

# A unique microporous copper trimesate selenite with high selectivity for CO<sub>2</sub>†

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A copper trimesate selenite compound is reported which shows a robust 3-D porous structure with unprecedented structural characteristics and represents a unique example of a metal inorganic–organic framework with considerable permanent microporosity and selective CO<sub>2</sub> sorption properties.

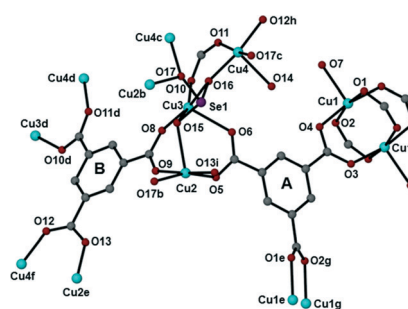
The synthesis and study of Metal Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs) have risen to the forefront of inorganic and materials science research.<sup>1,2</sup> This is not surprising taking into account the exceptional properties of these compounds and potential applications in various fields including gas storage and separation, catalysis, sensing, drug delivery, *etc.*<sup>1,2</sup> Besides tuning the properties of existing MOFs, it is also of great importance to discover new compounds that may exhibit features not observed for the already reported materials.

A strategy that can afford MOFs with unprecedented structures and properties involves the simultaneous use of polytopic organic ligands and inorganic anions with metal binding capability, such as SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>3</sub><sup>2-</sup>, SeO<sub>3</sub><sup>2-</sup>, TeO<sub>3</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, *etc.*<sup>3</sup> Such MOFs, which can be called Metal Inorganic Organic Frameworks (MINOFs), may show not only unique structural characteristics but also properties arising from the presence of inorganic anionic ligands, making them a distinct class of metal organic framework materials. For example, it is well known that the incorporation of QO<sub>3</sub><sup>2-</sup> (Q = S, Se, Te)

anions often leads to non-centrosymmetric structures due to the lone pair of electrons of these ligands and many acentric compounds with these anions display interesting non-linear optical properties (*e.g.* Second Harmonic Generation, SHG).<sup>4</sup> So far, MOFs containing bridging inorganic anionic groups in combination with organic polytopic ligands have been reported sporadically<sup>3</sup> and in addition, the vast majority of such materials described in the literature are nonporous with very few exceptions.<sup>3k</sup>

Herein we present the compound [Cu<sub>4</sub>(btc)<sub>2</sub>(SeO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]-6H<sub>2</sub>O (**MINOF-1**) (H<sub>3</sub>btc = 1,3,5-benzenetricarboxylic acid), which exhibits a robust 3-D open framework structure and also adopts a highly unusual structural topology as a result of the insertion of SeO<sub>3</sub><sup>2-</sup> ligands into the copper trimesate net. Importantly, **MINOF-1** represents a unique example of a coordination polymer based on both organic and inorganic polytopic ligands that shows significant permanent microporosity and high CO<sub>2</sub> uptake and selectivity *vs.* CH<sub>4</sub>.

Compound **MINOF-1** was isolated as plate-like crystals (Fig. S1, ESI†) by the reaction of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, H<sub>3</sub>btc and KSeCN in EtOH:H<sub>2</sub>O (1:1) at 90 °C. The SeO<sub>3</sub><sup>2-</sup> ligands are presumably formed *in situ* by the decomposition of SeCN<sup>-</sup>



**Fig. 1** Representation of the connectivity of the Cu<sup>2+</sup> ions, btc<sup>3-</sup> ligands (A and B) and SeO<sub>3</sub><sup>2-</sup> group in **MINOF-1**. The H atoms were omitted for clarity. Symmetry codes: a: 3/2 - x, 1/2 - y, 1 - z; b: 1 - x, -y, -z; c: 1 - x, y, 1/2 - z; d: x, 1 - y, z - 1/2; e: x, -y, z - 1/2; f: x, y, z - 1; g: 3/2 - x, y - 1/2, 1/2 - z; h: x, y, 1 + z; i: x, -y, 1/2 + z.

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† Electronic supplementary information (ESI) available: Experimental details, structural figures, sorption isotherms, SEM images and thermal analysis, IR, and PXRD data (Fig. S10–S13). CCDC 968879 and 968880 contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00091a

under hydrothermal conditions. Note that **MINOF-1** cannot be isolated using  $\text{SeO}_3^{2-}$  instead of  $\text{SeCN}^-$ ; reactions in the presence of  $\text{SeO}_3^{2-}$  led to mixtures of  $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$  (**HKUST-1**)<sup>5a</sup> and chalcocite  $[\text{Cu}(\text{SeO}_3)_2(\text{H}_2\text{O})_2]$ .<sup>5b</sup> Therefore, the slow transformation of  $\text{SeCN}^-$  to  $\text{SeO}_3^{2-}$  seems to be the key for the successful synthesis of the metal-organic selenite compound.

The compound crystallizes in the monoclinic space group  $C2/c$ .<sup>‡</sup> There are four crystallographically unique  $\text{Cu}^{2+}$  ions in the structure, all adopting a square pyramidal coordination geometry (Fig. 1): Cu1 is coordinated with four carboxylic oxygen atoms (O1–O4) and one terminal water (O7) solvent; Cu2 and Cu3 are connected with three carboxylate oxygen atoms (O9, O5, O13; O8, O6, O10, respectively) and two oxygen atoms from  $\text{SeO}_3^{2-}$  groups (O15, O17; O15, O16, respectively); and Cu4 is linked with two carboxylate (O11, O12) and two  $\text{SeO}_3^{2-}$  oxygen atoms (O16, O17) and one terminal water (O14) ligand. The structure is a 3-D framework, which is constructed by the combination of paddle-wheel  $[\text{Cu}_2(\text{COO})_4]$  SBUs and a double  $\text{Cu}^{2+}$ – $\text{SeO}_3^{2-}$ – $\text{btc}^{3-}$  layer and exhibits large channels running along the  $c$ -axis (Fig. 2). The dinuclear SBUs are formed by two symmetry-equivalent Cu1 ions and four trimesate anions (A), whereas the double layer is composed of a trinuclear unit  $[\text{Cu}_3]$  comprising the Cu2, Cu3 and Cu4 ions, the  $\mu_5$ - $\text{SeO}_3^{2-}$  ligands and trimesate anions of the second type (B) (Fig. 1 and 2). The underlying topology of this framework is quite complex as evidenced by the high number of the different nodes (Fig. S2<sup>†</sup>). Specifically, this 5-nodal network consists of an 8-connected node corresponding to the  $[\text{Cu}_3]$  subunits (Cu2, Cu3 and Cu4), two 3-connected nodes corresponding to the  $\text{SeO}_3^{2-}$  anions and the trimesate anion B and two 4-connected nodes corresponding to the second trimesate anion A and the  $[\text{Cu}_2]$  paddle wheel subunits, respectively. The point symbol for this 3,3,4,4,8-connected network is  $(4^{10}\cdot6^{15}\cdot8^3)_2(4^3)_2(4^4\cdot6^2)_2(6^2\cdot8^3\cdot10)(6^2\cdot8)_2$  and it is, as expected, unique so far. The structure of the MOF presented (**MINOF-1**) is special and unique for several reasons: a) **MINOF-1** adopts a unique and highly unusual structural type (see above); b) this MOF is a rare example of a coordination polymer combining  $\text{SeO}_3^{2-}$  and organic polytopic ligands (the known ones are very few examples of non-porous vanadium or lanthanide coordination polymers<sup>3i,j</sup>); and c) the combination of the well-known paddle wheel  $[\text{Cu}_2(\text{COO})_4]$  SBUs and layers of  $\text{Cu}^{2+}$  ions connected with both inorganic and organic polytopic ligands in **MINOF-1** is unprecedented.

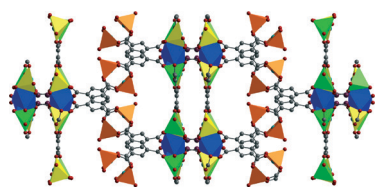


Fig. 2 The 3-D framework of **MINOF-1** with a polyhedral representation of the  $\text{Cu}^{2+}$  ions. (Cu1, orange; Cu2, blue; Cu3, green; Cu4, yellow; Se, purple; O, red; C, grey.) Guests and H atoms were omitted for clarity.

To investigate whether it is possible to remove the lattice and coordinating solvents from the **MINOF-1** without the collapse of the porous structure, a high temperature (200 °C) crystallographic study has been performed on a single crystal of the compound. The results indicate that the structural integrity of the compound is retained upon the removal of the solvents and the dry material (**MINOF-1'**) crystallizes in the same space group as that of the pristine compound with slight changes in the cell parameters.<sup>§</sup> The underlying network of **MINOF-1'** is quite similar to that of the pristine material, but there are some striking differences between the two structures. Thus, the connectivity of the  $[\text{Cu}_3]$  subunits, the trimesate anion B and  $\text{SeO}_3^{2-}$  within the double layer is exactly the same in both **MINOF-1** and **MINOF-1'** (Fig. S3<sup>†</sup>). However, the removal of the coordinated water molecule (O14) from Cu4 is accompanied by a flip of one carboxylate unit of the trimesate anion A which now bridges two  $[\text{Cu}_3]$  subunits. This, in turn, increases the connectivity of the  $[\text{Cu}_3]$  nodes from 8 to 9 and the connectivity of the respective trimesate anion A from 3 to 4 (Fig. S4<sup>†</sup>). Therefore, the resulting network is again 5-nodal but it is now 3,4,4,4,9-connected with the point symbol  $(4^{17}\cdot6^{18}\cdot8)_2(4^2\cdot8^4)(4^3\cdot6^2\cdot8)_2(4^3)_2(4^4\cdot6^2)_2$ ; it is, as expected, unique (Fig. S5<sup>†</sup>).

Nitrogen physisorption measurements recorded at 77 K for the activated sample (**MINOF-1'**) reveals a type-I isotherm, characteristic of a microporous material, as shown in Fig. S6<sup>†</sup>. The apparent Langmuir surface area is  $504 \text{ m}^2 \text{ g}^{-1}$  (BET,  $400 \text{ m}^2 \text{ g}^{-1}$ ) and the total pore volume is  $0.21 \text{ cm}^3 \text{ g}^{-1}$  at 0.98  $p/p_0$ . Analysis of the  $\text{N}_2$  adsorption data using the non-local density functional theory (NLDFT) gives a pore size of ca. 6 Å, which correlates well with the crystal structure of **MINOF-1'** (calculated pore size from PLATON:<sup>6</sup> ~6.1 Å). To further investigate the gas sorption properties of **MINOF-1'**, gas adsorption isotherms were measured for  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$  at different temperatures. **MINOF-1'** showed significant hydrogen uptake at 1 atm and 77 K (0.88 wt%) and even at 87 K (0.67 wt%), which is higher than those of mesoporous MCM-41 silica (0.57 wt%),<sup>7a</sup> zeolite ZSM-5 (0.71 wt%)<sup>7b</sup> and ICP particles (0.56–0.69 wt%)<sup>7c</sup> and comparable to those of several microporous MOFs (0.8–1.2 wt%).<sup>7d–g</sup> The isosteric heat of  $\text{H}_2$  adsorption ( $q_{\text{st}}$ ), as calculated by fitting the adsorption data at 77 and 87 K to appropriate virial-type

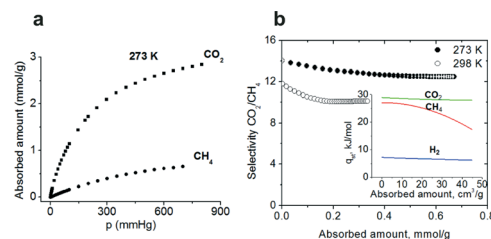


Fig. 3 (a) The  $\text{CO}_2$  and  $\text{CH}_4$  adsorption isotherms at 273 K. (b) The  $\text{CO}_2/\text{CH}_4$  selectivities for **MINOF-1'** predicted by applying IAST to the  $\text{CO}_2$  and  $\text{CH}_4$  single-component isotherms at 273 and 298 K. Inset: the isosteric heat of adsorption ( $q_{\text{st}}$ ) for  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$  as a function of the loading amount.

equations, is  $\sim 7$  kJ mol<sup>-1</sup> at zero coverage (Fig. 3b inset and S7†), which is comparable to the corresponding values obtained for many MOFs promising for hydrogen storage.<sup>7g</sup> More interestingly, MINOF-1' showed a remarkable ability to selectively sorb carbon dioxide from a gas mixture with methane at near ambient temperature. The CO<sub>2</sub> uptake at 1 bar and 273 K is 2.8 mmol g<sup>-1</sup> (Fig. 3a), while at 298 K it is 1.9 mmol g<sup>-1</sup>. This adsorption capacity exceeds those of some well-known MOFs such as MOF-5 and ZIF-100 (1.5 and 1.7 mmol g<sup>-1</sup>, respectively, at 273 K and 1 bar) and compares well with those of some of the best CO<sub>2</sub> sorbents.<sup>7h</sup> The CH<sub>4</sub> uptake is 0.7 mmol g<sup>-1</sup> (Fig. 3) and 0.25 mmol g<sup>-1</sup> at 273 and 298 K, respectively. Analysis of the adsorption data using the ideal adsorption solution theory (IAST)<sup>7i</sup> (Fig. S8†) reveals that the CO<sub>2</sub>/CH<sub>4</sub> selectivity in MINOF-1' is  $\sim 14$  at 273 K and  $\sim 12$  at 298 K for a CO<sub>2</sub>:CH<sub>4</sub> = 50:50 mixture in the low-pressure limit (near zero coverage) (see Fig. 3b). These CO<sub>2</sub>/CH<sub>4</sub> selectivity values of MINOF-1' compare well with those of MOFs showing great promise for CO<sub>2</sub> separation.<sup>7h</sup> The CO<sub>2</sub>/CH<sub>4</sub> gas mixture separation in MINOF-1' may be attributed to the preferential adsorption of quadrupolar CO<sub>2</sub> by the coordinatively unsaturated Cu<sup>2+</sup> sites (Lewis acids) of the metal-organic framework; such induced-dipole interactions are not favourable for nonpolar CH<sub>4</sub> molecules. As for the strength of these interactions, the isosteric heat of CO<sub>2</sub> and CH<sub>4</sub> adsorption, obtained by fitting the adsorption data at 263, 273 and 298 K to appropriate virial-type equations (Fig. S9†), was found to be  $\sim 29$  and  $\sim 27$  kJ mol<sup>-1</sup> at the limit of zero coverage, respectively (Fig. 3b inset). Considering that the kinetic diameters of CO<sub>2</sub> and CH<sub>4</sub> molecules are  $\sim 3.3$  Å and  $\sim 3.8$  Å, respectively, *i.e.* smaller than the pore size of MINOF-1' (*ca.* 6 Å), these results indicate preferential adsorption interactions between the surface functionalities of MINOF-1' and CO<sub>2</sub> molecules, thus supporting solubility separation of CO<sub>2</sub> over CH<sub>4</sub>.

In conclusion, the amalgamation of copper trimesate and copper trimesate selenite moieties in MINOF-1 led to a structure with features unprecedented in MOF chemistry. The new compound exhibits a highly robust open framework structure, which is retained upon the removal of guest and coordinated water solvents. Interestingly, the dehydration can even be achieved in a single crystal of the material heated at 200 °C. This single-crystal-to-single-crystal (SCSC) transformation is accompanied by a flip of a carboxylate unit which, in effect, leads to a dehydrated material with different topological features. Remarkably, MINOF-1 displays considerable permanent microporosity, which has been rarely observed so far in coordination polymers combining both inorganic and organic polytopic ligands. The high CO<sub>2</sub> uptake and its selective adsorption over CH<sub>4</sub> under near ambient conditions as well as the significant isosteric heat of adsorption for H<sub>2</sub> are also important properties of MINOF-1. Furthermore, the synthetic approach presented in this paper provides a means for the discovery of many new porous MOFs with novel structural features and possibly unusual and interesting physical properties. Our research efforts are now focused towards this direction.

## Acknowledgements

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## Notes and references

‡ Crystal data for MINOF-1: C<sub>18</sub>H<sub>22</sub>Cu<sub>4</sub>O<sub>23</sub>Se, *M* = 939.48, monoclinic, *C2/c*, *a* = 41.0363(18) Å, *b* = 12.1733(4) Å, *c* = 14.1609(5) Å,  $\beta$  = 100.869(3)°, *V* = 6947.1(5) Å<sup>3</sup>, *T* = 293(2) K, *Z* = 8, 17 377 reflections measured, 6115 independent reflections (*R*<sub>int</sub> = 0.0875). The final *R*<sub>1</sub> and *wR*(*F*<sup>2</sup>) values are 0.0639 (*I* > 2σ(*I*)) and 0.1371 (*I* > 2σ(*I*)), respectively; GOF = 1.093. § Crystal data for MINOF-1': C<sub>18</sub>H<sub>6</sub>Cu<sub>4</sub>O<sub>15</sub>Se, *M* = 795.39, monoclinic, *C2/c*, *a* = 38.391(6) Å, *b* = 12.3697(11) Å, *c* = 14.1757(14) Å,  $\beta$  = 90.165(10)°, *V* = 6732(2) Å<sup>3</sup>, *T* = 473(2) K, *Z* = 8, 26 274 reflections measured, 5938 independent reflections (*R*<sub>int</sub> = 0.2794). The final *R*<sub>1</sub> and *wR*(*F*<sup>2</sup>) values are 0.1312 (*I* > 2σ(*I*)) and 0.2912 (*I* > 2σ(*I*)), respectively; GOF = 1.071.

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