# A NbO-type Metal-Organic Framework Exhibiting High Deliverable Capacity for Methane Storage

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### 1. Materials and General Methods

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- $d_6$  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,  $\delta_{\text{DMSO-}d6}$  = 2.50 ppm) and <sup>13</sup>C spectra ( $\delta_{\text{CDCl}^3}$  = 77.16 ppm,  $\delta_{\text{DMSO-d6}}$  = 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 Xray diffraction (PXRD) patterns were carried out by a Philips PW3040/60 automated powder diffractometer, using Cu-K<sub>a</sub> radiation ( $\lambda = 1.542$  Å) with a 2 $\theta$  range of 5–45°. A micromeritics ASAP 2020 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 6  $\mu$ mHg min<sup>-1</sup> 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. X-ray Crystallography

The crystal data were collected on a Bruker Apex II CCD diffractometer equipped with a graphite-monochromatized Mo-K<sub>a</sub> radiation ( $\lambda = 0.71073$  Å) 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.<sup>2</sup> 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<sup>3</sup> program implemented in PLATON was used to remove these electron densities. The SQUEEZE function of the program PLATON reveals a residual electron density of 2628 electrons/cell (Z = 18) in cell-remaining voids where the residual electron density was tentatively assigned to 3 DMF and 3.5 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 benzene 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 1058417 contains the supplementary crystallographic data for ZJNU-50. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

#### 3. Synthesis and Characterization of the Organic Linker



*Scheme S1.* The synthetic route to the organic linker H<sub>4</sub>L.

**5-bromoisophthalic acid**: Isophthalic acid (20.00 g, 0.12 mol) was taken up in concentrated H<sub>2</sub>SO<sub>4</sub> (60 mL) and heated to 60 °C. To this was added NBS (25.71 g, 0.14 mol) in three portions each in 20 min. When the mixture was stirred at this temperature for 24 h, the mixture was poured into crushed ice. The resulting precipitation was collected by filtration, washed with water, and dried under vacuum at 70 °C. The product was purified by recrystallization with ethyl acetate, affording 5-bromoisophthalic acid as a white solid in 67.3% yield (19.80 g, 80.81 mol). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 600.1 MHz)  $\delta$  (ppm): 13.673 (s, br, 1H), 8.420 (t, *J* = 1.2 Hz, 1H), 8.258 (d, *J* = 1.2 Hz, 2H).

**Dimethyl 5-bromoisophthalate**: To 5-bromoisophthalic acid (19.80 g, 80.81 mol) in methanol (300 mL) was added concentrated H<sub>2</sub>SO<sub>4</sub> (15 mL). The mixture was refluxed for 24 h, and then cooled to room temperature. After the solvent was ratoevaporated, CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and H<sub>2</sub>O (100 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, washed with saturated NaHCO<sub>3</sub> solution and brine sequentially, dried over anhydrous MgSO<sub>4</sub> and filtered. The volatile was removed by rato-evaporation, and residue was recrystallized with methanol to give pure dimethyl 5-bromoisophthalate as a white solid in 95.6% yield (21.10 g, 77.27 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz)  $\delta$  (ppm): 8.627 (t, *J* = 1.6 Hz, 1H), 8.376 (d, *J* = 1.6 Hz, 2H), 3.980 (s, 6H).

**Dimethyl 5-(pinacolboryl)isophthalate:** Dimethyl 5-bromoisophthalate (10.00 g, 36.62 mmol), B<sub>2</sub>Pin<sub>2</sub> (10.23 g, 40.28 mmol), KOAc (10.78 g, 109.86 mmol), and Pd(dppf)Cl<sub>2</sub> (0.81 g, 1.09 mmol) were placed in a 500 mL round-bottom flask. The flask was evacuated and refilled with N<sub>2</sub> three times. The dry dioxine (300 mL) was added *via* syringe. The mixture was heated at 80 °C for 24 h, and then cooled to room temperature. The solvent was rato-vaporated, and CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and H<sub>2</sub>O (200 mL) was 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, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and filtered. After removal of the solvent, the residue was purified using silica gel column chromatography with petroleum ether/ethyl acetate (10/1, *v/v*) as eluent to afford dimethyl 5-(pinacolboryl)isophthalate as a white solid in 92% yield (10.80 g, 33.69 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz)  $\delta$  (ppm): 8.788 (t, *J* = 1.6 Hz, 1H), 8.657 (d, *J* = 1.6 Hz, 2H), 3.970 (s, 6H), 1.388 (s, 12H).

5-(2-(trimethylsilyl)ethynyl)isophthalate: Dimethyl Dimethyl 5bromoisophthalate (10.00 g, 36.62 mmol), CuI (0.35 g, 1.83 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (1.28 g, 1.83 mmol) were placed in a 500 mL round-bottom flask. The flask was evacuated under vacuum and refilled with N<sub>2</sub> for three times, and then ethynyltrimethylsilane (7.6 mL, 54.93 mmol), dry THF (200 mL) and triethylamine (7.7 mL, 54.93 mmol) were added via syringe sequentially. The resulting solution was stirred under nitrogen at room temperature for 24 h. After removal of the volatile, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and H<sub>2</sub>O (100 mL) was 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, washed with brine, dried over anhydrous MgSO4 and filtered. The solvent was ratoevaporated, and the residue was purified using silica gel column chromatography with petroleum ether/ethyl acetate (30/1, v/v) as eluent, affording dimethyl 5-(2-(trimethylsilyl)ethynyl)isophthalate as a yellow solid in 98.7% yield (10.50 g, 36.16 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz)  $\delta$  (ppm): 8.626 (t, J = 1.6 Hz, 1H), 8.315 (d, J= 1.6 Hz, 2H), 3.972 (s, 6H), 0.288 (s, 9H).

**Dimethyl 5-ethynylisophthalate**: A mixture of dimethyl 5-(2-(trimethylsilyl)ethynyl)isophthalate (10.50 g, 36.16 mmol),  $K_2CO_3$  (1.00 g, 7.20 mmol) in a mixed solvent of THF (80 mL) and MeOH (200 mL) was stirred under a

nitrogen atmosphere at room temperature for 24 hrs. After that, the solvent was removed by rato-evaporation. CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and H<sub>2</sub>O (100 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, washed with brine, dried over anhydrous MgSO<sub>4</sub> and filtered. The removal of volatile gave dimethyl 5-ethynylisophthalate in 98% yield (7.73 g, 35.43 mmol), which is pure enough for the next reactions. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz)  $\delta$  (ppm): 8.661 (t, *J* = 1.6 Hz, 1H), 8.343 (d, *J* = 1.6 Hz, 2H), 3.976 (s, 6H), 3.194 (s, 1H).

**Dimethyl 5-(2-(4-bromophenyl)ethynyl)isophthalate**: 1-bromo-4-iodobenzene (2.00 g, 7.07 mmol), dimethyl 5-ethynylisophthalate (1.54 g, 7.07 g), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.25 g, 0.35 mmol), CuI (0.067 g, 0.35 mmol) were mixed in a 250 mL round-bottom flask. The flask was evacuated under vacuum and refilled with N<sub>2</sub> for three times, and then 100 mL of a degassed solution of triethylamine and THF (1:1,  $\nu/\nu$ ) were added. The mixture was refluxed for 48 h. After removal of the solvents, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and H<sub>2</sub>O (100 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, washed with brine, dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed, and the product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (10/1,  $\nu/\nu$ ) as eluent, affording the dimethyl 5-(2-(4-bromophenyl)ethynyl)isophthalate in 68.2% yield (1.80 g, 4.82 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz)  $\delta$  (ppm): 8.657 (t, *J* = 1.6 Hz, 1H), 8.380 (d, *J* = 1.6 Hz, 2H), 7.538 (d, *J* = 8.4 Hz, 2H), 7.432 (d, *J* = 8.4 Hz, 2H), 3.993 (s, 6H).

Tetramethyl 5,5'-(benzene-1,4-diyl-ethyne-1,2-diyl) diisophthalate: То а mixture of dimethyl 5-(2-(4-bromophenyl)ethynyl)isophthalate (1.00 g, 2.68 mmol), dimethyl (pinacolboryl)isophthalate (0.94 g, 2.95 mmol), K<sub>3</sub>PO<sub>4</sub> (1.37 g, 6.43 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.16 g, 0.14 mmol) was added dry dioxane (80 mL) under a nitrogen atmosphere. The resulting mixture was refluxed under nitrogen for 48 h. After removal of the solvent, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and H<sub>2</sub>O (100 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, washed with brine, dried over anhydrous MgSO<sub>4</sub> and filtered. After volatile was removed by rato-evaporation, the residue was purified using silica gel column chromatography with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (2/1, v/v) as eluent, affording the tetramethyl intermediate as a pure white solid in 69% yield (0.90 g, 1.85 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600.1 MHz)  $\delta$  (ppm): 8.710 (t, J = 1.8 Hz, 1H), 8.673 (t, J = 1.8 Hz, 1H), 8.516 (d, J = 1.8 Hz, 2H), 8.426 (d, J = 1.8 Hz, 2H), 7.671-7.731 (m, 4H), 4.021 (s, 3H), 4.009 (s, 3H).

**5,5'-(benzene-1,4-diyl-ethyne-1,2-diyl) diisophthalic aicd (H<sub>4</sub>L)**: The tetramethyl intermediate (0.90 g, 1.85 mmol) was dissolved in MeOH (25 mL) and THF (25 mL), and then 20 mL 6 M NaOH aqueous solution was added. The solution was stirred under reflux for 12 hrs. After that, the solution was cooled to room temperature, and concentrated by rato-evaporation. The residue was dissolved in H<sub>2</sub>O, and acidified

with concentrated HCl under ice-water bath. The resulting precipitation was collected by filtration, washed with water, and dried under vacuum at 70 °C. The target compound was obtained as an off-white solid in quantitative yield. <sup>1</sup>H NMR (DMSO $d_6$ , 400.1 MHz)  $\delta$  (ppm): 8.489 (t, J = 1.6 Hz, 1H), 8.463 (t, J = 1.6 Hz, 1H), 8.439 (d, J = 1.6 Hz, 2H), 8.295 (d, J = 1.6 Hz, 2H), 7.872 (d, J = 8.4 Hz, 2H), 7.783 (d, J = 8.4Hz, 2H); <sup>13</sup>C NMR (DMSO- $d_6$ , 100.6 MHz)  $\delta$  (ppm): 166.884, 166.304, 140.481, 139.320, 136.063, 132.946, 132.654, 132.495, 131.734, 130.267, 129.679, 127.734, 123.730, 122.051, 91.059, 89.023.

#### 4. Synthesis and characterization of ZJNU-50

A mixture of the organic linker H<sub>4</sub>L (5.0 mg, 11.6  $\mu$ 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 24 h. Blue rhombic crystals were obtained in 51% yield. Selected FTIR (KBr, cm<sup>-1</sup>): 1655, 1560, 1419, 1371, 1253, 1105, 1047, 775, 719; TGA data for loss of 6DMF+7H<sub>2</sub>O, calcd: 50.5%, found: 49.5%; anal. for C<sub>42</sub>H<sub>70</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>23</sub>, calcd: C, 43.71%, H, 6.11%, N, 7.28%; found: C, 45.23%, H, 6.02%, N, 7.55%.



*Fig. S1* PXRD pattern of as-synthesized **ZJNU-50** (red), together with the one (black) simulated from its single-crystal X-ray diffraction structure.



*Fig. S2* TGA curve of as-synthesized **ZJNU-50** under a nitrogen atmosphere with a heating rate of 5 °C min<sup>-1</sup>.



*Fig. S3* Experimental (circles), Le Bail fitted (line), and difference (line below observed and calculated patterns) PXRD profile for activated **ZJNU-50a** at 298 K (Cu K<sub> $\alpha$ </sub> radiation). Vertical bars indicate the calculated positions of Bragg peaks. Refined lattice parameters: *a* = 18.464(4) Å and *c* = 46.73(2) Å. Goodness of fit: *R*<sub>p</sub>=0.0994, *R*<sub>wp</sub> = 0.1522.



*Fig. S4*  $N_2$  adsorption-desorption isotherm of **ZJNU-50a** at 77 K. Solid and open symbols represent adsorption and desorption, respectively.



*Fig. S5* BET plot of **ZJNU-50a**. Only the range below  $P/P_0 = 0.035$  satisfies the first consistency criterion for applying the BET theory.

 $S_{BET} = 1/(6.02087 \times 10^{-6} + 0.00131)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 3308 \ m^2 \ g^{-1}$ 



*Fig. S6* Excess (a) and absolute (b)  $CH_4$  adsorption-desorption isotherms of **ZJNU-50a** at 273 K (red) and 298 K (blue). Solid and open symbols represent adsorption and desorption, respectively. The solid lines were used to guide the eye.



Fig. S7 The isosteric heat of CH<sub>4</sub> adsorption as a function of methane loadings.



*Fig. S8* FTIR spectra of the organic ligand  $H_4L$  (black) and as-synthesized **ZJNU-50** (red).









Fig. S9 NMR spectra of the intermediates and the target compound.

MOFs	BET (m²/g)	V <sub>p</sub> (cm <sup>3</sup> /g)	Total CH <sub>4</sub> uptake at 35 bar		Total CH <sub>4</sub> uptake at 65 bar		CH <sub>4</sub> working capacity From 65 to 5 bar		Q <sub>st, ini</sub>	Ref.
			(cm <sup>3</sup> /cm <sup>3</sup> )	(g/g)	(cm <sup>3</sup> /cm <sup>3</sup> )	(g/g)	(cm <sup>3</sup> /cm <sup>3</sup> )	(g/g)	(kJ/mol)	
UTSA-40	1630	0.65	156	0.135	193	0.167	139	0.120		4
NOTT-100	1661	0.677	195	0.150	230	0.177	139	0.107	18.1	5
PCN-14	2000	0.85	195	0.169	230	0.197	157	0.136	18.7	6
UTSA-80	2280	1.03	192	0.198	233	0.240	174	0.178	15.95	7
NJU-Bai14	2383	0.925	173	0.165	206	0.196	151	0.144	16.6	8
PCN-46	2500	1.012	172	0.198	206	0.238	166	0.191		9
NU-135	2530	1.02	187	0.178	230	0.219	170	0.161	16.6	10
NOTT-101	2805	1.080	194	0.202	239	0.249	183	0.191	15.5	5
UTSA-76	2820	1.09	211	0.216	257	0.263	197	0.201	15.44	11
ZJU-5	2823	1.074	190	0.200	228	0.240	168	0.177	15.3	12
NOTT-103	2958	1.157	193	0.214	236	0.262	183	0.203	15.9	5
ZJNU-50	3308	1.184	178	0.213	229	0.274	184	0.220	15.0	This work
NOTT-102	3342	1.268	181	0.220	237	0.288	192	0.233	16.0	5

*Table S1* High-pressure CH<sub>4</sub> adsorption in some NbO-type MOFs.

Empirical formula	C <sub>21</sub> H <sub>35</sub> CuN <sub>3</sub> O <sub>11.5</sub>				
Formula weight	577				
Temperature (K)	150				
Wavelength (Å)	0.71073				
Crystal system	Trigonal				
Space group	<i>R</i> -3m				
	a = 18.4830(17)  Å .				
	b = 18.4830(17) Å				
Unit call dimensions	c = 46.758(11)  Å				
Onit cen dimensions	$\alpha = 90^{\circ}$				
	$\beta = 90^{\circ}$				
	$\gamma = 120^{\circ}$				
Volume (Å <sup>3</sup> )	13833(4)				
Ζ	18				
Calculated density (g cm <sup>-3</sup> )	1.242				
Absorption coefficient (mm <sup>-1</sup> )	0.764				
F(000)	2628				
Crystal size (mm)	0.06  imes 0.04  imes 0.03				
$\theta$ range for data collection (°)	1.31 to 25.02				
	$-21 \le h \le 21,$				
Limiting indices	$-20 \le k \le 21,$				
	$-55 \le l \le 55$				
Reflections collected / unique	35186 / 3006				
R <sub>int</sub>	0.4795				
Completeness to $\theta = 25.02$	100.0 %				
Absorption correction	Semi-empirical from equivalents				
Refinement method	Full-matrix least-squares on $F^2$				
Data / restraints / parameters	3006 / 46 / 124				
Goodness-of-fit on $F^2$	1.072				
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.1081, wR_2 = 0.2625$				
<i>R</i> indices (all data)	$R_1 = 0.1515, wR_2 = 0.2771$				
Largest diff. peak and hole (e.A-	0.623 and -0.883				
3)					
CCDC	1045458				

Table S2 Crystal data and structure refinement for ZJNU-50.

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.

## 5. Reference

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