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Calix[4]arene-based metal-organic frameworks: towards hierarchically porous materials†

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An upper rim-functionalised calix[4]arene dicarboxylic acid (H₂caldc) has been used to prepare four metal-organic frameworks, three of which have been structurally
10 **characterised and shown to form two- or three-dimensional network structures. Simulations suggest that such networks are likely to display interesting selectivity to guest molecules.**
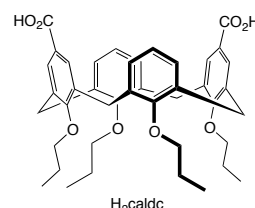
Metal-organic frameworks (MOFs) are currently attracting high levels of attention in inorganic and materials chemistry.[1] Many
15 MOFs are porous solids on removal of solvent from the as-synthesised materials, and as such they have a wide range of potential applications[2] including hydrogen storage,[3] catalysis[4] and drug delivery.[5]

Calix[4]arenes are macrocyclic structures capable of forming
20 hydrophobic cavities that bind apolar guests.[6] In the solid-state calix[4]arenes can act as porous entities allowing gases[7] or solvents[8] to be adsorbed. The formation of MOFs with calix[4]arene-based ligands opens up the possibility of forming hierarchically-porous materials, with *two levels* of porosity
25 associated with both the *ligand* and the *structural framework*.

Extended structures containing calixarenes have started to attract attention. Upper-rim *p*-sulfonated calix[4]arenes[9] and calix[6]arenes[10] have been used to prepare coordination networks, as have lower-rim appended calix[4]arenes containing pyridine
30 groups.[11] Similarly, calixarene analogues with sulfur-bridged aryl groups also form coordination networks.[12] Carboxylates are the most commonly used groups for constructing MOFs, but interestingly there are very few reports of metal complexes of calixarene-based polycarboxylates. Brechin and Dalgarno *et al*
35 reported that dimeric upper-rim *p*-carboxylatocalix[4]arenes self-assemble into infinite hydrogen-bonded nanotubes or bilayers, depending on the metal,[13] whereas *p*-carboxylatocalix[4]arene-O-methyl ethers generate nanocapsules.[14] Huang and Che *et al* reported that lower-rim functionalised calix[4]arenes form three-
40 dimensional networks with cobalt(II), with the metal centres linking the ligands into a non-interpenetrated (10,3)a net.[15]

In this communication, we demonstrate how the upper-rim appended 1,3-dicarboxylic acid H₂caldc[16] can be used to prepare MOFs containing copper, zinc, cobalt and cadmium. The
45 compounds [Cu₂(caldc)₂(DMF)₂] **1**, [Zn₂(caldc)₂(DMF)₂] **2**, [Cd₂(caldc)₂(DMF)₂]·3DMF **3** and [Co₅(caldc)₄(OH)₂(H₂O)₄]·4DMF **4** were prepared from the reactions of the appropriate metal(II) salts with H₂caldc in DMF

50 under solvothermal conditions. Compounds **1**, **3** and **4** were characterised by single crystal X-ray crystallography, whereas **2** was shown by powder X-ray diffraction to be isomorphous with **1**.

The structure of **1** consists of Cu₂(O₂CR)₄ secondary building
55 units (SBUs) that are linked by the dicarboxylates into sheets as shown in Figure 1a. The sheets have a (4,4) topology, though the curvature present within the caldc dianion gives each pore an hourglass shape. The copper 'paddle-wheel' dimers are also coordinated to DMF molecules, so there are no strong
60 interactions between the sheets, which stack in a staggered manner, as shown in Figure 1b. This means that the structure does not contain significant channels.

The structure of **3** contains square Cd₄(O₂CR)₈ SBUs, in which two carboxylates bridge each edge of the square in a bridging
65 chelating (κ^1O,κ^2O,O'-) coordination mode, as shown in Figure 2a. The SBUs are connected into (4,4) sheets in the *bc* plane, shown in Figure 2b, but unlike in **1**, these are connected into a three-dimensional network by further caldc dianions, which pair-wise link the SBUs into chains along the *a* axis, as depicted in
70 Figure 2c.

The structure of **4** contains infinite SBUs, running along the *a* axis. These SBUs consist of Co₄(μ₃-OH)₂(O₂CR)₆ units, that are linked together via single cobalt centres into chains, as shown in Figure 3a. Each of the single cobalt centres is coordinated to two
75 terminal aqua ligands, with the Co₄ and Co tectons bridged by a carboxylate and an aqua ligand. Although the hydrogen atoms on the hydroxides and aqua ligands were not observed in the crystal structure, the identification of these groups is unambiguous, based on bond length analysis and charge balance. There are two
80 independent caldc dianions within the structure of **4**, and these play different roles. One is solely coordinated to the cobalt centres within a chain, with two of these ligands coordinated to each Co₄(μ₃-OH)₂ unit via both carboxylates, as shown in Figure 3b. The second independent caldc ligand connects the chains into
85 sheets, as shown in Figure 3c. There are no strong interactions
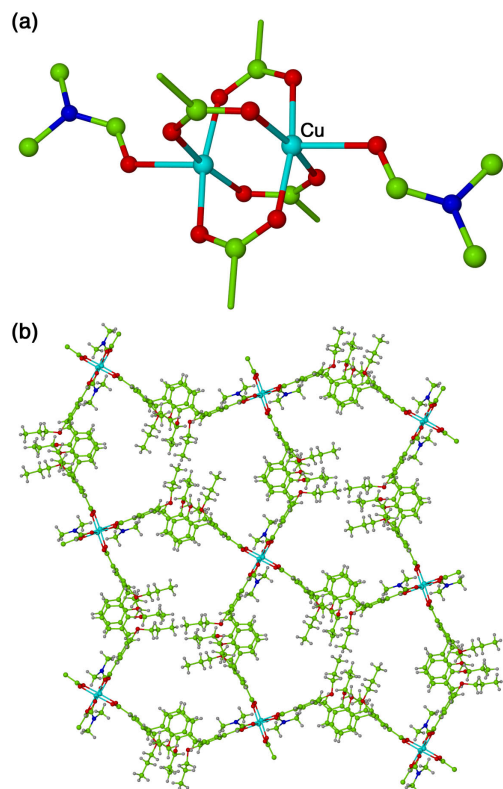
Figure 1. The structure of [Cu₂(caldc)₂(DMF)₂] **1**, showing (a) part of one of the (4,4) sheets, and (b) the manner in which the sheets stack together.

between the sheets. Although this appears to be the first observation of $Co_4(\mu_3\text{-}OH)_2(O_2CR)_6$ units in an extended structure, a similar core has been observed in the structure of $[Co_4(\mu_3\text{-}OH)_2(O_2CBu^t)_6(C_4H_6N_2O)_4]$.[17]

In the structures of **1**, **3** and **4**, the caldc dianion adopts a *pinched cone* conformation, which is similar to that observed in the free acid.[16] In **1**, the angle between the planes of the phenyl rings in the calixarene is 26°, whereas that between the carboxyphenyl rings is 120°. In **3**, there are two crystallographically independent caldc ligands. For the one connecting the SBUs into sheets, the angle between the planes of the phenyl rings in the calixarene is 13°, whereas that between the carboxyphenyl rings is 105°. For the caldc ligands connecting the sheets into the three-dimensional structure, the conformation is closer to that of a regular cone, with the angle between the planes of the phenyl rings in the calixarene 26°, and the angle between the carboxyphenyl rings 76°. Both independent caldc dianions in **4** adopt *pinched cone* conformations, though they differ in orientation. Coordination of both carboxylate groups to the same chain ensures that this ligand has the angle between the carboxyphenyl rings much lower (22°) than that of the phenyl rings (101°). For the ligand bridging the chains, it is the phenyl rings that are almost parallel, with an angle between them of 9° whereas the carboxyphenyl rings are more splayed (101°).

The (4,4) sheets present in the structure of **1** with hourglass-shaped pores are reminiscent of those in the structures of MOFs containing the camphorate (cam) linker, such as $[Cd_2(cam)_2]$[18] and $[Zn_2(cam)_2(dabco)]$.[19] This can be explained on the basis of the similar angles between the carboxylate groups in the two ligands – approximately 120° for both camphorate and the
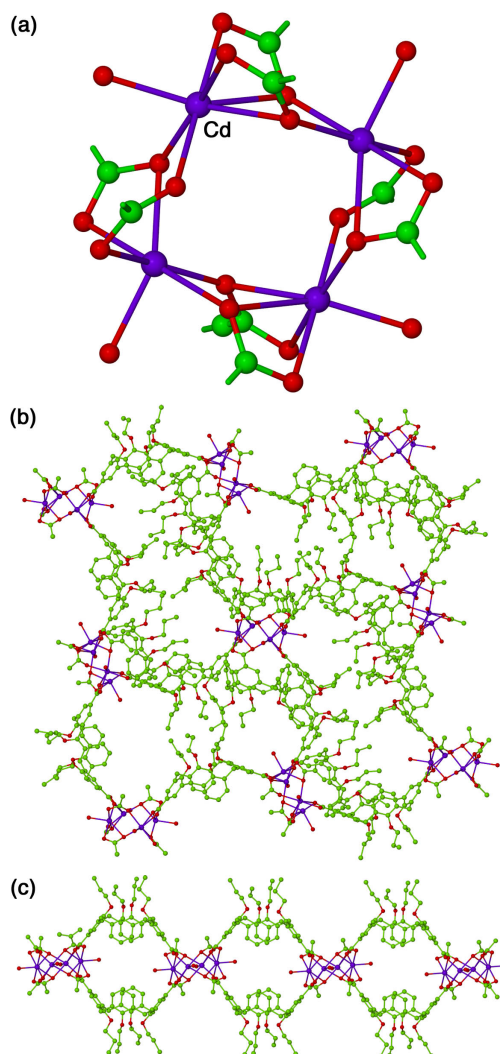
**Figure 2.** The structure of [Cd₂(caldc)₂(DMF)₂]·3DMF **3** showing (a) the $Cd_4(O_2CR)_8$ SBU, (b) the (4,4) sheets present in the *bc* plane, and (c) the chains running along the *a* axis that bridge the sheets into a three-dimensional network.

conformation adopted by caldc in **1**. The calixarene backbone ensures that caldc is a more flexible ligand than camphorate, as witnessed by the differences in conformations in the structures of **3** and **4**.

Simulations show that the accessible surface areas for these structures are relatively modest, with a N₂ probe molecule giving calculated values of 190 m² g⁻¹ for **1**, 410 m² g⁻¹ for **3** and 441 m² g⁻¹ for **4**. The experimental values obtained for **1**, **3** and **4** are lower than these calculated values, and in combination with the TGA and PXRD data suggest that it is difficult to remove the coordinate DMF molecules without some degree of framework collapse and concomitant loss of porosity. To assess whether incorporating porosity in the bowls of the caldc linkers leads – at least in principle – to interesting adsorption behaviour, we carried out molecular simulation of methane and hydrogen adsorption in **1**, **3**, and **4** with all solvent molecules removed. The bowl of the caldc ligand is not accessible to methane and only in **3** accessible to hydrogen, as shown in Figure 4. This is consistent with the structural data that shows only **3** has a relatively open
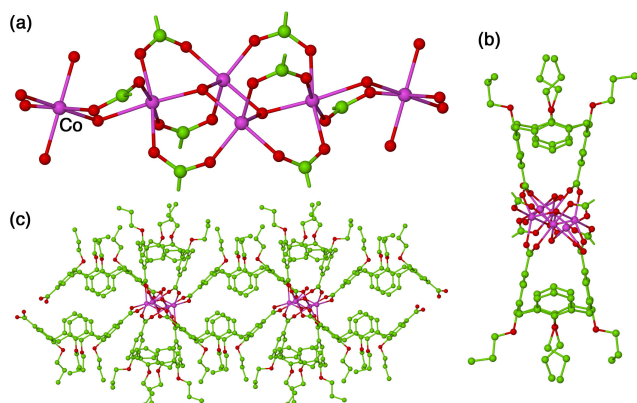
Figure 3. The structure of $[Co_5(caldc)_4(OH)_2(H_2O)_4]\cdot 4DMF$ **4** showing (a) part of the infinite chains formed by alternating $Co_4(\mu_3\text{-}OH)_2(O_2CR)_6$ and $Co(H_2O)_4(O_2CR)_2$ units, (b) coordination of caldc dianions to the SBU, and (c) caldc dianions bridging the SBUs into a two-dimensional network.
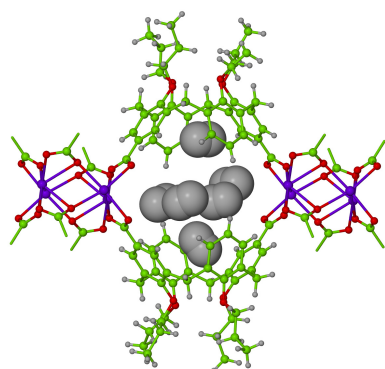
Figure 4. Simulated hydrogen adsorption for desolvated $[Cd_2(caldc)_2(DMF)_2]\cdot 3DMF$ **3**, showing adsorption into the calix[4]arene bowl.

conformation of the calix[4]arene bowl. Molecular simulation of adsorption of equimolar H_2/CH_4 mixtures at 300 K in **1**, **3**, and **4** show that all three structures exhibit very similar selectivities varying between 120 and 150 at 0.1 bar to between 40 and 50 at 20 bar. These selectivities are higher than observed in many other MOFs by molecular simulation (*e.g.* $Zn_4O(bdc)_3$ (IRMOF-1, bdc = 1,4-benzenedicarboxylate): ~5,[20] $Cu_3(btc)_2$ (HKUST-1, btc = 1,3,5-benzenetricarboxylate): ~18 - 12,[20] Zn(imidazolate)$_2$ (ZIF-3): ~31 − 25,[21]) and are in the same order of magnitude of what is observed in Zn(tbip) (tbip = 5-*tert*-butylisophthalate) where the selectivity varies between 200 and 125.[22] Here, as in Zn(tbip), the high selectivities are mainly due to the small size of the pores.

The observation that the calix[4]arene bowl in **3** is accessible to some but not all components of a mixture could in principle be exploited for separations.

Conclusions

Four metal-organic frameworks based on an upper-rim functionalised calixarene dicarboxylate have been prepared and characterised. Although to date it has not been possible to activate these MOFs by removing the coordinated solvent molecules, simulations suggest that these MOFs will display interesting selectivity in their gas adsorption behaviour. Future work will concentrate on changing the solvent system, adding neutral bridging co-ligands in order to prevent the formation of structures with coordinated DMF ligands and using more rigid calixarene ligands.

Notes and references

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