Supporting Information for the manuscript

A Microporous Metal-Organic Framework of a Rare sty Topology for High CH_4 Storage at Room Temperature

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Materials and Measurements: All the chemicals were commercially available and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Advance DMX 500 spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 3\text{-}30^{o}$ range on an X'Pert PRO diffractometer with Cu K_{α} radiation ($\lambda = 1.542$ Å) at room temperature. Thermogravimetric analyses (TGA) were conducted on a Netszch TGA 209 F3 thermogravimeter with a heating rate of 10 ^{o}C min^{-1} in a N_2 atmosphere.

Gas Sorption Measurements: A Micromeritics ASAP 2020 surface area analyzer was used to measure N_2 sorption isotherms. To have a guest–free framework, the fresh sample was guest–exchanged with dry acetone at least 10 times, filtered and vacuumed at room temperature for 24 h and then at 383 K until the outgas rate was 5 μmHg min^{-1} prior to measurements. A sample of 121 mg was used for the sorption measurements and was maintained at 77 K with liquid nitrogen. High-pressure CH_4 sorption isotherms were measured using a computer controlled Sieverts-type apparatus, details of which have been published elsewhere.[1]

X-ray Collection and Structure Determination: Crystallographic measurements for **ZJU-25** were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Mo K_{α} radiation ($\lambda = 0.71073$Å) at 140 K. The determinations of the unit cells and data collections for the crystals of **ZJU-25** were performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[2] All structures were determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 programpackage.[3] All non-hydrogen atoms, including solvent molecules, were located successfully from Fourier maps and were refined anisotropically. H atoms on C atoms were generated geometrically. Because the lattice DMF and water molecules are highly disordered in **ZJU-25**, the SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.[4] The resulting new files were used to further refine the structure. However, distortion still exists for the 9*H*-fluorene unit of the ligand even we used the lower symmetry space groups for structural solution, such as P3, P-3, P-3m1, P6(3), etc. These results suggest that the distortion is from the inherent nature of the crystals. The 9*H*-fluorene unit was modeled as a disordered unit that was cleaved into two parts with half occupancy. The contribution of disordered solvent molecules of seven DMF and one water molecules removed by the SQUEEZE process were included in the overall formula, formula weight, density, F(000), etc., calculations reported in crystallographic data summarized in Table S1.

Grand Canonical Monte Carlo (GCMC) Simulations: To locate other major CH_4 adsorption sites, we performed grand canonical Monte Carlo (GCMC) simulations of methane adsorption in ZJU-25 (with the open Cu sites preoccupied by methane) using the classical force-field method.[14] In the simultaion, both the CH_4 molecules and the frameworks were treated as rigid bodies. The standard universal force field was used to describe the methane-framework interaction and the methane-methane interaction. A 2×2×1 MOF supercell was used as the simulation box. 2×10^7 steps were used for equilibration and additional 2×10^7 steps were used to calculate the ensemble average of CH_4 adsorption sites and thermodynamic properties. More technical details of our GCMC simulations can also be found in our previous work.[15] Simulations were performed at T = 200 K, 300K and various pressures. The probability distribution of adsorbed CH_4 was generated from the simulation after the equilibrium stage, and representative results are shown in Figure S5 as examples. It is clear from the results that CH_4 molecules get adsorbed inside the small cage first, then the surfaces of the two large cages get populated, and the central voids of the large cages get filled last.

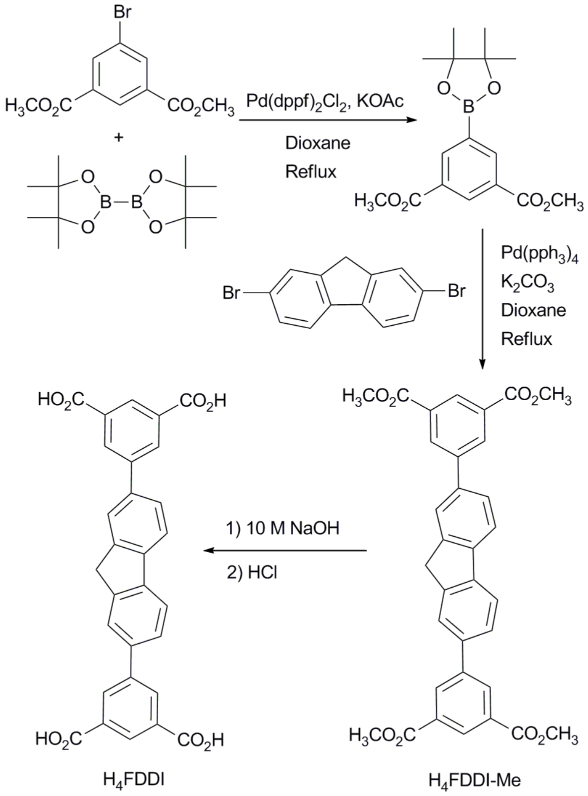
Derivation of the Isosteric Heat of Adsorption: A virial type expression of the following form was used to fit the combined CH_4 isotherm data for ZJU-25 at 240 K, 270 K and 300 K.

$$\ln P = \ln N + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1).$$

Here, P is the pressure expressed in bar, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represents 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, as determined using 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.

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

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 J $K^{-1}mol^{-1}$.



Scheme S1. Synthetic route to the organic linker used to construct **ZJU-25**.

Synthesis of the organic linekr H4FDDI: H_4FDDI was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in *Scheme S1*.

Dimethyl (5-pinacolboryl)isopthalate was synthesized by stirring the mixture of dimethyl 5-bromo-benzene-1,3-dicarboxylate (5.4 g, 19.8 mmol), bis(pinacolato)diborane (6.0 g, 23.6 mmol), potassium acetate (5.6 g, 57.2 mmol), Pd(dppf)$_2$Cl$_2$ (0.2 g, 0.28 mmol), and dried 1,4-dioxane (50 mL) at 80^{o}C for 24 h and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed in a vacuum. The crude product was purified by column chromatography (silica gel, ethylacetate/petroleum ether, 1:8 *v*/*v*). Yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (m, 12 H), 3.95 (s, 6 H), 8.64 (d, 2 H), 8.76 (s, 1H) ppm.

2, 7-dibromo-9*H*-fluorene (3.28 g, 10.0 mmol), dimethyl (5-pinacolboryl)isopthalate (9.26 g, 30.0 mmol), and K_2CO_3 (13.82 g, 100.0 mmol) were added to 1,4- dioxane (250 mL), and the mixture deaerated under Ar for 15 min. Pd(PPh$_3$)$_4$ (0.47 g,0.43 mmol) was added to the reaction mixture with stirring, and the mixture heated to 80°C for 3 days under Ar. The resultant mixture was evaporated to dryness and taken up in $CHCl_3$ which had been dried over $MgSO_4$. The $CHCl_3$ solution was evaporated to dryness and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10 *v*/*v*). Yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 4.00 (s, 12 H), 4.08 (s, 2H), 7.73 (d, 2 H), 7.89 (d, 2H), 7.93 (d, 2H) 8.54 (s, 4H), 8.67 (s, 2H) ppm.

Tetramethy 5,5’-(9H-fluorene-2,7-diyl)diisophthalate (H_4FDDI-Me) (3.31g, 6.00mmol) was then suspended in a mixture of 1,4-dioxane (20 mL), to which 50 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at *p*H = 2. The solid was collected by filtration, washed with water, and dried to give 5, 5'-(9H-fluorene-2,7-diyl) diisophthalate (H_4FDDI) (2.87 g, 97% yield). ^{1}H NMR (500 MHz, DMSO), δ = 4.14 (s, 2 H), 7.83 (d, 2H), 8.04 (s, 2 H), 8.11 (d, 2H), 8.47(s, 2H) 8.54 (s, 4H) ppm. MS (ESI) exact mass calcd for $C_{29}H_{18}O_8$ $(M-H^+)^-$: 494.45, Found 493.0.

Synthesis of ZJU-25: A mixture of H_4FDDI (1 mg, 0.0020 mmol) and $Cu(NO_3)_2{\cdot}2.5H_2O$ (1.949 mg, 0.0080 mmol) was dissolved in DMF/H_2O (3 mL, 9:1, *v*/*v*) in a screw-capped vial. After HNO_3 (35 μL) (69%, aq.) were added to the mixture, the vial was capped and placed in an oven at 60°C for 72 h. The resulting hexagonal flake-shaped single crystals were washed with DMF several times to give **ZJU-25**. Elementalanalysis: Calcd. For $[Cu_2(C_{29}H_{14}O_8)(H_2O)_2](DMF)_7(H_2O)$ ($C_{50}H_{69}N_7O_{18}Cu_2$): C, 50.75; H, 5.88; N, 8.29; Found: C, 50.26; H, 6.02; N: 8.57%.

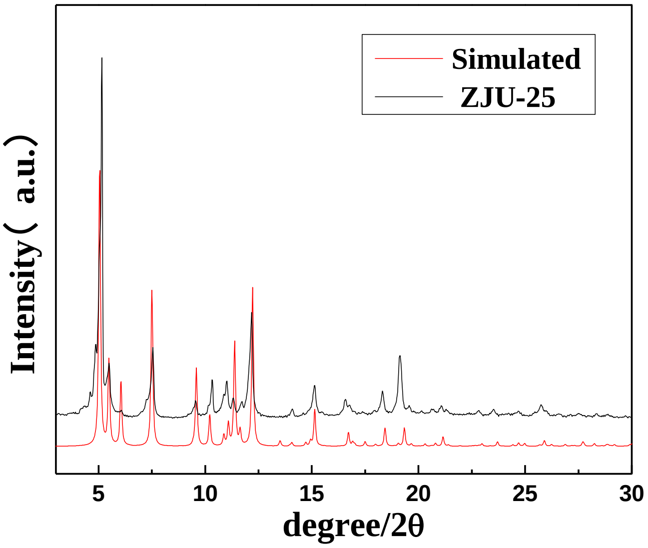


Figure S1. PXRD patterns of as-synthesized **ZJU-25** (black) and the simulated XRD pattern from the single-crystal X-ray structure (red).

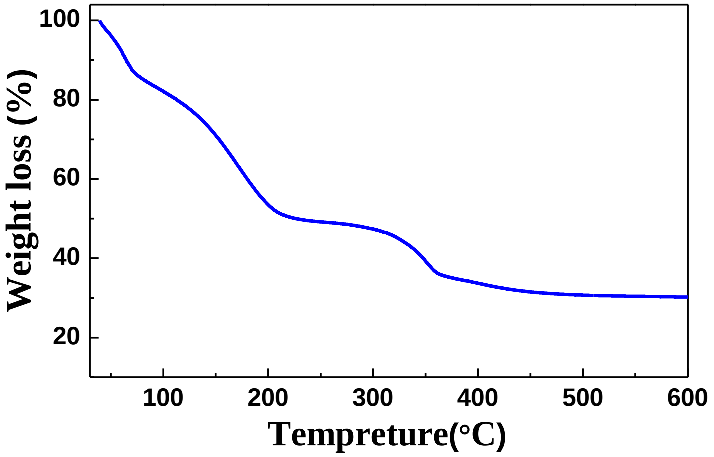


Figure S2. TGA curves of as-synthesized **ZJU-25** under a nitrogen atmosphere at a heating rate of 10 K min^{-1} .

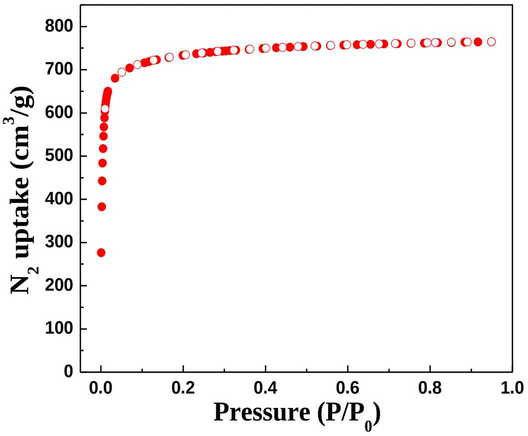


Figure S3. N_2 sorption isotherm of **ZJU-25a** at 77 K. Solid and open symbols represent adsorption and desorption, respectively.

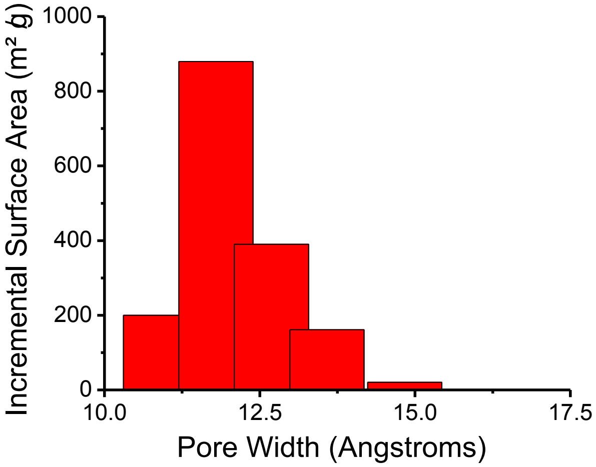


Figure S4. Pore size distributions in **ZJU-25** evaluated by DFT model from N_2 sorption isotherm at 77 K.

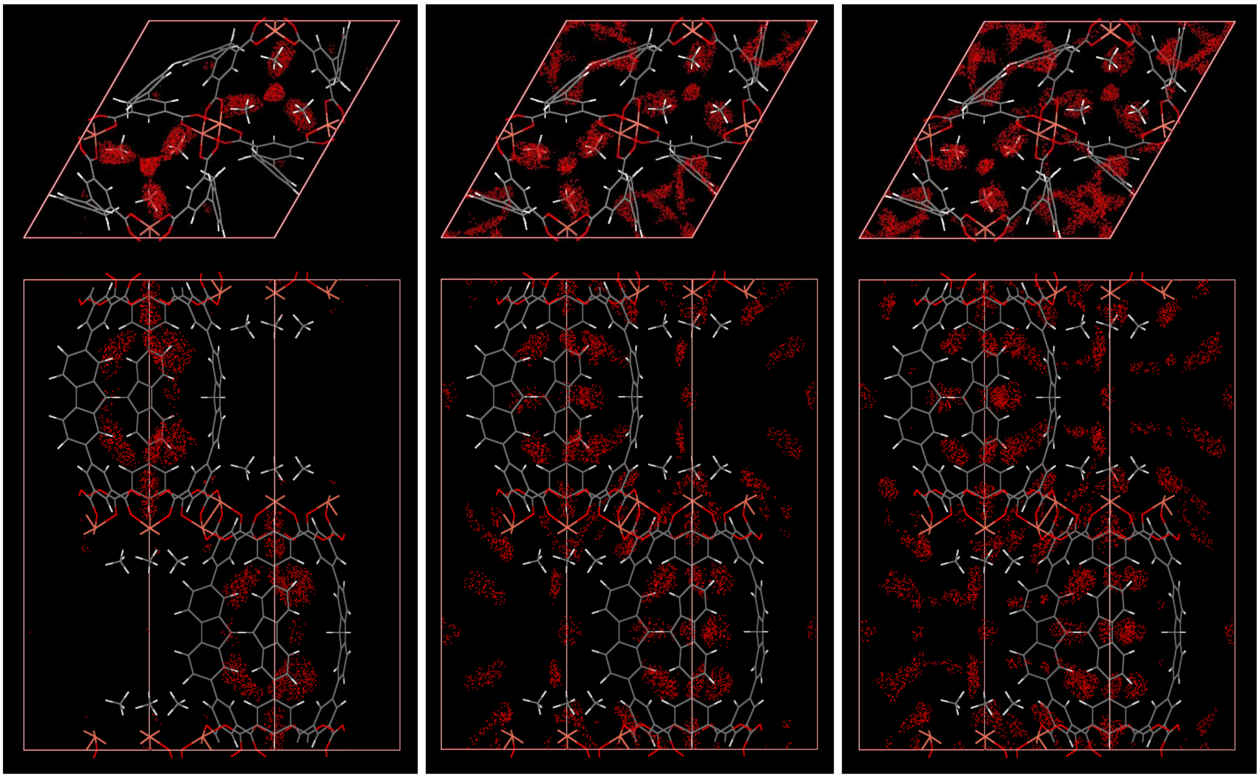
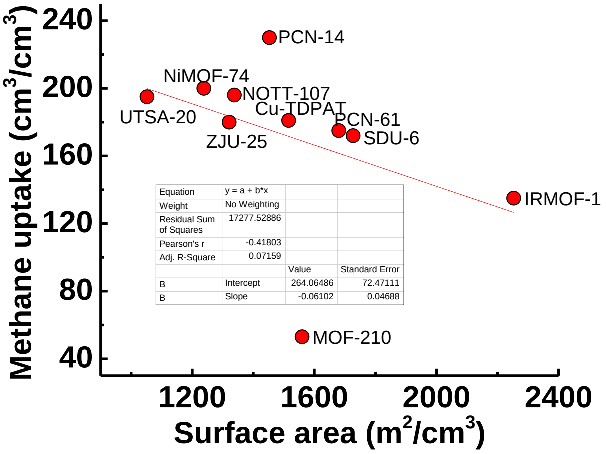


Figure S5. Probability distribution of the CH_4 center of mass in **ZJU-25** unit cell (top view and side view), obtained from GCMC simulation at 200 K and (from left to right) 0.02, 0.06, and 0.10 bar. The red regions represent the places where methane molecules are populated in the MOF structure. Note that the open-Cu site is preoccupied with CH_4 molecules in order to focus our effort on the search of other strong methane adsorption sites.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	17277.52886		
Pearson's r	-0.41803		
Adj. R-Square	0.07159		
		Value	Standard Error
B	Intercept	264.06486	72.47111
B	Slope	-0.06102	0.04688

Figure S6. Absolute volumetric methane uptake capacity at 35 bar and ambient temperature *versus* volumetric surface area in the selected porous MOFs. The solid line represents linear fitting results.

Table S1. Crystallographic data collection and refinement results for **ZJU-25.**

	ZJU-25
Chemical formula	$C_{50}H_{69}Cu_2N_7O_{18}$
Formula weight	1183.20
Temperature (K)	140(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a (Å)	18.2512(8)
b (Å)	18.2512(8)
c (Å)	34.2802(12)
V (Å^3)	9889.1(7)
Z	6
Density (calculated g/cm^3)	1.192
Absorbance coefficient (mm^{-1})	0.710
F(000)	3720
Crystal size(mm^3)	0.48x0.45x0.09
Goodness of fit on F^2	1.222
R_1, wR_2 [I>2σ(I)]	0.0696,0.1712
R_1, wR_2 (all data)	0.1067,0.1836
Largestdifference peak and hole(e/Å^3)	0.585,-0.341
CCDC	913334

Table S2 Virial coefficients employed to fit the 240 K, 270 K and 300 K CH_4 adsorption isotherm data of **ZJU-25**

Coefficient	**Value**		**Coefficient**	**Value**
a0	-1.83425544e+03		b0	6.50909111e+00
a1	3.19079349e+01		b1	-1.99553805e-01
a2	-2.81767534e+00		b2	7.12346584e-02
a3	-3.01301116e-01		b3	-8.57637940e-03
a4	2.34025398e-02		b4	5.35552949e-04
a5	-9.89230848e-04		b5	-8.97715566e-06

***Table S3*:** Comparison of the methane uptake in porous MOFs.

MOFs	S_{BET} (m^2/g)	S_{BET} (m^2/cm^3)	D_c[a] (g/cm^3)	Methane uptake[b] (cm^3/g)	Methane uptake[b] (cm^3/cm^3)	Reference
ZJU-25a	2124	1321	0.622	289	180	This work
PCN-14	1753	1453	0.829	264	230[c]	5
NiMOF-74	1027	1238	1.206	166	200	6
NOTT-107	1770	1338	0.756	259	196	7
UTSA-20	1156	1052	0.910	214	195	8
PCN-61	3000	1680	0.560	312	175	9
SDU-6	2826	1727	0.611	282	172	10
Cu-TDPAT	1938	1516	0.782	231	181	11
IRMOF-1	3800	2253	0.593	228	135	12
MOF-210	6240	1560	0.250	212	53	13

[a] framework density; [b] absolute methane uptake at 35 bar and ambient temperature; [c] 290 K.

Reference:

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