

## High methane storage and working capacities in a NbO-type metal-organic framework

Chengling Song,<sup>a</sup> Huimin Liu,<sup>a</sup> Jingjing Jiao,<sup>a</sup> Dongjie Bai,<sup>a</sup> Wei Zhou,<sup>b</sup> Taner Yildirim<sup>bc</sup> and Yabing He<sup>a\*</sup>

<sup>a</sup> College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: [heyabing@zjnu.cn](mailto:heyabing@zjnu.cn)

<sup>b</sup> NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102, USA

<sup>c</sup> Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, USA

### 1. General Remarks

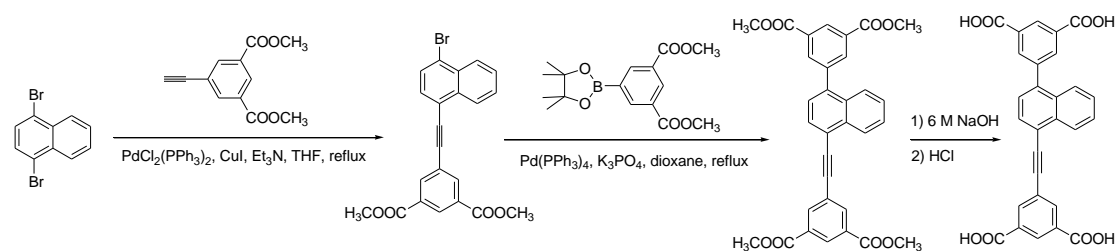
All starting materials and reagents are commercially available and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured at room temperature in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> with a Bruke AV400 or AV600 spectrometer. Chemical shifts are given in ppm with use of residual solvent as an internal standard for <sup>1</sup>H ( $\delta_{\text{CDCl}_3} = 7.26$  ppm,  $\delta_{\text{DMSO-}d_6} = 2.50$  ppm) and <sup>13</sup>C spectra ( $\delta_{\text{CDCl}_3} = 77.16$  ppm,  $\delta_{\text{DMSO-}d_6} = 39.52$  ppm). Coupling constants are reported in Hz. Fourier transform infrared (FTIR) spectra were acquired *via* a Nicolet 5DX FT-IR spectrometer with KBr discs in 4000-400 cm<sup>-1</sup> range. Elemental analyses (C, H, and N) were measured by a Perkin–Elmer 240 CHN analyzers. Thermogravimetric analyses (TGA) were collected using a Netzsch STA 449C thermal analyzer at 25-800 °C range with a heating rate of 5 °C min<sup>-1</sup> in a flowing nitrogen atmosphere (10 mL min<sup>-1</sup>). Powder X-ray diffraction (PXRD) patterns were carried out by a Philips PW3040/60

automated powder diffractometer, using Cu-K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) with a  $2\theta$  range of 5–45 °. A micromeritics ASAP 2020 HD88 surface area analyzer was used to obtain N<sub>2</sub> sorption isotherms at 77 K, which is maintained by a liquid nitrogen bath. To have a guest-free framework, the fresh sample was guest-exchanged with dry acetone at least 10 times, filtered and vacuumed at 373 K until the outgas rate was 3  $\mu\text{mHg min}^{-1}$  prior to measurements. High-pressure methane sorption measurements were performed at the Center for Neutron Research, National Institute of Standards and Technology (NIST) using a computer-controlled Sieverts apparatus, detail of which can be found in a previous publication.<sup>1</sup> Research-grade methane was used for high-pressure measurements with purity of 99.999%.

## 2. Single-crystal X-ray Crystallography

The crystal data were collected on a Bruker Apex II CCD diffractometer equipped with a graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K. 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. There are large solvent accessible void volumes in the crystals which are occupied by highly disordered DMF, and H<sub>2</sub>O molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities. The SQUEEZE function of the program PLATON reveals a residual electron density of 2283 electrons/cell ( $Z = 9$ ) in cell-remaining voids where the residual electron density was tentatively assigned to 6 DMF and 2 H<sub>2</sub>O. The numbers of solvents were also proved by the TGA. Structures were then refined again using the data generated. Due to the asymmetry of the ligand, the naphthalene ring and the triple bond are position disordered. In order to give an intuitive asymmetric unit and easy to understand, the occupancies of the ring and triple bond atoms are adjusted to 10.25 according to the formula of the asymmetric unit. CCDC 1407440 contains the supplementary crystallographic data for ZJNU-53. The data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html).

### 3. Synthesis and characterization of the organic linker



**Scheme S1** Synthetic route to the organic linker H<sub>4</sub>L used to construct **ZJNU-53**.

#### Dimethyl

#### 5-(2-(4-bromonaphthalen-1-yl)ethynyl)isophthalate:

1,4-dibromonaphthalene (1.00 g, 3.50 mmol), dimethyl 5-ethynylisophthalate (0.92 g, 4.20 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.123 g, 0.17 mmol), and CuI (0.0333 g, 0.17 mmol) were placed in a 250-mL flask. The flask was evacuated and refilled with nitrogen. The process was repeated with three times. A mixed solvent of triethylamine and THF (40 mL/40 mL) was added by syringe. The resulting mixture was refluxed under nitrogen for 48 h and then cooled to room temperature. The solvent was removed by ratio-evaporation, and the residue was extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous MgSO<sub>4</sub>, and filtered. The solvent was removed by ratio-evaporation, and the residue was purified with silica gel column chromatography with petroleum ether/dichloromethane (2/5, v/v) as eluent, affording dimethyl 5-(2-(4-bromonaphthalen-1-yl)ethynyl)isophthalate as a white solid (0.35 g, 0.83 mmol) in 24% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.1 MHz)  $\delta$  (ppm): 8.699 (t, *J* = 1.8 Hz, 1H), 8.499 (d, *J* = 1.8 Hz, 2H), 8.450-8.475 (m, 1H), 8.313-8.336 (m, 1H), 7.826 (d, *J* = 7.8 Hz, 1H), 7.690-7.734 (m, 2H), 7.651 (d, *J* = 7.8 Hz, 1H), 4.023 (s, 6H).

**Tetramethyl 5,5'-(naphthalene-1,4-diyl-ethyne-1,2-diyl) diisophthalate:** dimethyl 5-(2-(4-bromonaphthalen-1-yl)ethynyl)isophthalate (0.35 g, 0.83 mmol), dimethyl 5-(pinacolboron)isophthalate (0.32 g, 0.99 mmol), K<sub>3</sub>PO<sub>4</sub> (0.42 g, 1.98 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.048 g, 0.041 mmol) were placed in a 250-mL flask, which was evacuated and refilled with nitrogen. The process was repeated three times. 60 mL of dioxane was added by syringe. The mixture was heated under reflux at nitrogen for 48 h and cooled to room temperature. After removal of the solvents, CH<sub>2</sub>Cl<sub>2</sub> (80 mL) and

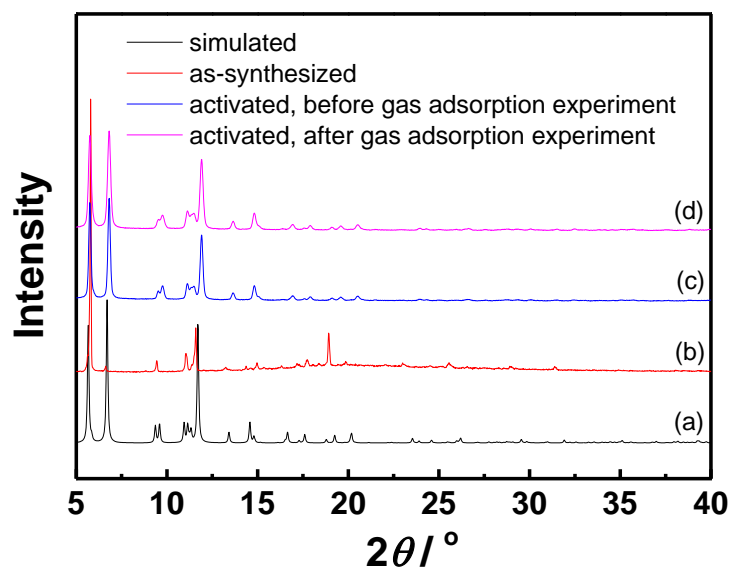
H<sub>2</sub>O (80 mL) were added. The organic phase was separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was combined, and washed with brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was ratio-evaporated, and the residue was purified by silica gel column chromatography with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (2/5, v/v) as eluent, affording tetramethyl 5,5'-(naphthalene-1,4-diyl-ethyne-1,2-diyl) diisophthalate as a white solid in 57% yield (0.25 g, 0.47 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz)  $\delta$  (ppm): 8.809 (t, *J* = 1.6 Hz, 1H), 8.705 (t, *J* = 1.6 Hz, 1H), 8.568 (d, *J* = 8.4 Hz, 1H), 8.531 (d, *J* = 1.6 Hz, 2H), 8.402 (d, *J* = 1.6 Hz, 2H), 7.886 (d, *J* = 7.6 Hz, 1H), 7.815 (d, *J* = 8.4 Hz, 1H), 7.708 (m, 1H), 7.566 (m, 1H), 7.473 (d, *J* = 7.2 Hz, 1H), 4.029 (s, 6H), 4.004 (s, 6H).

**5,5'-(naphthalene-1,4-diyl-ethyne-1,2-diyl) diisophthalic acid (H<sub>4</sub>L):** To the tetramethyl ester intermediate (0.25 g, 0.47 mmol) in a mixed solvent of THF (20 mL) and methanol (20 mL) was added 6 M NaOH (20 mL, 120 mmol). The resulting solution was heated under reflux overnight and cooled to room temperature. After the solvent was removed by ratio-evaporation, the residue was dissolved in H<sub>2</sub>O, and acidified with concentrated HCl under ice-water bath. The precipitation was filtered, washed with water, and dried under vacuum at 70 °C, affording the target compound as a white solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600.1 MHz)  $\delta$  (ppm): 8.599-8.581 (m, 2H), 8.508 (t, *J* = 1.8 Hz, 1H), 8.443 (d, *J* = 1.8 Hz, 2H), 8.247 (d, *J* = 1.8 Hz, 2H), 8.034 (d, *J* = 7.2 Hz, 1H), 7.833-7.793 (m, 2H), 7.673 (t, *J* = 7.2 Hz, 1H), 7.620 (d, *J* = 7.2 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 150.9 MHz): 166.911, 166.433, 140.506, 139.508, 136.132, 134.699, 133.240, 132.747, 132.355, 131.200, 130.876, 130.433, 129.772, 128.178, 127.459, 126.814, 125.958, 123.720, 120.084, 93.548, 89.127; Selected FTIR (KBr, cm<sup>-1</sup>): 1701, 1597, 1448, 1406, 1267, 1217, 837, 760, 669.

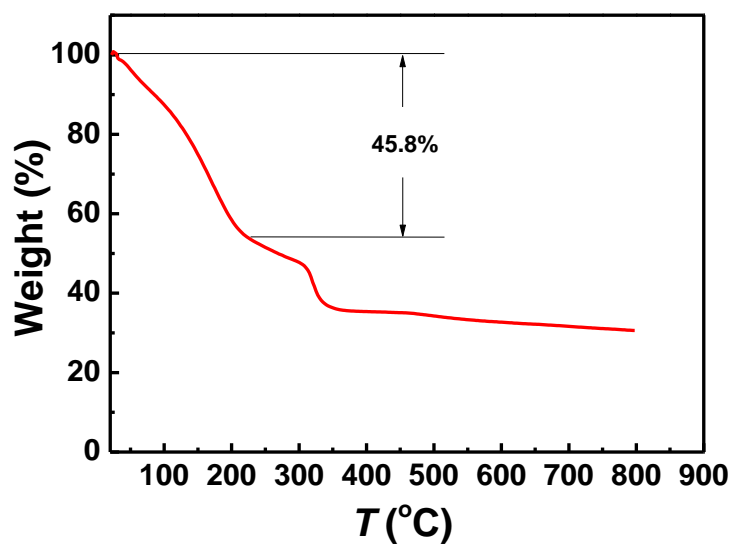
#### 4. Synthesis and characterization of ZJNU-53

A mixture of the organic linker H<sub>4</sub>L (5.0 mg, 10.4  $\mu$ mol) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (15.0 mg, 62.1  $\mu$ mol) was dissolved into a mixed solvent of *N,N*-dimethylformamide (DMF), methanol and H<sub>2</sub>O (1.5 mL / 0.5 mL / 0.08 mL) in a screw-capped vial (20 mL). 50  $\mu$ L of 6 M HCl were then added. The vial was capped and heated at 353 K for

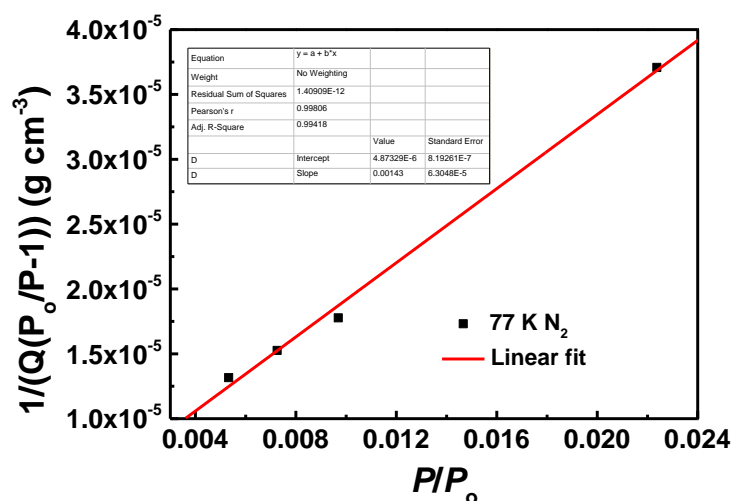
22 h. Blue rhombic crystals were obtained in 51% yield. Selected FTIR (KBr,  $\text{cm}^{-1}$ ): 1655, 1571, 1432, 1371, 1255, 1099, 1047, 775, 729; anal. for  $\text{C}_{46}\text{H}_{62}\text{Cu}_2\text{N}_6\text{O}_{18}$ , calcd: C, 49.59%, H, 5.61%, N, 7.54%; found: C, 49.62%, H, 5.57%, N, 7.45%.



**Fig. S1** PXRD patterns: (a) simulated from its cif file, (b) as-synthesized **ZJNU-53**, (c) activated **ZJNU-53a**, before gas adsorption experiment, and (d) activated **ZJNU-53a**, after gas adsorption experiment.

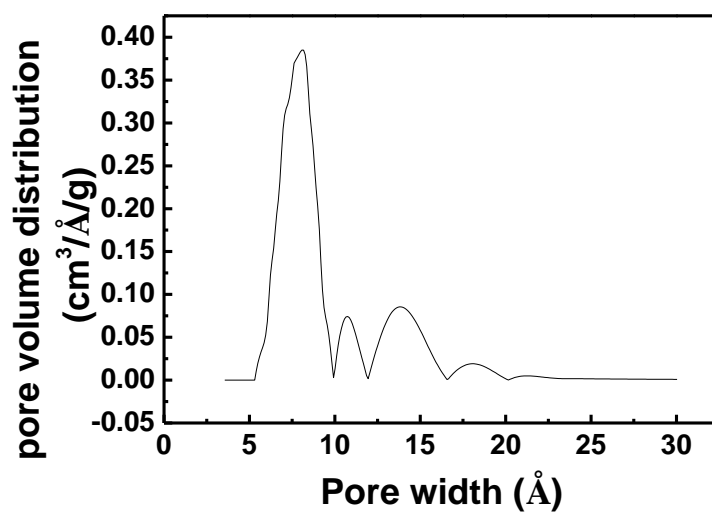


**Fig. S2** TGA curve of **ZJNU-53** at a nitrogen atmosphere with a heating rate of 5  $^\circ\text{C min}^{-1}$ . A weight loss of 45.8% up to 498 K corresponds to the loss of free solvent molecules and terminal water molecules ( $6\text{DMF}+4\text{H}_2\text{O}$ ).

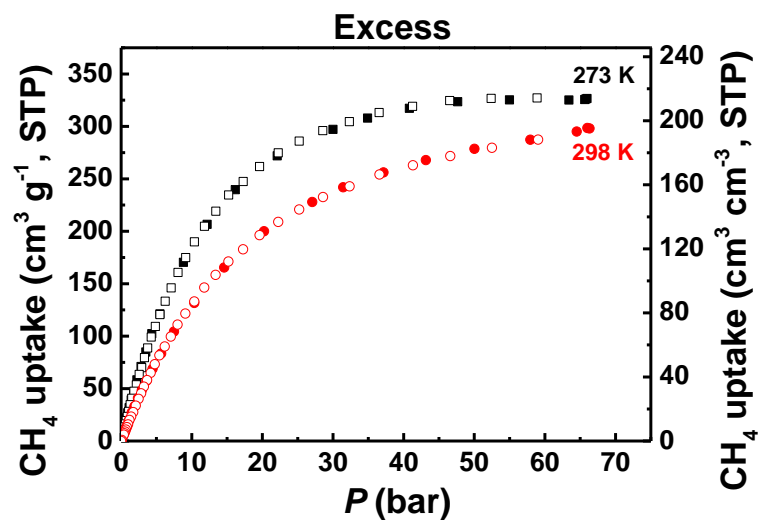


$$S_{\text{BET}} = 1/(4.87329 \times 10^{-6} + 0.00143)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 3034 \text{ m}^2 \text{ g}^{-1}$$

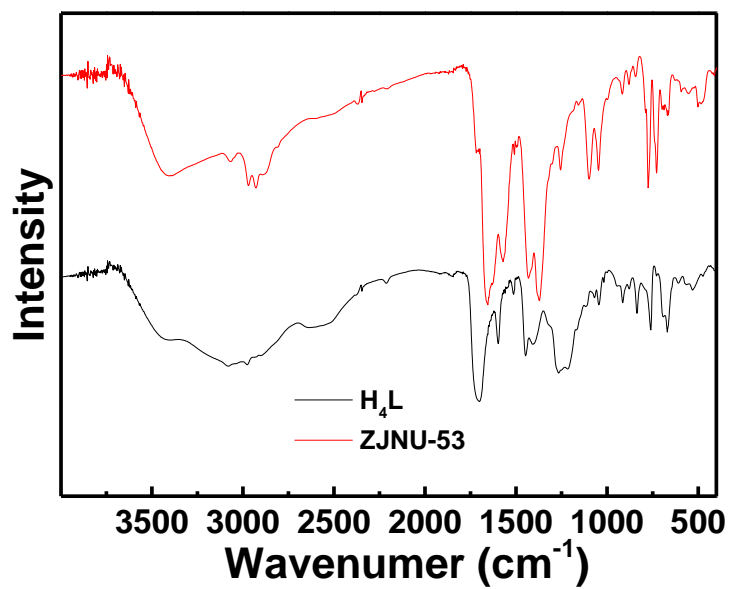
**Fig. S3** BET plot. Note that the BET surface area was determined using the consistency criteria reported by Rouquerol *et al.* on a nitrogen isotherm at 77 K.



**Fig. S4** Pore size distribution of **ZJNU-53a**, derived from the 77 K N<sub>2</sub> isotherm, based on the NLDFT model.

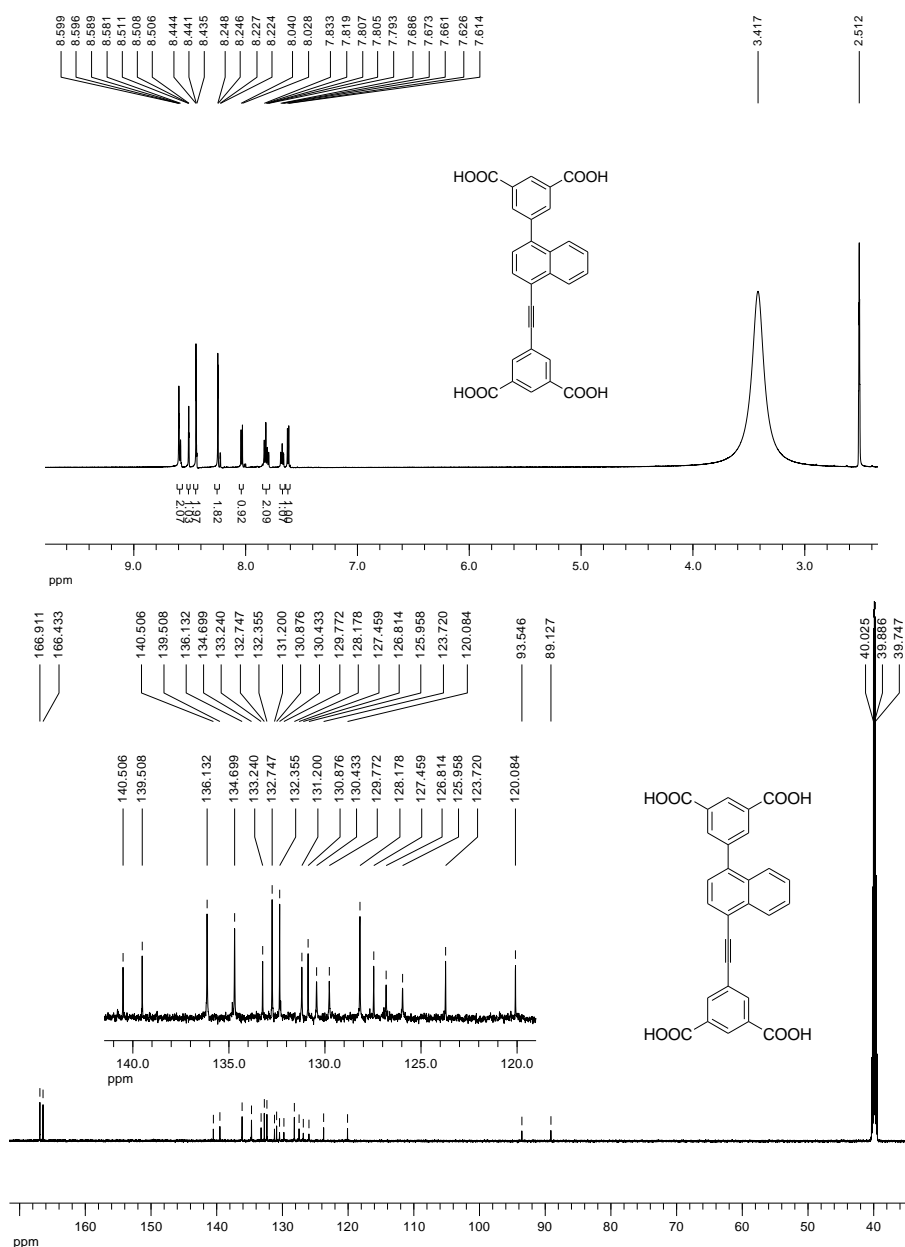


**Fig. S5** High-pressure excess methane adsorption isotherms of **ZJNU-53a** at 273 K and 298 K.

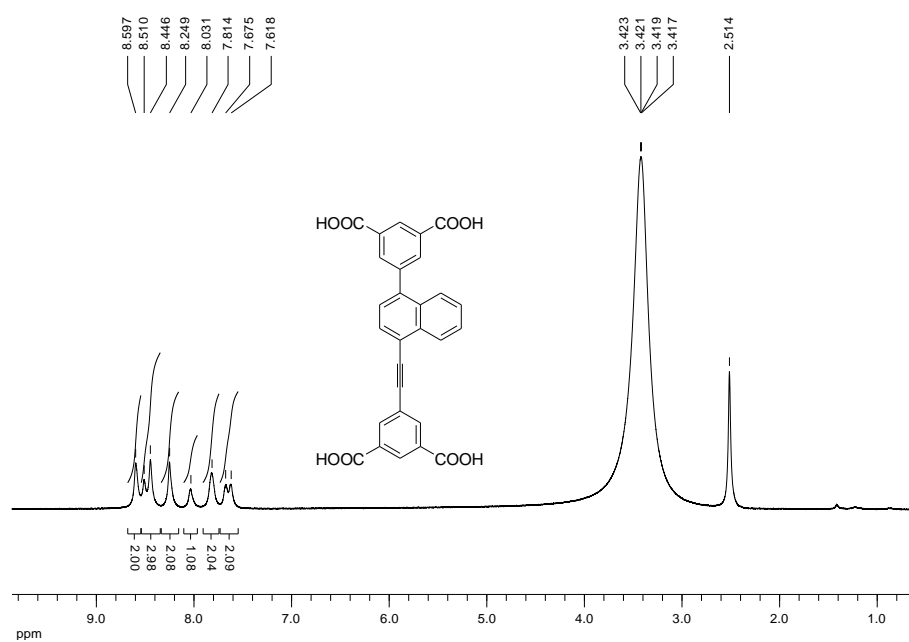


**Fig. S6** FTIR spectra of the organic linker (black) and the as-synthesized **ZJNU-53** (red).





**Fig. S7**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the organic linker  $\text{H}_4\text{L}$  in  $\text{DMSO-}d_6$



**Fig. S8**  $^1\text{H}$  NMR spectra of the acid-digested sample in  $\text{DMSO}-d_6$

**Table S1** Crystal data and structure refinement for **ZJNU-53**.

Empirical formula	C <sub>28</sub> H <sub>16</sub> Cu <sub>2</sub> O <sub>10</sub>
Formula weight	639.49
Temperature (K)	100(2)
Wavelength (Å)	1.54184
Crystal system	Trigonal
Space group	<i>R</i> -3m
Unit cell dimensions	$a = 18.4039(2) \text{ Å}$ $b = 18.4039(2) \text{ Å}$ $c = 46.9176(12) \text{ Å}$ $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 120^\circ$
Volume (Å <sup>3</sup> )	13762.1(4)
<i>Z</i>	9
Calculated density (g cm <sup>-3</sup> )	0.694
Absorption coefficient (mm <sup>-1</sup> )	1.080
<i>F</i> (000)	2898
$\theta$ range for data collection (°)	3.35 to 66.53
Limiting indices	$-16 \leq h \leq 21$ , $-21 \leq k \leq 21$ , $-51 \leq l \leq 55$
Reflections collected / unique	16512 / 2980
<i>R</i> <sub>int</sub>	0.0177
Completeness to $\theta = 25.02$	99.8 %
Absorption correction	Empirical
Max. and min. transmission	0.8814 and 0.7741
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	2980 / 260 / 222
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.436
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0700, <i>wR</i> <sub>2</sub> = 0.2456
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0765, <i>wR</i> <sub>2</sub> = 0.2617
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.973 and -0.650
CCDC	1407440

**Disclaimer:** Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

