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Unprecedented bilayer topologies in 5- and 6-connected framework polymers†

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Three bilayer structures with unprecedented 6-connected topology and a single example of a bilayer structure with 5-connected topology have been generated by co-ordination of 4,4′-bipyridine-*N*,*N*′-dioxide at La(III), Yb(III) or Er(III) nodes.

Correlation between topology and connectivity[1] in co-ordination polymer architectures is a topic of intense current interest in solid state materials chemistry.[2] Most effort has been directed to the controlled synthesis of architectures based on metal centres with 2-, 3-, 4- or 6-connectivity. However, metal–organic materials based upon 5-, 7- or 8-connected nodes are much rarer,[3–7] and are generally limited to metal centres with high co-ordination numbers and sterically non-demanding bridging ligands. We have previously prepared highly-connected nets using a combination of lanthanide (Ln) metal centres, which typically have co-ordination numbers ranging from 7 to 9, and 4,4′-bipyridine-*N*,*N*′-dioxide (L). L has flexible angular geometries at the O-donor and provides longer metal–aromatic ring distances than the corresponding pyridyl donors, thus reducing inter-ligand repulsions at a potential metal ion node.[6–9] This choice is supported by the complementarity of the hard acid metal centre and hard base ligand which leads to highly stable yet sterically and conformationally flexible complex geometries. 5- and 6-connected nets normally adopt 3-D topologies,[7–11] and there are very few examples of 5-connected topologies having 2-D structures.[3,4] To the best of our knowledge, the only 2-D 6-connected structure reported thus far is a 3^6 net.[10] We report herein four unprecedented 2-D bilayer networks that, for the first time, define non-3-D double-layered topologies for 5- and 6-connected solid state materials. In all four structures, 4^4 nets as observed in the 4-connected complex $\{La(L)_2[(NO_3)_3]\}_\infty$, **1**, (Fig. 1) formed by treatment of $La(NO_3)_3$ with L in MeOH, are linked by bridging ligands to form bilayer architectures.

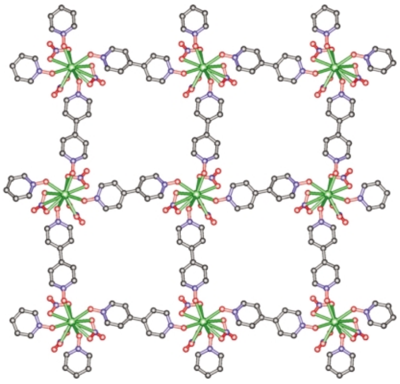

Fig. 1 View of the 4^4 grid structure of compound **1**.

$\{[Yb(L)_3](CF_3SO_3)_3\}_\infty$, **2**, was synthesised by layering a solution of L in MeOH on top of a layer of $CHCl_3$ covering solid $Yb(CF_3SO_3)_3$. $\{[Er(L)_5](I_3)_3(L)_{0.5}(MeOH)\}_\infty$, **3**, was synthesised by mixing $ErCl_3$, NaI, I_2 and L in MeOH. $\{[La(L)_4](ClO_4)_3\cdot C_6H_5Cl\cdot CH_3OH\}_\infty$, **4**, was obtained by layering a solution of L in MeOH on top of a layer of chlorobenzene covering solid $La(ClO_4)_3\cdot xH_2O$, while $\{[La(L)_{2.5}(CH_3OH)_2(C_7H_{11}CH_2CO_2)](BPh_4)_2\cdot 2.7CH_3OH\}_\infty$, **5**, was synthesised by adding consecutively solutions of $NaBPh_4$ and L in MeOH to a previously prepared solution of $LaCl_3$ in MeOH and sodium norbornyl acetate.†‡

In **2**, the Yb(III) centre is located in an 8-co-ordinate square anti-prismatic geometry provided by six molecules of L and two water molecules (Fig. 2a). Four of the molecules L bridge Yb(III) centres to give a 4^4 net, similar to that in **1** but with the remaining two molecules of L bridging on the same side of the 4^4 plane (Fig. 2a) to separate Yb(III) centres of an identical 4^4 net. This affords two-fold bridges between 6-connected nodes to generate a 2-D bilayer of 4^4 nets (Fig. 3b). The two water molecules which complete the co-ordination sphere at Yb(III) are located on the opposite side of the 4^4 net to the two bridging L molecules.†

Compounds **3** and **4** have the same topology as **2** (Fig. 3b). The water ligands in **2** are replaced by non-bridging molecules L in **3** with the Er(III) centre in **3** bound by eight molecules of L in a square anti-prismatic geometry (Fig. 2b). The two non-bridging L molecules are located on the opposite side of the 4^4 net to the inter-layer bridging ligands and are involved in π–π interactions with their counterparts in the adjacent bilayer. A possible explanation for this arrangement of the two pendant ligands is the need to incorporate I_3^- anions within cavities between the bilayers bounded by the pendant ligands.† The asymmetric unit of **4** contains two independent La(III) centres both of which are co-ordinated by eight molecules of L in square anti-prismatic

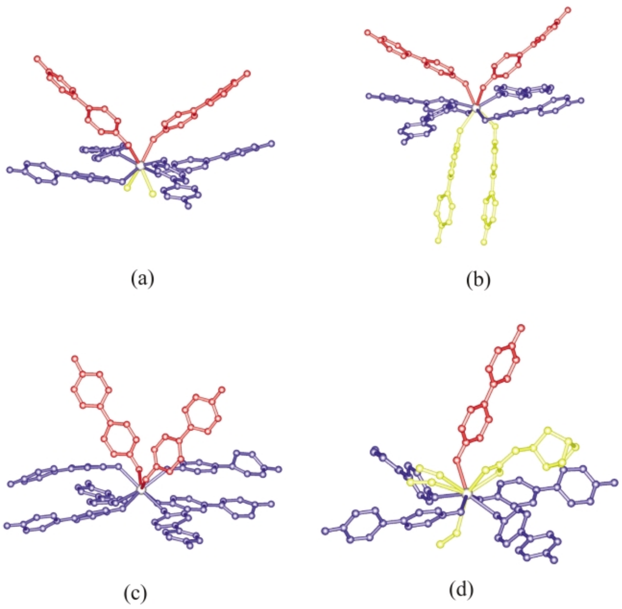

Fig. 2 Views of the co-ordination spheres of (a) **2**, (b) **3**, (c) **4** and (d) **5**. Ligands involved in the 4^4 nets are shown in blue, ligands connecting the 4^4 nets are shown in red, and ligands not involved in the bilayer structure are shown in yellow.

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† Electronic supplementary information (ESI) available: synthesis, characterisation, additional views and crystallographic details. See http://www.rsc.org/suppdata/cc/b4/b407554d/

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geometries (Fig. 2c) similar to that in **3**. Unlike the arrangements in **2** and **3** where four molecules of L bridge Ln(III) centres to give a 4^4 net, in **4** six molecules of L are involved in forming the 4^4 net; thus, two double-bridges, similar to the double-bridges observed in $[La(L)_4](C_4H_{22}B_{18}Co)_3$,[7] are incorporated within the 4^4 net. As in **2** and **3**, the two remaining molecules of L co-ordinate on the same side of the plane (Fig 2c) and bridge to an identical 4^4 net {rather than on opposing sides to form a NaCl-type 3-D network as observed in $[La(L)_4](C_4H_{22}B_{18}Co)_3$[7]} to afford the 2-D bilayer 6-connected architecture (Fig. 3b).†

The asymmetric unit of **5** comprises a single 5-connected La(III) node ligated by five molecules of L, a chelating carboxylate anion and two molecules of MeOH to give a total co-ordination number of nine (Fig. 2d). The choice of the 2-norbornane acetate as a co-ligand was based on its ability to bind and block sufficient coordination sites at the Ln(III) node to encourage the formation of the observed bilayer structure. The structure of **5** is related to those of **2–4**, but with two 4^4 nets being linked through a single bridging molecule L (Fig. 3c).† This type of 2-D bilayer architecture has been observed previously in $[Ag(pz)_2][Ag_2(pz)_5](PF_6)_3$[3] (pz = pyrazine) and in $[Cu_4\{1,4\text{-}C_6H_4(COO)_2\}_3(4,4'\text{-bipy})_2]$,[4] although not with *N*,*N*′-dioxide bridging ligands.

The related bilayer topologies observed for 8-, 7-, 6- and 5-connected structures are summarised schematically in Fig. 3 and form an elegant family of co-ordination polymers constructed from two parallel 4^4 nets. There are four, three, two and one bridges between the two parallel 4^4 nets for the 8-, 7-, 6- and 5-connected topologies, respectively. Thus, all the networks can be derived from the parent 8-connected compound[8] by removal of appropriate connections, suggesting that with careful selection of reactants a known topological motif can be designed and generated. The formation of these highly unusual bilayer topologies is based on the use of a flexible bridging *N*-oxide ligand which can adjust to the co-ordination sphere of the metal ion. This flexibility is reflected in the angles subtended at the O-donors of the bridging *N*,*N*′-dioxide ligand L (∠N–O–La), which range from 128 to 135° in **2**, from 128 to 144° in **3**, from 124 to 149° in **4** and from 123 to 135° in **5**. Furthermore, in **1** and **4** all ligands L have a *syn* conformation, in **2** and **3** they are all *anti*, while in **5** the ligands L adopt a *syn* conformation within the 4^4 net but are *anti* in the inter-layer bridges

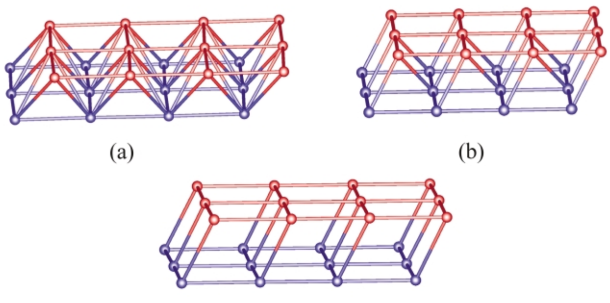

Fig. 3 Topological networks of (a) an 8-connected bilayer,[8] (b) a 6-connected bilayer and (c) a 5-connected bilayer. The 4^4 nets are shown in red and blue. 7-connectivity can be generated by removal of one bridge from (a).[8]

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‡ CCDC 239605–239609. See http://www.rsc.org/suppdata/cc/b4/b407554d/ for full crystallographic data in .cif or other electronic format.

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