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Ligand flexibility and framework rearrangement in a new family of porous metal–organic frameworks†

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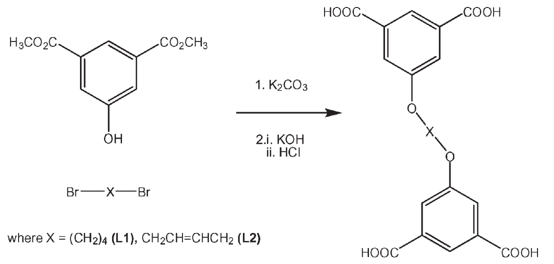
Ligand flexibility permits framework rearrangement upon evacuation and gas uptake in a new family of porous MOFs.

Porous metal–organic frameworks (MOFs) have attracted considerable interest owing to their potential applications in a variety of areas, including gas storage, separations and catalysis.[1] A pervasive design strategy involves the use of *rigid* di-[2] or tri-carboxylates[3] as ligands to bridge between mono- or multinuclear metal nodes, leading to robust neutral frameworks. MOFs constructed from tetracarboxylates are far less prevalent, but again rigid spacer units have been employed, for example based on poly(phenylene)[4] or 4,4′-bipyridyl units.[5] Here we report a new approach to MOF synthesis based upon the introduction of framework flexibility with a view to developing more responsive and adaptable materials. The approach is based upon a modular ligand design in which carboxyl-bearing aromatic groups are appended to a central core *via* a flexible ether link. Framework flexibility implemented by other means has been shown to be effective in applications for gas storage.[6] In this Communication our approach is illustrated with two examples wherein *flexible* tetracarboxylates are employed in MOF construction. These are derived from tetracarboxylic acid precursors in which flexible butane or butene spacers are used to link oxyisophthalic acid units (Scheme 1).



Scheme 1 Synthesis of tetraacids H_4**L1** and H_4**L2**.

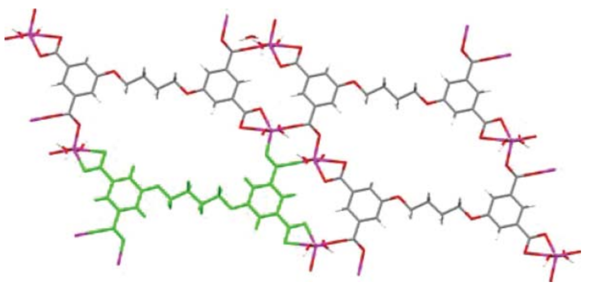


Fig. 1 Crystal structure of **1** with *planar* ligand **L1** highlighted in green. Water molecules in channels are not shown.

Ligand flexibility is specifically highlighted by structural characterisation of MOFs involving a planar form and an alternative twisted form of one ligand, which led to 2D and 3D frameworks respectively. In one instance characterisation involves *ab initio* structure determination using X-ray powder diffraction, which is rare for frameworks of this complexity. The porosity and CO_2 uptake of these MOFs are described and the relationship between these measurements and the ligand (and framework) flexibility is explored.

Tetracarboxylic acids H_4**L1** and H_4**L2** ligands have been synthesised as illustrated in Scheme 1 (see also ESI). The solvothermal reaction of $Zn(ClO_4)_2·6H_2O$ with H_4**L1** using a DMF–EtOH–H_2O solvent mixture‡ gave the 2D MOF $[Zn_2($**L1**$)(H_2O)_4]·2H_2O$ (**1**), whereas reaction with H_4**L2** under identical conditions‡ affords the 3D MOF $[Zn_4($**L2**$)_2(DMF)_3(H_2O)_3]·4H_2O$ (**2**). The crystal structures§ of compounds **1** and **2**

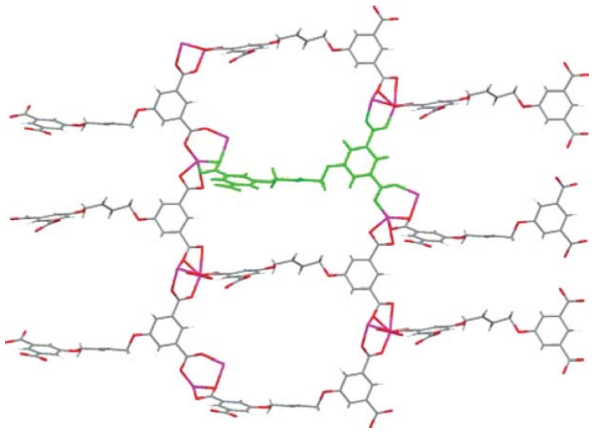


Fig. 2 Part of one network from crystal structure of **2** with *twisted* ligand **L2** highlighted in green. Water and DMF molecules are not shown.

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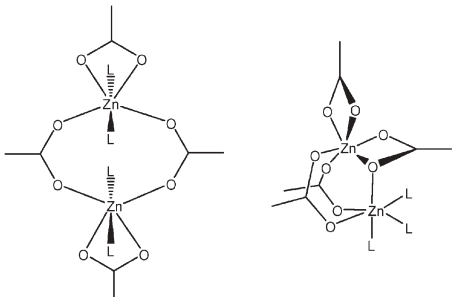
† Electronic supplementary information (ESI) available: Full experimental details of synthesis, crystallography, TGA and CO_2 sorption measurements. See DOI: 10.1039/b618796j



Square planar SBU I [L = H_2O]   Tetrahedral SBU II [L_3 = $(H_2O)_2(DMF)$ or $(DMF)_2(H_2O)$]

Scheme 2

are shown in Figs. 1 and 2, respectively. The principal difference between the two frameworks arises from the difference in conformation between ligands **L1** and **L2**.[7] Ligand **L1** adopts a planar conformation in **1** and is connected through each of the four carboxylate groups to dizinc centres either *via* a bridging interaction or by chelation to one of the two zinc atoms. The overall network is two-dimensional and can be described as having 4^4 topology with each ligand and each Zn_2 moiety adopting inversion symmetry and serving as a planar four-connected node (**I**, Scheme 2). By contrast, ligand **L2** adopts a twisted conformation in **2** whereby the two isophthalate moieties are orthogonal to each other. Again each ligand is linked to four separate Zn_2 units, in this case leading to a two-fold interpenetrated diamondoid network in which each ligand and each Zn_2 unit serves as a distorted tetrahedral node (**II**, Scheme 2). Two independent ligands and two independent Zn_2 units are present in the crystal structure; each node necessarily lacks inversion symmetry.

Each Zn centre in **1** adopts a distorted octahedral coordination sphere comprising four bonds to carboxylate oxygen atoms within the plane of the network and completed by two H_2O molecules arranged in a *trans* orientation protruding above and below the plane. Together with additional channel water molecules (one per Zn centre) these provide links between adjacent layers *via* O–H···O hydrogen bonds to carboxylate oxygen atoms [(O)H···O 1.79, 2.14 Å; O–H···O 171, 143°], ether oxygen atoms [(O)H···O 1.90 Å; O–H···O 158°] or to other H_2O molecules [(O)H···O 1.91, 1.99, 2.18 Å; O–H···O 159, 135, 141°].

Distorted tetrahedral SBUs in framework **2** comprise dizinc centres, each bridged by three carboxylate ligands with a fourth group chelating one of the two zinc atoms. The second zinc atom completes its coordination sphere with three solvent molecules. There are two independent Zn_2 SBUs, one containing two water and one DMF molecules and the other with two DMF and one water molecules (Scheme 2). Two independent **L2** ligands of similar conformation connect the SBUs. Channels are populated by additional water molecules (one per Zn atom).

The thermal stability of the frameworks and their porosity and potential for gas sorption have been explored using TGA and CO_2 sorption measurements. TGA indicates that both frameworks are stable to removal of all channel and coordinated solvent molecules and the evacuated frameworks are then stable to temperatures in excess of 400 °C (see ESI).[8] The sorption isotherms for **1** and **2** obtained with CO_2 at 198 K (after heating under high vacuum overnight to remove solvent molecules) revealed a typical Type I adsorption curve as defined by the IUPAC classification[9] (Figs. 3 and S5). The CO_2 sorption increases abruptly at very low pressures for both samples and reaches a maximum mass uptake of 17.2 wt % for **1** and **2**. The sorption isotherm data were fitted to the BET equation to give a BET surface area of 265(4) m^2 g^{-1} for **1** and 255(5) m^2 g^{-1} for **2**. The similarity in surface area is surprising given the difference in structure between **1** and **2** (calcd. free volume excluding solvent is 18% and 34%, for **1** and **2** respectively). Application of the Dubinin–Radushkevich equation to the isotherm data allowed the calculation of the pore volume. Given the similarity of surface areas for both samples, it is perhaps not surprising that the values obtained are identical at 0.11 ml g^{-1}. A possible explanation for the apparent similarity in porosity and gas sorption behaviour of **1** and **2** would be the rearrangement of **2** upon evacuation to yield a 2D framework structure analogous to that of **1** but employing ligand **L2** in a planar conformation. Such a rearrangement would require cleavage and reformation of Zn–O bonds, which could be enabled upon heating in the presence of solvent molecules in the framework channels. Indeed we have recently observed reversible formation of coordination bonds in crystalline solids in a non-framework system.[10]

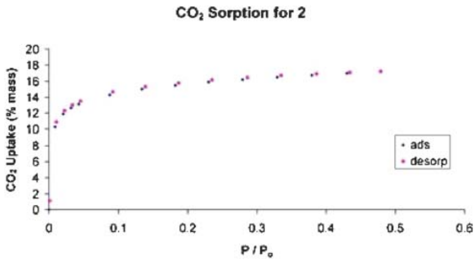


Fig. 3 Sorption–desorption isotherm of **2** at 198 K obtained with CO_2 gas over the pressure range 2–1000 mbar (relative pressure 6 × 10^{-5} to 0.5) (a very similar isotherm is obtained for **1** – see ESI Fig. S5).

Although such a mechanism cannot be confirmed without further studies, we are able to report that a planar structure similar to that of framework **1** can be achieved with the butenyl ligand **L2**. Indeed solvothermal synthesis under the same reaction conditions as used to prepare **2** led on one occasion to a homogeneous microcrystalline material **3** whose powder pattern differs from that obtained for **2** (see Fig. 4). Upon indexing the obtained pattern using DICVOL91,[11] a triclinic unit cell with dimensions similar to that of **1** were obtained.¶ On the hypothesis that a framework similar to **1** but with ligand **L2** in a planar conformation had formed, a suitable model was constructed to enable *ab initio*

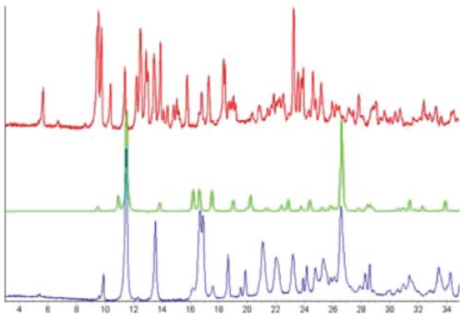


Fig. 4 Experimental X-ray powder pattern for **2** (red), calculated pattern for **1** (green) and experimental pattern for **3** (blue).

solution from the powder diffraction data. The structure was solved using the simulated annealing (SA) global optimisation procedure, described previously, and now implemented in the DASH program.[12] A restrained Rietveld refinement implemented using TOPAS[13] led to a good fit to the observed pattern (see ESI).¶ The structure of **3** shows a formulation of $[Zn_2(\mathbf{L2})(H_2O)_2]\cdot 2H_2O$, with a framework that is indeed similar to **1** although not isostructural. Ligand **L2** adopts a planar arrangement leading to a 4^4 sheet network employing dizinc-tetracarboxylate SBUs. However, the Zn centres have a tetrahedral coordination geometry in **3** that is related to the distorted octahedral environment in **1** through loss of one coordinated water molecule and conversion of the chelating carboxylate into a monodentate binding mode (See Fig. S4). As in **1**, there is also one H_2O molecule per Zn centre situated in the framework pores.

Reflecting on the plausibility of a structural rearrangement of **2** to a planar framework analogous to that in **3** upon heating and evacuation of solvent molecules it is instructive to examine the coordination environments of the Zn centres in **1** and **2** that would result from direct loss of coordinated solvent molecules. Specifically, loss of coordinated H_2O in **1** would generate four-coordinate zinc centres. Facile rearrangement of the chelating carboxylates supported by interlayer Zn–O bonding could be postulated as a means of stabilising the layered structure. Precedence for stability imparted by interlayer Zn–O bonding upon solvent removal is provided by Yaghi and coworkers in their study of $Zn_2(\text{terephthalate})_4(H_2O)_2$.[14] By contrast, direct loss of coordinated solvent from **2** would leave half of the zinc centres highly unsaturated and in an unusual pyramidal coordination geometry. Facile formation of additional supporting Zn–O bonding is not easily envisaged in this diamondoid structure. Thus, (solvent mediated) framework rearrangement to a layered structure (*cf.* **3**) presents a highly plausible consequence of removal of solvent molecules, and is consistent with the CO_2 sorption data.

A new family of torsionally flexible tetracarboxylic acids $H_4\mathbf{L1}$ and $H_4\mathbf{L2}$, with central butyl and butenyl spacer units, respectively, have been synthesised and used to construct thermally stable porous MOFs, which upon thermal desolvation show rapid uptake of CO_2 gas at low pressures. An explanation for the highly similar sorption behaviour of the square grid network formed using **L1** and the diamondoid network formed using **L2**, employing planar and twisted ligand conformations, respectively, has been proposed based upon a framework rearrangement from a 3D network in **2** to a 2D network. The flexibility of the tetracarboxylate **L2** and the plausibility of the proposed rearrangement have been confirmed by *ab initio* structure solution from X-ray powder data of a square grid network (**3**) employing **L2** in a planar conformation.

Support from the EPSRC, the University of Sheffield, CCLRC CMSD and CCDC is gratefully acknowledged. We are also grateful to CCLRC Daresbury Laboratory for beamtime at SRS station 16.2smx, during which the crystal structures of **1** and **2** were determined, and station 2.3, which enabled collection of preliminary powder data on compound **3**.

Notes and references

‡ Synthesis of **1** and **2**: $Zn(ClO_4)_2\cdot 6H_2O$ (0.112 g, 0.30 mmol) and either $H_4\mathbf{L1}$ or $H_4\mathbf{L2}$ (0.042 g, 0.10 mmol) were added to a 23 ml Teflon liner in a Parr acid digestion vessel, followed by DMF (3 ml), ethanol (3 ml) and H_2O (2 ml). The vessel was sealed and heated at 95 °C for 48 hours before being cooled down to room temperature at 0.1 °C min^{-1}. The colourless crystalline product was collected by filtration (yield: 60% for **1**, 36% for **2**) and included crystals suitable for single crystal diffraction study.

§ Crystal data for **1**, $C_{20}H_{26}O_{16}Zn_2$: $M = 653.18$, triclinic, $P\bar{1}$, $a = 7.962(2)$, $b = 8.511(2)$, $c = 9.827(2)$ Å, $\alpha = 68.56(3)$, $\beta = 79.47(3)$, $\gamma = 86.62(3)°$, $V = 588.7(2)$ Å^3, $Z = 1$, $D_c = 1.842$ Mg m^{-3}, $\mu = 2.121$ mm^{-1}, 4270 [R(int) = 0.0357] reflections used in refinement of which 2358 have $F^2 > 2\sigma(F^2)$. Final $R1 = 0.0460$ ($F^2 > 2\sigma(F^2)$), $wR2 = 0.127$ (all data). Crystal data for **2**, $C_{49}H_{59}N_3O_{30}Zn_4$: $M = 1431.47$, triclinic, $P\bar{1}$, $a = 13.0757(6)$, $b = 14.1157(7)$, $c = 16.6631(8)$ Å, $\alpha = 66.602(1)$, $\beta = 87.138(1)$, $\gamma = 89.757(1)°$, $V = 2818.7(2)$ Å^3, $Z = 2$, $D_c = 1.867$ Mg m^{-3}, $\mu = 1.779$ mm^{-1}, 19414 [R(int) = 0.0403] reflections used in refinement of which 10334 have $I > 2\sigma(I)$. Final $R1 = 0.0487$ ($F^2 > 2\sigma(F^2)$), $wR2$ (all data) = 0.134. CCDC 632264–632265. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618796j

¶ Crystal data for **3**, $C_{20}H_{20}O_{12}Zn_2$: $M = 583.13$, triclinic, $P\bar{1}$, $a = 9.5471(7)$, $b = 7.8520(7)$, $c = 8.4756(6)$ Å, $\alpha = 91.891(4)$, $\beta = 107.086(3)$, $\gamma = 91.891(4)°$, $V = 593.90(8)$ Å^3, $Z = 1$, $D_c = 1.695$ Mg m^{-3}, $R_{wp} = 0.0630$. CCDC 632266. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618796j

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7 (*a*) In the crystal structures of the corresponding tetraesters $Me_4\mathbf{L1}$ and $Me_4\mathbf{L2}$ both ligands adopt a planar conformation[7b]; (*b*) S. M. Hawxwell and L. Brammer, unpublished work.

8 Framework **1**: sharp mass loss of 15.9% before 55 °C, *cf.* 16.5% expected for loss of all water molecules. Framework **2**: gradual mass loss of 25.1% over a large temperature range, *cf.* 24.2% expected for loss of all DMF and H_2O molecules.

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