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

Sean P. Bew,a Andrew D. Burrows,a,b Tina Düren,a,c Mary F. Mahon,b Peyman Z. Moghadam,c Viorica M. Sebestyenb and Sean Thurstona

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An upper rim-functionalised calix[4]arene dicarboxylic acid (H_2caldc) has been used to prepare four metal-organic frameworks, three of which have been structurally 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 MOFs are porous solids on removal of solvent from the as-synthesised materials, and as such they have a wide range of potential applications, including hydrogen storage, catalysis and drug delivery.2 Calix[4]arenes are macrocyclic structures capable of forming hydrophobic cavities that bind apolar guests.3 In the solid-state calix[4]arenes can act as porous entities allowing gases or solvents 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 associated with both the ligand and the structural framework.

Extended structures containing calixarenes have started to attract attention. Upper-rim p-sulfonated calix[4]arenes4 and calix[6]arenes5 have been used to prepare coordination networks, as have lower-rim appended calix[4]arenes containing pyridine groups.6 Similarly, calixarene analogues with sulfur-bridged aryl groups also form coordination networks.7 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 reported that dimeric upper-rim p-carboxylatocalix[4]arenes self-assemble into infinite hydrogen-bonded nanotubes or bilayers, depending on the metal,8 whereas p-carboxylatocalix[4]arene-O-methyl ethers generate nanocapsules.9 Huang and Che et al reported that lower-rim functionalised calix[4]arenes form three-dimensional networks with cobalt(II), with the metal centres linking the ligands into a non-interpenetrated (10,3) network.10

In this communication, we demonstrate how the upper-rim appended 1,3-dicarboxylic acid H_2caldc11 can be used to prepare MOFs containing copper, zinc, cobalt and cadmium. The compounds [Cu_2(caldc)_2(DMF)_2]_n 1, [Zn_2(caldc)_2(DMF)_2]_n 2, [Cd_2(caldc)_2(DMF)_2]_n 3 and [Co_2(caldc)_4(OH)_2(H_2O)_4]·4DMF 4 were prepared from the reactions of the appropriate metal(II) salts with H_2caldc in DMF 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 Cu_2(O_2CR)_4 secondary building 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 caldic dianion gives each pore an hourglass shape. The copper ‘paddle-wheel’ dimers are also coordinated to DMF molecules, so there are no strong 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 Cd_4(O_2CR)_8 SBUs, in which two carboxylates bridge each edge of the square in a bridging chelating (κ^3-O,κ^3-O,κ^3-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 caldic dianions, which pairwise link the SBUs into chains along the a axis, as depicted in Figure 2c.

The structure of 4 contains infinite SBUs, running along the a axis. These SBUs consist of Co_4(μ_3-OH)_2(O_2CR)_8 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 terminal aqua ligands, with the CoO 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 independent caldic 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 Co_4(μ_3-OH)_2 unit via both carboxylates, as shown in Figure 3b. The second independent caldic ligand connects the chains into sheets, as shown in Figure 3c. There are no strong interactions.
between the sheets. Although this appears to be the first observation of Co₄(H₂O)(O₂CR)₆ units in an extended structure, a similar core has been observed in the structure of [Co₄(H₂O)₂(O₃CBu′)₂(C₂H₄N₂O₂)₄].

In the structures of 1, 3 and 4, the calde dianion adopts a pinched cone conformation, which is similar to that observed in the free acid. 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 calde 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 calde 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 calde dianions in 4 adopt pinched cone conformations, though they differ in orientation. Coordination of both carboxylate groups to the same SBU ensures that 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 [Cd₃(cam)₂]₃ and [Zn₃(cam)₂(dabco)]. 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 1. The structure of [Cu(calde)₂(DMF)₃] 1, showing (a) part of one of the (4,4) sheets, and (b) the manner in which the sheets stack together.

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 calde 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 calde 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 conformation adopted by calde in 1. The calixarene backbone ensures that calde is a more flexible ligand than camphorate, as witnessed by the differences in conformations in the structures of 3 and 4.
neutral bridging co-ligands in order to prevent the formation of structures with coordinated DMF ligands and using more rigid calixarene ligands. The EPSRC are thanked for financial support.

Notes and references


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