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A microporous metal–organic framework of a rare sty topology for high CH_4 storage at room temperature†

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A rare sty type microporous metal–organic framework, Cu_2(FDDI) (ZJU-25; H_4FDDI = tetramethyl 5,5′-(9*H*-fluorene-2,7-diyl)diisophthalate acid), was solvothermally synthesized and structurally characterized. With open metal sites and suitable pore space for their interactions with methane molecules, ZJU-25a exhibits absolute methane storage of 180 cm^3(STP) cm^{-3} at room temperature and 35 bar, enabling it to be one of the very few porous MOFs whose methane storage capacities have met and/or approached the DOE target of 180 cm^3(STP) cm^{-3} for material-based methane storage.

Materials for high methane storage are highly in need because of the great promise and significant value of methane (the main component of natural gas) as an alternative clean fuel/energy, particularly for natural gas vehicles. In fact, U.S. Department of Energy (DOE) recently initiated a new program called "MOVE" (Methane Opportunities For Vehicular Energy) to facilitate the development of transformational technologies that reduce the barriers to mass adoption of natural gas use in vehicles. Of particular interest are technologies that enable at-home refueling and low-cost, high energy density on-board storage for natural gas vehicles.[1] Among the diverse materials for methane storage, porous metal–organic frameworks (MOFs) are very promising ones.[2] This is because (a) such porous framework materials can be readily self-assembled from metal ions/clusters with organic linkers with high porosities, (b) the pores can be systematically varied and/or tuned by the interplay between the metal containing secondary building units and organic linkers of different lengths and geometries, and (c) the pore surfaces can be functionalized for their strong recognition of substrate molecules through the immobilization of different functional sites, particularly open metal sites.[3]

Porous MOFs for methane storage were pioneered by Kitagawa *et al.* and Yaghi *et al.* during 2000–2002.[4,5] Although highly porous MOFs can gravimetrically take a large amount of methane, their volumetric storage capacities are significantly limited because of their high porosities and low densities of the frameworks.[6] The significant progress in porous MOFs for methane storage was realized during 2008–2009 in which two porous MOFs, namely **PCN-14** by Ma *et al.*[7] and **Ni-MOF-74** by Wu *et al.*,[8] were established for their extraordinarily high volumetric methane storage (220 and 200 cm^3(STP) cm^{-3}, respectively), surpassing the DOE target of 180 cm^3(STP) cm^{-3} for methane storage at room temperature and 35 bar.[9] The high methane storage capacities within these two porous MOFs are apparently attributed to their high density of open metal sites and suitable pore space for their efficient storage of methane molecules. This very important concept (high density of open metal sites and optimized pore space) has been further confirmed by Guo *et al.* by demonstrating a MOF material with the very high methane storage density of 0.22 g cm^{-3} in the pores and methane storage of 195 cm^3(STP) cm^{-3} (Scheme 1).[10]

Among diverse porous MOFs, those assembled from copper paddle-wheel $Cu_2(COO)_4$ clusters and tetracarboxylates, typically of **nbo** topologies,[11] have attracted extensive attention for gas storage, particularly for methane and acetylene storage.[11f,g,i] This series of MOFs have two unique features: (a) the readily available open Cu^{2+} sites and (b) the systematically varied pore spaces, making them very suitable to study the effects of both open metal sites and variable pore spaces on gas storage.

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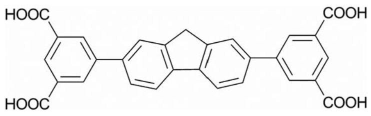

Scheme 1 Schematic structure of the organic linker H_4FDDI.

Herein we have developed a new tetracarboxylic acid, H_4FDDI (5,5′-(9*H*-fluorene-2,7-diyl) diisophthalic acid), and its corresponding microporous MOF, Cu_2(FDDI) (**ZJU-25**; ZJU = Zhejiang University). Interestingly, this new framework displays a topology derived from **ssb** instead of **nbo**, and exhibits high methane storage of 180 cm^3(STP) cm^{-3} at room temperature and 35 bar.

ZJU-25 was synthesized with $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_4FDDI in DMF/H_2O with addition of a small amount of nitric acid at 60 °C for 3 days as small blue hexagonal flake-shaped crystals. The structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD, Fig. S1, ESI†) and thermogravimetric analysis (TGA, Fig. S2, ESI†).

A single-crystal X-ray diffraction analysis revealed that **ZJU-25** crystallizes in the hexagonal space group *P*6$_3$/*mmc*.‡ As expected, the organic linkers are connected with paddle-wheel $Cu_2(COO)_4$ secondary building units (SBUs) (Fig. 1a) to form three-dimensional (3D) framework structures (Fig. 1b and c). The 3D framework of **ZJU-25** has three different types of pore apertures. One runs through the *a* axes of about 4.4 × 8.6 Å^2 (Fig. 1b) and the other two can be visualized along the *c* axes of about 3.6 and 5.4 Å in diameter, taking into account the van der Waals radii, respectively (Fig. 1c). PLATON calculations indicate that the void spaces are 68.3% for **ZJU-25** (6753 Å^3 out of the 9889.1 Å^3 per unit cell volume).[12]

The most interesting structural feature of **ZJU-25** is that its framework topology is different from well-established **nbo** ones assembled from $Cu_2(COO)_4$ SBUs and a number of tetracarboxylates.[9] If the linker is considered as one 4-coordinated vertex of the underlying net, then in combination with the 4-coordinated vertex corresponding to the metal paddle-wheels, the net is the one with RCSR symbol **ssb**,[13] one of several ways of linking vertices with planar 4-coordination with just one kind of link.[14] The only previous example of this topology in a MOF of which we are aware is that of **PCN-12** although that MOF was not so described.[15] We prefer, for reasons given earlier,[16] to consider the linker as having two 3-coordinated branch points which act as 3-coordinated vertices of the underlying net which is now the (3,4)-coordinated net with RCSR symbol **sty**. Fig. 1d shows the net in its augmented form, **sty-a**, in which the original vertices are replaced by their vertex figures (squares and triangles in this case).

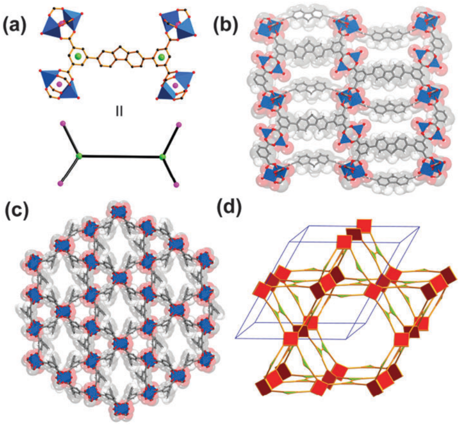

Fig. 1 X-ray single crystal structure of **ZJU-25**, indicating (a) each tetracarboxylate ligand connects with four paddle-wheel $Cu_2(COO)_4$ clusters; (b) the structure viewed along the *a* axes indicating irregular pores of about 4.4 × 8.6 Å^2; (c) the structure viewed along the *c* axes showing the small and the large pores of about 3.6 and 5.4 Å in diameter, respectively; (d) the framework topology of **sty-a** net.

The N_2 sorption isotherm at 77 K showed that the suitably activated **ZJU-25a** exhibits reversible Type-I sorption behaviour, characteristic of microporous materials with an adsorbed amount of N_2 of 765 cm^3 g^{-1} (Fig. S3, ESI†). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas of **ZJU-25a** are 2124 and 3304 m^2 g^{-1}, respectively. As expected, these values are higher than those of **MOF-505** because of the longer linker in **ZJU-25**; but slightly lower than those of **NOTT-102** because of the bending of the FDDI linker in **ZJU-25**. **ZJU-25a** has a pore volume of 1.183 cm^3 g^{-1}.

The moderately high porosity of **ZJU-25a** might enable it to be a very promising material for methane storage; we thus examine the methane sorption of **ZJU-25a**. As shown in Fig. 2 **ZJU-25a** takes up a large amount of methane. At 240 K, the methane uptake of **ZJU-25a** can reach 302 cm^3(STP) cm^{-3} under 63 bar. At 300 K and 35 bar, the practical conditions for methane storage, the absolute uptake of methane for **ZJU-25a** reaches the DOE target of 180 cm^3(STP) cm^{-3}. The methane storage capacity of **ZJU-25a** is significantly higher than those of most examined porous MOFs. In fact, **ZJU-25a** is among the very few porous MOFs whose methane storage capacities have met the DOE target at room temperature and 35 bar,[8–10,17] indicating the promise of this new porous MOF for practical methane storage applications. The methane storage is still not saturated, and can be further increased to 227 cm^3(STP) cm^{-3} under 63 bar.

The initial Q_{st} of CH_4 adsorption in **ZJU-25** is ~15.1 kJ mol^{-1}, comparable to those in other MOFs with copper paddlewheels.[2] Computational grand canonical Monte Carlo (GCMC) simulations indicate that all the open Cu sites are accessible and the

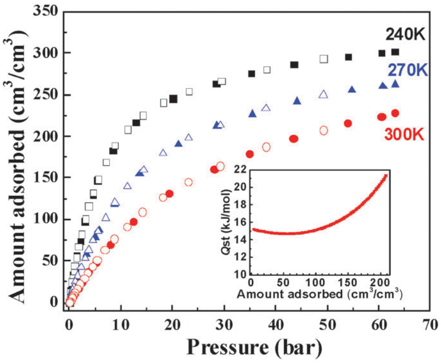

Fig. 2 High-pressure CH_4 absolute sorption isotherms of **ZJU-25a** at 240 K, 270 K and 300 K. Solid symbols: adsorption, open symbols: desorption. Inset: isosteric heats of adsorption of methane, calculated using the virial method.

primary CH_4 adsorption sites, which can take up $\sim$45 cm^3 cm^{-3} at RT and 35 bar. Other methane molecules are mainly located within the small cages (Fig. S5, ESI†). From the crystal structure, it can be observed that the pore sizes are in the range of 5 to 9 Å which are favorable for methane storage, as pointed out by Wilmer *et al.*[17b] It is interesting to note that these porous MOFs exhibiting high methane storage at room temperature and 35 bar have volumetric surface areas in the range of 1000 to 1500 cm^2 cm^{-3} (Fig. S6, ESI†). Apparently, open metal sites, pore/cage sizes, volumetric surface areas (a combined parameter from gravimetric surface area and framework density) should be collaboratively considered and enforced in order to secure high methane uptake under such practical methane storage conditions (room temperature and 35 bar), although MOF materials of higher volumetric surface areas can take up more methane under higher pressures such as 65 bar.

In summary, we have developed a new organic linker, aromatic tetracarboxylic acid, and incorporated it into a three-dimensional porous metal–organic framework. Interestingly, **ZJU-25** displays a very rare **sty-a** framework topology. The activated **ZJU-25a** exhibits moderately high porosity with a BET surface area of 2124 m^2 g^{-1}. The open Cu^{2+} sites and suitable pore spaces within **ZJU-25** have enabled this new MOF to take up a large amount of methane, reaching the DOE methane storage target of 180 cm^3(STP) cm^{-3} at 300 K and 35 bar.

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‡ Crystal data for **ZJU-25**: $C_{50}H_{69}Cu_2N_7O_{18}$, M = 1183.20, $P6_3/mmc$, $a = b$ = 18.2512(8) Å, c = 34.2802(12) Å, V = 9889.1(7) $Å^3$, Z = 6, D_c = 1.192 g cm^{-3}, μ(Mo-K_α) = 0.710 mm^{-1}, F(000) = 3720, GoF = 1.222, final R_1 = 0.0696 for $I > 2\sigma(I)$, wR_2 = 0.1836 for all data. CCDC 913334.

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