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COMMUNICATION

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

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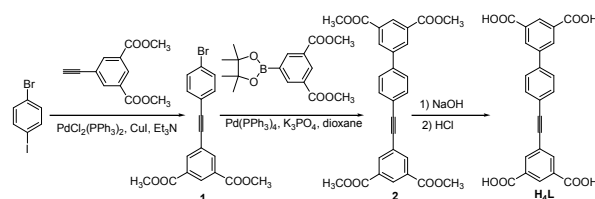
A copper-based NbO-type metal-organic framework ZJNU-50 constructed from a tetracarboxylate incorporating phenylethyne as spacer exhibited exceptionally high methane working capacity of 184 cm³ (STP) cm⁻³ for methane storage. The value is among the highest reported for MOF materials.

Growing concerns on depletion of conventional energy sources and environmental issue associated with CO₂ emission have triggered tremendous studies to develop new cleaner energy carries. 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 its mild operating condition 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 development 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 merits 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 NbO-type 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 as **ZJNU-50**, which is based on the following



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

considerations. 1) Under 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≡C triple bond, expecting to achieve a low methane uptake at a low pressure of say 5 bar and thus a high methane 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 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-(pinacolboronyl)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(NO₃)₂·3H₂O in a mixed solvent of *N,N*-dimethyl formamide (DMF), methanol and H₂O under acidic conditions afforded **ZJNU-50** as blue rhombic crystals in a good yield. The single-crystal X-ray structure was characterized and the phase purity was confirmed by powder X-ray diffraction studies (PXRD, Fig. S1). **ZJNU-50** can be best formulated as [Cu₂(L)(H₂O)₂]₆DMF·7H₂O based on single-crystal X-ray diffraction studies, thermogravimetric analysis (TGA, Fig. S2), and microanalysis.

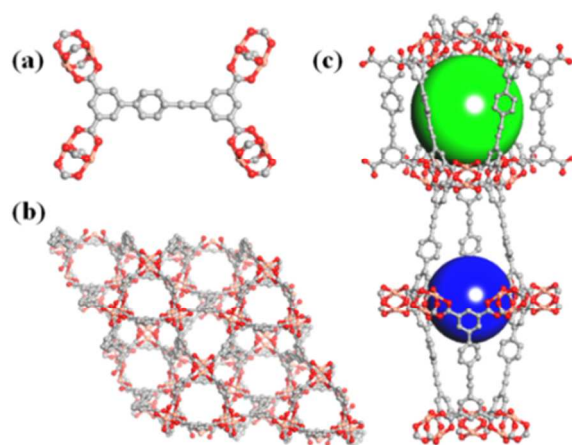


Fig. 1 Single-crystal X-ray diffraction structure showing that each organic ligand connects four dicopper paddlewheel SBUs to form a 3D network (b) containing two different types of cages (c). The hydrogen atoms are omitted for clarity.

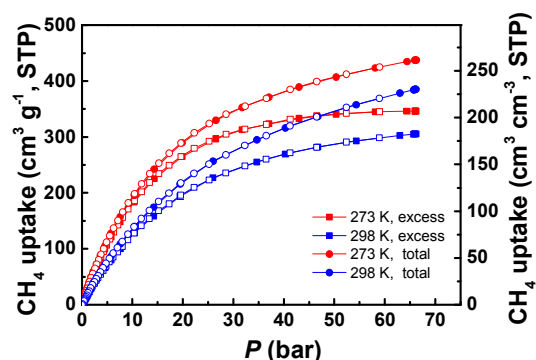


Fig. 2 High-pressure excess (square) and total (circle) methane sorption isotherms of **ZJNU-50a** at 273 K (red) and 298 K (blue). Solid and open symbols represent adsorption and desorption, respectively.

Single-crystal X-ray diffraction studies reveal that **ZJNU-50** crystallizes in the space group *R-3m*. As expected, the Cu²⁺ ions form dicopper paddlewheel Cu₂(COO)₄ clusters serving as square-planar 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 the rotation of the central phenyl ring around the molecular long 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). The textural feature was characterized by N₂ adsorption isotherm at 77 K. As shown in Fig. S4, 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). These values are systematically higher than those of **NOTT-101a**, and are among the highest reported for NbO-type MOFs (Table S1).

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). 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.

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

MOFs	Total uptake at 65 bar (35 bar)		Working capacity at 65 bar ^a		Ref.
	cm ³ cm ⁻³	g g ⁻¹	cm ³ cm ⁻³	g g ⁻¹	
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	^{3b}
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

The working capacity is defined as the difference in total uptakes between 65 and 5 bar.

At 298 K and 35 bar, the excess gravimetric methane adsorption capacity is 256 cm³ (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 to 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} **SDU-6**¹⁵ (Table 1). When the pressure increases to 65 bar, the total volumetric 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 at 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** of 0.216 g g⁻¹ and **UTSA-76** of 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 on 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 capacity. The volumetric 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 equation. As shown in Fig. S7, 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), 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 framework.

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Notes and references

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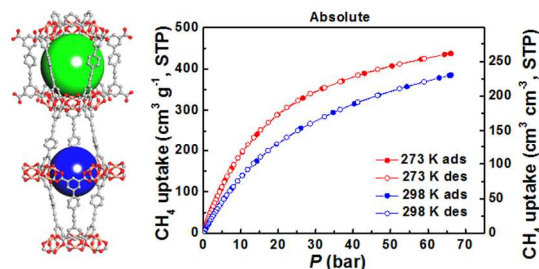
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TOC Figure



A NbO-type MOF incorporating phenylethyne moieties exhibits high methane working capacity for methane storage at room temperature.