Two highly-connected, chiral, porous coordination polymers featuring novel heptanuclear metal carboxylate clusters†

Lei Hou,[a] Jie-Peng Zhang,*[a] Xiao-Ming Chen*[a] and Seik Weng Ng[b]

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Two novel (3,12)-connected, chiral porous coordination polymers featuring 3D intersecting pore structures, selective sorption and solvothermal resistance properties are constructed by linking 3-connected benzene-1,3,5-tribenzoic acid with two types of 12-connected heptanuclear metal carboxylate clusters.

Metal carboxylate clusters, owing to their high thermostability and favouring the formation of noninterpenetrated frameworks, have been proven to be useful secondary building units (SBUs) for constructing coordination frameworks with characteristically promising applications in separation, storage and catalysis.[1] Noteworthily, zinc carboxylate SBUs, such as di-, tri-, tetra- and pentazinc carboxylate clusters, have been widely used to build interesting topological networks and functional materials with multi-topic carboxylates as linkers.[2] Usually, the expansion of the clusters favours highly-connected networks.[3] However, the high-nuclear clusters, such as hexa-, hepta- and octazinc clusters, are rarely incorporated into infinite frameworks due to difficulties in the formation of such clusters,[4] hence higher-connected networks are still scarce. On the other hand, Na^+ and K^+ cations have been introduced as a heterometallic and viable strategy to change the size and geometry of the clusters, to tune acidic pore surface and magnetic properties of coordination frameworks.[5]

Increasing the size of a ligand is another strategy to obtain highly-connected frameworks. Benzene-1,3,5-tribenzoic acid (H_3BTB) is selected as a linker from the following considerations: (i) the large size (two carboxylate groups are separated by $\sim$1.2 nm, see Fig. 1) and multiple coordination sites are of benefit for generating highly porous frameworks; (ii) the considerable distortion away from planarity arising from the steric repulsion between central and outer ring H atoms can prohibit interligand π-stacking interactions to generate non-interpenetrated frameworks;[6] (iii) the ample phenyl rings can introduce hydrophobic pore surfaces to improve sorption selectivity and solvothermal resistance. Despite so many merits, only six 3D porous frameworks constructed from H_3BTB have been studied since 2001,[1c,7] in which BTB tends to act as a 3-connected SBU to link metal clusters to form highly porous (3,4)-, (3,6)- and (3,8)-connected frameworks. With these considerations, we have succeeded in the construction of two unprecedented (3,12)-connected coordination networks through introducing alkali metal ions into the reaction system of Zn^{2+} and H_3BTB.

Solvothermal reaction of $Zn(NO_3)_2$ and $NaNO_3$ with H_3BTB in a 3 : 2 : 1 molar ratio in DMF–EtOH–H_2O medium at 90 °C for 48 h afforded a metal carboxylate framework $[Na_{0.5}Zn_{4.75}(\mu_3\text{-}OH)_2(BTB)_2(HBTB)(H_2O)_{0.5}]\cdot 5DMF\cdot 1.5EtOH\cdot 10H_2O$ (MCF-24, **1**).

X-Ray crystal structure analysis‡ reveals that **1** crystallizes in the chiral tetragonal space group $I4_122$. It exhibits a (3,12)-connected 3D non-interpenetrated framework built from two types of distinct heptanuclear clusters and BTB. The asymmetric unit of **1** consists of six unique Zn and one Na atoms, one $HBTB^{2-}$ and two fully-deprotonated BTB^{3-} ligands, two hydroxyl groups, one aqua ligand and disordered solvent molecules (Fig. S1†). All three independent $BTB^{3-}/HBTB^{2-}$ are non-planar with the inter-ring dihedral angles within the range 29.5–63.3°. Interestingly, two heptanuclear clusters $[NaZn_6(\mu_3\text{-}OH)_2(O_2C–)_{12}]$ (SBU1) and $[Zn_7(\mu_3\text{-}OH)_4(H_2O)_2(O_2C–)_8(HO_2C–)_4]$ (SBU2) are formed. In SBU1 (Fig. 1a), each Zn atom is tetrahedrally coordinated to three carboxylate O atoms and one μ_3-OH group, three crystallographically distinct Zn atoms are held together by six corner-sharing carboxylate and one μ_3-OH groups into

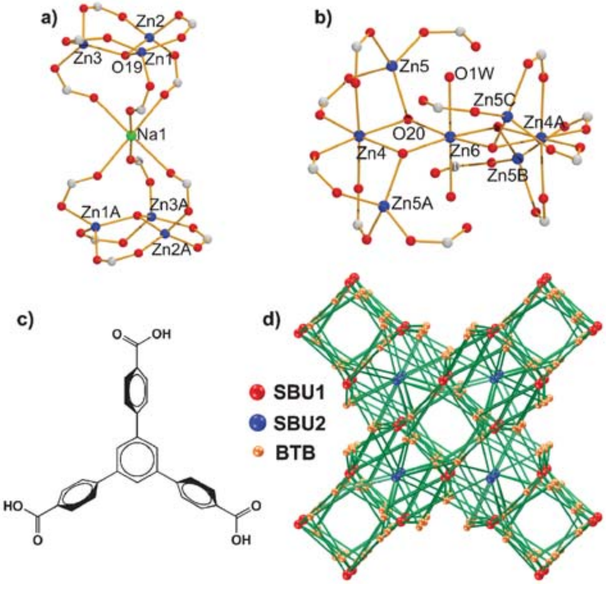

Fig. 1 Perspective views of the two heptanuclear clusters $[NaZn_6(\mu_3\text{-}OH)_2(O_2C–)_{12}]$ (a) and $[Zn_7(\mu_3\text{-}OH)_4(O_2C–)_8(HO_2C–)_4(H_2O)_2]$ (b) as 12-connected SBU1 and SBU2 in **1**, respectively, green Na, blue Zn, gray C, red O. Schematic representation of H_3BTB ligand (orange) (c) and (d) (3,12)-connected topological framework of **1**.

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[a] *MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: cxm@mail.sysu.edu.cn; Fax: +86 20 8411-2245; Tel: +86 20 8411-2074*

[b] *Department of Chemistry, University of Malaya, Kuala Lumpur, 50603, Malaysia*

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$[Zn_3(\mu_3\text{-}OH)(O_2C\text{–})_6]$ motifs, and two of such symmetry-related trinuclear motifs are further connected to a Na ion through six pairs of *syn–anti* carboxylate bridges into a heterometallic heptanuclear cluster. The Na–O distances are at 2.442(5)–2.500(5) Å. To the best of our knowledge, this kind of heterometallic heptanuclear cluster has not been reported before this work. Additionally, as shown in Fig. 1b, seven Zn atoms are connected by four μ_3-OH groups, two aqua ligands, eight carboxylate groups and four carboxylic groups to furnish the second heptazinc cluster with Zn6 residing on a two-fold axis, which also represents one type of unprecedented heptanuclear clusters.

Several compounds have been assembled by heptazinc carboxylate clusters $[Zn_7(\mu_4\text{-}O)_2(O_2C\text{–})_{10}L_2]$,[4a,8] in which, apart from ten carboxylate groups, two additional sites of the heptazinc clusters are occupied by terminal H_2O or N-containing ligands. The lock-in of terminal ligands not only prevents the expansion of the framework, but also constrains the construction of a higher-connected topological network. Comparably, both SBU1 and SBU2 in **1** incorporate twelve carboxylate/carboxylic groups from twelve BTB, and are further extended by these ligands to generate a 3D porous framework. The ratio of SBU1 to SBU2 in **1** is two because each BTB links to two SBU1 and one SBU2. The overall framework of **1** can be simplified as a (3,12)-connected network of $(4^3)_{12}(4^{12}6^{36}8^{18})_2(4^{12}6^{24}8^{30})$ topology by OLEX,[9] upon considering BTB ligands as 3-connected nodes and SBU1 and SBU2 as 12-connected nodes (Fig. 1d). Recently, several 12- and (4,12)-connected networks, mostly based on Cu^+ clusters, have been reported.[10] To the best of our knowledge, **1** is the first (3,12)-connected net observed so far, and SBU1 and SBU2 are the first examples of truly 12-connected metal carboxylate clusters.[4c] There are chiral 4_1 helical channels along the [001] direction with effective diameter of 6.0 Å (excluding van der Waals radii) (Fig. 2 and S5†). Moreover, helical channels (6.6 × 9.1 Å^2) exist along the [110] and $[1\bar{1}0]$ directions (Fig. S6†). These three channels are perpendicular to each other, and interconnected *via* cavities ($d \approx 7.0$ Å) to form a 3D intersecting pore structure. While the cavities and junctions between the cavities and channels are viewed as triangular and T-shaped 3-connected nodes, a rare 3-connected $(9^3)(9^212)_3$ topology can be rationalized (Fig. S7†). Notably, the pore surfaces of these cavities and channels are mainly surrounded by phenyl rings of BTB, furnishing a mostly hydrophobic channel system.

The TGA curve of **1** reveals a weight loss of 26.6% from 30 to 225 °C corresponding to the removal of 10 free H_2O, 1.5 EtOH and 5 DMF guest molecules (calc. 26.9%), and no further weight loss before the decomposition at 320 °C (Fig. S8†). The guest molecules of **1** can also be removed by soaking in CH_3OH for 48 h and subsequent heating at 150 °C under vacuum for 8 h, which is verified by TGA on the desolvated **1**, and a weight loss of 0.6% (calc. 0.5%) within 220–250 °C corresponding to the release of aqua ligands (Fig. S8†). Meanwhile, the lack of a C=O stretching peak at 1660 cm^{-1} in the IR spectrum of desolvated **1** (Fig. S12†) also confirms the complete release of DMF guests. X-Ray powder diffraction (PXRD) reveals that the framework is retained after evacuation (Fig. S9†).

The N_2 sorption isotherm of **1** at 77 K reveals type I behavior typical for microporous materials upon activation at 150 °C (Fig. 3a). The Langmuir surface area is fitted to be 1272 m^2 g^{-1} (BET, 1093 m^2 g^{-1}), which is higher than the highest value for zeolites, zeolite Y being 904 m^2 g^{-1},[11] and comparable to those of many porous coordination polymers and mesoporous silica materials (BET, 500–1160 m^2 g^{-1}).[12] The maximum N_2 uptake of 318 cm^3 g^{-1} (STP) (397 mg g^{-1}) is available at 1 atm, being equal to 23.6 molecules per formula unit. The MP-plot model indicates a pore diameter of ~6.0 Å for **1**, being consistent with the X-ray analysis. Using the *t*-plot model, the pore volume is 0.47 cm^3 g^{-1}.

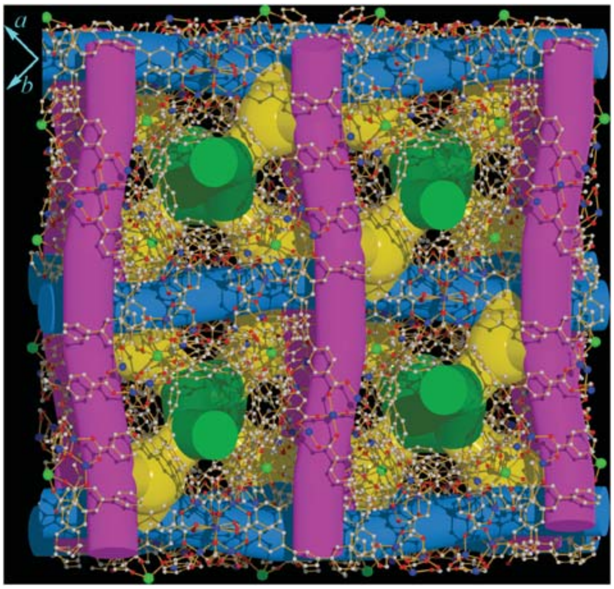

Fig. 2 3D porous network of **1** viewed along the [001] direction with three helical channels along the [001], [110] and $[1\bar{1}0]$ directions (green, azure and purple columns, respectively) connected by a cavity (yellow ball) as a 3-connected node (gray C, red O, green Na, blue Zn).

Regarding the considerable gas sorption capability and the hydrophobic pore surfaces of **1**, we further examined solvent uptake ability for hydrophilic and hydrophobic guests by TGA and PXRD techniques. In spite of the small molecular sizes of H_2O and CH_3OH, only 98 and 121 mg g^{-1} H_2O and CH_3OH (Fig. 3b, weight losses of 8.9 and 10.8%, respectively) can be adsorbed by **1**, respectively. The small uptakes should arise from the hydrophobic pore surfaces of **1**. On the other hand, **1** exhibits better sorption capability for larger benzene molecules (3.3 × 6.6 Å^2)[13] with a weight loss of 18.2% or a sorption amount of 222 mg g^{-1}, approximately twice those for H_2O and CH_3OH. Moreover, the complete release of benzene at 155 °C outclasses its boiling point (80.1 °C), indicating the existence of strong guest–host interactions by virtue of compatibility between hydrophobic benzene guests and host pore surfaces. Meanwhile, 1,3,5-trimethylbenzene, in spite of its even larger size, can also be adsorbed with a comparable amount (112 mg g^{-1}, weight loss of 10.1%) with those for H_2O and CH_3OH, revealing at least a free-passage[13] of *ca.* 4.1 × 8.2 Å^2 available in **1**. In addition, PXRD patterns of the guest-adsorbed samples reveal no significant structure transformation (Fig. S13†).

The hydro(solvo)thermal stability of **1** is also explored. The PXRD patterns (Fig. 4) of **1** refluxed in different solvents indicate that the framework is solvothermally resistant to boiling benzene and CH_3OH solvents, even for 24 h. It is known that the Zn_4O node is sensitive to H_2O and even moisture at 300 K, and collapsed within a very short time due to H_2O molecules attacking the zinc ions.[14] In contrast, the PXRD pattern reveals that **1** is

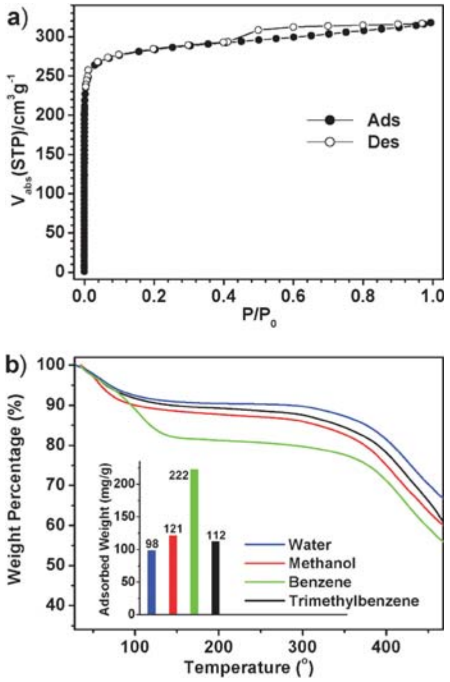

Fig. 3 Gas sorption isotherms of **1** for N_2 at 77 K (a), and TGA plots of H_2O, CH_3OH, benzene and 1,3,5-trimethylbenzene adsorbed samples of **1** (b). The inset shows the corresponding sorption amounts for per gram desolvated samples.

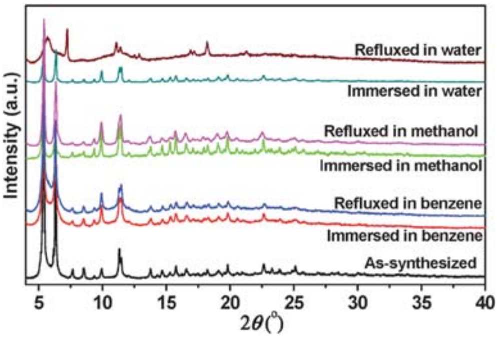

Fig. 4 PXRD patterns of **1** treated with different solvents at room temperature for 24 h and at their boiling points for 24 h (benzene and methanol) and water for 1 h, respectively.

resistant to H_2O at room temperature, which may be attributed, to some extent, to the hydrophobic pore surfaces in **1** preventing H_2O molecules from attacking SBU1 and SBU2. However, the PXRD pattern of **1** upon refluxing in H_2O for 1 h reveals a different pattern, implying that under violent conditions, water molecules, having a smaller size and stronger coordination ability, can attack the Zn–O bonds and change the framework to some extent.

It should be noted that, when we use KNO_3 to replace $NaNO_3$ in the reaction system, an isomorphous potassium analogue (K–O = 2.699(5)–2.742(5) Å) of **1** can also be readily prepared and fully characterized by single-crystal X-ray diffraction, PXRD, elemental analysis, IR spectroscopy and TGA,† indicating that the framework composition and structural features of this newly discovered (3,12)-connected frameworks can be finely tuned.

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Notes and references

‡ Crystal data: both **1** and **2** belong to the tetragonal, space group $I4_122$ (No. 91) with Z = 16 at T = 293(2) K. For **1**: $C_{81}H_{49}Na_{0.5}Zn_{4.75}O_{20.5}$, M = 1672.20, a = 32.4729(7), c = 47.6641(18) Å, V = 50 261(2) Å^3, ρ = 0.884 g cm^{-3}, μ = 0.940 mm^{-1}, total reflections = 80 929, unique reflections = 24 575 (R_{int} = 0.1136), final R_1 = 0.0592 and wR_2 = 0.1128 for $I > 2\sigma[I]$, and S = 0.945 (after SQUEEZE), Flack parameter = 0.06(1). For **2**: $C_{81}H_{49}K_{0.5}Zn_{4.75}O_{20.5}$, M = 1680.26, a = 32.441(2), c = 47.814(3) Å, V = 50 320(4) Å^3, ρ = 0.887 g cm^{-3}, μ = 0.954 mm^{-1}, total reflections = 79 454, unique reflections = 22 182 (R_{int} = 0.1177) final R_1 = 0.0594 and wR_2 = 0.1273 for $I > 2\sigma[I]$, S = 0.947 (after SQUEEZE), Flack parameter = 0.03(1). CCDC 689748 and 689749. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b809069f

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