

Supporting Information

A Microporous Metal-Organic Framework with Both Open Metal and Lewis Basic Pyridyl Sites for High C₂H₂ and CH₄ Storage at Room Temperature

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1.1 Materials and Measurements

All the chemicals were commercially available and used without further purification. Dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (**1**) was synthesized according to Ref. [1]. ¹H NMR spectra were recorded on a Bruker Advance DMX 500 spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10 °C/min in N₂ atmosphere. Infrared spectrum (IR) was recorded on Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 3-40° range on an X'Pert PRO diffractometer with Cu Kα (λ = 1.542Å) radiation at room temperature.

1.2 Gas Sorption Measurements

A Micromeritics ASAP 2020 surface area analyzer was used to perform the gas sorption measurements. In order to remove guest solvent molecules in the framework, a freshly prepared sample of **ZJU-5** was exchanged with dry acetone 10 times and then activated at 373 K under high vacuum for 12 h until the outgas rate was 5 μmHg min⁻¹ prior to measurements to get the activated **ZJU-5a** for gas sorption studies. The sorption measurement was maintained at 77 K with liquid nitrogen and 273 K with ice-water bath (slush), respectively. As the center-controlled air condition was set up at 25.0 °C, a water bath of 25.0 °C was used for adsorption isotherms at 298.0 K. High-pressure CH₄ sorption isotherms were measured using a computer controlled Sieverts-type apparatus, details of which have been published elsewhere.²

Isotherm data were analysed using the virial equation⁶:

$$\ln(n/p) = A_0 + A_1n + A_2n^2 + \dots$$

where the *p* is pressure, *n* is the amount adsorbed, and *A*₀, *A*₁, etc., are virial coefficients.

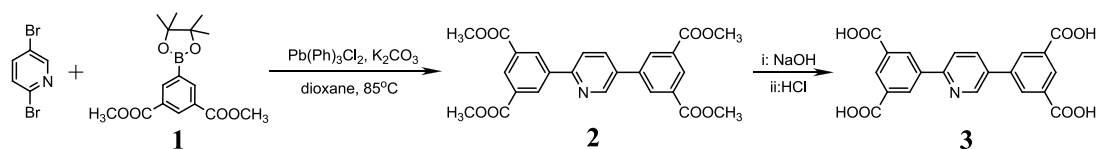
1.3 X-ray Collection and Structure Determination

Crystallographic measurements for **ZJU-5** were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Mo K_α radiation (λ = 0.71073Å) at 293 K. The determination of the unit cell and data collection for the crystal of **ZJU-5** was performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.³

The structure of ZJU-5 was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package.⁴ All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The central ring of the PDDI component is disordered, which was refined as disordered model with occupancies of 0.375 for C7, 0.125 for N1, 0.375 for C7' and 0.125 for N1'. The three disordered lattice DMF and four water molecules could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package.⁵ The resulting new files were used to further refine the structure. The composition of the as-synthesized **ZJU-5** was figured out based on the elemental analysis, TGA and single crystal structure. The lattice molecules were added to account for the formula in the CIF file. H atoms on benzene C atoms of PDDI were generated geometrically, while H atoms on the C atoms of the disordered central PDDI ring were not generated. Crystallographic data are summarized in Table S1.

1.4 Synthesis of the organic linker H₄PDDI

H₄PDDI was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in Scheme S1.



Scheme S1. Synthetic route to the organic linker H₄PDDI used to construct **ZJU-5**.

Tetramethyl 5,5'-(pyridine-2,5-diyl)diisophthalate (2): 2,5-dibromopyridine (3.54 g, 15 mmol), **1** (14.41 g, 45 mmol) and K_2CO_3 (27.8 g, 200 mmol) were mixed in 1,4-dioxane (100 mL), and the mixture was purged with argon and stirred for half an hour at room temperature. Then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.30 g, 0.4 mmol) was added and the mixture heated at 85°C for 24 h under argon. The resultant mixture was extracted with water and CHCl_3 , and the water phase was then removed. Organic solvent was removed under reduced pressure, and the crude product was purified with toluene recrystallization to obtain pure tetramethyl 5,5'-(pyridine-2,5-diyl)diisophthalate (**2**, 5.48g). Yield: 79%. ¹H NMR (500 MHz, CDCl_3), δ = 4.02 (s, 12 H), 8.01 (d, 1H), 8.12 (d, 1H), 8.53 (s, 2H), 8.78 (d, 2H), 8.96 (s, 2H), 9.05 (s, 1H) ppm. Anal. Calcd for $\text{C}_{25}\text{H}_{21}\text{O}_8$: C, 64.79; H,

4.57; N, 3.02. Found: C, 64.49; H, 4.54; N, 2.98.

5,5'-(pyridine-2,5-diyl)diisophthalic acid (H₄PDDI, 3): **2** (4.63 g, 10 mmol) was then suspended in a mixture of THF (20 mL) and H₂O (50 mL), to which 100 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF was removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration, washed with water, and dried to give H₄PDDI (3.93 g, 96.5% yield). ¹H NMR (500 MHz, CDCl₃): δ = 8.53 (d, 1H), 8.56 (s, 1H), 8.58 (d, 2H), 8.63 (s, 1H), 8.83 (d, 2H), 8.87 (d, 1H), 9.29 (s, 1H). Anal. Calcd for C₂₁H₁₃NO₈: C, 61.92; H, 3.22; N, 3.44. Found: C, 61.31; H, 3.68; N, 3.41.

1.5 Synthesis of ZJU-5:

A mixture of H₄PDDI (15 mg, 0.037 mmol) and Cu(NO₃)₂(H₂O)_{2.5} (30 mg, 0.129 mmol) was dissolved in DMF/H₂O/MeCN (8 mL, 6:1:1, v/v) in a screw-capped vial. After HCl (50 μL) (37%, aq.) were added to the mixture, the vial was capped and placed in an oven at 80°C for 72 h. The resulting rhombic prism shaped single crystals were washed with DMF several times to give **ZJU-5** (28 mg, 78% yield base on H₄PDDI). Elemental analysis: Calcd. For [Cu₂(C₂₁H₉NO₈)(H₂O)₂](DMF)₄(H₂O)₆ (C₃₃H₅₃N₅O₂₀Cu₂, %): C, 40.99; H, 5.53; N, 7.24; Found: C, 40.94; H, 5.27; N, 7.38. IR (KBr, cm⁻¹): 3422(s), 2363(w), 1624(s), 1559(s), 1448(m), 1377(s), 1306(w), 1090(w), 773(m), 727(m), 474(w).

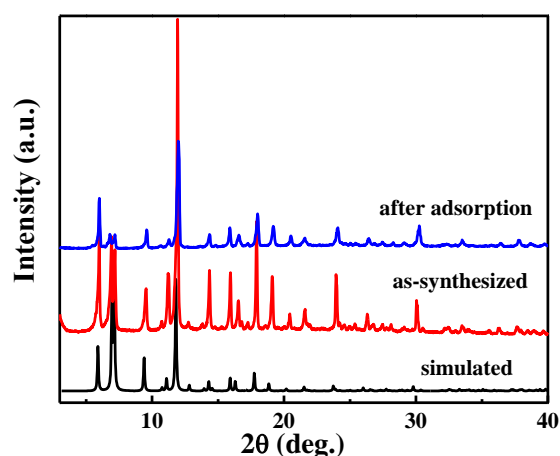


Figure S1. PXRD patterns of as-synthesized **ZJU-5** (red) and the simulated XRD pattern from the single-crystal X-ray structure (black) and XRD pattern of the sample after absorption (blue).

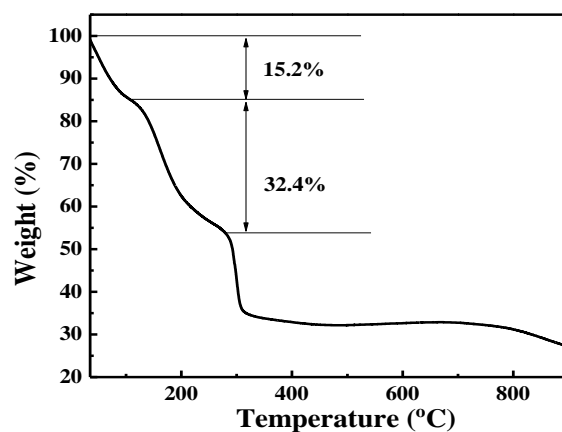


Figure S2. TGA curves of as-synthesized **ZJU-5** under a nitrogen atmosphere at a heating rate of 10 K min⁻¹.

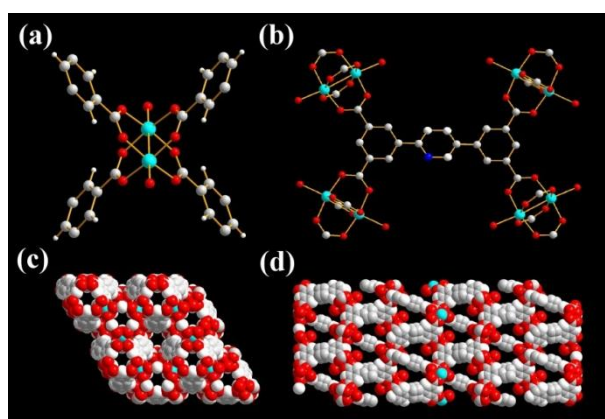


Figure S3. X-ray single crystal structure of **ZJU-5** indicating (a) the 4-connected $\{\text{Cu}_2(\text{O}_2\text{CR})_4\}$ paddle-wheel unit; (b) each tetracarboxylate ligand connects with four paddle-wheel $\text{Cu}_2(\text{COO})_4$ clusters; (c) the hexagonal channels viewed along the c axes; (d) triangular windows viewed along the a axes.

Table S1 Crystallographic Data collection and Refinement result for **ZJU-5**.

| ZJU-5 | |
|--|--|
| chemical formula | C ₃₀ H ₄₂ Cu ₂ N ₄ O ₁₇ |
| formula weight | 857.76 |
| temperature (K) | 293(2) |
| wavelength (Å) | 0.71073 |
| crystal system | Trigonal |
| space group | R-3m |
| <i>a</i> (Å) | 18.8163(13) |
| <i>b</i> (Å) | 18.8163(13) |
| <i>c</i> (Å) | 38.079(4) |
| <i>α</i> (°) | 90 |
| <i>β</i> (°) | 90 |
| <i>γ</i> (°) | 120 |
| <i>V</i> (Å ³) | 11675.7(16) |
| <i>Z</i> | 9 |
| density (calculated g/cm ³) | 1.098 |
| absorbance coefficient (mm ⁻¹) | 0.876 |
| <i>F</i> (000) | 3996 |
| crystal size (mm ³) | 0.45 × 0.32 × 0.22 |
| goodness of fit on <i>F</i> ₂ | 1.086 |
| R1, wR2 (I > 2σ(I)) ^a | 0.0935, 0.2063 |
| R1, wR2 (all data) ^a | 0.1297, 0.2233 |
| largest difference peak and hole (e/Å ³) | 1.035, -0.606 |

^aR1 = Σ(|*F*_o| - |*F*_c|) / Σ|*F*_o|; wR2 = [Σw(|*F*_o| - |*F*_c|)² / Σw*F*_o²]^{1/2}.

Table S2. Comparison of some microporous MOFs for acetylene storage (at 298 K and 1 atm)

| Material | <i>S</i> _{BET} (<i>S</i> _{Langmuir}) [m ² g ⁻¹] | <i>V</i> _p ^a [cm ³ g ⁻¹] | <i>D</i> _c ^b [g cm ⁻³] | C ₂ H ₂ uptake [cm ³ g ⁻¹]([cm ³ cm ⁻³]) | <i>d</i> ^c [g cm ⁻³] | -Δ <i>H</i> ^e [kJ mol ⁻¹] | Ref. |
|---------------|---|--|---|--|--|---|-----------|
| ZJU-5a | 2823(3118) | 1.074 | 0.679 | 193(131) | 0.21 | 37.0 | This work |
| HKUST-1 | 1401(2095) | 0.76 | 0.879 | 201(177) | 0.21 | 30.4 | 7 |
| MOF-505 | 1139(1694) | - | 0.927 | 148(137) | 0.16 | 24.7 | 7 |
| CoMOF-74 | 1018(1504) | - | 1.169 | 197(230) | 0.27 | 50.1 | 8 |
| MnMOF-74 | 695(993) | - | 1.085 | 168(182) | 0.21 | 39.0 | 8 |
| MgMOF-74 | 927(1364) | - | 0.909 | 184(167) | 0.19 | 34.0 | 8 |
| FeMOF-74 | 1350 | 0.63 | 1.126 | 156(176) | 0.20 | 47.0 | 9 |
| PCN-16 | (2810) | 1.00 | 0.718 | 176(126) | 0.15 | 44.2 | 10 |
| NOTT-101 | (2930) | 1.05 | 0.684 | 184(126) | 0.15 | 37.1 | 10 |

| | | | | | | | |
|--------------------------------|------------|------|-------|----------|------|------|----|
| NOTT-102 | (3590) | 1.28 | 0.587 | 146(86) | 0.10 | - | 10 |
| UTSA-20 | (1894) | 0.67 | 0.910 | 150(136) | 0.16 | 30.8 | 10 |
| UTSA-34b | 991(1532) | 0.54 | 0.840 | 121(102) | 0.12 | 50.0 | 11 |
| Cu ₂ (ebtc) | 1852(2844) | 1.00 | 0.718 | 160(115) | 0.13 | 34.5 | 12 |
| Cu ₄ L ^d | 1115(1722) | 0.61 | 0.833 | 154(128) | 0.15 | - | 13 |

^a Pore volume. ^b Crystal density calculated from the single-crystal structure without molecules and terminal ligands. ^c Density of adsorbed acetylene in bulk material. ^d H₈L = tetrakis[(3,5-dicarboxyphenoxy)methyl]methane. ^e Isothermic heats of adsorption at low coverage.

Table S3. Comparison of some microporous MOFs for the high-pressure methane storage (at 298-300 K and 35 atm)

| Material | S_{BET} (S_{Langmuir}) [m ² g ⁻¹] | V_p^a [cm ³ g ⁻¹] | D_c^b [g cm ⁻³] | CH ₄ uptake ^d [cm ³ g ⁻¹]([cm ³ cm ⁻³]) | d^c [g cm ⁻³] | $-\Delta H^e$ [kJ mol ⁻¹] | Ref. |
|-------------------------|---|---|----------------------------------|---|--------------------------------|--|-----------|
| ZJU-5a | 2823(3118) | 1.074 | 0.679 | 280(190) | 0.19 | 15.3 | This work |
| PCN-11 | 1931(2442) | 0.91 | 0.749 | 228(171) ^g | 0.18 | 14.6 | 14 |
| PCN-14 | 1753(2176) | 0.87 | 0.871 | 264(230) ^f | 0.21 | 30.0 | 15 |
| PCN-61 | 3000(3500) | 1.36 | 0.560 | 312(175) | 0.16 | | 16 |
| NOTT-107 | 1770 | | 0.756 | 259(196) | | | 17 |
| CoMOF-74 | 1018(1504) | | 1.169 | 149(174) ^g | 0.22 | 19.6 | 18 |
| NiMOF-74 | 1027 | | 1.206 | 166(200) | 0.26 | 20.2 | 18 |
| MIL-53(Al) | 1235(1627) | 0.54 | | (186) | | | 19 |
| UTSA-20 | 1156(1894) | 0.67 | 0.910 | 214(195) | 0.22 | 17.7 | 20 |
| SNU-50' | 2300(2450) | 1.08 | 0.650 | 267(173) ^g | 0.18 | 26.8 | 21 |
| SDU-6 | 2826 | 1.17 | 0.611 | 282(172) | 0.17 | | 22 |
| HKUST-1 | 1502(2216) | 0.76 | 0.880 | 200(176) ^g | 0.19 | | 23 |
| Cu ₃ (tdpat) | 1938(2608) | 0.93 | 0.782 | 231(181) | 0.18 | | 24 |

^a Pore volume. ^b Crystal density calculated from the single-crystal structure without molecules and terminal ligands. ^c Density of adsorbed acetylene in bulk material. ^d absolute, at ambient temperature and 3.5MPa. ^e Isothermic heats of adsorption at low coverage. ^f At 290 K. ^g Excess

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