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## COMMUNICATION

# Extending the family of Zn-based MOFs: synthetic approaches to chiral framework structures and MOFs with large pores and channels†

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**Tri- and pentanuclear, kinetically stable SBUs were exploited for the preparation of the novel MOFs  $[\text{Zn}_3(\text{BTEB})_2(\text{DMF})_2]$  and  $(\text{Me}_2\text{NH}_2)[\text{Zn}_5(\text{BTEB})_3(\mu_3\text{-OH})_2(\text{DMF})_2]$ . The applied synthetic approach results in topologies that are stabilised by tritopic benzene-trisethynylbenzoic acid (BTEB) linkers giving rise to chiral frameworks with large pores or channels.**

Metal–organic frameworks (MOFs) are classified as crystalline materials consisting of clusters or metal ions linked coordinatively through organic ligands and resulting in microporous networks.<sup>1</sup> The interest in MOFs is a result of their advantageous characteristics which include facile synthesis, high porosity, and amenability to chemical modification for targeting purposes.<sup>2</sup> MOFs are regarded as key materials related to energy storage<sup>3</sup> and efficient usage of resources, as their unprecedented surface areas make them promising alternative materials for gas storage,<sup>4</sup> gas separation<sup>5</sup> and catalysis purposes.<sup>6</sup> Current activities focus on the development of synthetic concepts to novel MOFs whereby increased hydrogen and CO<sub>2</sub> storage capabilities may provide scientific concepts to initiate a shift towards more sustainable energy concepts. Most employed synthetic approaches to MOFs rely on self-assembly using simple inorganic metal ions as starting materials that may aggregate into oligonuclear complexes in the presence of suitable, cross-linking multi-dentate ligands. Careful selection of the metal ions, the nature of the assembled coordination clusters and ligands and consideration of their preferred coordination modes and geometries provide control over the resulting network topologies. Rigid, aromatic polycarboxylate ligands whose backbone structures can be extended modularly for instance through insertion of phenylene or ethynyl moieties are attractive ligands that give rise to ultra-high surface area materials with amenable pore structures and interpenetration patterns.

To explore the formation of new open-framework materials that give rise to high surface areas and interesting interpenetration patterns, the tri-functional ligand, 1,3,5-benzene-trisethynylbenzoic acid (BTEB), was chosen.<sup>7</sup> Its tritopic, triangular topology is characterized by a carboxylate–carboxylate and centroid–carboxylate separation distance of *ca.* 18 Å and 10 Å. The only

BTEB coordination compounds previously synthesized and structurally characterized comprise of a {Ni/cylam} 2D-network polymer<sup>8</sup> and a highly porous MOF containing octahedral  $\{\text{Zn}_4\text{O}(\text{O}_2\text{C})_6\}$  SBUs.<sup>9</sup> Here we report two new BTEB-based MOFs,  $[\text{Zn}_3(\text{BTEB})_2(\text{DMF})_2]$  (**TCM-1**) and  $(\text{Me}_2\text{NH}_2)[\text{Zn}_5(\text{BTEB})_3(\mu_3\text{-OH})_2(\text{DMF})_2]$  (**TCM-2**), whose topologies and interpenetration patterns are determined by the nuclearity of kinetically stable, tri- and pentanuclear Zn(II) SBUs. In the former case the observed helical interpenetration patterns results in supramolecular chirality.

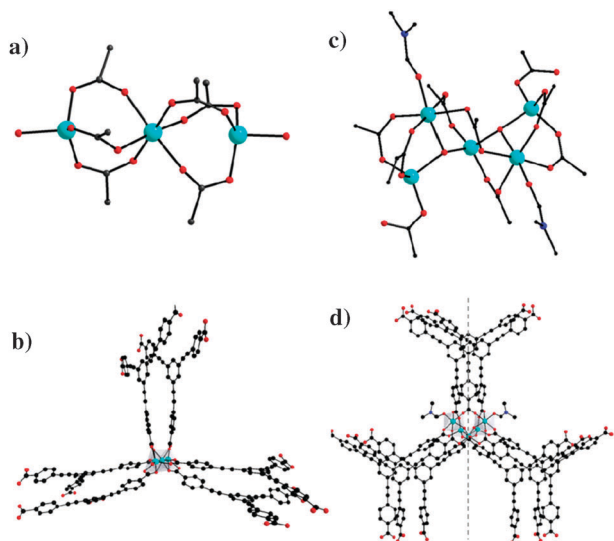
**TCM-1** and **-2** form under solvothermal reaction conditions at 80 °C in DMF (ESI†). Phase-pure, colourless, needle-like crystals of **[TCM-1].solv** are obtained at a molar Zn<sup>2+</sup>/BTEB ratio of 2 : 1. The MOF can be also obtained at a Zn<sup>2+</sup>/BTEB ratio of 3.3 : 1. Above a molar reactant ratio of 3.8/1, **[TCM-2].solv** starts to co-crystallise as yellowish block crystals. Phase-pure samples of **[TCM-2].solv** can be obtained when the molar ratio is raised to 6 : 1. Further increased Zn<sup>2+</sup> concentrations, *e.g.* Zn<sup>2+</sup>/BTEB ratios of 9 : 1, result in the formation of MOF-180 that contains tetranuclear SBUs and whose structure was previously reported.<sup>9</sup>

**TCM-1** contains trinuclear  $\{\text{Zn}_3(\text{O}_2\text{C})_6\}$  SBUs (Fig. 1a and b) in which the Zn-atoms are linearly arranged and triply bridged by bidentate carboxylate moieties that originate from six different fully deprotonated BTEB ligands. The central zinc atom is in an almost ideal octahedral coordination environment. The outer two Zn atoms adopt distorted tetrahedral coordination geometries whose remaining terminal sites are provided by O-donors from coordinating DMF molecules. Similar complexes have previously been isolated as 0D systems and used to prepare 3D-network structures.<sup>10</sup> **[TCM-1].solv** crystallizes either in the space group *P*<sub>4</sub><sub>3</sub><sub>2</sub> or *P*<sub>4</sub><sub>1</sub><sub>2</sub> (enantiomeric) representing a chiral supramolecular system in which the shape and topology of SBUs promote the formation of optical isomers. Each trinuclear Zn moiety is linked *via* π–π interacting BTEB pairs to three neighbouring Zn SBUs. Two carboxylate functionalities of each organic ligand link the complexes along 4<sub>3</sub> (or 4<sub>1</sub>)-screw axes that coincide with the crystallographic *c*-axes (as seen in Fig. 2); the third deprotonated acid functionality connects the helical chains according to the 4-fold screw symmetry in the other directions of space to form a 3D network structure. **TCM-1** is 2-fold interpenetrated consisting of two symmetry equivalent nets that are not connected through covalent or coordination bonds (Fig. 2c and d). The symmetry of **TCM-1** and of the observed interpenetration pattern results in double

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**Fig. 1** (a, b) Trinuclear Zn(II) building unit in **TCM-1** that is stabilised by six carboxylate moieties (only O-donor atoms of the coordinating DMF molecules are represented); (c, d) pentanuclear Zn(II) SBU in **TCM-2** that is stabilised by nine carboxylate moieties ( $C_2$  symmetry axis indicated as intersected line). Colour code: Zn cyan, O red, C grey.

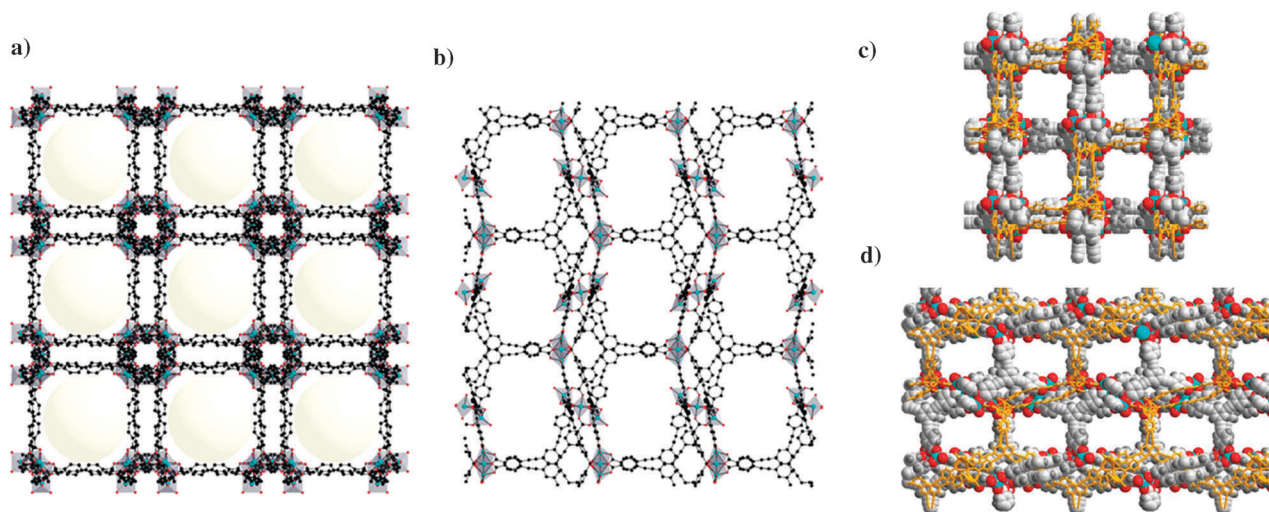
helical arrangements in which dispersion forces between the aromatic ligand moieties promote close inter-ligand contacts. Thus, the observed interpenetration mode stabilises the observed topology and does not significantly affect pore and channel diameters of the supramolecular assembly. **TCM-1** forms an open-framework structure whose void spaces are accessible from all directions of space. This feature distinguishes **TCM-1** from previously reported related structures that are stabilised by the less extended ligands, *e.g.* 4,4',4''-*s*-triazine-2,4,6-triyltri-benzoate (TATB) or chiral derivatives.<sup>11</sup> In comparison to  $[Zn_3(TATB)_2(HCOO)]$ , the use of extended BTEB ligands results in a significant increase of the solvent-accessible void space from *ca.* 4535 Å<sup>3</sup> (54% of the unit cell volume) to *ca.* 11 135 Å<sup>3</sup> (72%). The cross-sectional diameter of the chiral

channels in **TCM-1** when viewed in the direction of the crystallographic *c*-axis doubles to *ca.* 12 Å. **TCM-1** has channel openings that are characterised by 16 × 11 Å and that are absent in the related  $[Zn_3(TATB)_2(HCOO)]$ -MOF.

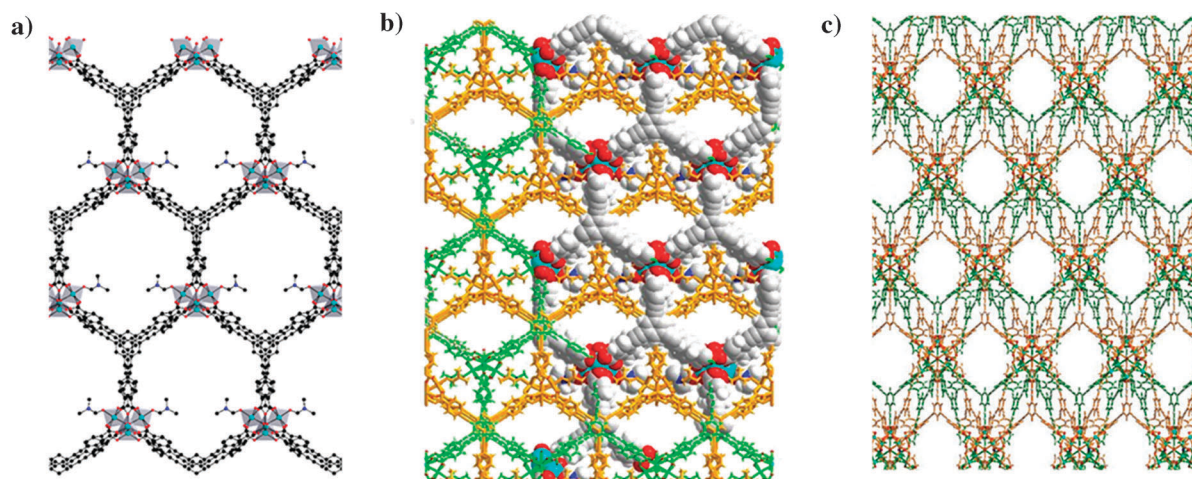
**TCM-2** contains novel pentanuclear  $\{Zn_5(\mu_3-OH)_2(O_2C)_9 DMF_2\}$ -SBUs in which two  $\mu_3-OH$  ligands stabilise two triangular Zn<sup>II</sup> arrangements (Fig. 1c and d). The atom positions of these triangular units are related by  $C_2$  rotational symmetry. The complex is stabilized by 9 deprotonated BTEB ligands: 7 carboxylate functions act in a bridging bidentate mode and two as monodentate ligands. The hydroxo and carboxylate O-donor atoms facilitate distorted tetrahedral coordination geometries for four Zn<sup>II</sup> atoms, including the central Zn atom. Two coordinating DMF molecules complete the octahedral coordination environments of the remaining two Zn<sup>II</sup> sites. Each complex unit in **TCM-2** carries an overall -1 charge which is most likely compensated by disordered dimethyl ammonium counterions  $Me_2NH_2^+$  which commonly form under solvothermal reaction conditions using DMF as solvent.

The new non-planar pentanuclear SBU in **TCM-2** acts as a 9-connecting node (Fig. 3). However, the 3-pointed, equilateral star symmetry of the organic ligand is further translated to the structure of the inorganic SBU. The ligands can be divided into 3 × 3 groups whose struts enclose *ca.* 120° angles and point in three distinct directions of space. This binding motif results in a 3D honeycomb topology when viewed in the [001] direction. As for **TCM-1**, **TCM-2** also contains two interpenetrated symmetry-equivalent frameworks, which are effectively interwoven with each other (Fig. 3). The observed interpenetration mode is highlighted in Fig. 3 and is stabilized by pairwise  $\pi$ - $\pi$ -interactions between central aromatic phenyl ring moieties of the tritopic organic BTEB ligands (centroid-centroid distance of 3.36 Å between the aromatic rings). Despite this interpenetration effect, **TCM-2** contains large void spaces accounting for 49% of the cell volume. Pore openings of the network structure when viewed in the [001] and [101] directions have cross-sectional diameters of 10.5 Å and 9.0 Å, respectively.

Freshly prepared crystals of **[TCM-1].solv** desolvate readily and elemental analyses suggest that samples that were stored for several



**Fig. 2** Crystal structure of **TCM-1**. (a) View in the direction of the crystallographic *c*-axis; (b) view in the direction of the crystallographic *b*-axis; (c and d) 2-fold interpenetration in **TCM-1** when viewed in the direction of the crystallographic *c*-axis and *a*-axis. One network shows in space filling representation whilst the second is shown as orange wireframe; constitutional solvent molecules neglected for clarity. Colour code: Zn cyan, O red, C grey.



**Fig. 3** View of the framework structure of **TCM-2** viewed in the direction of the crystallographic  $c$ -axis (Zn cyan, O red, C grey). (b) Interpenetration pattern in **TCM-2** with the view in the direction of the crystallographic  $c$ -axis (independent frameworks highlighted in different colours). (c) Interpenetrated networks (green and brown) with the view in the  $[101]$ -axis.

weeks at room temperature only retain one constitutional DMF and two water molecules per formula unit. Thermogravimetric analyses of freshly prepared samples in an air atmosphere confirm a weight loss of *ca.* 50% between 20 and 120 °C attributable to the loss of constitutional solvent molecules from the network structure. A thermogravimetric step of 7 wt% most likely originates from the removal of the two coordinated DMF molecules. Above 370 °C the oxidative degradation of the organic ligand is observed. **TCM-2** reveals a very similar decomposition behaviour. A weight loss of 37% between 20 and 120 °C is the result of the desolvation of the compound. A weight loss of 9% between 120 and 200 °C stems from the removal of the coordinated DMF molecules before the oxidative degradation of the  $\text{Me}_2\text{NH}_2^+$  cations (4% between 200 °C and 350 °C) and the organic ligands above 350 °C destroy the framework structure. Elemental analyses suggest that bulk samples of **TCM-2** that were stored for several weeks at room temperature retain five DMF and nine constitutional water molecules per formula unit.

The most important attributes of these MOFs which relate to energy applications stem from their surface areas available for gas sorption applications. The structural analysis of **TCM-1** and its calculated void volume give rise to a relatively high surface area (2000–4000  $\text{m}^2 \text{g}^{-1}$ ) whilst the chiral framework structure can be maintained. However, our preliminary activation and BET experiments using **[TCM-1].solv** show that the structure tends to collapse due to the capillary forces that prevail upon solvent removal or due to the loss of the coordinating terminal DMF molecules and associated phase transitions. Preliminary drying attempts using supercritical  $\text{CO}_2$  suggest that the framework structure may be maintained upon desolvation. Activation of **[TCM-2].solv** involved the exchange of constitutional solvent molecules by acetone and by dichloromethane. Outgassing was achieved under vacuum conditions at 30 °C.  $\text{N}_2$  sorption studies gave a BET surface area of 1338  $\text{m}^2 \text{g}^{-1}$  and a corresponding Langmuir surface area of 1393  $\text{m}^2 \text{g}^{-1}$ . Outgassing attempts at 60 °C or 100 °C did not improve the surface areas and may be associated with the removal of the coordinating DMF molecules or the decomposition of the counterions and an accompanying phase change resulting in closure of the pores.  $\text{H}_2$  adsorption studies on **TCM-2** were carried out at

77 K at  $p/p_0 \approx 1$  ( $p_0$  near 1 atm). The absorbed  $\text{H}_2$  quantity correlates to 150  $\text{cc g}^{-1}$ , corresponding to 13  $\text{mg g}^{-1}$  or *ca.* 1.3 wt%.

In summary, we report the syntheses, structures and properties of two unprecedented Zn-based MOFs. The applied synthetic approach takes advantage of kinetically stable SBUs that form selectively and phase-pure depending on the molar ratios of the reactants. We are currently devising approaches to exploit their chiral framework structures and large pores and channels for gas storage and catalysis purposes.

## Notes and references

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