Unusual parallel and inclined interlocking modes in polyrotaxane-like metal–organic frameworks†

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We describe here two unusual polyrotaxane-like metal–organic frameworks of $[Co_2(1,3\text{-bix})_2(bpea)_2]$ 1 and $[Cd_4(1,4\text{-bix})_4(bpea)_4]\cdot 4H_2O$ 2, where both species contain loops and rods that are interlaced in a highly rare "parallel" fashion in 1, but, uniquely, in an "inclined" fashion in 2.

Entangled systems have attracted considerable interest because of their intriguing topological structures and potential applications.[1] Interpenetrating nets, being an important subject in the area of entanglement, have provided a long-standing fascination for chemists, and many fascinating structures have been constructed and well discussed in comprehensive reviews by Robson and Batten.[2] Besides the common catenated arrays **I**, particular attention has been recently focused on Borromean architectures **II**, and rotaxane-like species **III** (Chart 1).[3] Polyrotaxanes, as the extended periodic version of rotaxane motifs, are viewed as particularly significant species for their mechanical links and potential applications in molecular machines or switches.[3] However, polyrotaxane-like networks are still quite rare, as evidenced in a review by Ciani and coworkers.[4] To date, only a few fascinating examples constructed from 1D or 2D motifs exhibit 1D or 2D polyrotaxane-like arrays involving a loop (Scheme S1†). Higher dimensional motifs in this facet are a challenge and remain largely unexplored.[4]

The basic design element of the polyrotaxane-like framework is the synthesis of a molecular unit with loops and insertion of a linear rod through those loops. Conformationally flexible ligand 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) has already has a proven ability to give unusual entanglements involving a loop.[5] Biphenylethene-4,4′-dicarboxylic acid (H_2bpea), as a long rigid ligand, is a good candidate for a rod in the assembly (Scheme S2†). Thus it may be possible to yield these new classes of entangled compounds through combining the two types of different precursors. Following this idea, we report here fascinating polyrotaxane-like frameworks of $[Co_2(1,3\text{-bix})_2(bpea)_2]$ **1** and $[Cd_4(1,4\text{-bix})_4(bpea)_4]\cdot 4H_2O$ **2**.‡ Both species contain loops and rods that are interlaced in a highly rare "parallel" fashion in compound **1**, but, uniquely, in an "inclined" fashion in compound **2**.§

The structure of **1** contains two unique Co(II) atoms, two unique 1,3-bix ligands, and two unique bpea ligands (Fig. S1†). However, the coordination environments of both Co(II) atoms and both unique ligands within each ligand type are basically the same. Each octahedral Co(II) atom coordinates to two imidazole groups of two different 1,3-bix ligands, and two chelating carboxylate groups of two different bpea ligands. In turn, each 1,3-bix and each bpea ligand bridges two Co(II) atoms. In this way 2D sheets are formed, in which each Co(II) atom is connected to three others, one each by two bpea ligands and a third by pairs of 1,3-bix ligands which adopt a curved geometry, creating a 'loop' (Fig. 1).

In isolation, the network topology could thus be described as having the 3-connected (6,3) topology. However, two such networks interpenetrate in a 2D → 2D parallel fashion,[2] but in a highly unusual way (Fig. 1). The $Co_2(1,3\text{-bix})_2$ 'loops' of each net are penetrated by one of the two types of bpea ligands of the other net, and *vice versa*. Reduction of the individual networks to (6,3) nets converts these loops into a single link, resulting in a network description which cannot properly describe the topology of interpenetration[2] as it would require links to pass through the middle of other links. Thus to obtain a network description that can be used to further describe the interpenetration, one must include the 2-membered rings (*i.e.* the 'loops'), resulting in a 4-connected (2.6^5) topology (Fig. 1). In other words, unlike the overwhelming majority of interpenetrating networks, the interpenetration cannot be properly described if the networks are first reduced to their simplest topology; topologically undesirable 2-membered rings must be introduced to show the rotaxane-like interactions between nets. Thus an unusual 2D polyrotaxane-like structure is formed containing rotaxane-like motifs.

Such interpenetrating networks are exceedingly rare. This interpenetration topology has only been reported once before,[5a] and a similar motif has been observed for one example of two parallel interpenetrating "(4,4)" sheets (better described as 6-connected ($2^2.4^8.6^5$) nets).[5b] It should be noted that rotaxane-like interactions can be defined in any interpenetrating network system, and that all these aforementioned

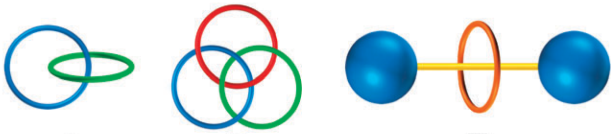

Chart 1

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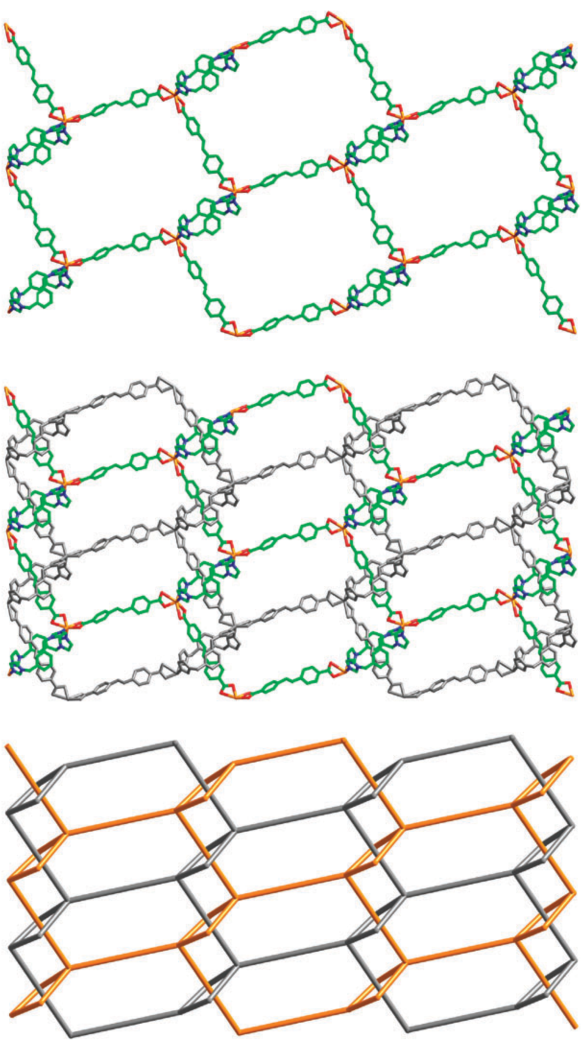

Fig. 1 (Top) A view of a single sheet in **1**, (middle) a view of the two interpenetrating nets in **1** and (bottom) schematic view of the interpenetration in **1**.

networks (and that of **2**, *vide infra*) are not true polyrotaxanes as they also contain catenated rings.[4] However the requirement of 2-membered loops in the topological description of the individual nets to adequately describe the interpenetration (due to their participation in the rotaxane motifs) is a significant and distinguishing feature. A small number of interpenetrating 1D polymers (true polyrotaxanes) have also been reported which also require 2-membered rings to describe their interpenetration topologies.[6]

The structure of **2** contains basically the same individual sheets as **1** (Fig. S2† and Fig. 2), apart from Cd(II) replacing Co(II), 1,4-bix replacing 1,3-bix and inclusion of four unique intercalated water molecule positions in the lattice. Even though there are four different metals, four different 1,4-bix ligands and five different bpea ligands, as before each type has basically the same environment—each octahedral metal is bound to two 1,4-bix ligands and two chelating carboxylate groups from two different bpea ligands. Each ligand in turn connects two metal atoms. In this way 2D sheets are formed, where a 'loop' is created by two 1,4-bix ligands and two Cd(II) atoms (Fig. 2).

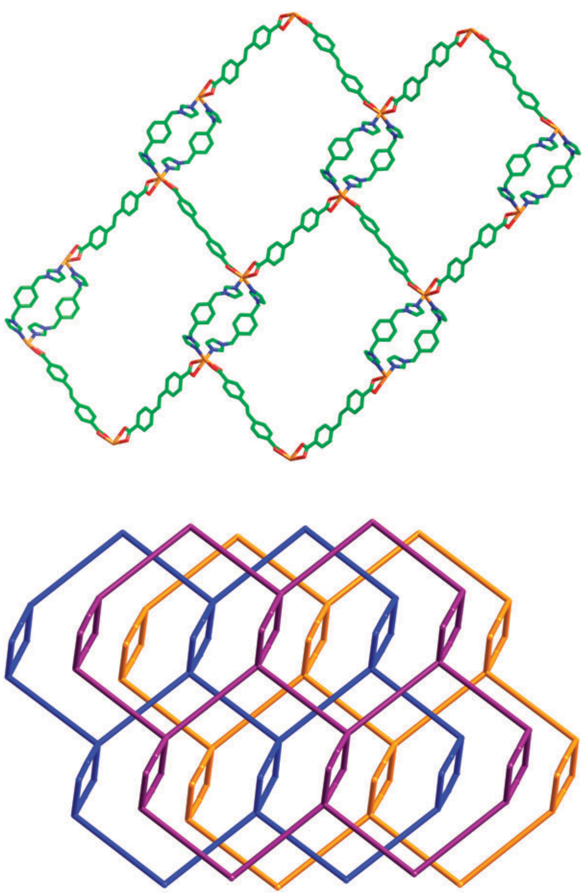

Fig. 2 (Top) A view of a single sheet in **2** and (bottom) schematic view of the ABC packing of sheets in **2**.

The way the networks interpenetrate, however, is very different to **1**, and is in fact the first example reported of its particular interpenetration topology. All sheets are identical, and stack in an ABC fashion (Fig. 2). Thus the largest windows of each sheet, through which interpenetration would normally occur (although not in the case of **1**), are blocked off by the sheets above and below (Fig. 2). However, a second, identical stack of sheets lies at an inclined angle and interpenetrates with the first stack, to give an overall 3D entanglement. What is unprecedented here is that it occurs in such a way that the 2-membered rings of the (2.6^5) nets are again important. Each 6-membered ring of each net is entangled with four inclined nets. As depicted in Fig. 3, the highlighted ring of the blue sheet has rods from different nets passing through each of the two 2-membered 'loops' on opposite sides of the ring (one loop is penetrated by the red net, the other by the orange net). Furthermore, two of the single rods (*i.e.* the bpea ligands) of this 6-membered ring participate in rotaxane-like interactions with 2-membered loops from two other inclined sheets (one with the pink net, the other with the green net depicted in Fig. 3). The other two single rods in the ring do not participate in any of these rotaxane-like interactions. 2D inclined interpenetration involving these types of rotaxane interactions is unprecedented.

As mentioned above, we believe this interpenetration topology is unique. We are not aware of any other example of inclined interpenetration of 2D nets which involves the

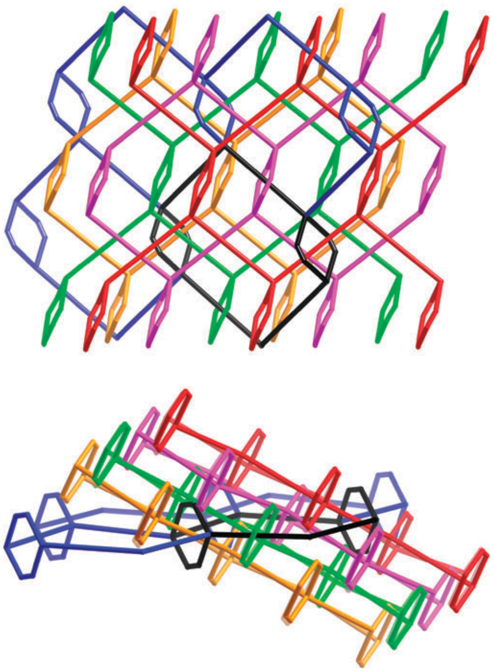

Fig. 3 (Top) The inclined interpenetration in **2** viewed from above and (bottom) side-on to the blue sheet. The highlighted ring in the blue sheet interpenetrates with the other four inclined sheets.

formation of rotaxane-like interactions with 2-membered loops, and there are only two previous examples for parallel 2D interpenetration.[5]

Notably, in both structures the sheets have the same topologies, and even the loops and the 6-membered rings of **2** are basically the same as ones of **1**, apart from 1,4-bix replacing 1,3-bix and Cd(II) replacing Co(II). Despite the change in both metal and bix ligand, it is difficult to determine the reason for the two different interpenetration motifs displayed here.

In summary, two unusual polyrotaxane-like frameworks have been successfully produced by using $M_2(bix)_2$ (M = Co(II) and Cd(II)) as the loops and the long rigid bpea as the rods. The loops and rods are interlocked in a highly rare "parallel" fashion in compound **1**, but, uniquely, in an "inclined" fashion in compound **2**. Also, the different entangled modes observed here provide new perspectives in topology of interpenetration.

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Notes and references

‡ *Experimental data*: for **1**: A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (145 mg, 0.5 mmol), H_2bpea (134 mg, 0.5 mmol), 1,3-bix (119 mg, 0.5 mmol), and water (12 mL) was placed in a 23-ml Teflon reactor and kept under autogenous pressure at 150 °C for three days. Then the mixture was cooled to room temperature, and pink crystals of **1** were obtained in 46% yield based on Co(II). $C_{60}H_{48}Co_2N_8O_8$: Calc.: C 63.95, H 4.29, N, 9.94. Found: C 63.74, H 4.41, N 9.83%. FTIR (KBr pellet, cm^{-1}): 3101 (w), 2924 (m), 2855 (w), 1678 (w), 1597 (s), 1549 (s), 1516 (m), 1370 (s), 1226 (w), 1087 (w), 945 (w), 779 (w), 632 (w). For **2**: Compound **2** was synthesized by a method similar to that for **1**, using $Cd(NO_3)_2 \cdot 4H_2O$ (154 mg, 0.5 mmol), 1,4-bix (119 mg, 0.5 mmol) and H_2bpea (134 mg, 0.5 mmol) as the reagents. Colorless crystals of **2** were obtained in 39% yield based on Cd(II). $C_{120}H_{96}Cd_4N_{16}O_{20}$: Calc.: C 56.93, H 3.82, N, 8.85. Found: C 56.59, H 3.52, N 8.93%. FTIR (KBr pellet, cm^{-1}): 3468 (m), 3104 (w), 2925 (w), 2849 (w), 1677 (s), 1604 (m), 1515 (s), 1423 (m), 1392 (w), 1232 (w), 1088 (w), 938 (w), 769 (w), 628 (w).

§ *Crystal data*: for **1**: triclinic, space group $P\bar{1}$, M_r = 1126.92, a = 11.039(4), b = 13.094(5), c = 19.901(7) Å, α = 100.224(7), β = 101.872(7), γ = 108.184(6)°, V = 2582.6(16) $Å^3$, Z = 2, μ = 0.709 mm^{-1}, D_c = 1.449 Mg m^{-3}, $F(000)$ = 1164, T = 183(2) K, 14496 reflections collected, 6176 unique with R_{int} = 0.0457, $R1$ = 0.0722, $wR2$ = 0.1362 ($I > 2\sigma(I)$) and GOF = 1.020. For **2**: monoclinic, space group $P2_1/c$, M_r = 2531.73, a = 15.0358(10), b = 34.679(2), c = 21.8823(14) Å, β = 94.8230(10)°, V = 11369.7(13) $Å^3$, Z = 4, μ = 0.814 mm^{-1}, D_c = 1.479 Mg m^{-3}, $F(000)$ = 5120, T = 183(2) K, 63711 reflections collected, 12590 unique with R_{int} = 0.0673, $R1$ = 0.0658, $wR2$ = 0.1370 ($I > 2\sigma(I)$) and GOF = 1.002.

Single-crystal X-ray diffraction data for **1** and **2** were recorded at a temperature of 183(2) K on a Bruker-AXS Smart CCD diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). All the structures were solved by the direct method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. The hydrogen atoms associated with the water molecules were not located from the difference Fourier maps.

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