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A NbO-type metal-organic framework exhibiting high deliverable capacity for methane storage[†]

Chengling Song,^a Yajing Ling,^a Yunlong Feng,^a Wei Zhou,^{bc} Taner Yildirim^{bd} and Yabing He*^a

A copper-based NbO-type metal-organic framework ZJNU-50 constructed from a tetracarboxylate incorporating phenylethyne as a spacer exhibited an exceptionally high methane working capacity of 184 cm³ (STP) cm⁻³ for methane storage. The value is among the highest reported for MOF materials.

Growing concerns on depletion of conventional energy sources and environmental issues associated with CO₂ emission have triggered tremendous studies to develop new cleaner energy carriers. Natural gas, whose main component is methane, is considered as an attractive fuel as compared with other conventional energy sources due to its increasing supply and lower emission of greenhouse gases and other pollutants. However, its comparatively low volumetric energy density under standard conditions presents a giant challenge for its wide utilization, especially as a transportation fuel in vehicular application. Realization of safe and efficient methane storage is thus highly desired. The physisorption based processes, involving adsorbing methane within the micropores of porous materials to achieve a density competitive with compressed natural gas (CNG) but at a lower storage pressure, offer an attractive technique due to their mild operating conditions and high energy efficiency. The key lies in finding an efficient adsorbent material. The past decade has seen great progress in methane storage material development. One of the key developments is the use of metal-organic frameworks (MOFs), a new class of highly porous materials assembled through the modular combination of inorganic and

organic building blocks, for storing methane providing improvement in the methane storage performance.¹ In fact, several MOFs exhibit methane adsorption capacities exceeding those of the conventional activated carbons.² Also, BASF has demonstrated model vehicles fuelled by natural gas using BASF MOF materials.

Of various MOFs, NbO-type MOFs constructed from dicopper paddlewheel secondary building units (SBUs) and tetracarboxylate have been increasingly explored for methane storage due to their salient features of high surface area, tuneable pore size and open copper sites suitable for gas adsorption. For example, Zhou group reported several NbO-type MOFs incorporating anthracene derivatives, double bond or triple bond moieties exhibiting good methane adsorption properties.³ Snurr et al. used molecule simulations to discover some very useful structure-property relationship regarding methane storage and to identify a NbO-type MOF with an exceptionally high methane adsorption capacity at room temperature and 35 bar.4 We recently investigated a series of NbOtype MOFs for methane storage and derived an empirical equation for predicting methane storage capacity.⁵ Undoubtedly, these results demonstrate that NbO-type MOFs are promising in terms of methane storage, and encourage us to further synthesize and explore more NbO-type MOFs for methane storage.

For vehicular application, an ideal MOF material should not only have high methane storage capacity, but more importantly should have high methane deliverable capacity. It is well known that the methane storage and deliverable capacities of MOF materials depend on a variety of factors such as pore space, pore size distribution, framework densities, and open metal sites. To optimize these factors to enhance the methane deliverable capacity, we developed a novel tetracarboxylate derivative H₄L, 5,5'-(benzene-1,4-diyl-ethyne-1,2-diyl) diisophthalic acid (Scheme 1), and used it to construct the corresponding NbO-type MOF termed ZINU-50, which is based on the following considerations. (1) On the premise of ensuring structural stability and no significant reduction of the framework density, we elongate the organic linker, 1,4-benzenediisophthalate, in NOTT-101^{5,6} by inserting a slim $C \equiv C$ triple bond, expecting to achieve a low methane uptake at a low pressure of say 5 bar and thus a high methane

^a College of Chemistry and Life Sciences, Zhejiang Normal University,

Jinhua 321004, China. E-mail: heyabing@zjnu.cn

^b NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102, USA

^c Department of Materials Science and Engineering, University of Maryland,

College Park, Maryland 20742, USA

^d Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, USA

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Scheme 1 Synthesis of tetracarboxylic acid H₄L used to construct ZJNU-50.

working capacity; (2) to our knowledge, no study based on this unsymmetrical organic linker has been reported. Our studies show the activated **ZJNU-50a** (thereafter, the letter "a" indicates activated MOF materials) exhibits an exceptionally high methane storage capacity of 178 and 229 cm³ (STP) cm⁻³ at 298 K under 35 and 65 bar, respectively. Suppose at 65 and 5 bar as the upper and lower limiting working pressures, respectively, up to 80% of the methane storage amount, namely, 184 cm³ (STP) cm⁻³ can be delivered at 298 K, which is among the highest reported for porous MOFs. As compared to **NOTT-101a**, **ZJNU-50a** has a higher gravimetric methane deliverable capacity, despite a similar volumetric one.

Scheme 1 outlines the synthesis of the ligand, 5,5'-(benzene-1,4-diyl-ethyne-1,2-diyl) diisophthalic acid. We began with the synthesis of dimethyl 5-(2-(4-bromophenyl)ethynyl)isophthalate 1 by Sonogashira coupling reaction of 1-bromo-4-iodobenzene with dimethyl 5-ethynylisophthalate. Subsequently, Suzuki coupling of dimethyl 5-(2-(4-bromophenyl)ethynyl)isophthalate with dimethyl 5-(pinacolboryl)isophthalate afforded the corresponding tetramethyl ester precursor 2, which was hydrolyzed and acidified to give the desired tetracarboxylic acid. The chemical structure was characterized unambiguously by ¹H NMR and ¹³C NMR spectroscopy.

A solvothermal reaction of the tetracarboxylic acid and $Cu(NO_3)_2 \cdot 3H_2O$ in a mixed solvent of *N*,*N*-dimethyl formamide (DMF), methanol and H_2O under acidic conditions afforded **ZJNU-50** as blue rhombic crystals in a good yield. The singlecrystal X-ray structure was characterized and the phase purity was confirmed by powder X-ray diffraction studies (PXRD, Fig. S1, ESI†). **ZJNU-50** can be best formulated as $[Cu_2(L)(H_2O)_2]$ ·6DMF·7H₂O based on single-crystal X-ray diffraction studies, thermogravimetric analysis (TGA, Fig. S2, ESI†), and microanalysis.

Single-crystal X-ray diffraction studies reveal that **ZJNU-50** crystallizes in the space group $R\bar{3}m$. As expected, the Cu²⁺ ions form dicopper paddlewheel Cu₂(COO)₄ clusters serving as squareplanar SBUs that are linked with the rectangular organic building blocks to give rise to a three-dimensional (3D) NbO-based network containing two different types of nanocages (Fig. 1). One consists of 12 ligands and 6 SBUs, and the diameter is about 14 Å, taking into account the van der Waals radii of the atoms; while the other is constructed from 6 ligands and 12 SBUs with dimensions of *ca.* 11 × 24 Å. Due to the elongation of the linker, the sizes of the two cages are systematically larger than those in **NOTT-101**. It is worth noting that the central phenyl ring was twisted out of the plane defined by the two terminal isophthalates with the dihedral angle smaller than the one observed in **NOTT-101**, suggesting that the rotation of the central phenyl ring around the molecular long



Fig. 1 Single-crystal X-ray diffraction structure showing that each organic ligand connects four dicopper paddlewheel SBUs (a) to form a 3D network (b) containing two different types of cages (c). The hydrogen atoms are omitted for clarity.

axis is relatively free. Such a low rotation barrier might play a role in optimizing gas adsorption at high pressure.⁷

Before gas adsorption measurement, the as-synthesized **ZJNU-50** was solvent-exchanged with dry acetone, and then evacuated at 100 °C under high vacuum, affording the activated **ZJNU-50a**. The integrity of the framework was confirmed by powder X-ray diffraction (Fig. S3, ESI†). The textural feature was characterized by N₂ adsorption isotherm at 77 K. As shown in Fig. S4 (ESI†), the N₂ sorption isotherm shows a type-I adsorption behaviour, characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) surface area and the total pore volume are estimated to be 3308 m² g⁻¹ and 1.184 cm³ g⁻¹ (Fig. S5, ESI†). These values are systematically higher than those of **NOTT-101a**, and are among the highest reported for NbO-type MOFs (Table S1, ESI†).

Given that the gravimetric surface area falls in the optimal range for methane storage,⁴ we evaluate the performance of ZJNU-50a for methane storage in detail. 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 (Fig. S6, ESI[†]). As shown in Fig. 2, the adsorption and desorption branches well overlapped with each other, suggesting that the adsorption process is reversible and the adsorbed methane can be fully recovered during the desorption process. At 298 K and 35 bar, the excess gravimetric methane adsorption capacity is 256 cm^3 (STP) g^{-1} . By using the N2-derived pore volume and the bulk phase density of methane, the total gravimetric CH₄ uptake is calculated to be 296 cm³ (STP) g^{-1} . In order to calculate the volumetric methane uptake, which is the most appropriate one to quantify the adsorption capacity of the adsorbents, especially for ANG vehicular application, the crystal density of 0.5978 g cm⁻³ was used. ZJNU-50a shows a total volumetric methane storage capacity of 178 cm³ (STP) cm⁻³ at 298 K and 35 bar. This capacity approaches the DOE's previous target of 180 cm³ (STP) cm⁻³ for methane storage when the packing loss is ignored, and is comparable with those of NU-125,¹⁶ NOTT-102,⁵ Cu-TDPAT,¹¹ ZJU-25,⁹ PCN-46,^{3b} and SDU-6¹⁵ (Table 1). When the pressure increases to 65 bar, the total volumetric



Fig. 2 High-pressure excess (square) and total (circle) methane sorption isotherms of **ZJNU-50a** at 273 K (red) and 298 K (blue). Solid and open symbols represent adsorption and desorption, respectively.

Table 1 Comparison of some MOFs for high-pressure methane storage

	Total uptal 65 bar (35	ke at bar)	Working ca at 65 bar ^a		
MOFs	$cm^3 cm^{-3}$	$g g^{-1}$	cm ³ cm ⁻³	$g g^{-1}$	Ref.
ZJNU-50	229 (178)	0.274 (0.213)	184	0.220	This work
HKUST-1	267 (227)	0.216 (0.184)	190	0.154	2a
UTSA-76	257 (211)	0.263 (0.216)	197	0.201	7
NOTT-102	237 (181)	0.288 (0.220)	192	0.233	5
UTSA-80	233 (192)	0.240 (0.198)	174	0.178	8
NU-125	232 (182)	0.287 (0.225)	183	0.227	2a
PCN-14	230 (195)	0.197 (0.169)	157	0.136	2a
UTSA-20	230 (184)	0.181 (0.145)	170	0.134	2a
ZJU-25	229 (180)	0.263 (0.206)	181	0.208	9
ZJU-5	228 (190)	0.240(0.200)	168	0.177	10
Cu-TDPAT	222 (181)	0.202 (0.165)	163	0.149	11
PCN-61	219 (171)	0.279 (0.218)	174	0.222	12
MOF-5	214 (150)	0.246 (0.172)	182	0.209	2b
PCN-46	206 (172)	0.237 (0.198)	166	0.191	3 <i>b</i>
NU-111	206 (138)	0.360 (0.241)	179	0.313	2a
ZJU-36	203 (142)	0.292 (0.204)	175	0.252	13
PCN-80	196 (147)	0.244 (0.183)	166	0.206	14
SDU-6	(172)	(0.201)			15

^{*a*} The working capacity is defined as the difference in total uptakes between 65 and 5 bar.

methane uptake reaches 229 cm³ (STP) cm⁻³, which is 87% of the DOE's new target of 263 cm³ (STP) cm⁻³ assuming no packing loss. The value is among the highest reported for all MOFs, and among the copper-based MOFs, is only lower than the adsorption capacities of the two best MOFs, **HKUST-1** (267 cm³ (STP) cm⁻³)^{2a} and **UTSA-76** (257 cm³ (STP) cm⁻³),⁷ under the same conditions, making **ZJNU-50a** as a promising MOF material for volumetric methane storage (Table 1). The methane storage capacity corresponds to 87% of the methane stored in a CNG tank at 248 bar and 298 K, and is equivalent to the amount of methane stored in a CNG tank at 210 bar and 298 K. Although **ZJNU-50a** has a lower volumetric methane storage capacity than **HKUST-1** and **UTSA-76**, it has a higher gravimetric methane storage capacity of 0.274 g g⁻¹ than **HKUST-1** (0.216 g g⁻¹) and **UTSA-76** (0.263 g g⁻¹) due to a larger pore volume and a lower framework density.

When evaluating the performance of an adsorbent for vehicular application, the deliverable capacity of methane gas is more important than the total storage capacity because it determines the driving range of natural gas vehicles. Taking 5 bar and 65 bar as specific lower and upper pressure limits, the deliverable capacity of **ZJNU-50a** is 184 cm³ (STP) cm⁻³ at 298 K; that is, a tank filled with **ZJNU-50a** can deliver 71.4% as much fuel as the CNG tank operating in the same lower pressure limit and 248 bar as the upper pressure limit, indicating **ZJNU-50a** as a potential material for methane delivery. As compared to **NOTT-101**, **ZJNU-50a** has a comparable volumetric methane deliverable amount, but a higher gravimetric methane deliverable amount is comparable to or even better than those of MOFs that show the most promise for deliverable methane storage: **PCN-14**,^{2a} **PCN-61**,¹² **PCN-80**,¹⁴ **ZJU-5**,¹⁰ **ZJU-25**,⁹ **ZJU-36**,¹³ **UTSA-20**,^{2a,17} **UTSA-80**,⁸ **NU-111**,^{2a} **MOF-5**^{2b} (Table 1).

To understand the gas-framework interaction, the adsorption isotherm at 273 K is also measured. The isosteric heat of methane adsorption was extracted from the temperature-dependent isotherms using Clausius–Clapeyron equations. As shown in Fig. S7 (ESI[†]), the isosteric heat of adsorption for methane does not decrease with the methane loading. The initial value is calculated to be 15.0 kJ mol⁻¹, which is slightly lower than that of most reported copper-based frameworks (Table S1, ESI[†]), thus responsible for a low methane uptake at low pressure and a high methane working capacity.

In summary, we developed a new organic linker and used it to construct a NbO-type MOF **ZJNU-50a** exhibiting exceptionally high volumetric methane storage and deliverable capacities. At 298 K and 65 bar, the volumetric methane storage and deliverable capacities reach 229 and 184 cm³ (STP) cm⁻³, respectively, which are among the highest reported for all MOFs. Such high storage and deliverable capacities are attributed to the balanced porosity and framework density, suitable pore/cage size, and the moderate density of open metal sites within **ZJNU-50a**. It is expected that this work will stimulate more investigation of porous MOFs for enhanced methane storage by tuning or optimizing the pore structure of the framework.

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

Chengling Song,^{*a*} Yajing Ling,^{*a*} Yunlong Feng,^{*a*} Wei Zhou,^{*b,c*} Taner Yildirim,^{*b,d*} Yabing He,^{*a**}

- ^{a.} College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, China. E-mail: <u>heyabing@zjnu.cn</u>.
- ^{b.} NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6102, USA.
- ^{c.} Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA.
- ^{d.} Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, USA.

1. Materials and General Methods

All starting materials and reagents are commercially available and used without further purification. ¹H NMR and ¹³C NMR spectra were measured at room temperature in CDCl₃ 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 ¹H (δ_{CDCl^3} = 7.26 ppm, $\delta_{\text{DMSO-}d6}$ = 2.50 ppm) and ¹³C spectra (δ_{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⁻¹ 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⁻¹ in a flowing nitrogen atmosphere (10 mL min⁻¹). Powder Xray diffraction (PXRD) patterns were carried out by a Philips PW3040/60 automated powder diffractometer, using Cu-K_a radiation ($\lambda = 1.542$ Å) with a 2 θ range of 5–45°. A micromeritics ASAP 2020 surface area analyzer was used to obtain N₂ 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 μ 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.¹ 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_a 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.² There are large solvent accessible void volumes in the crystals which are occupied by highly disordered DMF, and H₂O molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE³ 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 H₂O. 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 H₄L.

5-bromoisophthalic acid: Isophthalic acid (20.00 g, 0.12 mol) was taken up in concentrated H₂SO₄ (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). ¹H NMR (DMSO-*d*₆, 600.1 MHz) δ (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 H₂SO₄ (15 mL). The mixture was refluxed for 24 h, and then cooled to room temperature. After the solvent was ratoevaporated, CH₂Cl₂ (150 mL) and H₂O (100 mL) were added. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂. The organic phase was combined, washed with saturated NaHCO₃ solution and brine sequentially, dried over anhydrous MgSO₄ 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). ¹H NMR (CDCl₃, 400.1 MHz) δ (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), B₂Pin₂ (10.23 g, 40.28 mmol), KOAc (10.78 g, 109.86 mmol), and Pd(dppf)Cl₂ (0.81 g, 1.09 mmol) were placed in a 500 mL round-bottom flask. The flask was evacuated and refilled with N₂ 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 CH₂Cl₂ (200 mL) and H₂O (200 mL) was added. The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂. The organic phase was combined, washed with brine, dried over anhydrous MgSO₄, 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). ¹H NMR (CDCl₃, 400.1 MHz) δ (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(PPh₃)₂Cl₂ (1.28 g, 1.83 mmol) were placed in a 500 mL round-bottom flask. The flask was evacuated under vacuum and refilled with N₂ 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, CH₂Cl₂ (100 mL) and H₂O (100 mL) was added. The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂. 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). ¹H NMR (CDCl₃, 400.1 MHz) δ (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. CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂. The organic phase was combined, washed with brine, dried over anhydrous MgSO₄ 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. ¹H NMR (CDCl₃, 400.1 MHz) δ (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(PPh₃)₂Cl₂ (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 N₂ for three times, and then 100 mL of a degassed solution of triethylamine and THF (1:1, ν/ν) were added. The mixture was refluxed for 48 h. After removal of the solvents, CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂. The organic phase was combined, washed with brine, dried over anhydrous MgSO₄ and filtered. The solvent was removed, and the product was purified using silica gel column chromatography with petroleum ether/ethyl acetate (10/1, ν/ν) as eluent, affording the dimethyl 5-(2-(4-bromophenyl)ethynyl)isophthalate in 68.2% yield (1.80 g, 4.82 mmol). ¹H NMR (CDCl₃, 400.1 MHz) δ (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), K₃PO₄ (1.37 g, 6.43 mmol) and Pd(PPh₃)₄ (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, CH₂Cl₂ (100 mL) and H₂O (100 mL) were added. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂. The organic phase was combined, washed with brine, dried over anhydrous MgSO₄ and filtered. After volatile was removed by rato-evaporation, the residue was purified using silica gel column chromatography with petroleum ether/CH₂Cl₂ (2/1, v/v) as eluent, affording the tetramethyl intermediate as a pure white solid in 69% yield (0.90 g, 1.85 mmol). ¹H NMR (CDCl₃, 600.1 MHz) δ (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 (H₄L): 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 H₂O, 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. ¹H NMR (DMSO d_6 , 400.1 MHz) δ (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); ¹³C NMR (DMSO- d_6 , 100.6 MHz) δ (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 H₄L (5.0 mg, 11.6 μ mol) and Cu(NO₃)₂·3H₂O (15.0 mg, 62.1 μ mol) was dissolved into a mixed solvent of *N*,*N*-dimethylformamide (DMF), methanol and H₂O (1.5 mL / 0.5 mL / 0.08 mL) in a screw-capped vial (20 mL). 50 μ 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⁻¹): 1655, 1560, 1419, 1371, 1253, 1105, 1047, 775, 719; TGA data for loss of 6DMF+7H₂O, calcd: 50.5%, found: 49.5%; anal. for C₄₂H₇₀Cu₂N₆O₂₃, 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⁻¹.



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_{α} 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*_p=0.0994, *R*_{wp} = 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 CH₄ 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 BE (m ²	BET	BET V _p (m ² /g) (cm ³ /g)	Total CH ₄ uptake at 35 bar		Total CH ₄ uptake at 65 bar		CH ₄ working capacity From 65 to 5 bar		$Q_{ m st,ini}$	Ref.
	(m²/g)		(cm ³ /cm ³)	(g/g)	(cm ³ /cm ³)	(g/g)	(cm ³ /cm ³)	(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 CH₄ adsorption in some NbO-type MOFs.

Empirical formula	C ₂₁ H ₃₅ CuN ₃ O _{11.5}				
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 ³)	13833(4)				
Ζ	18				
Calculated density (g cm ⁻³)	1.242				
Absorption coefficient (mm ⁻¹)	0.764				
F(000)	2628				
Crystal size (mm)	$0.06 \times 0.04 \times 0.03$				
θ 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 _{int}	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.

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