

# CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

# Coordination Assembly of Borromean Structures

Cite this: DOI: 10.1039/x0xx00000x

Mei Pan<sup>a,b\*</sup>, and Cheng-Yong Su<sup>a,c\*</sup>Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Borromean link constitutes an intriguing type of entanglement and knot in both discrete coordination architectures (Borromean or Borromean) and infinite coordination assemblies (Borromean networks), characteristic of nontrivial three-ring links which are inseparable as a whole while cleavage of any ring makes the whole fall apart. This highlight paper covers recent advances in the assembly of coordination supramolecular structures showing Borromean-linking topological characters.

## 1. Introduction

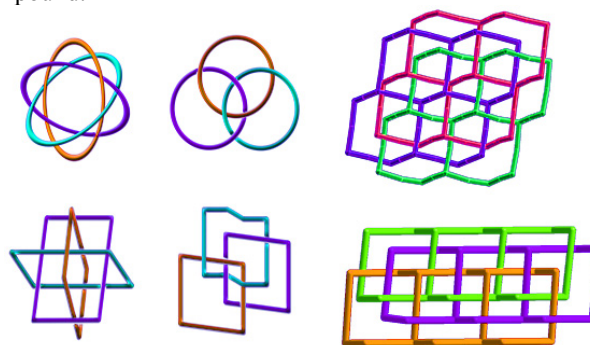
Among different types of topological entanglements, Borromean link represents one of the most intriguing styles because of its complexity, structural integrity and aesthetic beauty. Many Borromean examples have existed in the history of human being to symbolize strength and unity, which were embodied in totems, arts, as well as science.<sup>1</sup> Such kind of links is unlike topological Hopf links, in which two closed rings are interlocked with each other and cannot be separated without breaking at least one of them. In the Borromean topology, three closed rings are entangled in such a fashion that none of any two rings are really interlocked with each other (trivial links), while by the linking of the third one, they cannot be separated (nontrivial links) any more. In another word, all the entangled components in a Borromean system can be separated just by breaking one of the closed items (Scheme 1).<sup>2</sup>

Since the earliest example of discrete molecular Borromean rings realized by Seeman *et al* in manipulation of the topological properties of DNA sequences in 1997,<sup>3</sup> the first chemical synthesis of the smallest Borromean rings was achieved by Stoddart *et al* in 2004 with an all-in-one assembly strategy.<sup>1b</sup> Meanwhile, the chemical assembly of Borromean links in coordination polymers (CPs) was actually accomplished even earlier, which was ignored in the original report but formally put forward and classified by Ciani *et al* through a thorough topological analysis in 2003.<sup>2b</sup> Since then, design and synthesis of this kind of fascinatingly entangled structures in both discrete supramolecular architectures or two- to three-dimensional (2D and 3D) networks has triggered intense interest to scientists, although the topological control of such entanglement is proven a great challenge.<sup>2,4-8</sup> This Highlight will cover recent advances in the assembly of above two kinds of Borromean structures involving coordination chemistry. Firstly, section 2 will give a short introduction to the

assembly of discrete Borromean ring compounds (Borromean or Borromean), and then in section 3, we will focus on the assembly of polymeric coordination Borromean networks, which are discussed in line with ligands, topologies and stabilizing interactions.

## 2. Assembly of Borromean ring compounds

Borromean structures in the discrete three-ring-entangled formats, which are nearly true representatives to their ancient graphical symbols, are especially fascinating but challenging to synthesis.<sup>1a,7</sup> Stoddart *et al* proposed the term 'Borromean ring compounds' as a general descriptor for molecules possessing Borromean topology, which is an accurate and accepted form of nomenclature. While Borromean ring compounds which are assembled using metal ions and retaining the metal ions as an intrinsic part of the structure can better be referred to as 'Borromeanes'. Upon removal of the metal ions, the term 'Borromean' is suggested for the resulting metal-free compound.<sup>7</sup>



Scheme 1. Various presentations of the Borromean links.<sup>4a</sup>

For a long time, the topological complexity of discrete Borromean ring compounds has posed a formidable challenge

to synthetic scientists. Up to now, successful syntheses of such topological molecules are still quite rare. Actually, as early as in the 60's of last century, Wasserman *et al*<sup>9,10</sup> started to pay attention to Borromean structures, and predicted that, in order to synthesize a Borromean ring, at least 30 carbon atoms are needed in one branch ring. And in 1993, Gulick<sup>11</sup> tried to synthesize a Borromean molecule through the method of triple-braiding. In 2003, Siegel *et al*<sup>12</sup> proposed an alternative strategy to synthesize Borromean rings according to their topological characters. They made a try to achieve this goal via multistep method using metal coordination as the template. Firstly, two key structural intermediates were synthesized from a principal base macrocycle with *endo*- or *exo*-oriented metal-binding sites. Then a threaded two-ring structure was completed, in which the two rings are orthogonal and at least one of the two rings possesses a second set of metal-binding sites which should be compatible with the threading and knitting together of the third ring. However, in the assembling step of the third ring, both ring-closing and covalent-bond formation are needed, which brought significant challenges thereof the final goal was not achieved. But this attempt gave insight into the assembly of human conceptive Borromean links in later synthesis.

In 2004, Stoddart *et al* realized the first wholly chemically-synthetic Borromean ring compounds using an all-in-one strategy (Fig. 1).<sup>1a,b</sup> The assembly of the Borromean links is from 18 components by the template-driven assembly of 12 imine and 30 dative bonds, and directed by the coordination of three interlocked macrocycles with six zinc(II) ions. The three macrocycles are each tetranucleating and decadentate, presenting diagonally in pairs, and containing six *exo*-bidentate bipyridyl and six *endo*-diiminopyridyl ligands in total. Both solid-state crystallographic and solution analyses manifest the formation of three-ring entangled Borromean structure with  $S_6$  symmetry. Later in 2005, the authors further demetalated the six Zn(II) by borohydride reduction to result in metal-template-free Borromean structures with real Borromean link structures.<sup>8</sup>

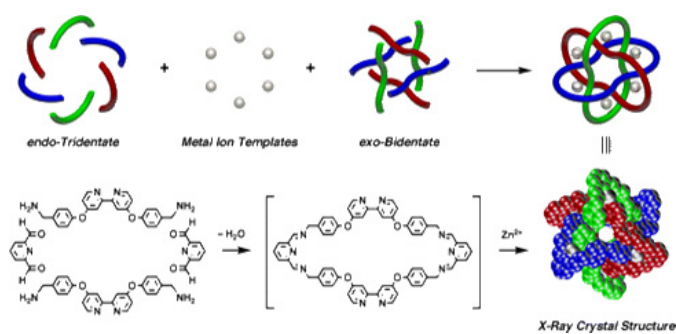
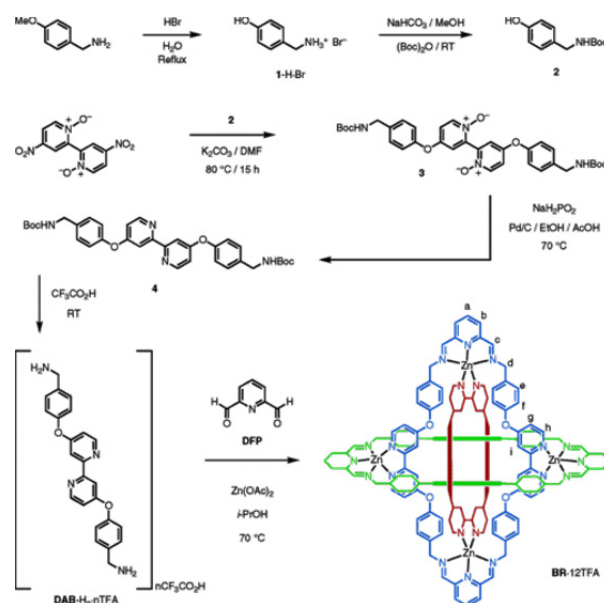


Fig. 1 Schematic assembly of a Borromean link from a combination of *endo*-tridentate and *exo*-bidentate ligands around metal ion templates. Reproduced from Ref. 1a with permission from the American Chemical Society.

After the successful synthesis of the first chemical Borromean molecule, Stoddart *et al* further expanded their ligands and accomplished a series of similar Borromean ring

compounds. They introduced alkyl group onto the 4-site of DFP (2,6-diformylpyridine) to result in BR(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OAc)<sub>6</sub>·12TFA and BR(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SMe)<sub>6</sub>·12TFA (Scheme 2, TFA = trifluoroacetic acid). In 2006, two stereo-active DFP molecules were used to assembly (R)<sup>12</sup> and (S)<sup>12</sup> Borromean enantiomers. And in 2007, pentenyloxy or p-tolylpentenyloxy was substituted to the 4-site of DFP to assemble BRO<sub>6</sub>·12TFA and BRS<sub>6</sub>·12TFA.<sup>13</sup>



Scheme 2. Synthesis of the Dibenzyllammonium Bipyridine Trifluoroacetate Salt (DAB) and BR·12TFA. Reproduced from Ref. 13a with permission from the American Chemical Society.

In above examples, an important finding is that the clever use of metal–ligand interactions could facilitate the assembly of Borromean structures. Based on the similar strategy, Schmittl *et al* applied spatial integration of both phenAr<sub>2</sub> and pyridyl units into a single ligand to result in the formation of a Borromean-ring-type hexanuclear cage (Fig. 2).<sup>14</sup> In this structure, two ligands **Phen3** and two Cu(I) ions form one rhombus (ring), and the resulting three rhombuses are interlocked with each other via Cu(I) coordination centers, at which the phenanthroline and pyridyl units act as *endo* and *exo* binding ligands, respectively.

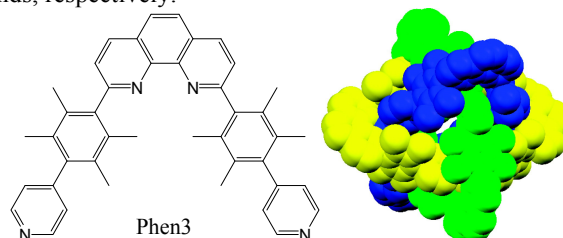


Fig. 2 Ligand **Phen3** containing both phenAr<sub>2</sub> and pyridyl units and the X-ray structure of Borromean-ring-type hexanuclear cage from it. Reproduced from Ref. 14 with permission from the American Chemical Society.

Different from above metal-templated strategy, Jin et al recently reported two coordination-driven self-assembled metallasupramolecules with real Borromean link structures.<sup>15</sup> The assembly was driven by the enhanced stability of interpenetrating structures with the compensation of weak coordination bonds. As shown in Fig. 3, through the stoichiometric (1:1) reaction of  $[\text{Cp}^*\text{RhCl}_2]_2$  with five ligands  $L_1$ – $L_5$  [ $L_1$  = pyrazine (pz);  $L_2$  = 4,4'-bipyridyl (bpy);  $L_3$  = 1,2-bis(4-pyridyl)ethylene (bpe);  $L_4$  = N,N'-4-dipyridyloxalamide (dpo);  $L_5$  = 1,4-bis(4-pyridyl)benzene (bpb)] five binuclear Rh-complexes with four coordination sites and different lengths can be obtained, which can serve as linear connecting units to further assemble with Cu-containing complex  $\text{Na}_2\text{L}^{\text{Cu}}$ . Finally, molecular rectangles based on the common  $[\text{4Rh}+2\text{Cu}]$  multinuclear structures with different Rh-component units were achieved. However, due to the variation in starting binuclear Rh-units, the obtained complexes **1–5** show distinct configurations: simple monomeric rings are obtained in complexes **1–3** with short ligands; while by the substitution of longer spacer N,N'-4-dipyridyloxalamide ( $L_4$ ), a special trimeric pattern is obtained in complex **4**. In this trimer, any two rectangles are not interlocked with each other, while each one is threading through one of the other two rectangles and cannot be separated as a whole. Break of any one of the three rings interrupts the union of all, thus bearing the intrinsic character of Borromean links. Changing the starting ligand to 1,4-bis(4-pyridyl)benzene ( $L_5$ ), which has almost identical N...N distance as in  $L_4$  but without an obvious hydrogen-bonding site, similar Borromean-linked structure was also obtained in complex **5**. This manifests that, the length of the Rh-component units is the driving force to determine the Borromean-type interpenetration in these two complexes, instead of the templated amide hydrogen bonds presenting in complex **4**.

### 3. Assembly of coordination Borromean networks

As mentioned above, coordination polymers of Borromean linkage came to scientists' notice only after the topological analysis and classification by Carlucci *et al.*<sup>2b</sup> Up to now, only a handful of extended coordination networks possessing Borromean topology have been reported.<sup>4,5</sup> Despite this paucity, some factors that may facilitate the formation of Borromean topologies, such as the shape and flexibility of the ligands, the pattern and size of the network topology, as well as the sustaining effects of different kinds of supramolecular interactions, have been explored and understood.<sup>4,5</sup> In general, honeycomb (hcb) networks of 2D (6,3) topology with high undulating character are mostly favored in formation of Borromean entanglement than any other 2D networks.<sup>4</sup> Especially, for a hollow (6,3)-hcb layer possessing regular  $C_3$ -symmetry and thick concavo-convex character, formation of Borromean links can even be solely driven by a void-filling process.<sup>4b,c</sup> The following section will focus on the formation of coordination Borromean networks from the view of above three

kinds of influencing factors, i.e. ligands, topologies and driving forces.

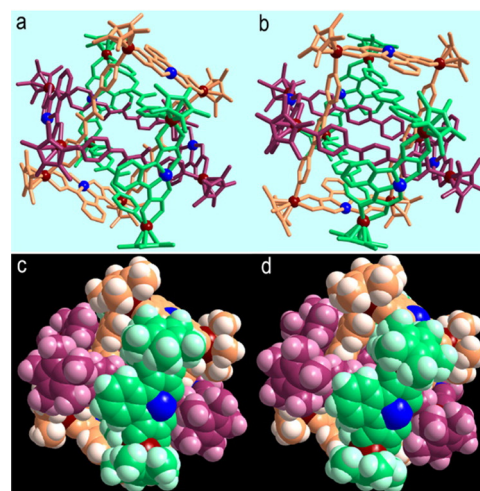
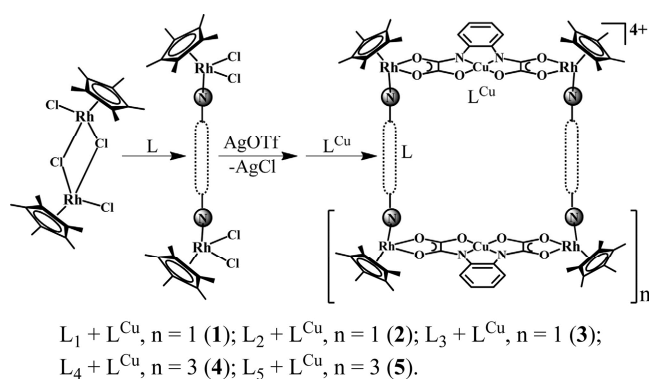


Fig. 3 (top) Synthesis of Complexes **1–5**. (bottom) View of the X-ray structures of Borromean-link structures in Complexes **4** (a,c) and **5** (b,d) as ball-and-stick and space-filling presentations. Reproduced from Ref. 15 with permission from the American Chemical Society.

#### 3.1 Ligands used in the assembly of Borromean networks

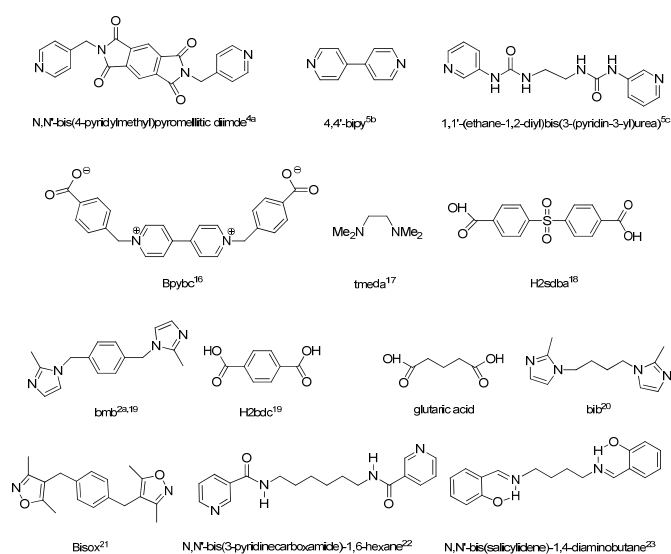
Generally, the assembly of Borromean networks can start from either ditopic linear (2-connecting) or triangle (3-connecting) ligands, since they are both commonly used in construction of 2D hcb-layers which are essential in most cases to build Borromean structures.<sup>4</sup> Some examples also involve the combination of coligands, macrocycles or other ancillary units. Scheme 3 and 4 summarize the 2-connecting linear ligands, 3-connecting triangle ligands and other ancillary ligands applied in the assembly of reported coordination Borromean networks.

##### 3.1.1 Type-I (2-connecting) linear ligands

One synthetic strategy of Borromean networks is to start from 2-connecting ligands (referred to Type-I) in combination with 3-connecting metal nodes to build 2D coordination hcb-layers. Using a flexible, charged-separated linear ligand Bpybc ( $\text{H}_2\text{Bpybc-Cl}_2=1,1'$ -



bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride), Zhang *et al* synthesized a series of metal-organic frameworks (MOFs) containing  $\text{Mn}^{\text{II}}$  and  $\text{Eu}^{\text{III}}$  with the metal-to-ligand ratio of 2:3. In these MOFs, each Bpybc ligand connects two metal ions by two terminal carboxylate groups, and each metal center can be seen as a 3-connecting node to link the whole framework into an infinite 2D honeycomb (hcb) network. This typical (6,3) net is comprised of large pseudo-hexagonal ring units, with metal ions occupying the corners and Bpybc ligands locating at the edges. Large free void (inner-diameters of 27.4–29.3 Å) existed in these 2D networks; however, interpenetration did not occur and none of the 2D honeycomb layers were mutually interlocked with other layers. Nevertheless, three adjacent layers formed an inextricable entanglement, and cannot be separated without breaking the intra-layer connections. In another word, the hcb layers in this MOF structure are entangled with each other to result in a so-called *n*-fold Borromean linkage showing 2D→3D dimension increase.<sup>16a</sup>



Scheme 3. Type-I (2-connecting) linear ligands applied in Borromean networks.

Such Borromean linkage based on 3-connecting metal centers and 2-connecting ligands were also observed in other coordination networks. For example, complex  $\{[\text{Ag}_2(\text{bmb})_3](\text{BF}_4)_2\}$  was obtained by reacting the flexible, *exo*-bidentate ligand bmb (1,4-Bis(2-methylimidazol-1-ylmethyl)benzene) with  $\text{AgBF}_4$ .<sup>2a</sup> The coordination environment around the Ag metal ion is trigonal planar and the three imidazole rings are oriented in a propeller-like arrangement with their 2-methyl groups located on the same side of the plane, which is defined by the coordinating nitrogen atoms. Therefore, each ligand bridges two silver ions which, in turn, each silver ion coordinates to three separate ligands. This coordination mode results in the formation of 2D layer containing large hexagonal rings; furthermore, three such separate honeycomb layers can be entangled to form a Borromean weave as demonstrated in Fig. 4.

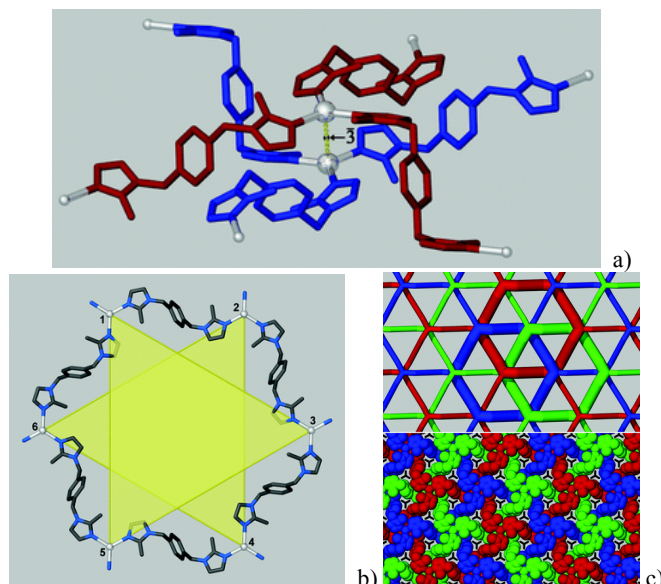


Fig. 4 Structure of  $\{[\text{Ag}_2(\text{bmb})_3](\text{BF}_4)_2\}$ : (a) Perspective view showing that each ligand bridges two silver ions and that each silver ion is coordinated to three ligands. The two “infinite” complexes (shown in red and blue) are attracted to one another by means of  $\text{Ag}\dots\text{Ag}$  interactions (fragmented yellow cylinder). (b) Projection along [001] showing the formation of a hexagonal ring consisting of six silver ions and six ligands. (c) The topology of an infinite Borromean weave (top) and a projection along [001] (bottom) showing a corresponding weave consisting of three separate honeycomb lattices of  $[\text{Ag}_2(\text{bmb})_3]^{2+}$ . Reproduced from Ref. 2a with permission from the Royal Society of Chemistry.

The combination of bmb and *p*-H<sub>2</sub>bdc ligands in reaction with Zn (II) can also result in similar 2D (6, 3) hcb network,  $[\text{Zn}(\text{bmb})_{0.5}(\text{p-bdc})_3\text{H}_2\text{O}]_n$ , in which the hexagonal ring involves four *p*-bdc<sup>2-</sup>, two bmb ligands and six Zn<sup>II</sup> ions.<sup>19</sup> As shown in Fig. 5, entanglement of three hcb networks affords a Borromean topological sheet.

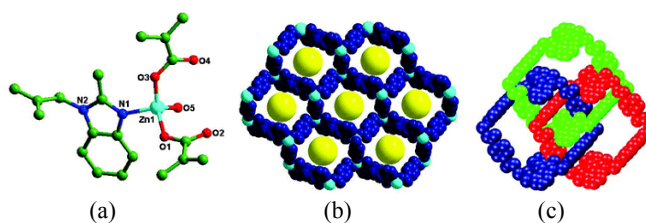


Fig. 5 (a) Coordination environment of  $\text{Zn}^{\text{II}}$  ion in  $[\text{Zn}(\text{bmb})_{0.5}(\text{p-bdc})_3\text{H}_2\text{O}]_n$  with hydrogen atoms and free water molecules omitted for clarity. (b) The 2D (6, 3) hcb network based on hexagonal ring, which involves four *p*-bdc<sup>2-</sup> anions, two bmb ligands, and six  $\text{Zn}^{\text{II}}$  ions. (c) Space-filling representation of a Borromean links in the honeycomb-like sheets. Reproduced from Ref. 19 with permission from the American Chemical Society.

Silver(I) coordination network (Fig. 6)<sup>21</sup> formed by the reaction of semi-rigid bis(isoxazolyl) ligand, 1,4-bis((3,5-dimethylisoxazol-4-yl)methyl)benzene (bisox), with Ag(I) perchlorate is quite similar to the case shown in Fig. 5. In this coordination network, each Ag(I)

center is trigonal planar and coordinated to three bisox ligands, and each ligand adopts *S*-conformations to link two Ag(I) centers into hcb-(6,3) layer. Thus formed layers are further stacked through Borromean links. Similar examples can also be found in other earlier reports.<sup>5d,e,21</sup>

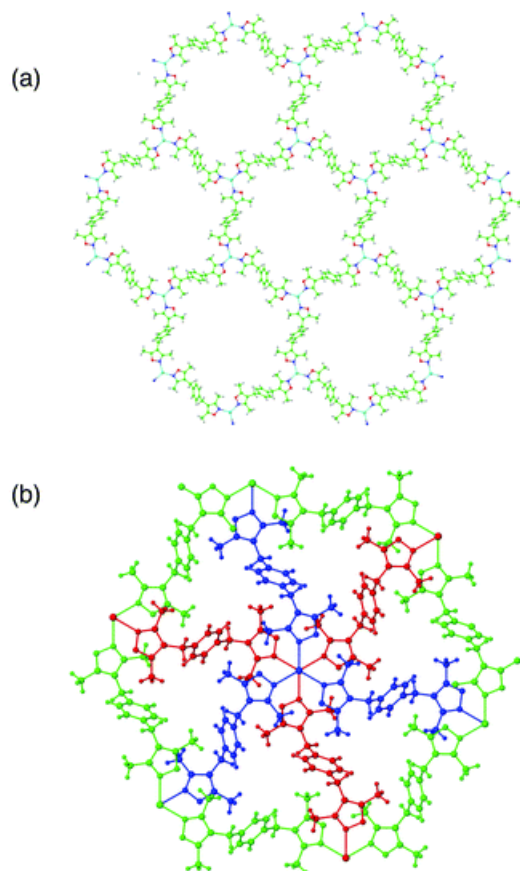
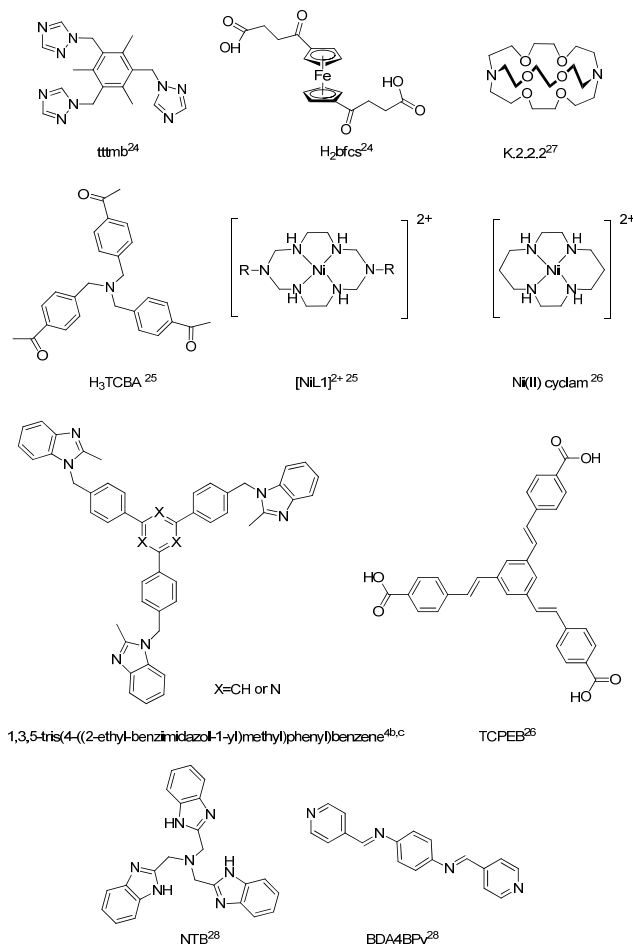


Fig. 6 The structure of  $[\text{Ag}_2(\text{bisox})_3](\text{ClO}_4)_2$  showing (a) one of the (6,3)  $\text{Ag}_2(\text{bisox})_3$  layers present in the structure, (b) the Borromean network with the independent sheets shown in different colours. Reproduced from Ref. 21 with permission from the Royal Society of Chemistry.

### 3.1.2 Type-II (3-connecting) triangle ligands

Different from the above Type-I linear ligands, the triangle ligands (referred to Type-II) can link three 2-connecting metal centers with metal-to-ligand ratio of 3:2 to form 2D (6,3) hcb-nets, which represents an alternative synthetic strategy to build Borromean networks. For example, by the solution reaction of a flexible tripodal ligand ttmb (1,3,5-tris(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene), a ferrocenyl bridging ligand  $\text{H}_2\text{bfcs}$  (1,1'-bis(3-carboxy-1-oxopropyl)ferrocene) and  $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  salts under room temperature, a trinodal, self-catenated layer-pillaring complex  $\{[\text{Cd}_3(\text{bfcs})_3(\text{ttmb})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}\}_n$  is obtained.<sup>24</sup> The complex shows (6,3) hcb-net structure, in which the basic  $(\text{ML})_6$  type hexagonal ring is comprised of six ttmb ligands and six  $\text{Cd}^{\text{II}}$  ions, serving as 3-connecting and 2-connecting nodes, respectively. In each layer, there are three identical  $\text{Cd}^{\text{II}}$ -ttmb hcb-networks which

are entangled in a Borromean-linking fashion. That means, any two of the three identical networks are not really catenated with each other, but by the involvement of the third network, the interweaving triple-network becomes inseparable. This shows the typical character of Borromean topology. However, in the crystal structure, the secondary ligands  $\text{bfcs}^{2-}$  further connect the above 2D layers together into a 3D layer-pillar framework. In this context, the (6,3) nets have direct connections by the linkage of  $\text{bfcs}^{2-}$  and do not present a true Borromean pattern any more.



Scheme 4. Type-II (3-connecting) triangle ligands and other ancillary ligands or compounds involved in Borromean networks.

Using azamacrocyclic Ni(II) complexes  $[\text{NiL}^1](\text{ClO}_4)_2$  and  $\text{TCBA}^{3-}$  as building blocks ( $\text{L}^1 = 3,10\text{-bis-(2-fluorobenzyl)-1,3,5,8,10,12-hexaazacyclotetradecane}$ ,  $\text{TCBA}^{3-} = \text{tri(4-carboxybenzyl)amine}$ ), a coordination polymer  $[\text{NiL}^1]_3(\text{TCBA})_2$  with 2D Borromean structure is obtained, in which each Ni(II) ion connects two individual bowl-shaped  $\text{TCBA}^{3-}$  anions to generate a 2D (6,3) undulating sheet containing  $(\text{ML})_6$ -type hexagonal ring. In each ring, there are six  $\text{TCBA}^{3-}$  anions at the corners and six macrocyclic  $[\text{NiL}^1]$  compounds at the edges as shown in Fig. 7. Thus formed 2D sheets are further entangled into a 3D Borromean structure.<sup>25</sup> It is noteworthy that this is one of the only two cases (the other can be found in reference 26) in which macrocyclic units are involved in the structure of Borromean nets.

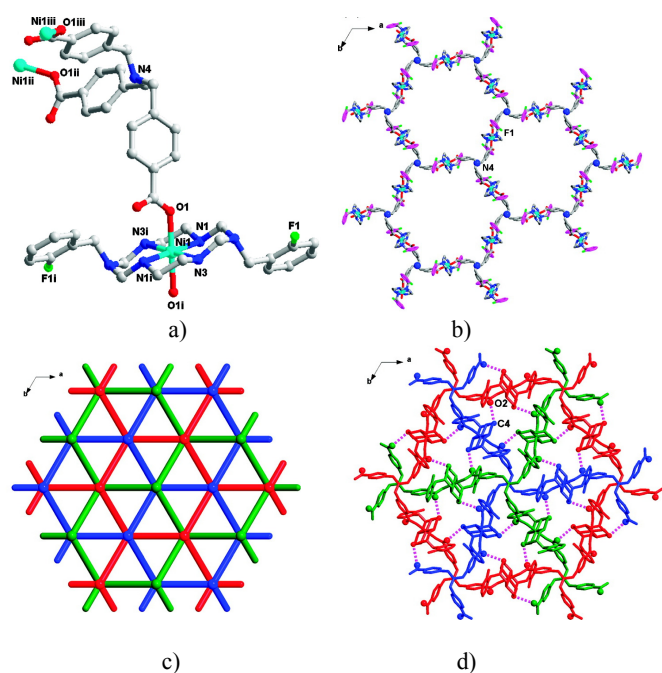
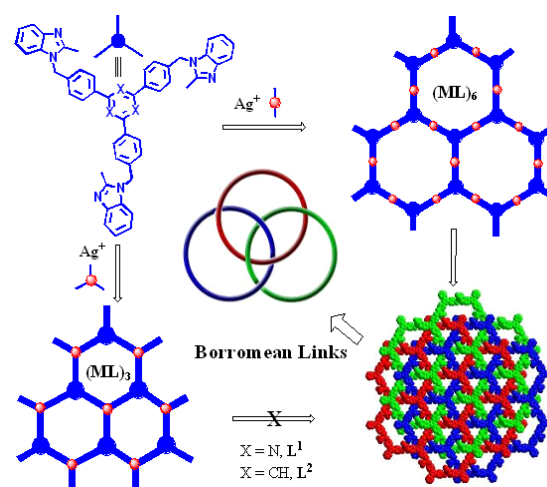


Fig. 7 Structure of complex  $[(\text{NiL})_3\text{-(TCBA)}_2]$ : (a) Coordination environments of Ni(II) and the coordination modes of bowl-shaped  $\text{TCBA}^{3-}$ . (b) 2D (6, 3) sheet, showing the large honeycomb-like cavities and the tropism of 2-fluorobenzyl groups (in pink). (c) The topological structure of the Borromean links. (d) The C-H $\cdots$ O hydrogen bonding interactions between the entangled sheets. Reproduced from Ref. 25 with permission from the American Chemical Society.

Our group has long been interested in assembly of Borromean coordination networks.<sup>4</sup> For example, reactions of two tripodal ligands, 2,4,6-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)-1,3,5-triazine ( $\text{L}^1$ ) and 1,3,5-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)benzene ( $\text{L}^2$ ), with  $\text{AgSbF}_6$  were found to be able to lead to formation of two types (6,3) networks in one single crystal with the overall formula  $[(\text{Ag}_3\text{L}_2)(\text{Ag}_2\text{L}_2)](\text{SbF}_6)_5 \cdot \text{solvents}$ .<sup>4b</sup> As shown in Scheme 5, the ligands act as tris-monodentate triangular connectors, while the  $\text{Ag}^+$  ions show two kinds of coordination geometries. One has a two-fold symmetry, thus acting as two-connecting linkers to form an  $(\text{ML})_6$  type network involving six ligands and six  $\text{Ag}^+$  ions in the basic hexagonal ring. The other one has a three-fold symmetry, thus behaving as a three-connecting node to join the three-connecting ligands into an  $(\text{ML})_3$  type network, comprising three ligands and three  $\text{Ag}^+$  ions in each basic ring. These two types of (6,3) networks show the same hcb-net topology but different chemical compositions. The subunits of the  $(\text{ML})_3$  net are  $\text{AgL}$  while those of  $(\text{ML})_6$  net are  $\text{AgL}_{2/3}$ , corresponding to metal-to-ligand ratios of 1 : 1 and 3 : 2, respectively. Further topological analysis revealed that the  $(\text{ML})_3$  network is independent in the crystal lattice, while the  $(\text{ML})_6$  networks display Borromean linking as depicted in Scheme 5, offering an interesting example showing co-occurrence of interweaving and non-interweaving polymeric networks in the same crystal. A similar structural diversity

in one single-crystal involving Borromean linked hcb-networks and independent  $(\text{ML})_3$  type network was also observed in assembly of tripodal ligand, 1,3,5-tris(4-((2-ethyl-benzimidazol-1-yl)methyl)phenyl)benzene and  $\text{Ag}^+$  ions.<sup>4c</sup> A noticeable find is that two kinds of 2D networks cocrystallize to resolve enantiomeric single-crystal tubes showing microscale crystal pores, which might be of interest in morphology control of crystal growth and property imbedding through coordination assembly, such as chirality, porosity, topology, and so on. In both cases, the crystal packing displays interesting sandwiched Borromean sheets stacking with the 3-fold Borromean  $(\text{ML})_6$  layer intercalated by two single  $(\text{ML})_3$  layers in a face-to-face fashion. The conformational chirality originated from the homogeneous propeller-like conformation of all ligands has been observed to transfer between two kinds of networks in the crystal lattice, resulting in the same handedness in the same crystal and finally giving rise to enantiomeric resolution.



Scheme 5. Schematic representation of two types of (6,3) nets and formation of three-fold interlocking network via Borromean links.<sup>4b</sup>

### 3.2 Net Topology in coordination Borromean networks

As mentioned and demonstrated by the examples in section 3.1, most Borromean-linked structures are based on the 2D (6,3) honeycomb coordination networks. To generate Borromean links, the 2D layered structures can either show 2D  $\rightarrow$  2D entanglements in a parallel manner, or, form 2D  $\rightarrow$  3D dimension increase by Borromean links, which has been previously classified by Carlucci *et al.*<sup>2b</sup> Moreover, there are other kinds of Borromean networks which can be built from 2D layers other than regular (6,3) honeycomb networks, which will be shown below.

#### 3.2.1 Borromean ladders from brick-wall type (6,3) networks

Reaction of a semi-rigid ditopic ligand, N,N'-bis(4-pyridylmethyl) pyromellitic diimide (Scheme 3), with  $\text{HgI}_2$  afforded the 2-D brick-wall type (6,3) networks, which feature in remarkably undulating 2D layers leaving large voids inside each network. A notable finding is that the brick-wall networks interlock in a specific



way, resulting in a three-fold parallel entanglement characteristic of Borromean links as shown in Fig. 8. The structural analysis revealed that normal interpenetration does not occur in these closely packed networks. Any two undulating brick-wall networks are independent and not interlocked, but appearance of the third network inevitably results in interweaving of three networks which can be schematized to a Borromean ladder links. From a topological view, the brick-wall network shows the (6,3) net topology, equivalent to that of the hcb-network. Therefore, assembly of both brick-wall and hcb-networks can be achieved from three metal ions and three ligands by forming a six-membered basic ring. However, the hcb-network contains the trigonal 'Y-shaped' nodes ( $C_3$  symmetry) while the brick-wall network possesses the 'T-shaped' nodes ( $C_2$  symmetry). Such geometric difference leads to hexagonal and rectangular basic six-membered rings, respectively, which subsequently determine the shape of the networks. In contrast to the Borromean links based on the hcb-networks containing trigonal  $C_3$  symmetrical building units in section 3.1, the present case offers a new approach to Borromean links based on the ladder-like  $C_2$  unsymmetrical building units. Such assembly process indicates that the lower unsymmetric  $C_2$  nodes and nonequivalent connectors can be utilized to build Borromean networks, implying the possibility of fabricating diversified Borromean networks other than typical hexagonal hcb-nets.<sup>4a</sup>

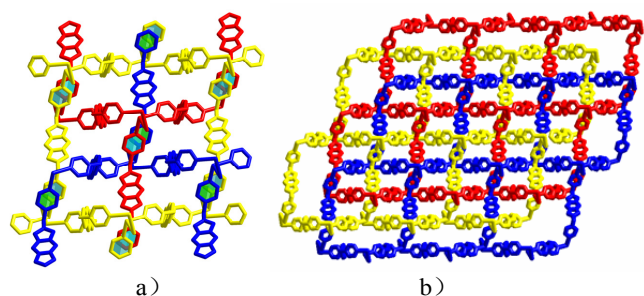


Fig. 8  $\pi \dots \pi$  stackings (highlight, a) formed between 'T-shaped' building blocks stabilizing Borromean brick-wall networks b).<sup>4a</sup>

### 3.2.2 Borromean networks from (4,4)-sql lattice

Alternatively, the Borromean links have also been found to be able to form from the 2D (4,4)-sql networks. Reaction of the ligand, 1,1'-bis(4-carboxybenzyl)-4,4'-bipyridinium dichloride ( $H_2BpybcCl_2$ ), with  $NiCl_2$  and potassium hydrogen phthalate (KHPTA) in the ratio 1 : 1 : 1 yielded a supramolecular compound  $\{[Ni(H_2O)_4(Bpybc)(PTA)] \cdot 9H_2O\}_n$ . The asymmetric unit of this complex contains a mononuclear coordination motif  $cis-[Ni(H_2O)_4(Bpybc)(PTA)]$  and nine lattice water molecules. Two enantiomeric mononuclear units were linked via hydrogen bonding to form a dimer, and each dimer is linked to four adjacent dimers, thus generating an undulating (4,4)-sql network containing large cavities (Fig. 9). The most remarkable structural feature is that three separable (4,4)-sql networks are entangled with each other to form a Borromean sheet (2D  $\rightarrow$  2D). Different from normal interpenetration, no two sql-networks are mutually interlocked, but, as a whole, three networks form an inextricable

entanglement. This is the first report of Borromean links comprising threefold entangled (4,4)-sql networks.<sup>16b</sup>

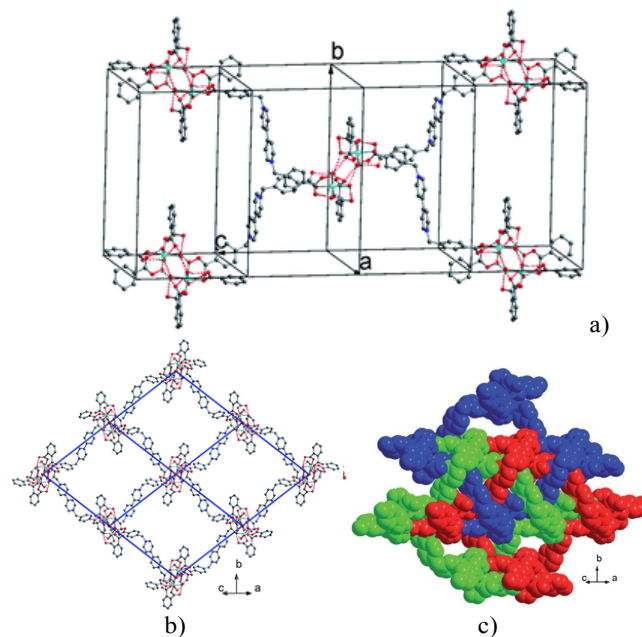


Fig. 9 Connection mode between hydrogen-bonded dimers (a), hydrogen-bonded (4,4)-sql layer (b), and space-filling representation of the Borromean links viewed along the [101] direction (c). Reproduced from Ref. 16b with permission from the Royal Society of Chemistry.

### 3.2.3 Pseudo-Borromean networks from $ThSi_2$ -type network

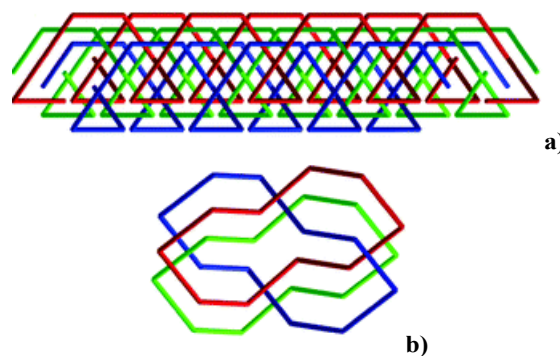


Fig. 10 Structure of  $\{[Co(\text{glutaric acid})(\text{bib})] \cdot 1.5H_2O\}_n$ : framework perspective showing the 3-fold interpenetrating motif with  $ThSi_2$ -type network (a); and view of pseudo-Borromean (b). Reproduced from Ref. 20 with permission from the American Chemical Society.

Liu *et al.*<sup>20</sup> reported another interesting coordination polymer with the topological links closely related to Borromean links. Flexible glutaric acid and bib (1,4-bis(2-methyl-imidazol-1-yl)butane, Scheme 3) were co-assembled with Co(II) to give a 3-connected  $ThSi_2$ -type coordination polymer  $\{[Co(\text{glutaric acid})(\text{bib})] \cdot 1.5H_2O\}_n$ . The large voids formed in a single 3D



network allow incorporation of other two identical networks, thus leading to a 3-fold interpenetrating motif showing pseudo-Borromean links as illustrated in Fig. 10.<sup>20</sup>

### 3.3 Supramolecular interactions in Borromean networks

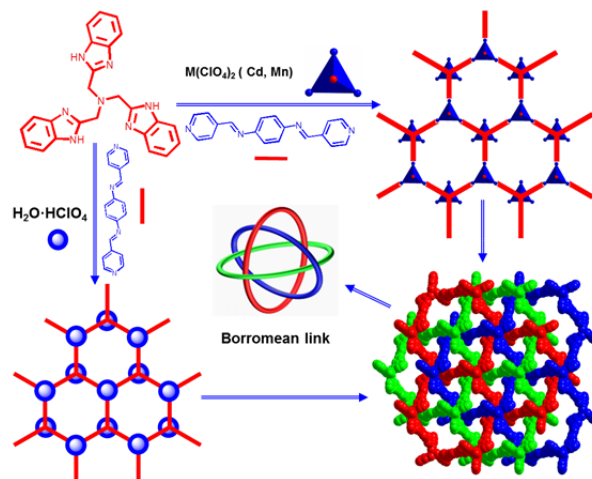
Up to now, predictable engineering of Borromean network is still a significant challenge. However, examination of available Borromean networks indicates that various supramolecular forces play important roles in the formation and stabilization of Borromean network topology. Moreover, these intermolecular interactions not only contribute to the stability of the Borromean linkage, but also provide opportunities to tune the structure-property relationship of the coordination frameworks.

#### 3.3.1 Hydrogen-bonding Borromean networks

Hydrogen bonds (HBs) are ubiquitous in both natural and synthetic self-assembly processes. For some reported Borromean networks, varied hydrogen bonds may exist between the component networks to solidify the overall coordination framework.<sup>16a,22,25</sup> To simplify the network linkage, some HBs are neglected in order to reach exact Borromean entanglements. In such cases, HBs should be the leading interactions in formation of 2D sheets responsible for Borromean-linking. One example has been shown in section 3.2.2, in which the Borromean networks are based on the (4,4)-**sql** lattices which are generated from mononuclear coordination units through the linking of abundant hydrogen bonds.<sup>16b</sup>

The first examples of real hydrogen-bonding Borromean links were reported by our group,<sup>4d</sup> in which assembly of a tripodal ligand tris(2-benzimidazolylmethyl)amine (NTB) with the long rod-like spacer, *N,N'*-bis(pyridin-4-ylmethylene)-benzene-1,4-diamine (BDA4BPY, Scheme 4), in the presence of  $M(\text{ClO}_4)_2$  ( $M = \text{Cd}^{2+}$  and  $\text{Mn}^{2+}$ ) or  $\text{H}_3\text{O}^+\cdot\text{ClO}_4^-$  led to the formation of (6,3)-hcb networks which interweave in a parallel fashion to give rise to hydrogen-bonding Borromean links (Scheme 6).

In complexes  $\{\text{Cd}(\text{NTB})\text{Cl}\cdot(\text{BDA4BPY})1.5\cdot(\text{ClO}_4)_2\}_\infty$ ,  $\{\text{Mn}(\text{NTB})\text{Cl}\cdot(\text{BDA4BPY})1.5\cdot(\text{ClO}_4)_2\}_\infty$  and  $\{\text{H}_2\text{O}\cdot\text{HNTB}\cdot(\text{BDA4BPY})1.5\cdot\text{ClO}_4\cdot 2\text{H}_2\text{O}\}_\infty$ , formation of  $[\text{M}(\text{NTB})\text{Cl}]^+$  or  $[\text{H}_2\text{O}\cdot\text{HNTB}]^+$  motifs provides a set of hydrogen-bonding donors (three -NH groups) pointing to the same direction. The BDA4BPY spacers acting as the HB acceptors join these HB donors to lead to a N-H...N hydrogen-bonded network with self-assembly propagation restricted in two dimensions. As a consequence, assembly of 2D (6,3)-hcb networks can be predefined. Thus formed (6,3)-hcb networks have large hexagonal rings with the edge length of 29 Å. Moreover, these networks are not coplanar, featuring in thick concave-convex “egg tray” layers. Since the networks possess  $C_3$ -symmetry and the hexagonal rings and the voids are uniformly distributed, interlocking of these hollow (6,3)-hcb networks prefers Borromean links to other entangling fashions. Therefore, formation of the 2D Borromean network can be solely driven by a void-filling process without any hydrogen bonding between the component networks.



Scheme 6. Schematic representation of two types of hydrogen-bonding hcb-networks and formation of 3-fold interlocking network via Borromean links.<sup>4d</sup>

Another type of Borromean entanglement is sustained by specific hydrogen bonding involving a ligand backbone and counter anions. Complex  $[\{\text{Zn}(\mu\text{-L1})_{1.5}(\text{SO}_4)\}_x\text{H}_2\text{O}]$  prepared from *N,N'*-bis(3-pyridyl)-*p*-phenylenebisurea (L1) displays a 3-fold 2D→2D Borromean topology with the (6,3) hcb-networks mainly sustained by interlayer urea-sulfate hydrogen bonding (Fig. 11).<sup>5d</sup> On the contrary, the Borromean-structured coordination polymer  $[\text{Ag}_2(\text{L1})_3](\text{NO}_3)_2\cdot 7\text{H}_2\text{O}$  ( $\text{L1} = 1,1'$ -(ethane-1,2-diyl)bis(3-(pyridin-3-yl)urea)) is held in a synergistic effect by coordination interactions, argentophilic interactions and saturated hydrogen bonding to nitrate counterions.<sup>5c</sup>

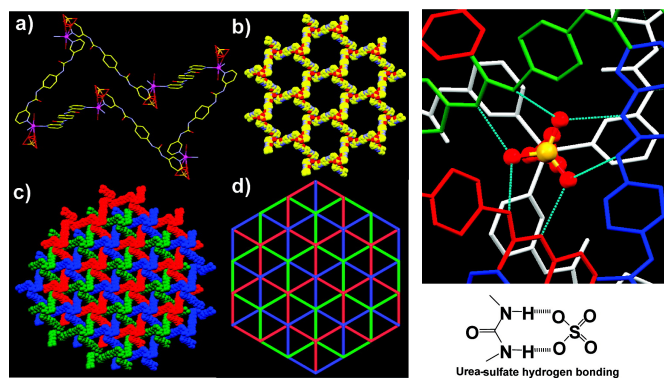


Fig. 11 Crystal structure illustration: (a) chair conformation of the hexagonal ring; (b) highly undulating (6,3) honeycomb layer; Borromean entanglement (c) in the space filling model and (d) in a TOPOS schematic representation (top) and urea-sulfate hydrogen bonding interactions (bottom) presenting in  $[\{\text{Zn}(\mu\text{-L1})_{1.5}(\text{SO}_4)\}_x\text{H}_2\text{O}]$ . Reproduced from Ref. 5d with permission from the American Chemical Society.

#### 3.3.2 $\pi$ - $\pi$ stacking Borromean networks

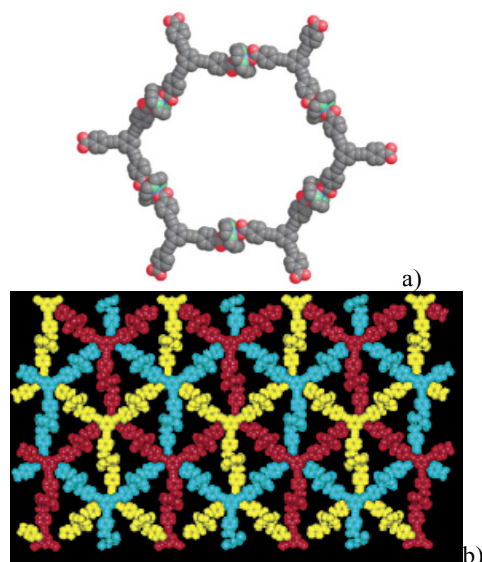


Fig. 12 Structure of  $[\{\text{Ni}(\text{cyclam})\}_3(\text{TCPEB})_2] \cdot 6\text{C}_5\text{H}_5\text{N}$ : the 6-membered ring of a (6,3) layer (hydrogen atoms omitted, a), and CPK representations for top view showing 3-fold parallel interwoven (6,3) nets (b). Reproduced from Ref. 2b with permission from the Royal Society of Chemistry and Ref. 26 with permission from the American Chemical Society.

The  $\pi$ - $\pi$  stacking also universally exists in the assembly of coordination polymers. In some specific cases,  $\pi$ - $\pi$  stacking can facilitate formation of Borromean links. As demonstrated in Fig. 8 (section 3.2.1), offset face-to-face  $\pi$ - $\pi$  stackings formed between pyridyl rings represent the major factor influencing Borromean interweaving. Each 'T-junction' involves three  $\pi$ - $\pi$  stackings and the Borromean links were stabilized by these multiple intermolecular interactions.<sup>4a</sup>

Another Borromean network with  $\pi$ - $\pi$  stacking as the major interactions was found in ref. 26. In this Borromean structure, the (6,3) networks are different from the undulated ones observed in other Borromean networks, which are rather flat, but nevertheless they are able to give Borromean links of three parallel motifs as shown in Fig. 12. Each entangled sheet is only ca. 4 Å thick. Within the triply interwoven networks, the central benzene units of TCPEB<sup>3-</sup> ligand in one layer display offset  $\pi$ - $\pi$  interactions with those of the other layers (shortest C $\cdots$ C distance, 3.470 Å). Moreover, there exist offset  $\pi$ - $\pi$  interactions between the central benzene rings of TCPEB<sup>3-</sup> in a layer and the 4-carboxyphenyl rings belonging to the adjacent layers (shortest C $\cdots$ C distance, 3.535 Å).<sup>26</sup>

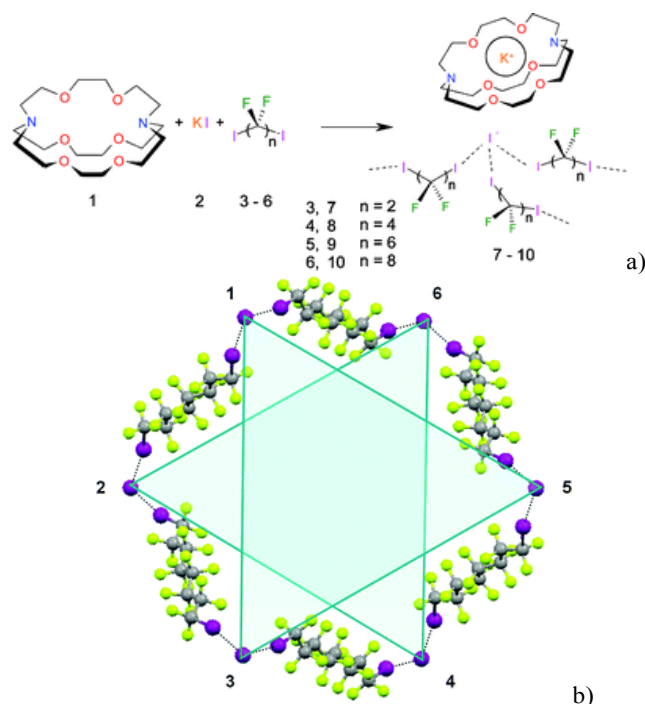
### 3.3.3 Coordination-bonding Borromean networks

For most of Borromean networks introduced in this highlight paper, the coordination-bonding is responsible mainly for construction of individual 2D networks which are further entangled by Borromean links. A special example has been shown in the beginning of section 3.2.1.<sup>24</sup> In addition to the weak  $\pi$ - $\pi$  interactions between the hcb-networks forming Borromean links, there are actually coordination interactions

from bridging ferrocenyl carboxylate  $\text{bfcs}^{2-}$ . It should be noted that, Borromean topology is envisaged in this case by neglecting the coordination bonding through the  $\text{bfcs}^{2-}$  ligands. If this coordination bonding is considered as a linkage, it is no longer a real Borromean entanglement anymore.

### 3.3.4 Halogen-bonding Borromean networks

The term halogen-bonding (XB) defines any non-covalent interaction that involves halogens as acceptors of electron density. Resnati *et al* has applied XB-driven metric engineering strategy to the prediction, design and synthesis of Borromean supramolecular architectures. For example, the assembly of K.2.2.2. (1) and potassium iodide (KI, 2) with 1,1,2,2,3,3,4,4-octafluoro-1,4-diiodobutane (4) and 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-1,8-diiodooctane (6) gave rise to three-component supramolecular complexes 8 and 10 as shown in Scheme 7. In both structures, iodide ions act as pyramidal tridentate XB acceptors to bridge three different iodine atoms belonging to three distinct perfluoroalkyl chains, which, in turn, behave as bidentate and telechelic XB donors. Such connectivity around the iodine ions assembles the structure into infinite and highly undulating 2D hcb-networks, in which each hexagon is comprised of six I<sup>-</sup> ions (as vertexes) and six diiodoPFAs (as sides). Three such layers entangle in 2D $\rightarrow$ 2D fashion sustained by Borromean links.<sup>27</sup>



Scheme 7. (a) Formation of three component supramolecular complexes through synergic  $\text{K}^+$  cryptation by K.2.2.2. and I<sup>-</sup>  $\cdots$ I-C XB. (b) A view down the crystallographic  $c$ -axis of a hexagonal ring, consisting of six I<sup>-</sup> ions and six diiodoPFA. Reproduced from Ref. 27 with permission from the Royal Society of Chemistry.

### 3.3.5 Argentophilic (Ag...Ag) or aurophilic (Au...Au) interactions-bonding Borromean networks

As a very early reported structure containing Borromean links,<sup>23</sup>  $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$  and  $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{ClO}_4)_2$  [ $\text{H}_2\text{L} = \text{N},\text{N}'\text{-bis}(\text{salicylidene})\text{-1,4-di-aminobutane}$ ] comprise highly undulated (6,3) hcb-networks with 6-membered rings of 3-connected silver centers (Fig. 13). The silver atoms display inter-layer unsupported Ag...Ag interactions with distances of 2.934(2) and 2.946(2) Å. As Carlucci stated, if the Ag...Ag interactions are neglected, the adjacent layers can be considered to be interlinked via Borromean links.<sup>2b</sup> Nevertheless, such argentophilic (Ag...Ag) interaction should contribute to the formation and stabilization of the Borromean linkage.

The Borromean link in complex  $\{[\text{Ag}_2\text{L}_3](\text{BF}_4)_2\}$  in section 3.1.1 is also stabilized by ligand unsupported Ag...Ag interactions. As shown in Fig. 4, each  $[\text{AgL}_3]$  motif is associated with an identical symmetry-related motif by means of argentophilic interactions ( $\text{Ag}\dots\text{Ag} = 3.0619(4)$  Å). It is believed that the Ag...Ag interactions can cooperate with one another to stabilize the structure in the same way that nature uses many weak interactions in order to stabilize biological systems.<sup>2a</sup>

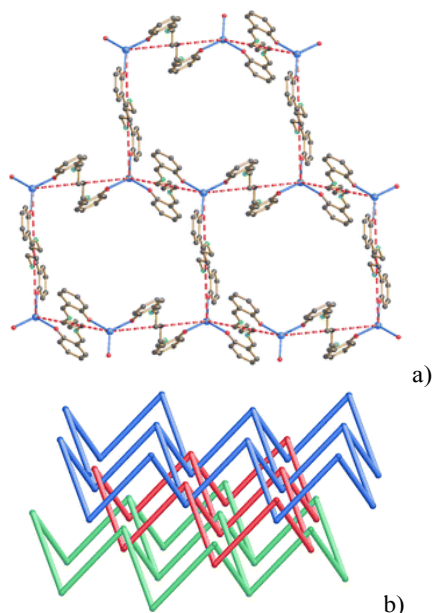


Fig. 13 View of the undulated single layers (a), and schematic view of the linkage of the layers (b) in complex  $[\text{Ag}_2(\text{H}_2\text{L})_3](\text{NO}_3)_2$ . Reproduced from Ref. 2b with permission from the Royal Society of Chemistry.

In complex  $[\text{Cu}_2(\text{tmeda})_2\{\text{Au}(\text{CN})_2\}_3](\text{ClO}_4)$  [ $\text{tmeda} = \text{N},\text{N},\text{N}',\text{N}'\text{-tetramethylethylenediamine}$ ],<sup>17</sup> the single-crystal structural analysis reveals the presence of (6,3) undulated networks in which the  $\text{Cu}(\text{tmeda})^{2+}$  nodes are linked by  $\text{Au}(\text{CN})_2^-$  linear motifs (Fig. 14). Three such networks are entangled via Borromean links, and further interconnected and

stabilized in the central plane by aurophilic Au...Au interactions, ranging in the interval of 3.40–3.60 Å.<sup>2b</sup>

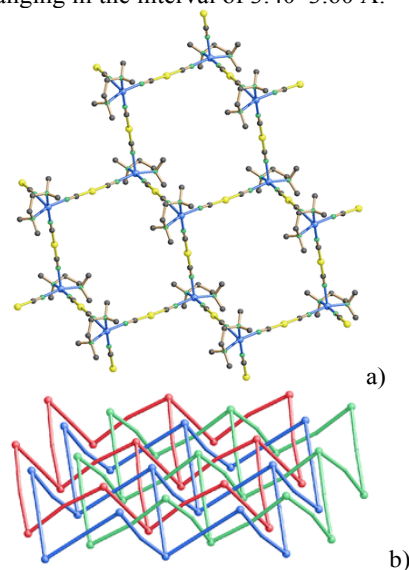


Fig. 14 A single layer (a) and schematic view of the Borromean links (b) in  $[\text{Cu}_2(\text{tmeda})_2\{\text{Au}(\text{CN})_2\}_3](\text{ClO}_4)$ . Reproduced from Ref. 2b with permission from The Royal Society of Chemistry.

### 3.3.6 Void-filling driven Borromean networks

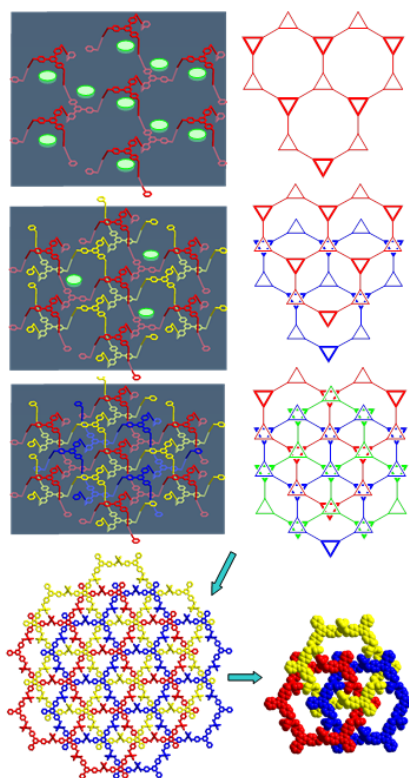


Fig. 15 Illustration of the formation of Borromean links via mutual interlocking of 2D hcb-networks through a void-filling process (voids are highlighted in green dishes). Reproduced from Ref. 4b with permission from the Royal Society of Chemistry.



Different from all above examples in this section, Borromean interweaving in references 4b-d is generated without assistance of any kinds of intermolecular interactions in between the component 2D networks, but simply driven by a void-filling process to achieve close-packing in the crystal lattice. This phenomenon is no wonder if we look into the popular interpenetration occurring frequently in the hollow coordination networks. Nevertheless, some preconditions must be met for formation of Borromean links in such cases.

As proposed in references 4b-d and demonstrated in Fig. 15, honeycomb networks of 2D (6,3) topology should be formed with high undulating character, for example, thick concavo-convex "egg tray" like networks. For such hollow (6,3)-hcb networks, the existence of intrinsic large ring cavities and uniform voids will induce them to mutually interlock to satisfy close-packing. Unless the (6,3) networks significantly deviate from  $C_3$  symmetry thus causing mismatch of the ring size and void shape, Borromean interlocking should be the most favored entanglement fashion in such a situation.

## Conclusions

In summary, various coordination Borromean ring compounds or networks, although they are still challenging targets for synthetic chemistry, have been constructed by appropriate design and control of the organic ligands, metal nodes, topological patterns, as well as assisting interactions between the sub-structures. Discrete Borromean ring compounds are available from ligands having both *endo* and *exo* binding sites via metal-templated strategy, or by template-free interpenetration of metallo-rectangles. Meanwhile, construction of 2D and 3D Borromean networks are achievable based on the interweaving of undulated (6,3) hcb-like network possessing large cavities, which can be assisted by various supramolecular interactions or even solely as a result of close-packing. Borromean networks built from other kind of topological patterns are still rare and waiting for further exploration. Nevertheless, examination of existing examples may provide hints for future synthesis. It might be expected that, as more and more Borromean structures are reported, synthesis of this kind of intriguingly topological structures will finally go from serendipitous discovery to rational design and prediction. Furthermore, the stabilization by entangled rings or porous networks, the chirality transfer among the Borromean structures, and intrigue ring entanglement and linkage topology might bring interesting properties in such fields as molecular motors or machines, guest adsorption, supramolecular catalysis, and so on.

## Acknowledgements

This work was supported by the 973 Program of China (2012CB821701), the NSFC Projects (91222201, 21373276, 21121061, 21173272), the NSF of Guangdong Province (S2013030013474), the FRF for the Central Universities, and the RFDP of Higher Education of China for funding.

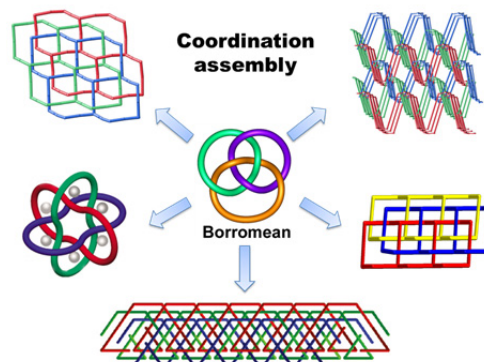
## Notes and references

- <sup>a</sup> MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, Lehn Institute of Functional Materials, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China  
panm@mail.sysu.edu.cn; cecsey@mail.sysu.edu.cn
- <sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China
- <sup>c</sup> State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China
- (a) S. J. Cantrill, K. S. Chichak, A. J. Peters and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 1; (b) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G.W. V. Cave, J. L. Atwood and J. F. Stoddart, *Science*, 2004, **304**, 1308; (c) J. S. Siegel, *Science*, 2004, **304**, 1256; (d) N. C. Seeman, *Angew. Chem., Int. Ed.*, 1998, **37**, 3220; (e) C. A. Schalley, *Angew. Chem., Int. Ed.*, 2004, **43**, 4399; (f) H. Wu, S. Brittain, J. Anderson, B. Grzybowski, S. Whitesides, and G. M. Whitesides, *J. Am. Chem. Soc.*, 2000, **122**, 12691.
  - (a) L. Dobrzańska, H. G. Raubenheimer and L. J. Barbour, *Chem. Commun.*, 2005, 5050; (b) L. Carlucci, G. Ciani, D. M. Proserpio, *CrystEngComm*, 2003, **5**, 269.
  - C. Mao, W. Sun and N. C. Seeman, *Nature*, 1997, **386**, 137.
  - (a) X.-Q. Lu, M. Pan, J.-R. He, Y.-P. Cai B.-S. Kang, C.-Y. Su, *CrystEngComm*, 2006, **8**, 827; (b) X.-L. Zhang, C.-P. Guo, Q.-Y. Yang, W. Wang, W.-S. Liu, B.-S. Kang, C.-Y. Su, *Chem. Commun.*, 2007, 4242; (c) X.-L. Zhang, C.-P. Guo, Q.-Y. Yang, T.-B. Lu, Y.-X. Tong, C.-Y. Su, *Chem. Mater.*, 2007, **19**, 4630; (d) J.-J. Jang, L. Li, T. Yang, D.-B. Kuang, W. Wang, C.-Y. Su, *Chem. Commun.*, 2009, 2387.
  - (a) R. Liantonio, P. Metrangolo, F. Meyer, T. Pilati, W. Navarrini, G. Resnati, *Chem. Commun.*, 2006, 1819; (b) J. Li, L. Song, S. Du, *Inorg. Chem. Commun.*, 2007, **10**, 358; (c) P. Byrne, G. O. Lloyd, N. Clarke, J. W. Steed, *Angew. Chem.*, 2008, **120**, 5845; *Angew. Chem. Int. Ed.*, 2008, **47**, 5761; (d) N. N. Adarsh, P. Dastidar, *Cryst. Growth Des.*, 2010, **10**, 483.
  - D. B. Amabilino and L. Pérez-García, *Chem. Soc. Rev.*, 2009, **38**, 1562.
  - (a) C. D. Meyer, C. S. Joiner, J. F. Stoddart, *Chem. Soc. Rev.*, 2007, **36**, 1705; (b) R. S. Forgan, J. P. Sauvage, J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434; (c) J. Fraser Stoddart, *Chem. Soc. Rev.*, 2009, **38**, 1802.
  - A. J. Peters, K. S. Chichak, S. J. Cantrill, J. F. Stoddart, *Chem. Commun.*, 2005, 3394.
  - H. L. Frisch, E. Wasserman, *J. Am. Chem. Soc.*, 1961, **83**, 3789.
  - E. Wasserman, *Sci. Am.*, 1962, **207**, 94.
  - N. van Gulick, *New J. Chem.*, 1993, **17**, 619.
  - J. C. Loren, M. Yoshizawa, R. F. Haldimann, A. Linden, J. S. Siegel, *Angew. Chem.*, 2003, **115**, 5880; *Angew. Chem. Int. Ed.*, 2003, **42**, 5702.
  - (a) K. S. Chichak, A. J. Peters, S. J. Cantrill, and J. F. Stoddart, *J. Org. Chem.*, 2005, **70**, 7956; (b) C. Pentecost, A. J. Peters, K. S. Chichak, G. W. V. Cave, S. J. Cantrill, and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2006, **45**, 4099; (c) C. R. Yates, D. Bentez, S. I. Khan, and J. F. Stoddart, *Org. Lett.*, 2007, **9**, 2433.

14. M. Schmittel, B. He, J. Fan, J. W. Bats, M. Engeser, M. Schlosser, H.-J. Deiseroth, *Inorg. Chem.*, 2009, **48**, 8192.
15. S.-L. Huang, Y.-J. Lin, T. S. Andy Hor, and G.-X. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 8125.
16. (a) J.-K. Sun, Q.-X. Yao, Y.-Y. Tian, L. Wu, G.-S. Zhu, R.-P. Chen, and J. Zhang, *Chem. Eur. J.*, 2012, **18**, 1924; (b) Q.-X. Yao, X.-H. Jin, Z.-F. Ju, H.-X. Zhang, J. Zhang, *CrystEngComm*, 2009, **11**, 1502.
17. D. B. Leznoff, B. Y. Xue, R. J. Batchelor, F. W. B. Einstein, B. O. Patrick, *Inorg. Chem.*, 2001, **40**, 6026.
18. D.-R. Xiao, Y.-G. Li, E.-B. Wang, L.-L. Fan, H.-Y. An, Z.-M. Su, and L. Xu, *Inorg. Chem.*, 2007, **46**, 4158.
19. C. Xu, Q. Guo, X. Wang, H. Hou, and Y. Fan, *Cryst. Growth Des.*, 2011, **11**, 1869.
20. J.-Q. Liu, Y.-S. Huang, Y.-Y. Zhao, and Z.-B. Jia, *Cryst. Growth Des.*, 2011, **11**, 569.
21. (a) A. D. Burrows, D. J. Kelly, M. F. Mahon, P. R. Raithby, C. Richardson, and A. J. Stevenson, *Dalton Trans.*, 2011, **40**, 5483; (b) A. D. Burrows, C. G. Frost, M. F. Mahon, P. R. Raithby, C. Richardson and A. J. Stevenson, *Chem. Commun.*, 2010, 46, 5064.
22. S. Muthu, J. H. K. Yip and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 2002, 4561.
23. M. L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2237.
24. X. Shi, W. Wang, H. Hou, and Y. Fan, *Eur. J. Inorg. Chem.*, 2010, 3652.
25. L. Jiang, X.-R. Meng, H. Xiang, P. Ju, D.-C. Zhong, and T.-B. Lu, *Inorg. Chem.*, 2012, **51**, 1874.
26. M. P. Suh, H. J. Choi, S. M. So and B. M. Kim, *Inorg. Chem.*, 2003, **42**, 676.
27. (a) R. Liantonio, P. Metrangolo, T. Pilati and G. Resnati, *Cryst. Growth Des.*, 2003, **3**, 355; (b) R. Liantonio, P. Metrangolo, F. Meyer, T. Pilati, W. Navarrin and G. Resnati, *Chem. Commun.*, 2006, 1819.

### TOP Graphic

The state-of-art advances in the assembly of coordination supramolecular structures featuring in Borromean topological characters have been introduced.



Dr. Mei Pan received her BSc in Chemistry from Shandong University in 1998 and earned her PhD in Microelectronics and Solid State Electronics from Shanghai Institute of Technical Physics (SITP), Chinese Academy of Sciences (CAS) in 2004. She joined Sun Yat-Sen University in 2006 and promoted to associate professor in 2010. She has published over 50 peer reviewed SCI papers and her current research interests include the design and synthesis of supramolecular coordination materials, focusing on the study of luminescent properties and applications.



Dr. Cheng-Yong Su is the Cheung Kong Professor of Chemistry at Sun Yat-Sen University since 2007. He obtained Ph.D from Lanzhou University in 1996, worked at Stuttgart University as an Alexander von Humboldt Research Fellow during 2001-2002 and the University of South Carolina as a Postdoctoral Fellow during 2002-2003. He is the author of over 200 peer reviewed publications and 6 book chapters. His current research interest is in the field of supramolecular coordination chemistry and materials, focusing on clean environment and energy related metal-organic materials, catalysis and nanoscience.