

## A robust microporous metal–organic framework constructed from a flexible organic linker for acetylene storage at ambient temperature†

Yun-Shan Xue,<sup>a</sup> Yabing He,<sup>b</sup> Shi-Bin Ren,<sup>a</sup> Yanfeng Yue,<sup>b</sup> Le Zhou,<sup>a</sup> Yi-Zhi Li,<sup>a</sup> Hong-Bin Du,<sup>\*,a</sup> Xiao-Zeng You<sup>a</sup> and Banglin Chen<sup>\*,b</sup>

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By using an octadentate ligand tetrakis[(3,5-dicarboxyphenoxy)methyl] methane ( $H_8L$ ), a new microporous metal–organic framework  $[Cu_4L(H_2O)_4](H_2O)_{31}$  (**1**) was solvothermally synthesized and structurally characterized. MOF **1** is built from the 4-connected square planar  $[Cu_2(O_2CR)_4]$  cluster and 8-connected cube ligand **L** to have a highly open framework with *scu* topology. It possesses permanent porosity as confirmed by  $N_2$ ,  $H_2$ ,  $C_2H_2$ ,  $CO_2$  and  $CH_4$  gas adsorption measurements and exhibits high acetylene storage of 193 and  $154\text{ cm}^3\text{ g}^{-1}$  at 273 and 296 K under 1 atm, respectively.

## 1. Introduction

Metal–organic frameworks (MOFs) have emerged as very promising materials for  $H_2$ ,  $CH_4$ ,  $CO_2$  and  $C_2H_2$  storage and capture.<sup>1–17</sup> This is because the high permanent porosities within MOFs can provide the necessary space to take up gas molecules, while the tunable pore sizes/curvatures and functionalized pore surfaces can be utilized to direct their strong interactions with gas molecules. In fact, some world record MOF materials for the gas storage have been realized over the past decade,<sup>8,9c</sup> Typically, it is necessary to have rigid organic linkers and metal-containing clusters (generally termed as secondary building units (SBUs)) to stabilize the frameworks and establish their permanent porosities for their gas uptake; thus previous research to construct robust MOFs has been mainly focused on the deliberate design and suitable choice of rigid organic linkers and SBUs. With these in mind, a variety of rigid organic linkers such as terephthalic acid, 1,4-naphthalenedicarboxylate, 1,1'-ethynebenzene-3,3',5,5'-tetracarboxylate (EBTC)<sup>8d</sup> and benzene-1,3,5-tricarboxylate, and SBUs such as paddlewheel cluster  $M_2(CO_2)_4$  ( $M = Cu, Zn, Co$  and  $Ni$ ) and  $Zn_4O(CO_2)_6$ <sup>17</sup> have been successfully incorporated into a series of robust MOFs. Further development on porous MOFs has motivated us to address the possibility of making use of flexible organic linkers to synthesize robust MOFs.<sup>18</sup> The success of this new strategy will significantly broaden the

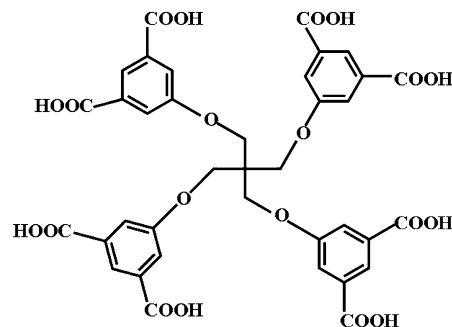
dictionary database of porous MOFs, providing the fundamental basis to tune and optimize pore structures to target high performance gas storage and separation of MOF materials. Given the fact that *m*-benzenedicarboxylate moieties are very powerful organic groups to stabilize the frameworks by the formation of paddlewheel  $Cu_2(CO_2)_4$  clusters and the corresponding cages of moderate sizes,<sup>2,3</sup> herein we report the synthesis of a new flexible organic linker tetrakis[(3,5-dicarboxyphenoxy)methyl] methane ( $H_8L$ , Scheme 1) and its resulting robust MOF  $[Cu_4L(H_2O)_4] \cdot (H_2O)_{31}$  (MOF **1**) of the rare (4,8)-connected *scu* topology for acetylene storage at ambient temperature.

## 2. Experimental section

## 2.1. Materials and methods

All the chemicals except the ligand  $H_8L$  were commercially purchased and used without further purification. The preparation of  $H_8L$  is described in the following section.

Elemental analyses of C and H were performed on an Elementar Vario MICRO elemental analyzer. Fourier transformed

Scheme 1 Schematic structure of the flexible linker  $H_8L$ .

<sup>a</sup>State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China. E-mail: hbdu@nju.edu.cn; Fax: +86 25-83314502

<sup>b</sup>Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas, 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: +1 210-458-7428

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infrared (FT-IR) spectra were obtained on a Bruker Vector 22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer under nitrogen with a heating rate of 10 °C min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5–50 degree range with a scan speed of 0.1 deg s<sup>-1</sup> on a Bruker D8 Advance instrument using a Cu Kα radiation (λ = 1.54056 Å) at room temperature. A Micromeritics ASAP 2020 surface area porosimetry system was used to measure gas adsorption. In order to remove guest solvent molecules in the framework, a freshly prepared sample was activated at 120 °C under dynamic vacuum. The sorption measurements for N<sub>2</sub> and H<sub>2</sub> were carried out at 77 K with liquid nitrogen, while those for C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> sorption were performed at 273 and 296 K with a water bath, respectively.

## 2.2. Synthesis

**Preparation of H<sub>8</sub>L.** A mixture of dimethyl 5-hydroxyisophthalate (19.24 g, 80.8 mmol), pentaerythrityl tetrabromide (7.68 g, 20.0 mmol) and K<sub>2</sub>CO<sub>3</sub> (33.20 g, 240.0 mmol) in DMF (150 mL) was stirred at 100 °C for about 96 h under a nitrogen atmosphere. The mixture was condensed to about 75 mL and then 1000 mL of water was added at 0 °C. The mixture was filtered after stirring for about 10 min and washed with aqueous NaOH (10%) and water. A white solid was obtained after drying in vacuum at 60 °C. The solid was added to a solution of 28 mL of 20% NaOH and 300 mL of methanol, and refluxed for about 96 h at 80 °C. The mixture was condensed to about 100 mL, then cooled to room temperature and filtered. The filtrate was acidified to pH 1–2 with aqueous HCl (6 mol L<sup>-1</sup>), and the precipitate was filtered, washed with water, and dried in vacuum to give a white solid H<sub>8</sub>L (12.5 g). Yield: 78%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ (ppm): 12.59 (s), 7.92 (d, 6H), 7.16 (d, 6H), 5.21 (s, 6H), 2.36 (s, 9H).

**Synthesis of 1.** A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.024 g, 0.1 mmol) and H<sub>8</sub>L (0.0158 g, 0.02 mmol) in 4 mL of H<sub>2</sub>O, 2 mL of EtOH and three drops of HNO<sub>3</sub> (2 mol L<sup>-1</sup>) was sealed in an autoclave equipped with a Teflon liner (25 mL), heated at 100 °C for 3 days, and then cooled to room temperature. Blue block single crystals of **1** were collected in a *ca.* 62% yield based on H<sub>8</sub>L. Elemental analysis for C<sub>37</sub>H<sub>90</sub>Cu<sub>4</sub>O<sub>55</sub>, calcd (%): C, 26.65; H, 5.44. Found (%): C, 26.74; H, 5.45. IR data (KBr, cm<sup>-1</sup>): 3422 (s), 2364 (m), 1709 (s), 1573 (s), 1376 (s), 1268 (s), 1135 (s), 1041 (s), 883 (m), 775 (s), 682 (m), 481 (w).

## 2.3. Single-crystal X-ray crystallography

A suitable crystal of **1** was selected for single crystal X-ray diffraction. The data collections were carried out on a Bruker Smart APEX II CCD diffractometer at 291 K, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reductions and absorption corrections were performed using the SAINT and SADABS programs,<sup>19</sup> respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on *F*<sup>2</sup> using the SHELXL-97 program.<sup>20</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in

geometrically calculated positions and refined using the riding model. Because of the highly disordered solvent molecules in **1**, the PLATON/SQUEEZE route was employed to calculate the diffraction contribution from the solvent molecules, and thereby to produce a set of solvent-free diffraction intensities.<sup>21</sup> The final formula was derived from crystallographic data combined with elemental and thermogravimetric analyses data. Details of the crystal parameters, data collection and refinement results are summarized in Table 1. Selected interatomic bond lengths and angles of **1** with their estimated standard deviations are given in Table S1 (ESI†). Further details can be obtained from the ESI†.

## 3. Results and discussion

### 3.1. Synthesis

**1** was prepared solvothermally under the acidic condition from corresponding Cu(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and H<sub>8</sub>L in an ethanol–water mixture at 100 °C even without using the typical solvent DMF. The as-synthesized product is of pure phase as further confirmed by XRPD and elemental analyses. MOF **1** loses 31 lattice water molecules and 4 coordinated water molecules in the temperature range from room temperature to about 150 °C with the experimentally determined water weight loss of 37.4% (Fig. S2†), which matches with the calculated one of 37.8%. The desolvated **1** can be thermally stable up to about 300 °C.

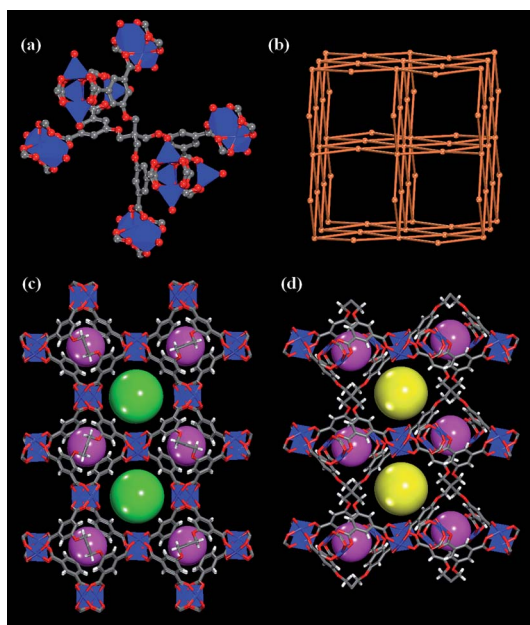
### 3.2. Crystal structure descriptions

MOF **1** crystallizes in the orthorhombic space group *Pbcm* with four asymmetric units in one cell. Each asymmetric unit contains a half L<sup>8-</sup> ligand, three Cu(II) ions, and three coordinated water molecules (Fig. S1†). As shown in Fig. 1a, the three Cu<sup>II</sup> are five-coordinated in a square pyramidal geometry by four carboxylate oxygen atoms from four different L<sup>8-</sup> ligands at the basal positions and one water molecule at the apical position. The two adjacent Cu<sup>II</sup> ions are linked together by four carboxylate groups

**Table 1** Crystallographic and structural data for **1**<sup>a</sup>

Compound reference	<b>1</b>
Chemical formula	C <sub>37</sub> H <sub>90</sub> Cu <sub>4</sub> O <sub>55</sub>
Formula mass	1669.26
Crystal system	Orthorhombic
<i>a</i> /Å	12.100(3)
<i>b</i> /Å	26.162(4)
<i>c</i> /Å	26.162(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Unit cell volume/Å <sup>3</sup>	8282(3)
Temperature/K	291(2)
Space group	<i>Pbcm</i>
No. of formula units per unit cell, <i>Z</i>	4
No. of reflections measured	42 618
No. of independent reflections	8312
<i>R</i> <sub>int</sub>	0.0613
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0468
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.1129
Final <i>R</i> <sub>1</sub> values (all data)	0.0627
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1200
Goodness of fit on <i>F</i> <sup>2</sup>	1.069

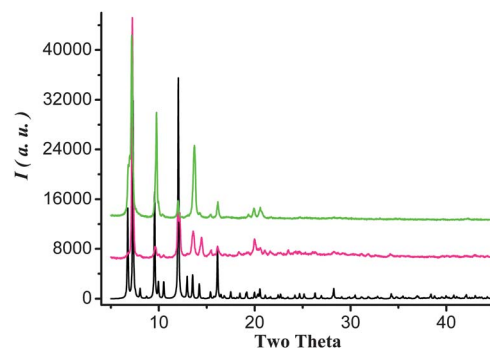
$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$



**Fig. 1** Single-crystal X-ray structure of **1**, showing (a) the organic ligand which is connected to eight  $[\text{Cu}_2(\text{O}_2\text{CR})_4]$  SBUs, (b) the resulting 4,8-connected framework with *scu* topology, and structures viewed along (c) the *a* axis and (d) the *c* axis to illustrate the pore windows and corresponding interconnecting cages (color scheme: C, gray; H, white; O, red; and Cu, blue).

to form a paddlewheel dinuclear cluster  $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ . The Cu–O, Cu–O<sub>w</sub> and Cu···Cu distances range 1.914(2)–1.969(2), 2.144(3)–2.162(2), and 2.6371(7)–2.6395(7) Å, respectively, which are consistent with those found in other  $[\text{Cu}_2(\text{O}_2\text{CR})_4]$  paddlewheel based MOFs.<sup>22</sup> The dicopper paddlewheel cluster is linked by four  $\text{L}^{8-}$  ligands *via* carboxylate groups in a square coordination geometry, while the  $\text{L}^{8-}$  ligand, with the center quaternary carbon atom sitting on a 2-fold symmetry axis, adopts a distorted cube coordination geometry to connect eight neighbouring dicopper paddlewheels. This gives rise to a non-interpenetrated (4,8)-connected network with the *scu* topology<sup>23</sup> (Schläfli symbol of  $\{4^46^2\}_2\{4^{16}6^{12}\}$ ) (Fig. 1b), in which the dicopper paddlewheel cluster and organic linker are regarded as 4-connected and 8-connected nodes, respectively. It is noted that **1** is one of the few known MOFs with *scu* topology reported to date.<sup>24</sup>

Viewed along the *a* and *c* axes in **1**, there exist two types of micropore windows of approximately  $5.5 \times 5.5 \text{ \AA}^2$  and  $5.5 \times 5.8 \text{ \AA}^2$ , respectively, taking into account van der Waals distances. Close examination of the structure reveals that **1** consists of two types of interconnecting cages: one is small octahedral cages (purple spheres in Fig. 1c and d) of approximately 4.7 Å in diameter, built from four dicopper paddlewheel clusters and two half L ligands; another is larger cuboctahedral cages (green and yellow spheres in Fig. 1) with an approximate diameter of 9.0 Å, composed of eight dicopper paddlewheel clusters and four half L ligands. Each cage connects with eight neighbouring ones of different types to form a highly porous framework. PLATON calculations show that the guest accessible void ( $5125.5 \text{ \AA}^3$  per unit cell) comprises 61.9% of the unit cell volume.



**Fig. 2** X-ray powder diffraction patterns of MOF **1**: (a) calculated (black), (b) as-synthesized (pink) and (c) after gas adsorption measurements (green).

### 3.3. Thermal properties

To investigate the thermal stability of the framework of **1**, thermogravimetric analyses (TGA) were carried out. As exemplified in Fig. S2†, the guest solvent molecules in **1** can be removed before *ca.* 100 °C, while the desolvated **1** is stable up to about 300 °C before the decomposition of the organic ligand. The robustness and thermal stabilities of the framework of **1** were further checked by X-ray powder diffraction. As shown in Fig. 2, the main XRD peaks of **1** heated at 120 °C under high vacuum for 12 h basically matched those of the pristine ones, indicating that the framework of **1** remains intact after desolvation and activation.

### 3.4. Adsorption properties

The permanent porosity of MOF **1** was confirmed by gas adsorption measurements of  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ . As shown in Fig. 3a, the  $\text{N}_2$  adsorption isotherm at 77 K for **1** shows type-I behavior with a steep rise in the very low pressure region, suggesting a microporous nature of the activated **1**. The Brunauer–Emmett–Teller (BET) area, the Langmuir surface area and pore volume were calculated from the  $\text{N}_2$  adsorption isotherm to be  $1115 \text{ m}^2 \text{ g}^{-1}$ ,  $1722 \text{ m}^2 \text{ g}^{-1}$ , and  $0.612 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The Horvath–Kawazoe (HK) model calculations indicate a median pore diameter of 5.8 Å, which is consistent with that calculated from the single crystal structure analysis.

The  $\text{H}_2$  sorption measurements at 77 K showed that the activated **1** exhibited reversible hydrogen adsorption isotherm curves (Fig. 3a), indicating a strong affinity of hydrogen molecules toward pore surfaces. At 77 K and 760 Torr, the  $\text{H}_2$  uptake of **1** is  $238 \text{ cm}^3 \text{ g}^{-1}$  (2.12 wt%), which is moderately high.<sup>25</sup> The activated **1** also takes up certain amount of carbon dioxide ( $140 \text{ cm}^3 \text{ g}^{-1}$ , 6.25 mmol  $\text{g}^{-1}$ ) and methane ( $32 \text{ cm}^3 \text{ g}^{-1}$ , 1.42 mmol  $\text{g}^{-1}$ ) at 273 K and 760 Torr (Fig. 3b).

The most important feature of MOF **1** is its high acetylene uptake of 193 and  $154 \text{ cm}^3 \text{ g}^{-1}$  under 1 atm at 273 K and 296 K, respectively (Fig. 3c). Although MOF **1** is less porous than MOF-505<sup>8c</sup> and  $\text{Cu}_2(\text{EBTC})$ ,<sup>8d</sup> the acetylene storage capacity of MOF **1** ( $154 \text{ cm}^3 \text{ g}^{-1}$ ) is comparable to  $148 \text{ cm}^3 \text{ g}^{-1}$  for MOF-505 and  $160 \text{ cm}^3 \text{ g}^{-1}$  for  $\text{Cu}_2(\text{EBTC})$ , and thus is amongst the few MOFs for high acetylene storage.<sup>8b–d,16</sup> The storage capacities of MOF **1** for acetylene are still not saturated, which means that

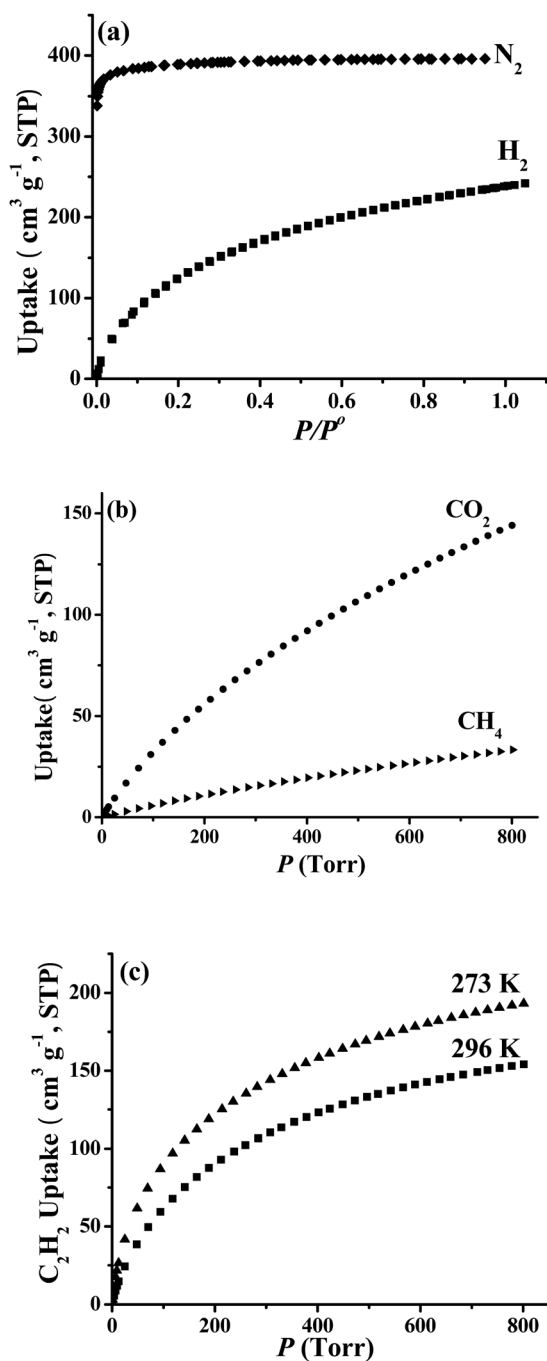


Fig. 3 Gas sorption isotherms of the MOF 1 for (a) N<sub>2</sub> and H<sub>2</sub> at 77 K; (b) CO<sub>2</sub> and CH<sub>4</sub> at 273 K; and (c) C<sub>2</sub>H<sub>2</sub> at 273 and 296 K.

their uptake can be further maximized until the limit of safe storage of acetylene under a pressure of 0.2 MPa.<sup>26</sup>

The high acetylene storage capacities of MOF 1 are attributed to the high density of open copper(II) sites within MOF 1. As established in HKUST-1 in which each open copper(II) site binds one acetylene molecule, the copper(II) site density of 3.85 mmol g<sup>-1</sup> in MOF 1 can contribute 86.3 cm<sup>3</sup> storage capacity of the total 154 cm<sup>3</sup> at 1 atm and 296 K. The remaining acetylene (67.7 cm<sup>3</sup>) can be easily stored inside the pore space of moderate sizes (cages of 4.7 and 9.0 Å) within MOF 1.

## 4. Conclusions

In summary, we have successfully synthesized a novel robust open metal-organic framework [Cu<sub>4</sub>L(H<sub>2</sub>O)<sub>4</sub>·(H<sub>2</sub>O)<sub>31</sub>] (1) with (4,8)-*scu* topology based on a flexible tetrahedrally branched octadentate ligand (H<sub>8</sub>L) and the paddlewheel Cu<sub>2</sub>(O<sub>2</sub>C)<sub>4</sub> cluster. The new MOF possesses interconnecting cages with unsaturated open metal sites after thermal activation. It exhibits permanent porosity and high acetylene uptake of 193 and 154 cm<sup>3</sup> g<sup>-1</sup> at 273 and 296 K under 1 atm, respectively, highlighting its potential as an acetylene storage material. This study shows that it is also feasible to construct robust MOFs from flexible organic linkers once the organic linkers are suitably decorated to favor the formation of robust metal-containing secondary building blocks, thus providing a new strategy to explore new porous MOF materials for high gas storage and separation in the near future.

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