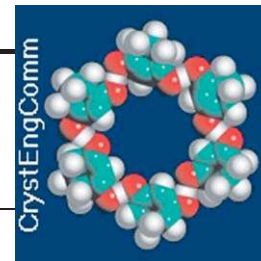


Borromean links and other non-conventional links in 'polycatenated' coordination polymers: re-examination of some puzzling networks†



Highlight

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A number of coordination networks, exhibiting novel and fascinating types of entanglements of individual motifs have been reported throughout the years by many groups. The structural complexity of these species has caused, in some cases, misinterpretations regarding the correct nature of the entanglement. In this article, we analyse the structures of some polymeric networks of the 'polycatenanes' class, which have the peculiar feature of all the constituent motifs having lower dimensionality than that of the overall array. Unexpected topological features and new linkages, that had previously been overlooked, have been discovered. The most relevant finding concerns the first observation of examples of Borromean links in 3D and 2D arrays. These systems are comprised of layers that are not catenated but, nonetheless, inseparably entangled in an uncommon topological fashion.

Introduction

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The use of crystal engineering principles has produced in the last years a variety of coordination networks,¹ many of which exhibit novel and fascinating types of entanglements of individual motifs.² The interest in these species is rapidly increasing not only for their potential properties as functional solid materials,³ in host-guest chemistry, ion exchange, catalysis, and for the development of optical, magnetic and electronic devices, but also for their intriguing and often

The early scientific interests of Lucia Carlucci, after the "Laurea" degree (1989) in Industrial Chemistry at the University of Bologna, were devoted to the synthesis and characterization of organometallic compounds, an activity that continued in the PhD thesis on dinuclear amino-carbene complexes of iron and ruthenium. She moved in 1992 to the University of Milano as a researcher joining DCSSI. In the recent years her main interests moved to the study of coordination polymers and supramolecular architecture. In this field her view is mainly focused on the development of new designed ligands with the aim to obtain coordination polymers with predictable topology and useful properties.



Gianfranco Ciani

Gianfranco Ciani, born in Ferrara, Italy, in 1944, is Full Professor of Inorganic Chemistry at the University of Milano and director of DCSSI. Since 1969 in Milano his activities have been devoted to X-ray crystallographic studies of coordination and organometallic compounds, mainly carbonyl metal clusters, including hydrido-carbonyl rhenium clusters, medium- and high-nuclearity rhodium and cobalt clusters, and metal clusters containing interstitial carbides and nitrides. Since 1993 his main interest has been the study of coordination polymers and their topologies and of the crystal engineering of mineralo-mimetic and nanoporous 2D and 3D networks. He is the author of over 210 publications.

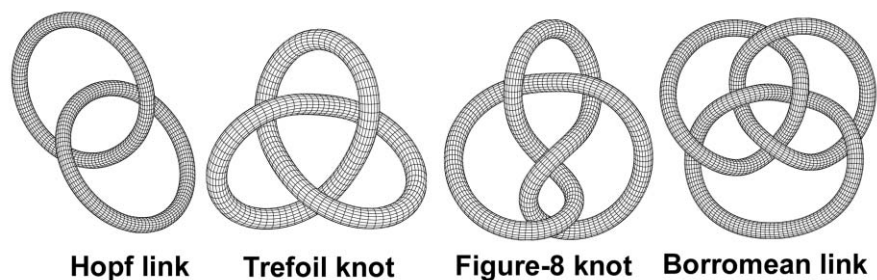
Davide M. Proserpio in 1981 entered the "Almo Collegio Borromeo" (the oldest university college in Italy) in Pavia where started being interested in Borromean links... and got the "Laurea" in Chemistry in 1986. In the next five years he was active in the field of applied theoretical chemistry under the supervision of Carlo Mealli (CNR-Florence, Italy) and Roald Hoffmann (Cornell University, USA), developing a package for EHT calculation CAAO. Since 1991 he has been a researcher at DCSSI with special interest in the topological problems that arise from the new complexity of the solid state coordination polymers: interpenetration, polycatenation, polythreading and polyknotting.



Davide M. Proserpio



Lucia Carlucci



Scheme 1 Various topological links and knots.

complicated architectures and topologies. The ‘network approach’ or topological approach to crystal chemistry^{1h,4,5} is an important achievement in this area—a useful tool for the analysis and design of network structures—in that it simplifies complex species to schematized reference nets. Topological investigation is necessary preliminary work to be accomplished in order to identify packing trends that may allow for the rational design of functional materials.

We will examine here some unusual aspects of the topology of ‘polycatenated’ networks, *i.e.* nets having the peculiarity that the whole array has a higher dimensionality than that of each of the component motifs. We have devoted particular attention to the analysis of the phenomena of mechanical interlocking, typical of molecular structures such as catenanes and knots,^{6,7} (see Scheme 1). The linkages in these entangled species are the subject of a number of topological investigations,⁸ especially those concerning the classification of isomers within complex organic molecules, organic polymers and biopolymers, natural and synthetic forms of DNA, *etc.* When discussing the complexity of entangled coordination polymers, it seems necessary to use concepts derived both from crystal chemistry, that has furnished the bases for the topological classification of inorganic nets,^{4,5,9} and from the mathematical theory of knots and links.

Our re-examination of known polycatenated networks has evidenced some misinterpretations and has allowed us to recognize the existence of unexpected and puzzling topological features, like Borromean links.

Polycatenated networks

The most popular among the different types of entangled polymeric systems are those described as ‘interpenetrating networks’.² The origin of interpenetration can be ascribed to the presence of large free voids in a single network, though it has been demonstrated that interpenetration does not prevent the possibility of obtaining open porous materials.¹⁰ The current world records for the degree of interpenetration belong to two recently reported diamondoid nets: within coordination polymers the maximum number of interpenetrating nets (10-fold diamondoid) has been observed in [Ag(ddn)₂](NO₃) (ddn = 1,12-dodecanedinitrile),¹¹ while a higher number of interpenetrating frames (11-fold diamondoid) has been reported for a hydrogen-bonded structure, with molecules of a tetraphenol as tetrahedral centres and benzoquinone units as rods.¹²

According to Batten and Robson,^{2a} interpenetrating networks that “can be disentangled only by breaking internal connections”, are characterized by the presence of infinite structurally regular motifs that must contain rings “through which independent components are inextricably entangled”.

We have previously observed¹³ that within structures consistent with the conditions described above, different subclasses can be envisaged and classified. We suggest, therefore, to consider the distinct subclass of polycatenanes, having the peculiar features that all the constituent motifs have lower dimensionality than that of the resulting architectures, and that

each individual motif is catenated only with the surrounding ones but not with all the others, as a single ring of a chain. The components can be, in principle, 0D, 1D or 2D species that must contain closed loops and that are interlocked *via* topological Hopf links (see Scheme 1).¹⁴

Real examples of these entanglements include interlocked 1D motifs (infinite molecular ladders¹⁵), giving increased dimensionality, both (1D → 2D) and (1D → 3D), and 2D motifs (interweaved in a ‘parallel’ or an ‘inclined’ fashion),² generating three-dimensional arrays (2D → 3D). More complex entanglements of this class are also known, involving motifs of different dimensionality (1D + 2D → 3D).¹³ Several noteworthy cases are illustrated in Fig. 1.

We have re-investigated in detail the known (2D → 3D) systems derived by parallel catenation. These species are comprised of independent layers whose average planes are parallel but displaced in a perpendicular direction, thus generating a polycatenated 3D architecture. Interlocking can occur either because the sheets are deeply undulated simple layers or because they are multiple layers, in both cases exhibiting some thickness. This interlocking mode has been discovered only recently (the first example was reported in 1997)¹⁸ but the number of examples is ever growing, both with single^{16,19} and with multiple^{17,18,20} layers.

A correct analysis of these, often complicated, crystal structures is fundamental in order to avoid misinterpretations, that

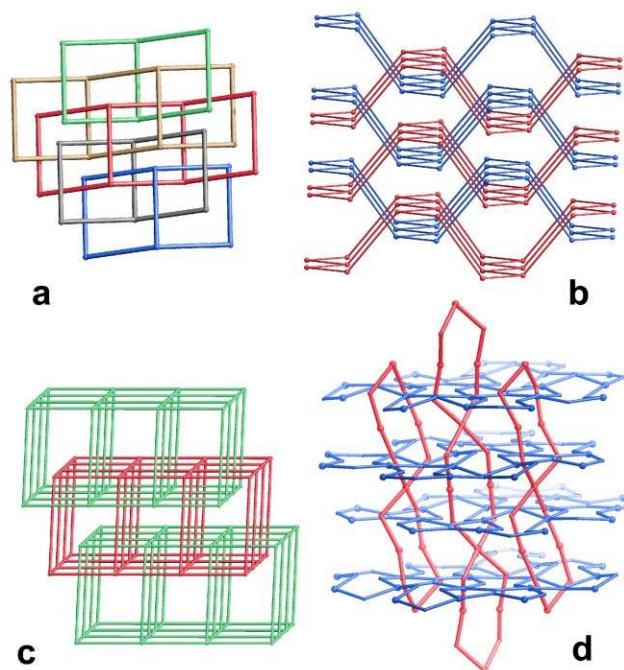


Fig. 1 Examples of polycatenated networks: (a) (1D → 2D) polycatenated ladders (ref. 15a); (b) (2D → 3D) polycatenation of simple layers (ref. 16); (c) (2D → 3D) polycatenation of double layers (ref. 17); (d) (1D + 2D → 3D) polycatenation of ribbons and layers (ref. 13).

can easily occur, about the nature and extent of the entanglements, as we shall see in what follows.

For instance, the polycatenated network of $[\text{Cu}_6(\text{CN})_5(\text{trz})]$ (trz = triazolate)^{19b} contains highly undulated single layers, comprised of large 36-membered $\{\text{Cu}_{14}(\text{CN})_{10}(\text{trz})_4\}$ rings that can be described in terms of square grids of (4,4) topology.^{4,9} The sheets give parallel (2D \rightarrow 3D) catenation, that was overlooked by the authors and recognized as such by Batten.^{2c} Any layer is catenated by two other adjacent layers. Moreover, each of the shortest (4,4) circuits is interlocked with twelve others, six from the 'upper' and six from the 'lower' layer. The structure is even more complicated, due to the presence of short interlayer $\text{Cu}\cdots\text{Cu}$ contacts, down to *ca.* 2.7 Å, that have been neglected in the above analysis.

Another noteworthy case is represented by the polycatenated (2D \rightarrow 3D) species $[\text{Ag}(\text{sebn})_2](\text{SbF}_6)$ and $[\text{Ag}(\text{sebn})_2](\text{CF}_3\text{SO}_3)$ [sebn = sebaconitrile, (1,10-decanedinitrile)],²¹ which are isomorphous in spite of the different nature of the anions. The 2D complex layers are based on distorted tetrahedral silver(I) centers disposed on four different levels. These layers are intertwined by simple translation in such a way that each one is catenated by the two adjacent identical motifs (the 'upper' and the 'lower' ones), as schematically illustrated in Fig. 2 (top), and exhibits also some interdigitation with the second nearest neighbouring sheets.

Due to the structural complexity, when we reported these results we overlooked a feature of great relevance. Re-examination of the 2D layers (see Fig. 2, middle) has now

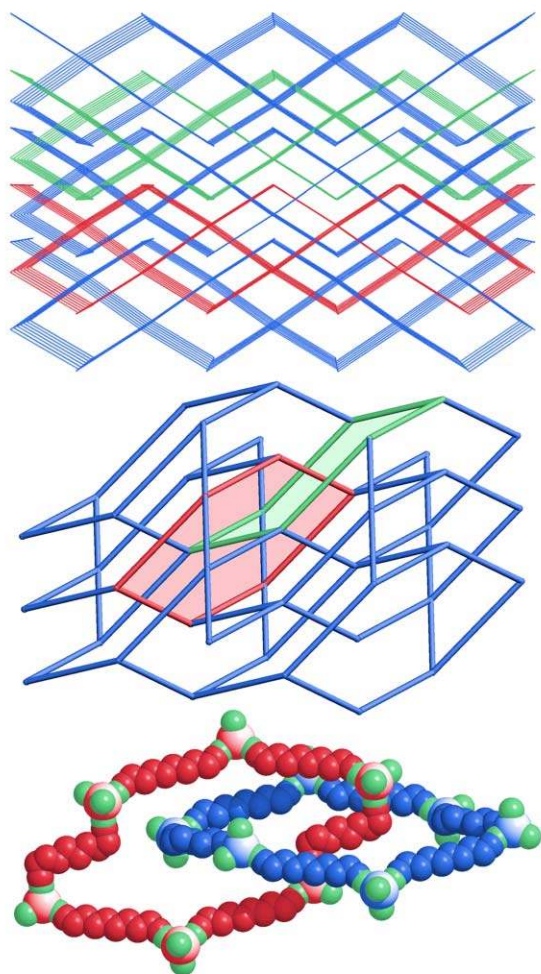


Fig. 2 The polycatenated (2D \rightarrow 3D) network in $[\text{Ag}(\text{sebn})_2]\text{X}$ (ref. 21) (top). An individual self-penetrated layer (middle) and the detail of the catenation of two 6-membered rings in the layer (bottom) are also shown.

revealed that these are uninodal self-penetrating nets. All the shortest circuits at each metal centre are 6-gons and the short topological symbol of the net is 6^6 , as diamond, but with a different long Schläfli symbol (6.6.6.6₂.6₂.6₂).⁹ In spite of the presence of two different types of silver ions in these layers (the internal ones and the surface ones), all the centres exhibit an identical topology. Self-penetrating 2D nets are a rarity but the contemporary presence of self-penetration and polycatenation phenomena is exceptional. A noteworthy consequence is that the shortest 6-membered rings (Fig. 2, bottom) are catenated by rings of the same size not only 'internal' but also 'external' to the layer.

Other quite remarkable cases, whose unique topological features were not previously noticed, are discussed below.

Borromean links in (2D \rightarrow 3D) entanglements

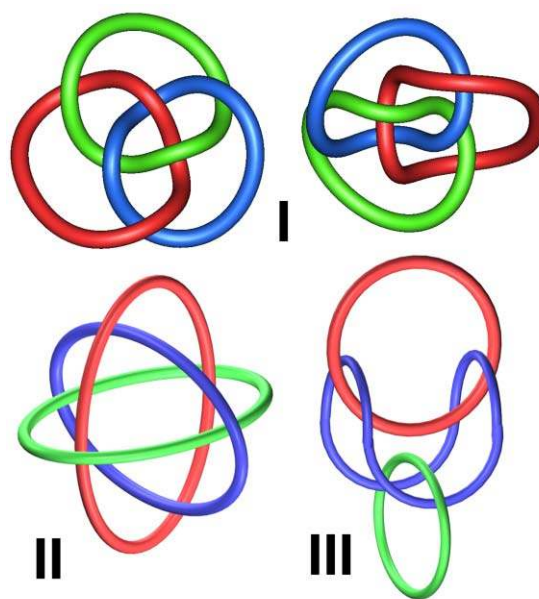
Molecular motifs containing rings could give inextricable entanglements not only *via* topological Hopf links, as those present in the above cases. One alternative way involving at least three closed circuits at a time is represented by the Borromean links²² (see Scheme 2).

These are non-trivial links in which three rings are entangled in such a way that any two component rings form a trivial link, *i.e.* if any one ring is cut the other two are free to separate. A single case is presently known in chemistry of a molecular system with such type of entanglement. This is a species constructed from single-stranded DNA by Seeman and co-workers in 1997,²³ that is comprised of three individual rings of 196, 206 and 216 nucleotides, entangled *via* Borromean links in a more complex fashion than in Scheme 2.

Using links of this type infinite 1D, 2D or 3D arrays can be imagined, two of which are illustrated in Fig. 3 (none actually observed).

The peculiar and intriguing topological feature of these extended entanglements is that none of the motifs is catenated to the other ones but altogether they are not separable. Links like these could appear only mathematical curiosities; indeed we have been able to identify real infinite examples of this interweaving phenomenon.

The structures of two isomorphous polymeric silver(I) complexes reported by Chen and coworkers in 1999, namely $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$ and $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{ClO}_4)_2$ [$\text{H}_2\text{L} = N,N'$ -bis(salicylidene)-1,4-di-aminobutane],²⁴ contain bis-monodentate phenol groups of a Schiff base ligand as bridges. They are



Scheme 2 Various presentations of the Borromean links.

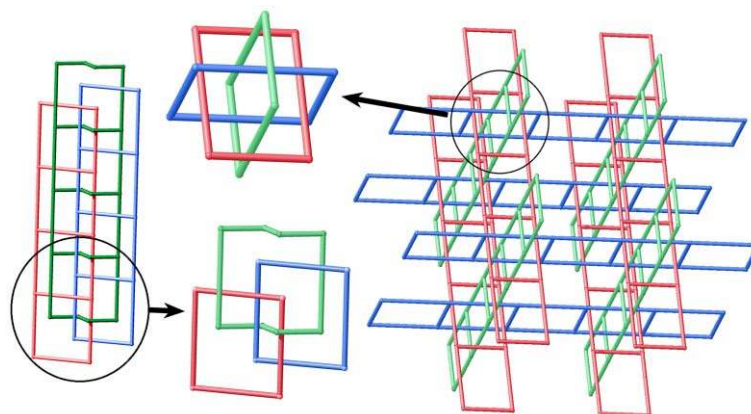


Fig. 3 Extended entanglements *via* Borromean links: (left) 'three Borromean ladders' and (right) a 3D 'Borromean array'. The different presentations of the Borromean rings in the two cases are evidenced. The individual motifs (ladders) are not catenated but cannot be disentangled.

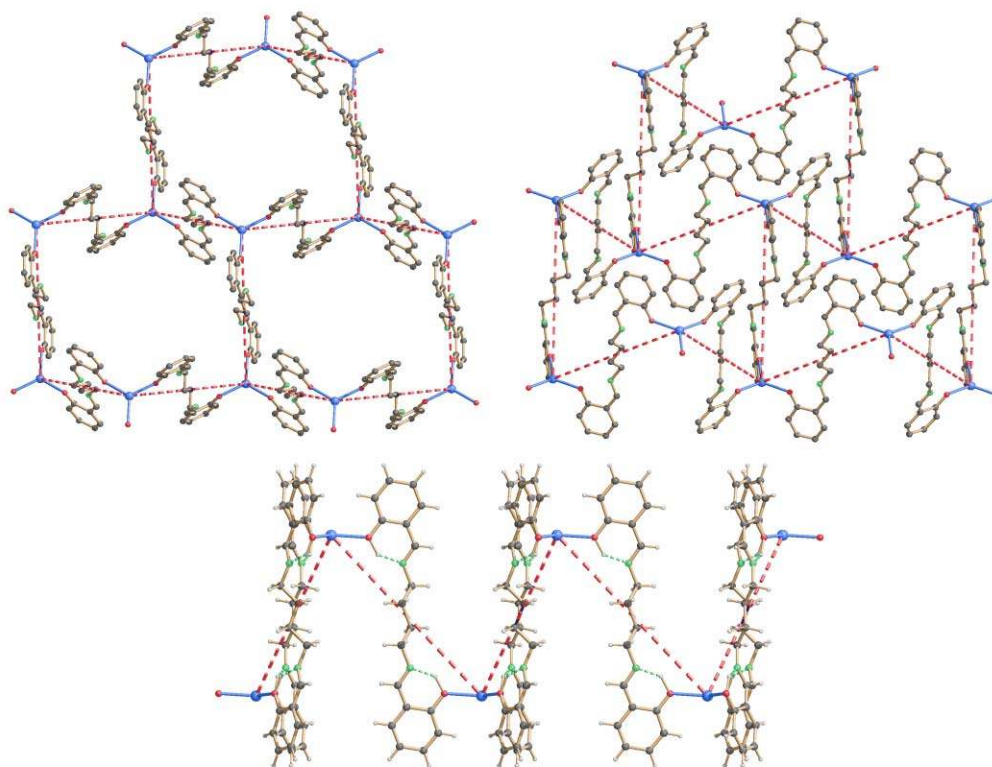


Fig. 4 Three views of the undulated single layers in the complex $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$, reported in ref. 24.

comprised of highly undulated (6,3) layers, with 6-membered rings of 3-connected silver centres (see Fig. 4). The silver atoms exhibit interlayer unsupported $\text{Ag}\cdots\text{Ag}$ interactions of 2.934(2) and 2.946(2) Å in the two species. Different topologies can be envisaged depending on which links are included in the topological model. Taking into account these $\text{Ag}\cdots\text{Ag}$ contacts a single 3D array results, that can be described as a 4-connected self-penetrating species (see later), or even as an overall 6-connected α -Po net, whose nodes are represented by the Ag_2 units (according to the description proposed by the authors).

On the other hand, and much more interestingly, if the $\text{Ag}\cdots\text{Ag}$ interactions are neglected, the array appears like a polycatenated (2D \rightarrow 3D) system, as previously noticed,^{2c,24} that is shown in Fig. 5. Each layer seems catenated by two others (one 'above' and one 'below'). However, a more careful examination leads to the exceptional finding that the adjacent layers are not catenated but are interlinked *via* Borromean links. This is evident on considering three hexagonal rings from three different adjacent layers (Fig. 6) that are entangled as the

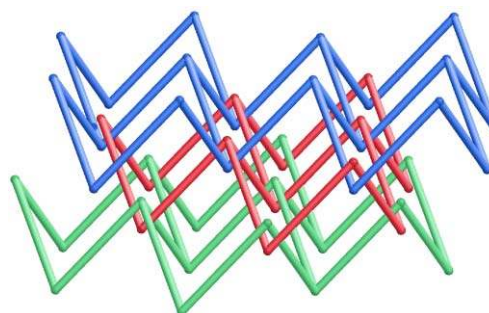


Fig. 5 Schematic view of the linkage of the layers in $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$.

three Borromean rings of Scheme 2 (type I presentation), in which no two individual rings are interlocked.

The three rings are highly undulated and this could seem a necessary condition for the formation of Borromean links with

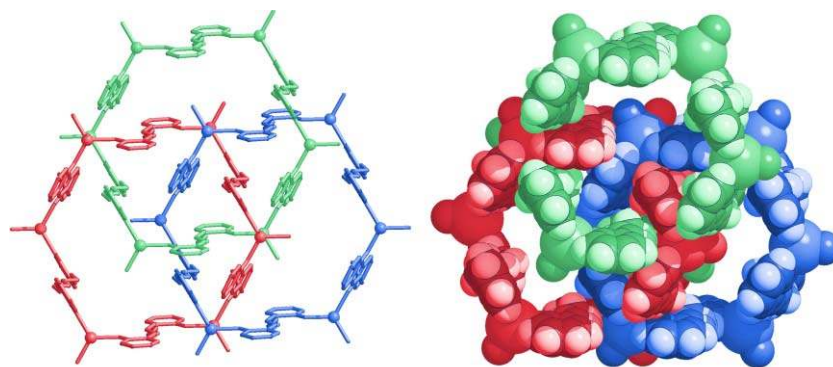


Fig. 6 Sticks and balls (left) and sphere packing (right) illustrations of the Borromean links of three 6-membered rings of different adjacent layers in $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$. Click here to access a 3D representation.

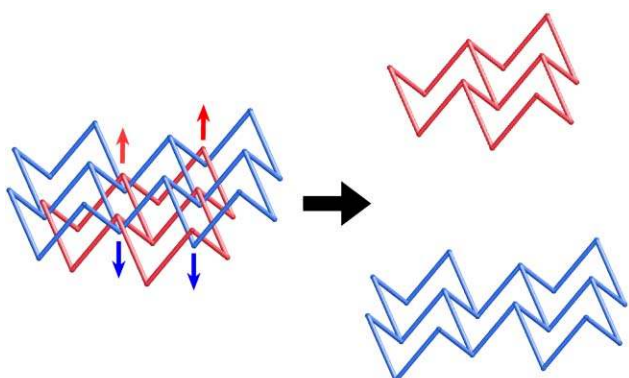


Fig. 7 Any two adjacent layers are not catenated and can be separated by a relative displacement in the perpendicular direction.

closed loops disposed on parallel average planes (but see also an exceptional case described below). Wasserman had also speculated that a minimum number of 30 carbon atoms are needed for organic molecular rings in order to give Borromean links;²⁵ the organic–inorganic loops in the present species are 90-membered rings.

In Fig. 7 we can see how two adjacent layers, being not catenated, can be readily separated.

What has been stated for three rings can be extended to the whole array, that represents an infinite case of *n*-Borromean links (Fig. 8). This chain of rings is such that no one ring is catenated to other ones but cannot be separated.

Theoretical examples of *n*-Borromean links have been described by Mislow,^{22a} for instance, the chain illustrated in Fig. 9 (top left) represents an entangled array that can be completely separated into the component rings by cutting only one ring, a property that is called ‘Brunnian’.^{22a,26} Obviously, three Borromean rings must have this property. On the other hand, the species here described, like the chain in Fig. 9 (right), does not show the Brunnian property, *i.e.* the cut of one ring separates the chain into two halves but leaves all the other rings inextricably entangled.

Borromean rings have always fascinated the human beings, and we can find many examples of their representation in history, arts, sciences and other human activities^{22b,27} (see Fig. 10). The name derives from the symbol of three entangled rings in the crest of the ancient noble Italian family of Borromeo.

Chemists since the early sixties have considered the realization of Borromean links in molecular form as a synthetic goal of great interest,^{7a,22,25,28} and we have already mentioned that it has been achieved in 1997 by means of DNA nanotechnology.²³ Our analysis has now revealed the possibility of such unusual entanglements also in an extended polymeric chemical species.

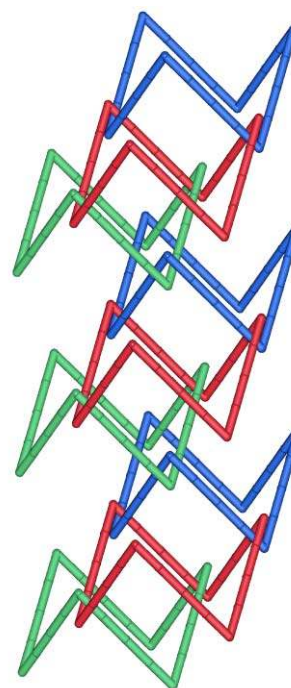


Fig. 8 Infinite stacking of entangled rings from different layers. Any group of three adjacent rings is interlocked *via* Borromean links.

Moreover, the coordination network above described is exceptional also from another point of view. If one adopts the above mentioned alternative bond model including the $\text{Ag}\cdots\text{Ag}$ interlayer linkages, a unique self-penetrating network results. An analysis of this net (Fig. 11) reveals the surprising feature that the short (6^6) and long ($6_26_26_26_26_2$) Schläfli symbols, as well as the coordination sequence up to the 10th neighbours, are identical to those of diamond.^{9a} In spite of the evident differences, it seems that we are unable, at present, to assign a distinct topological classification to the two nets.

After finding the above case of Borromean links in a coordination network we were encouraged to investigate for other examples. In the recent literature another 3D ‘polycatenated’ array shows an identical entanglement topology, namely $[\text{Ag}_2\text{L}_3(\text{OH})](\text{ClO}_4)\cdot 2.5\text{H}_2\text{O}$ [$\text{L} = N,N'$ -bis(3-pyridine-carboxamide)-1,6-hexane].²⁹ This network is comprised of highly undulating (6,3) sheets, that contain two types of Ag centres lying, respectively, at the top and at the bottom of each layer (thickness *ca.* 16.6 Å, see Fig. 12), that the authors have described as an ‘egg tray’.

As in the network previously considered, none of the layers is interlocked with other layers, but any group of three adjacent layers forms an inextricable entanglement. Again, we have an

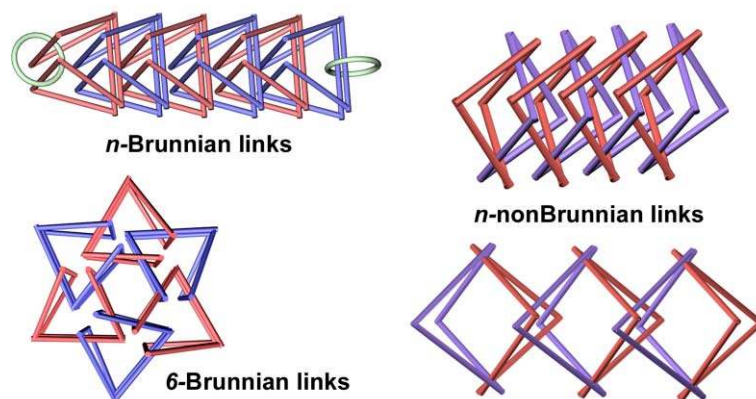


Fig. 9 Examples of Borromean links with the Brunnian property (left) or without (right, two views of the same chain). The top left n -Brunnian chain can have a variable number of rings and the two external closing ones are necessary only for a finite chain but no more if we imagine to extend the chain to infinity.

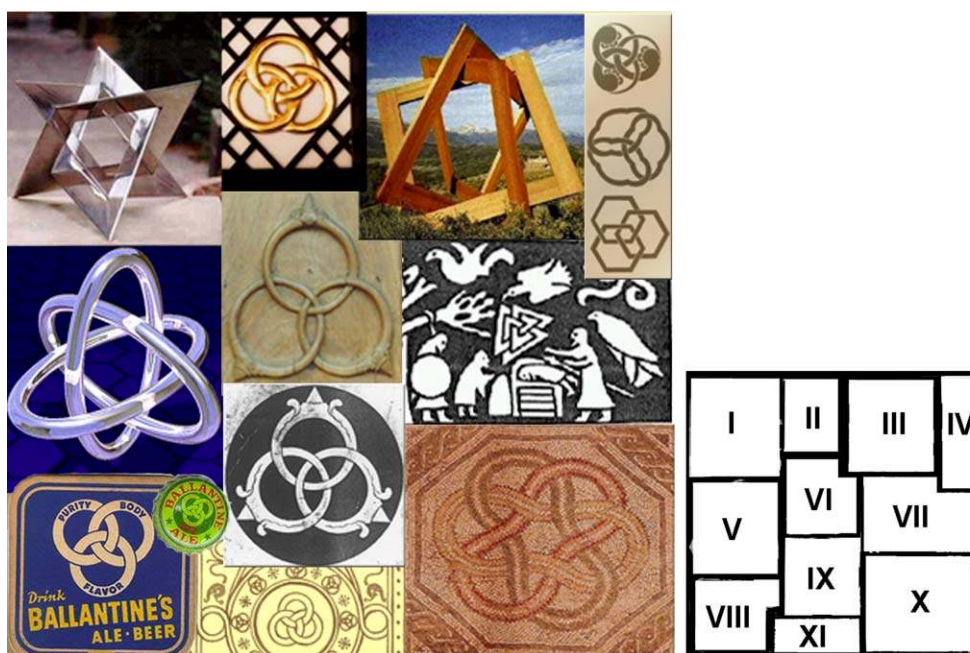


Fig. 10 Collage of pictures of Borromean rings that can be found on the web (see ref. 26). **I** and **III**, Borromean sculptures by the Australian artist John Robinson; **II**, decoration on a lantern of a Shinto temple in Japan; **IV**, Japanese designs of symbols used as family crests; **V**, picture by Mark Lengowski of Cabletron; **VI**, rings on the door of the church of San Sigismondo, Cremona (Italy); **VII**, a Viking symbol with Borromean triangles from a stone picture in Gotland Island; **VIII**, the trade-mark of the Ballantine beer; **IX**, rings appearing in the Cappella Rucellai in the Church of San Pancrazio in Florence; **X**, a mosaic of the 4th century in the Villa at Piazza Armerina in Sicily; **XI**, a logo of Ricordi, a music printing company in Milano.

infinite case of n -Borromean links (see Fig. 13). This feature was overlooked by the authors, but Batten, in the last updating of his website,^{2d} has noticed the peculiarity of the system, recognizing that no layer is effectively catenated to other ones.

With the above considerations in mind, as a natural extension, we have also examined in detail the examples of 3-fold parallelly ‘interpenetrated’ sheets listed by Batten.^{2d} We have thus discovered a new class of (2D \rightarrow 2D) 3-fold entangled ‘Borromean layers’.

3-fold Borromean layers in (2D \rightarrow 2D) entanglements

We have been able to identify three cases of 3-fold entangled 2D layers that are neither interpenetrated nor catenated (no Hopf links) but exhibit Borromean links, which were previously unrecognized and described as parallel 3-fold interpenetrated layers. In all cases the layer topology is (6,3).

In $[\text{Cu}_2(\text{tmeda})_2\{\text{Au}(\text{CN})_2\}_3](\text{ClO}_4)$ [tmeda = N,N,N',N' -tetramethylethylenediamine],³⁰ the crystal structure reveals the

presence of (6,3) undulated layers in which the nodes are represented by $\text{Cu}(\text{tmeda})^{2+}$ units linked by $\text{Au}(\text{CN})_2^-$ linear complexes (see Fig. 14).

Three such layers are entangled *via* Borromean links, as schematically shown in Fig. 15. One can easily realize this point observing that the blue net is completely located above the red one, the green net above the blue one, but the red net lies above the green one. This is a general criterion for Borromean links involving three parallel motifs at a time (see also the three ‘Borromean ladders’ in Fig. 3, left).

Indeed, the three nets are possibly interconnected in the central plane by aurophilic $\text{Au}\cdots\text{Au}$ interactions, ranging in the interval 3.40–3.60 Å.

The same type of topological entanglement has been found also in the recently reported complex $[\{\text{Ni}(\text{cyclam})\}_3(\text{TCPEB})_2 \cdot 6\text{C}_5\text{H}_5\text{N} \cdot 4\text{H}_2\text{O}]$ [TCPEB = 1,3,5-tris(2-(4-carboxyphenyl)-1-ethynyl)benzene].³¹ Also in this case, the network contains (6,3) layers; the nodes are represented by the trigonal tridentate ligands, that are connected *via* the Ni(cyclam) units acting as spacers. A single 6-membered ring is illustrated in

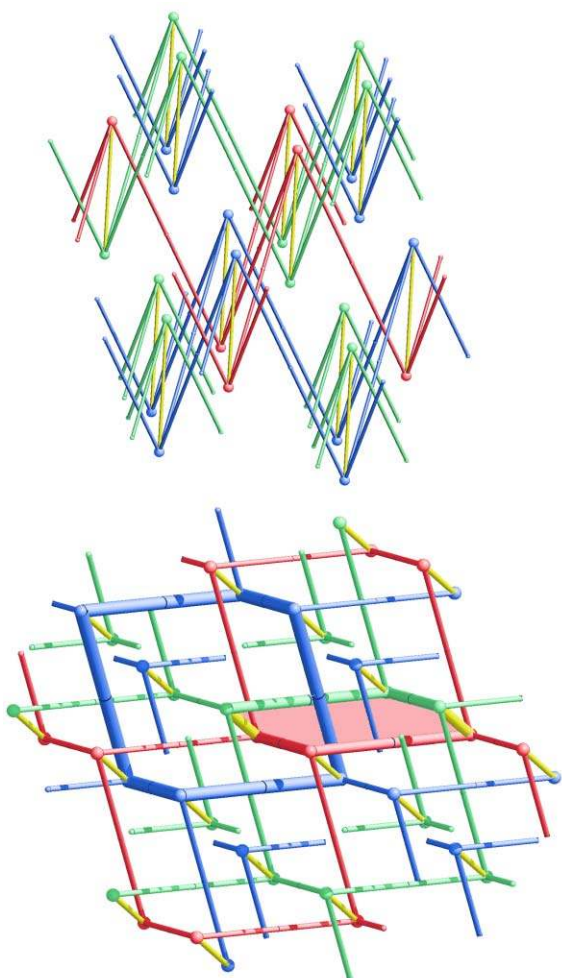


Fig. 11 Top, a distorted side view of the layers to enhance the Ag...Ag contacts (in yellow); bottom, a view of the network with two catenated 6-rings (bolded) showing the self-penetration.

Fig. 16. Interestingly, these layers, different from the undulated sheets found in the other species already described, are rather flat, but nevertheless they are able to give Borromean links of three parallel motifs (Fig. 17). Each entangled sheet is only *ca.* 4 Å thick.

The third species of this class is a framework belonging to the realm of supramolecular chemistry. In $[\text{K}(\text{K}.2.2.2)]\text{I}(\text{1,8-diodoperfluorooctane})_{1.5}$ ($\text{K}.2.2.2 = 4,7,13,16,21,24\text{-hexoxa-1,10-diazabicyclo}[8,8,8]\text{-hexacosane}$)³² the strong halogen bonding $\text{I}^- \cdots \text{I}$ between naked iodide ions and the diiodoperfluoroalkanes generates 2D layers of (6,3) topology, having the I^- anions as nodes. Three such layers give a (2D \rightarrow 2D)

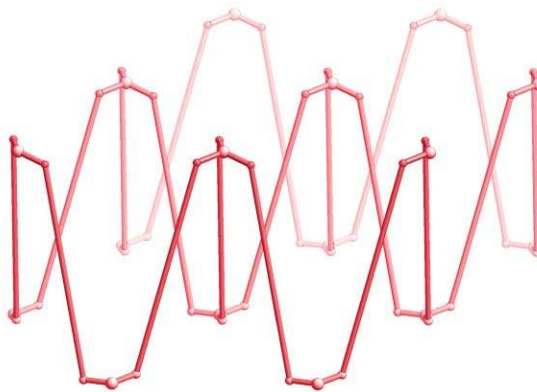
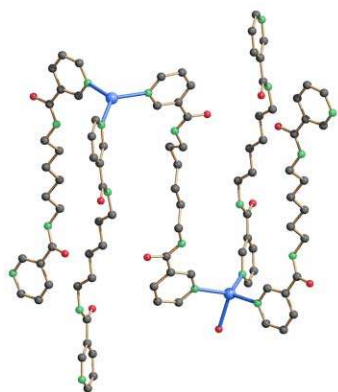


Fig. 12 A portion of a single layer in $[\text{Ag}_2\text{L}_3(\text{OH})](\text{ClO}_4).2.5\text{H}_2\text{O}$, showing the coordination of the Ag centres (ref. 29) (left) and a schematic view of a whole layer (right).

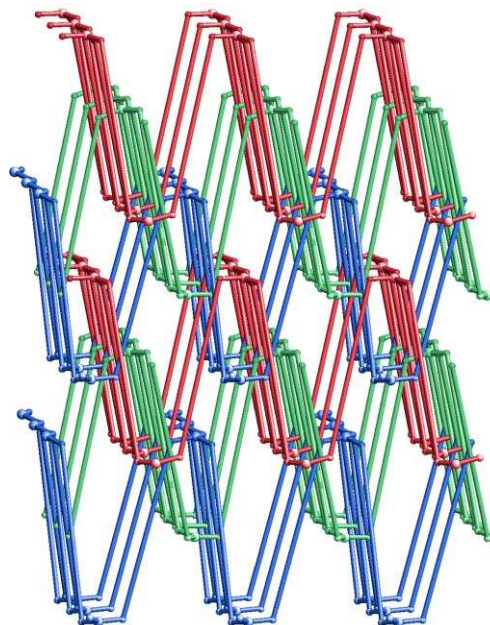


Fig. 13 The overall *n*-Borromean layer entanglement in $[\text{Ag}_2\text{L}_3(\text{OH})](\text{ClO}_4).2.5\text{H}_2\text{O}$. Any group of three differently coloured adjacent layers forms a minimal Borromean linkage.

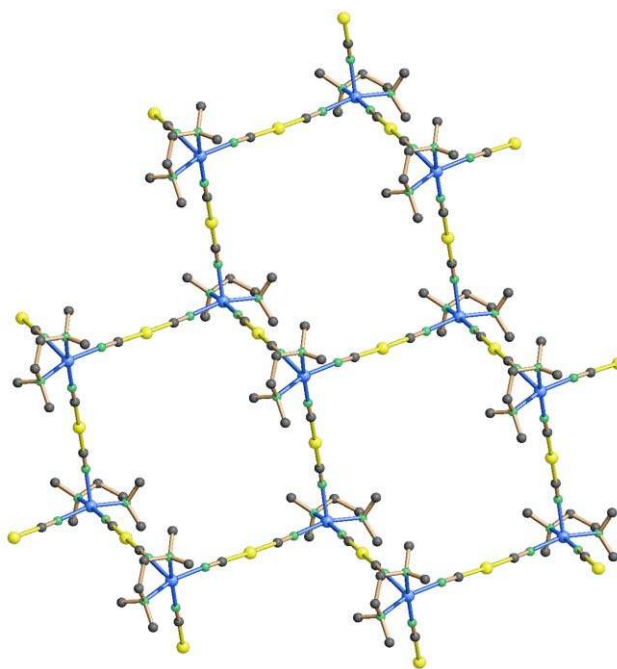


Fig. 14 A single layer in $[\text{Cu}_2(\text{tmeda})_2\{\text{Au}(\text{CN})_2\}_3](\text{ClO}_4)$.

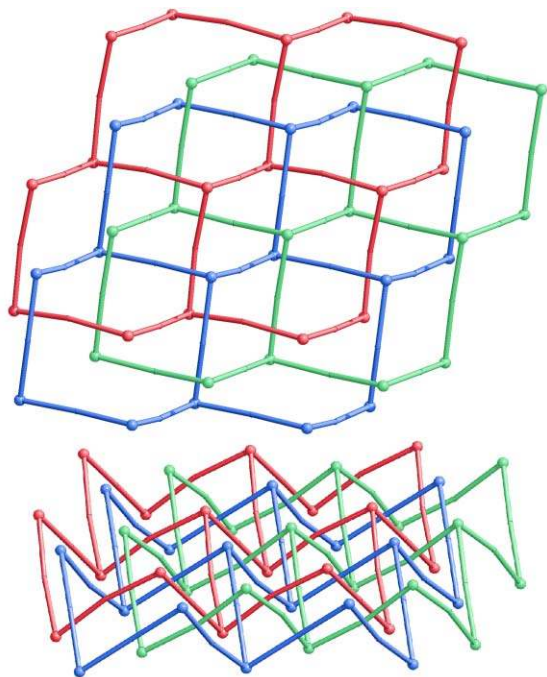


Fig. 15 Two schematic views of the Borromean links in $[\text{Cu}_2(\text{tmeda})_2\text{-}\{3\text{Au}(\text{CN})_2\}_3](\text{ClO}_4)$.

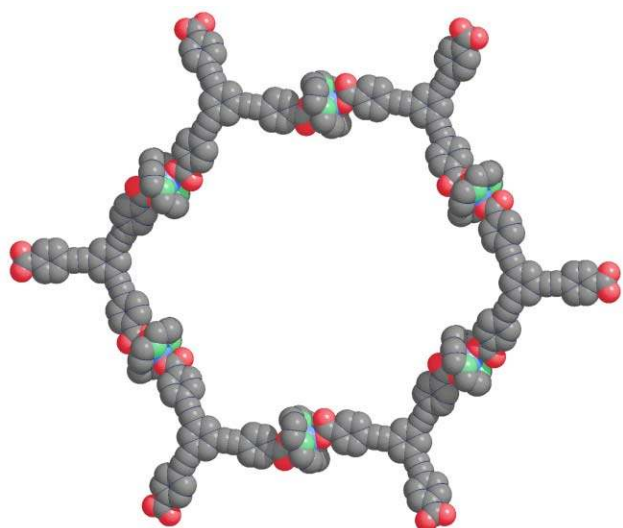


Fig. 16 A 6-membered ring of a (6,3) layer of $[\{\text{Ni}(\text{cyclam})\}_3(\text{TCPEB})_2 \cdot 6\text{C}_5\text{H}_5\text{N}$ (hydrogen atoms omitted).

entanglement sustained by Borromean links, like in the two examples described above. Though the authors classify this system as a case of 3-fold parallel interpenetration, they have noticed that “two of the nets are not interpenetrating as they can be separated without any bond breakage. It is only the addition of the third net that ties them all together in the observed structure”. A similar comment on this “unusual mode of interpenetration” has been reported by Batten.^{2d} Note that, differently from the 3D Borromean arrays previously described, these 2D entanglements must be obviously of the Brunnian type.

Another case of non-conventional links

A recently reported network assigned to the class of polycatenated systems, $[\text{Ag}(\text{bpe})(\text{L})_{0.5}]\cdot\text{H}_2\text{O}$ [bpe = 1,2-bis(4-pyridyl)ethane; L = 4,4'-biphenyldicarboxylate],³³ exhibits quite unusual and puzzling topological features. This polymeric

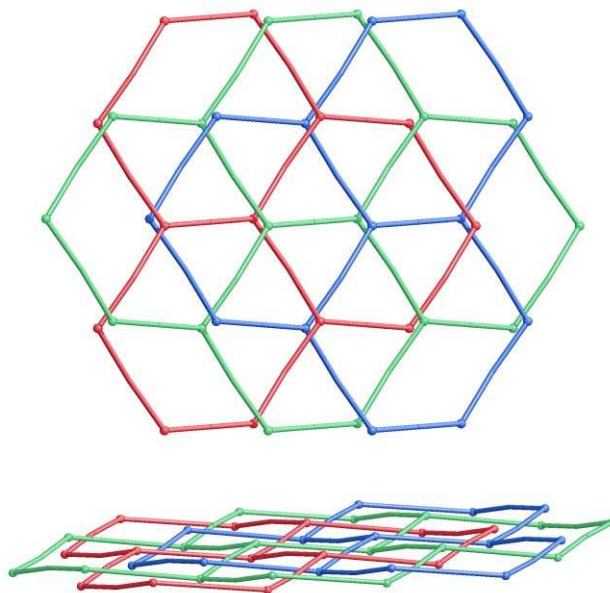


Fig. 17 Two schematic views of the three entangled Borromean layers in $[\{\text{Ni}(\text{cyclam})\}_3(\text{TCPEB})_2 \cdot 6\text{C}_5\text{H}_5\text{N} \cdot 4\text{H}_2\text{O}$. Click here to access a 3D representation.

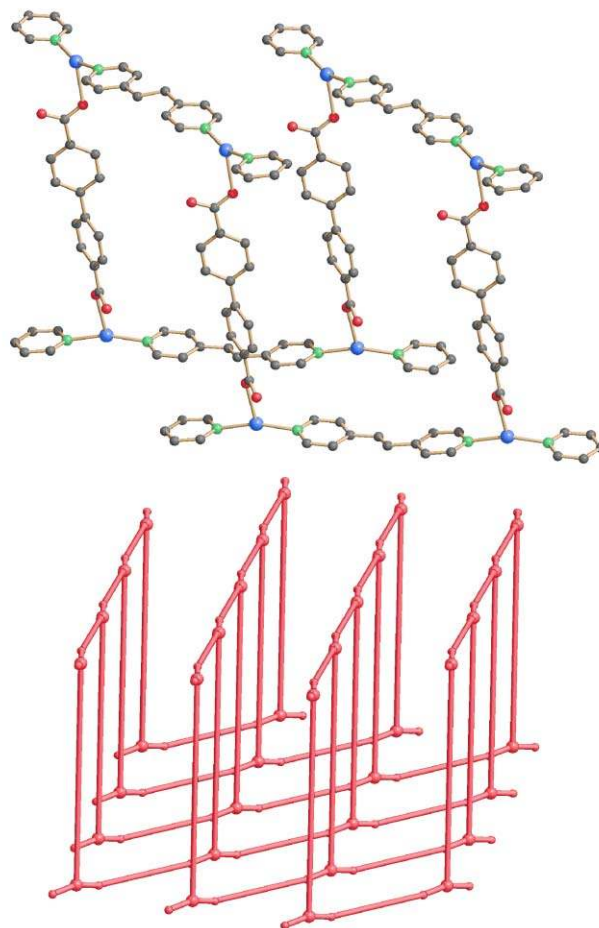


Fig. 18 A single ‘cell’ (top) and the individual bilayer in $[\text{Ag}(\text{bpe})(\text{L})_{0.5}]\cdot\text{H}_2\text{O}$ (see ref. 33).

species is comprised of catenated 2D bilayers of $8^2.10$ topology (see Fig. 18), previously observed also in non-entangled structures.³⁴

At a first glance the structure, illustrated in Fig. 19, seems like another case of parallel catenation involving thick multiple

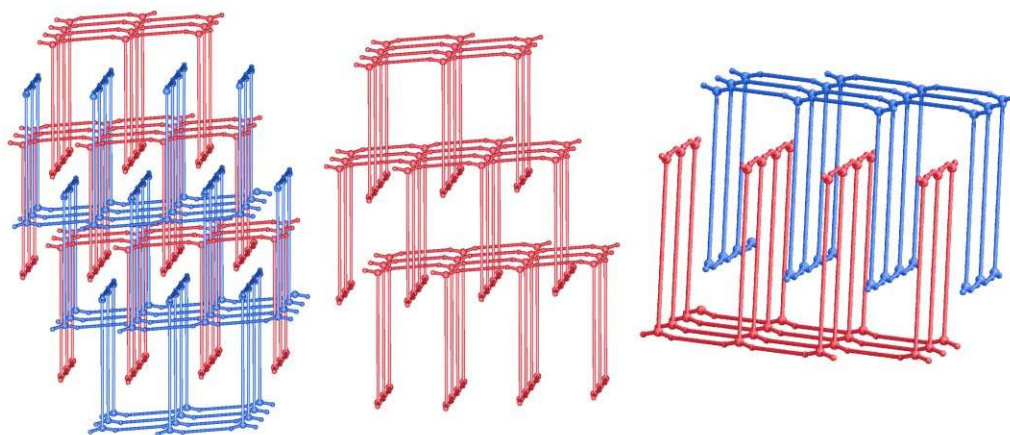


Fig. 19 The schematized overall network showing the two catenated sets of layers in blue and red (left), a view of a single set of catenated layers (middle) and the tongue-and-groove interdigitation of two single layers belonging to the different sets (right).

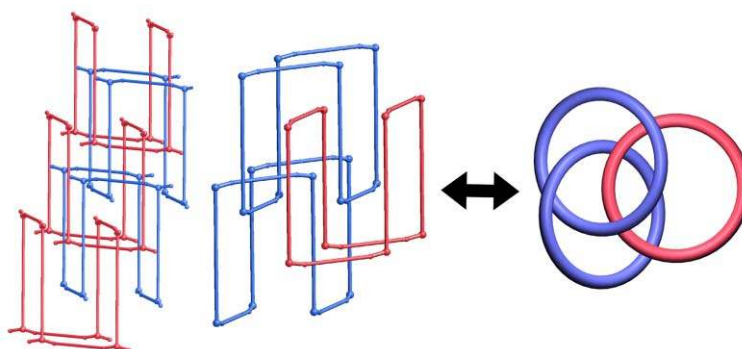


Fig. 20 A sequence of 'cells' of the two sets along the direction of catenation (left); three adjacent 'cells' (middle) are topologically equivalent to the three entangled rings (right) corresponding to two catenated rings (blue) + one free ring (red).

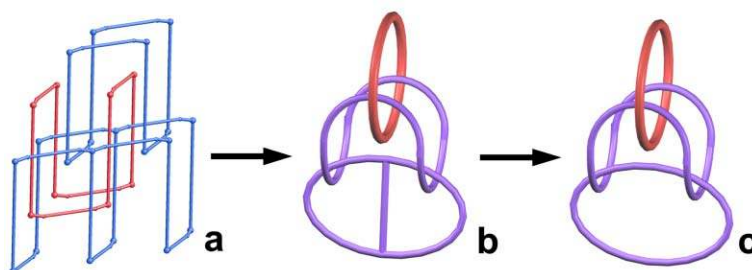


Fig. 21 The fundamental entanglement (a) in the network corresponds to the nontrivial linkage (b), which, in turn, is related to the Borromean links (c).

layers, similar to those previously discussed.^{17,18,20} Each sheet was erroneously described by the authors as interlocked by four adjacent ones (two 'upper' and two 'lower').

A careful analysis shows that the entanglement is comprised of two sets of polycatenated layers (in blue and red, respectively), with each individual 2D motif interlocked only by the two nearest neighboring ones of the same set. Quite surprisingly, no motifs of one set (see Fig. 19, middle) are catenated by individual motifs of the other set, and the closest layers belonging to the different sets are simply interdigitated in pairs (Fig. 19, right), in the tongue-and-groove fashion.³⁴

In a sequence of 'cells' (*i.e.* 8-membered loops) along the direction of catenation only those of the same colour are interlocked (Fig. 20, left)

Three adjacent such 'cells' (two blue and one red) are shown in Fig. 20 (middle) and display the identical entanglement of the three (*pseudo*-Borromean) rings illustrated in the same figure (right), *i.e.* an assembly of two catenated rings (Hopf link) plus one free ring.^{22b} Our considerations are entirely of topological nature: this means that the closed loops can

undergo 'ideal' continuous deformations (like rubber rings), without taking into account metrical factors (dimensions of the components, geometrical rigidity) or energetical factors (barriers to deformation), that do not belong to the realm of topology.^{8,14}

However, what is the nature of the linkage between the two sets of 'non-catenated' layers? This can be clearly seen in Fig. 21: the elemental link between them (a) is equivalent to the non-trivial entanglement (b), in which the catenation of the blue rings prevents the disentanglement of the (non-catenated) red one; the way in which this entanglement can be transformed into Borromean links (c) is also shown.

Conclusions

Entangled structures are becoming increasingly common within coordination polymers, and many new topologies are being reported. Among the ones we consider particularly fascinating, besides the 'polycatenanes' here discussed, other species that can be described as polyrotaxanes³⁵ and *pseudo*-polyrotaxanes³⁶ as well as

uncommon topological phenomena like polyknotted (self-penetrating) networks,³⁷ and intertwined one-dimensional chains woven like wool and weft threads in a cloth,³⁸ or multiple infinite helices.³⁹ In an attempt to establish useful relationships between structures and properties for these species^{2e,40} a careful analysis of the topology is unavoidable, particularly for the more complex types of entanglements.⁴¹

We have shown here that also in the case of coordination networks an approach based on concepts from the theory of links and knots has been useful to evidence some overlooked features, that are likely to be frequently encountered in the near future, and could also inspire new methods for dealing with more complex systems.

Appendix

To help the reader into the field of links, we report in Fig. 22 the complete list of the simplest possible links formed with 2 or 3 rings. In the notation A.B.C the letters correspond to: A = number of crossings, B = number of rings, C = ordering number (note that there are no links 4.2.2 or 5.2.2). These pictures and similar ones within the paper have been produced with KnotPlot.⁴²

In the search for possible *n*-nonBrunnian links we found, besides the one shown in Fig. 9, also the chain illustrated in Fig. 23.

Fabrication of a metallic microstructure (ca. 1.5 × 4 mm) of Borromean rings (as well as of other complex links and knots) was achieved by “soft lithography” by G. M. Whitesides and coworkers.⁴³

Further pictures concerning the subject of this Highlight

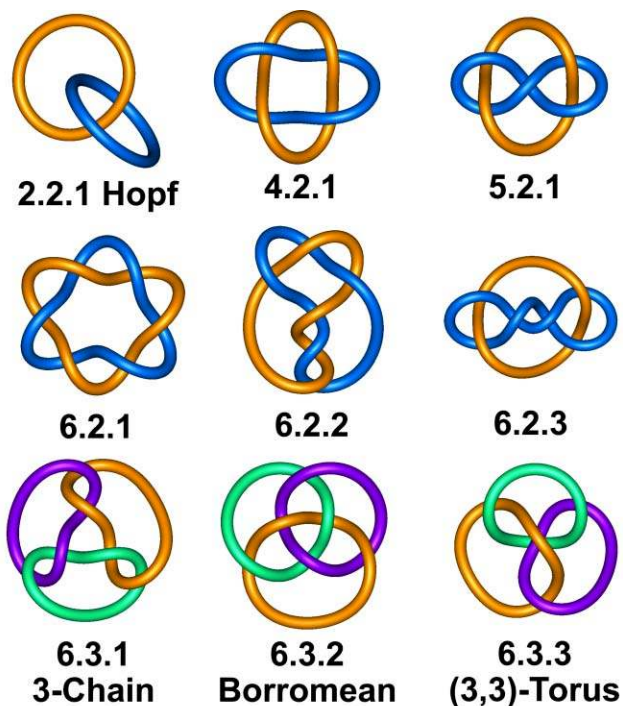


Fig. 22 Simplest links with 2 or 3 rings.

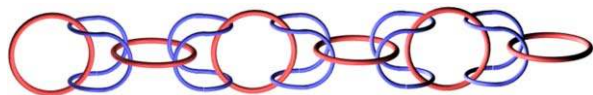


Fig. 23 A new example of *n*-nonBrunnian links. The cut of one blue ring separates the chain in two halves, while the cut of one red ring allows the separation of two half chains plus two blue rings.

(and more) can be found on the website <http://dessi.istm.cnr.it/research/webmar.ppt> based on the presentation made at the European Research Conference (EURESCO) on “Molecular Crystal Engineering—EuroConference on Design and Preparation of Molecular Materials” (Acquafredda di Maratea, Italy, 31 May – 5 June 2003).

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