]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE^[2] to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; the structure was then refined again using the data generated. A summary of the crystallographic data is given in Table S1. CCDC 2142041 contains the supplementary crystallographic data for SNNU-Bai69.

Table S1. Crystallographic Data of SNNU-Bai69

MOFs	SNNU-Bai69
Empirical formula	C ₄₈ H ₄₂ Cl ₁₂ Cu ₈ N ₈ O ₂₅ Sc ₄
Formula weight	2244.46
T [K]	153(2)
Wavelength [Å]	1.54178
Crystal system	Triclinic
Space group	<i>P</i> ₁
a [Å]	19.6298(1)
b [Å]	20.2011(1)
c [Å]	20.3398(1)
α [deg]	82.881(2)
β [deg]	78.746(2)
γ [deg]	87.263(2)
V [Å ³]	7847.2(8)
Z	2
ρ_{calc} [g cm ⁻³]	0.95
μ [mm ⁻¹]	4.740
F(000)	2212
Crystal size [mm ³]	0.11 × 0.08 × 0.05
Theta range [deg]	2.20 – 61.41
Limiting indices	-21 ≤ h ≤ 22

	-22 ≤ k ≤ 22
	-22 ≤ l ≤ 19
Reflections collected	62440
Reflections unique	23269 [R(int) = 0.0676]
Completeness	95.8 %
Data/restraints/parameters	23269 / 0 / 951
Goodness-of-fit on F ²	1.066
R1, wR2 ^a [I > 2σ(I)]	0.0695, 0.2168
R1, wR2 ^a [all data]	0.0837, 0.2312
Δρ _{max} / Δρ _{min} [e. Å ⁻³]	-0.731 / 1.282

^a R1 = $\Sigma||F_o| - |F_c||/|F_o|$; wR2 = $[\Sigma w(\Sigma F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

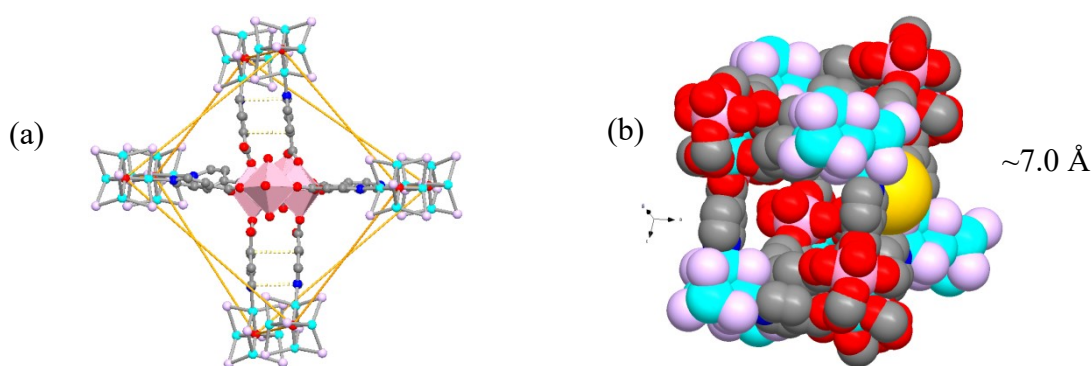


Figure S1. (a) The π ... π stacking role between two couples of neighbouring isonicotinic acids around the torsional cubic 8-c $\text{Sc}_4\text{O}_2(\text{COO})_8$ cluster and (b) the pore size of 1D pore channel in SNNU-Bai69. H atoms have been omitted for clarity.

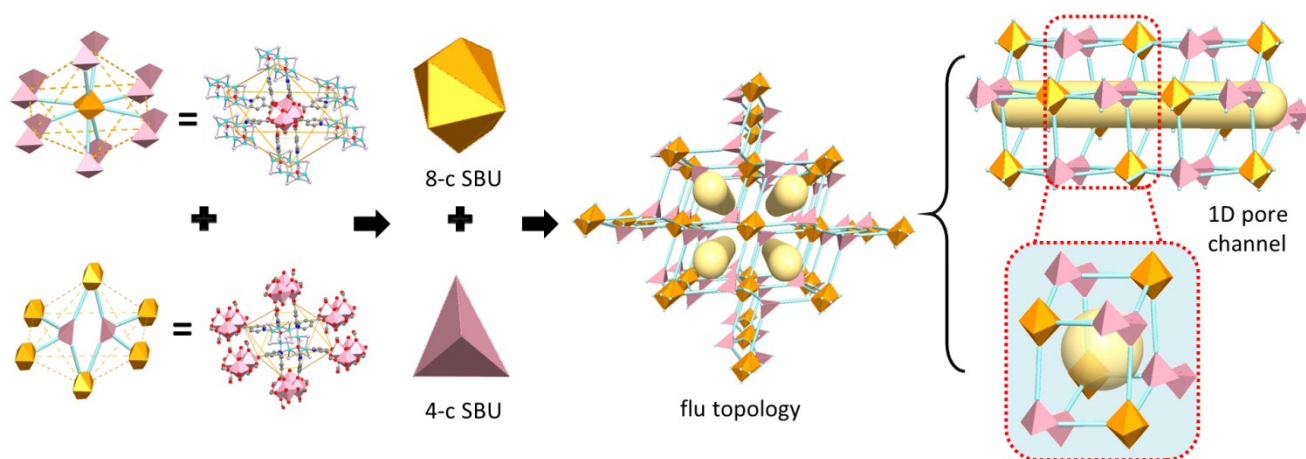


Figure S2. The simplification of *flu* topological network of SNNU-Bai69 with the point symbol of $\{4^{12}.6^{12}.8^4\} \{4^6\}_2$.

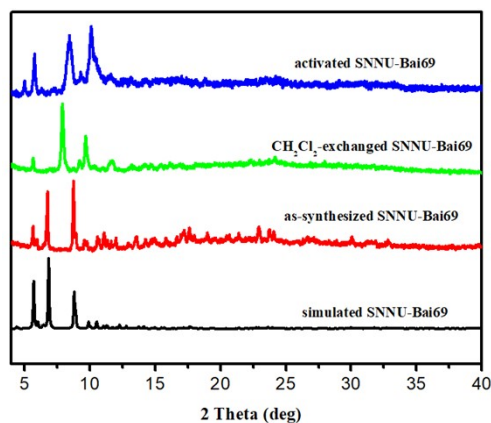


Figure S3. The simulated and experimental PXRD patterns of SNNU-Bai69.

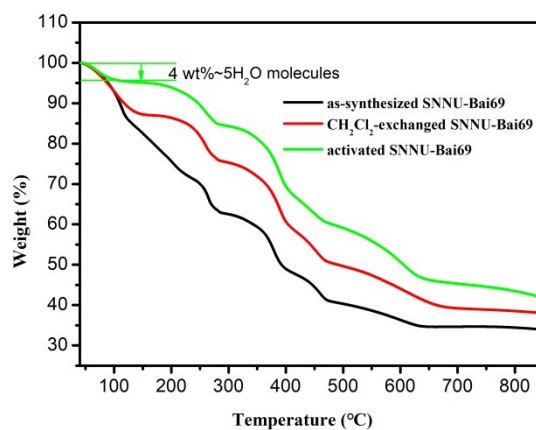


Figure S4. TGA curves of as-synthesized (black), CH_2Cl_2 -exchanged and activated (green) of SNNU-Bai69. The weight loss of 4 wt% of activated SNNU-Bai69 at 100 °C is attributed to five coordinated H_2O molecules on two Sc^{3+} ions. Note: Due to the rapid volatilization of MeCN and CH_2Cl_2 solvent in the pore channels of as-synthesized and CH_2Cl_2 -exchanged SNNU-Bai69, respectively, the loss weight before 100 °C are not able to indicate the real loss weight of MeCN and CH_2Cl_2 solvent in the pore channels.

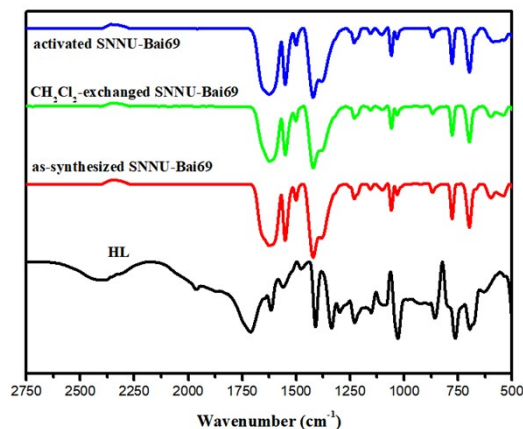


Figure S5. Infrared spectra of ligand (black), as-synthesized (red), CH_2Cl_2 -exchanged (green), and activated (blue) of SNNU-Bai69.

Gas sorption measurements. Low-pressure adsorption isotherms of N₂ (99.999%), C₃H₈ (99.99%), C₂H₆ (99.999%) and CH₄ (99.999%) gases were performed on Micromeritics 3Flex surface area and pore size analyzer. Before analysis, about 50 mg samples were activated by using the “outgas” function of the surface area analyzer. For all isotherms, ultra-high purity He gas (UHP grade 5.0, 99.999% purity) was used for the estimation of the free space (warm and cold), assuming that it is not adsorbed at any of the studied temperatures. The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) and the Langmuir equation from the N₂ sorption data at 77 K. When applying the BET theory, we made sure that our analysis satisfied the two consistency criteria as detailed by Walton and co-workers.^[3] For the Langmuir surface area, data from the whole adsorption data were used.

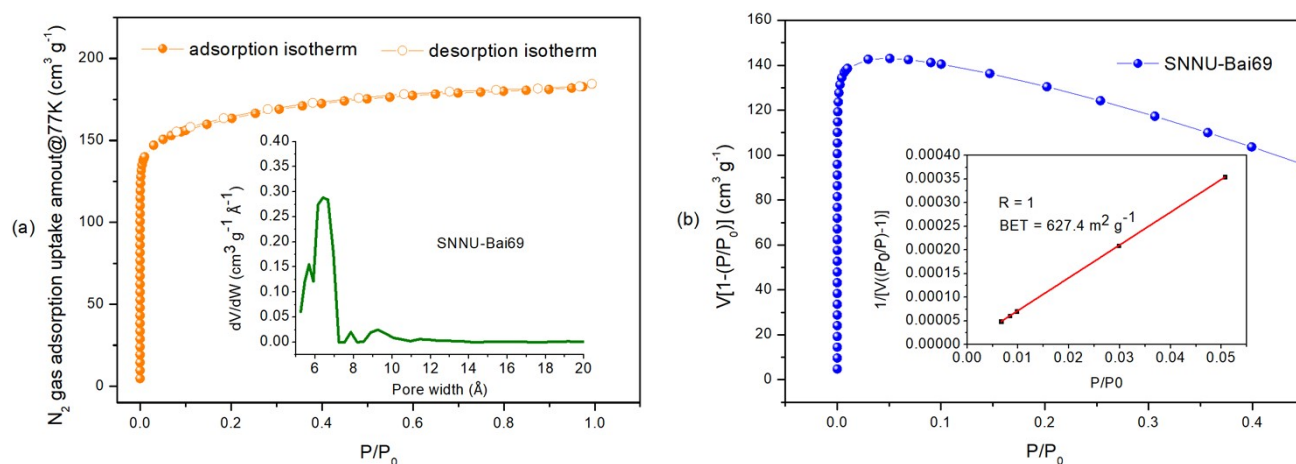


Figure S6. (a) The N₂ adsorption isotherms at 77 K (Inset: DFT pore size distribution plot) and (b) $V[1-(P/P_0)]$ vs. P/P_0 for SNNU-Bai69, only the range below $P/P_0 = 0.04$ satisfies the first consistency criterion for applying the BET theory (Inset: Plot of the linear region for the BET equation).

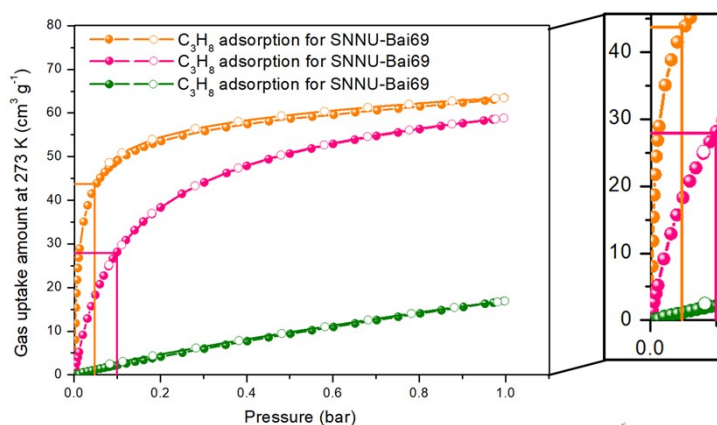


Figure S7. The C₃H₈, C₂H₆ and CH₄ adsorption isotherms for SNNU-Bai69 at 273 K (right, the enlarged view of gas adsorption isotherms at ultra-low pressures); Filled and open symbols represent adsorption and desorption, respectively.

Estimation of the isosteric heats of gas adsorption. A virial-type^[4] expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for C₃H₈, C₂H₆ and CH₄ (at 273 and 298 K) of activated SNNU-Bai69. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \quad (1)$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m , n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of C₃H₈, C₂H₆ and CH₄ sorption for activated SNNU-Bai69 in the manuscript are determined by using the sorption data measured in the pressure range from 0-1 bar (273 and 298 K), which is fitted by the virial-equation very well ($R^2 > 0.9999$).

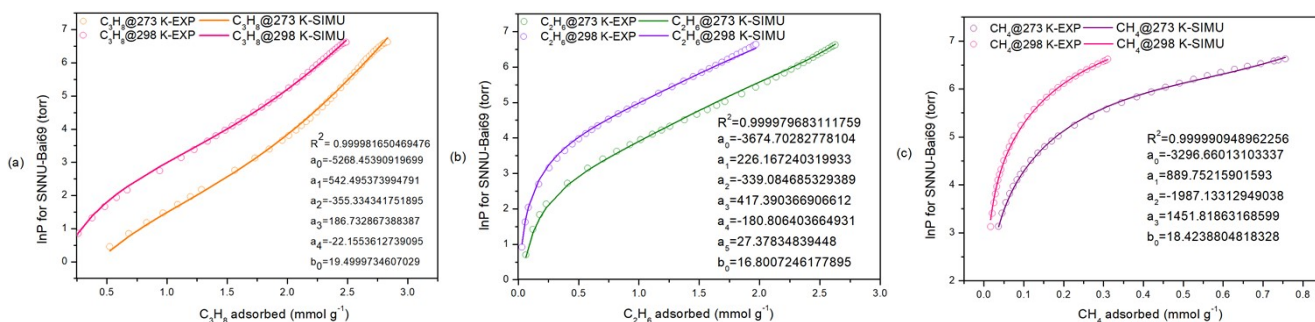


Figure S8. The details of virial equation (solid lines) fitting to the experimental C₃H₈ (a), C₂H₆ (b), and CH₄ (c) adsorption data (symbols) for activated SNNU-Bai69.

Prediction of the Gas Adsorption Selectivity by IAST. IAST (ideal adsorption solution theory)^[5] was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. In practice, several methods to do this are available. We found for this set of data that the dual-site Langmuir-Freundlich equation was successful in fitting the data. As can be seen in Figure S9 and Table S2, the model fits the isotherms very well ($R^2 > 0.9999$).

$$q = \frac{q_{m,1} b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + \frac{q_{m,2} b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}} \quad (3)$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol/g), $q_{m,1}$ and $q_{m,2}$ are the saturation capacities of sites 1 and 2 (mmol/g), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multi-component adsorption with IAST.

The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as $(x_A/y_A)/(x_B/y_B)$, where x_i and y_i are the mole fractions of component i ($i = A, B$) in the adsorbed and bulk phases, respectively.

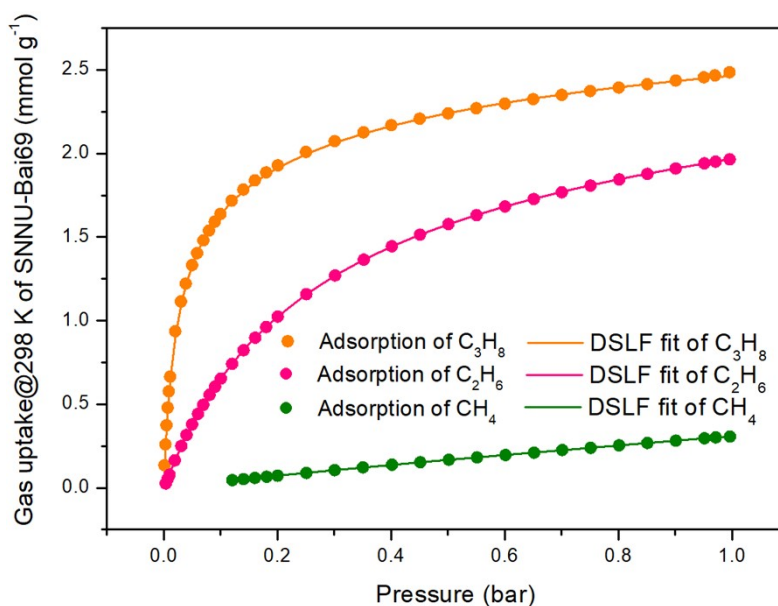


Figure S9. Low pressure gas adsorption isotherms and the dual-site Langmuir-Freundlich (DSLFL) fit lines of C_3H_8 , C_2H_6 and CH_4 in SNNU-Bai69 at 298 K.

Table S2. Dual-site Langmuir-Freundlich parameters for pure C₃H₈, C₂H₆ and CH₄ isotherms in activated SNNU-Bai69 at 298 K

	SNNU-Bai69		
	C ₃ H ₈	C ₂ H ₆	CH ₄
R ²	0.999901252032284	0.999992655795133	0.999969255620802
q _{m,1}	1.64558891096833	2.28209582909371	0.00524644304478482
q _{m,2}	1.57618317711217	616.954875574045	3.43099893472945
b ₁	0.0614805318315383	0.0405489098007078	2.30928362383002E-28
b ₂	0.483565594448545	2.03105555485444E-06	0.0014976922963507
n ₁	1.50567705	1.01405966194158	0.06932982
n ₂	1.054339267	0.944205288808884	1.100673544

Breakthrough experiment. The breakthrough experiments were performed on a gas-separation apparatus which was designed by Xuzhou North Gaorui Electronic Equipment Co., Ltd. In the breakthrough system. All flow rates of all gases can be regulated by the mass flow controllers. According to a protocol established by the literatures,^[6] the breakthrough curves in this investigation were collected at 298 K. An activated sample of SNNU-Bai69 (653 mg) was packed into a stainless-steel column (0.40 cm internal diameter × 15 cm length) and the remaining volume in the column was filled by glass wool. Helium gas (with a flow rate of 10 mL/min for 20 min) was initially purged into the packed column to ensure that no other gases were detected in the effluent. Then, the desired gas mixture with a flow rate of 10 mL/min (C₃H₈/C₂H₆/CH₄: 5/10/85) was dosed into the column. Effluent from the bed was monitored by a gas chromatography (GC). A complete breakthrough of C₃H₈ or C₂H₆ gas was defined when the concentration of effluent C₃H₈ or C₂H₆ reaches 1% of the feed concentration. Breakthrough time was calculated by subtracting the time to breakthrough based upon a sample bed packed only with stainless steel beads and cotton plugs from the observed breakthrough time. The C₃H₈ and C₂H₆ separation capacities were determined by their amounts fed through the bed during the breakthrough time, respectively.^[6a, 6b]

Reference

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