Formation of two (6,3) networks showing structural diversity, Borromean topology and conformational chirality in the same crystal†

Xue-Li Zhang,[a] Cui-Ping Guo,[a] Qing-Yuan Yang,[a] Wei Wang,[b] Wei-Sheng Liu,[b] Bei-Sheng Kang[a] and Cheng-Yong Su*[a]

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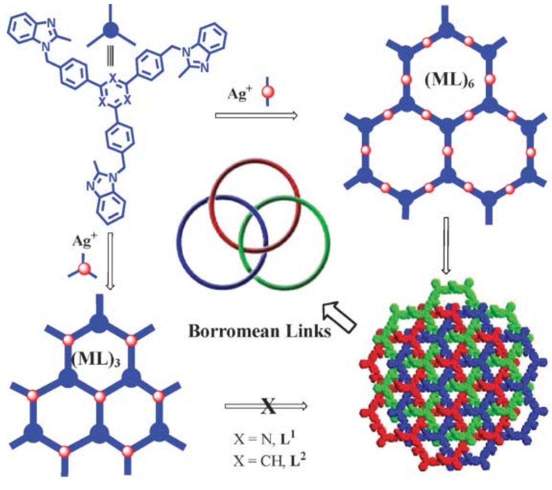
Reaction of two tripodal ligands, 2,4,6-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)-1,3,5-triazine (L^1) and 1,3,5-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)benzene (L^2), with $AgSbF_6$ led to formation of two types (6,3) networks in one single crystal, of which one is three-fold Borromean topologically entangled while the other is independent, showing the same chirality and sandwiched Borromean stacking.

Assembly of topological molecules showing structural integrity and aesthetic beauty, such as catenanes, rotaxanes and knots, has been appealing to chemists aiming at molecular devices or machines.[1] Similar topological analyses have been applied to identifying entanglements in coordination networks.[2] The even intriguing molecular topology, Borromean rings, characteristic of nontrivial three-ring links which are inseparable as a whole while cleavage of any ring makes the whole fall apart, is now becoming one of the most challenging synthetic targets.[3] Existence of Borromean topology in coordination networks has recently been well documented,[4] and this finding motivated chemists to realize topological control over the Borromean networks. However, although a few examples have been reported to explore various influencing factors that facilitate formation of Borromean topology,[5] predictable assembly of Borromean networks remains a challenge. Difficulties often encountered in coordination network assembly are occurrences of supramolecular isomerism and structural diversity from the same building units.[6] In this paper we report two interesting examples which show Borromean topology and structural diversity in the same crystal. In addition, a conformational chirality was found to be consolidated within the network and transferred between the networks.

Two semi-rigid tripodal ligands, 2,4,6-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)-1,3,5-triazine (**L^1**) and 1,3,5-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)benzene (**L^2**), which contain a large four-ring plane and three free-rotating pendants of benzimidazole rings (Bim), were prepared. Reaction of the ligands with $AgSbF_6$ afforded complexes $[(Ag_3L_2)(Ag_2L_2)](SbF_6)_5\cdot$solvents (**1**, **L** = **L^1**, solvents = $2CHCl_3\cdot H_2O$; **2**, **L** = **L^2**, solvent = $1.5H_2O$. synthetic details see ESI†).

Single-crystal X-ray diffraction study‡ revealed a similar structural feature for the two complexes: simultaneous formation of two types of (6,3) networks in a single crystal *via* different connecting ways between ligand **L** and Ag^+ ion as shown in Scheme 1, Fig. 1 and S1–2, ESI†. In both complexes, the ligands lie about a three-fold axis acting as a tris-monodentate triangular connector, while the Ag^+ ions are located at two different sites. Ag1 has a two-fold symmetry, thus each connecting two ligands to form an $(\mathbf{ML})_6$ type network involving six ligands and six Ag^+ ions in the basic hexagonal ring. Ag2 has a three-fold symmetry, thus also acting as a three-connecting node to join ligands into an $(\mathbf{ML})_3$ type network comprising three ligands and three Ag^+ ions in each basic ring. Therefore, the Ag^+ ions provide two distinct coordination modes which in combination with the triangular ligands lead to formation of two types of (6,3) networks showing the same net topology but different compositions. The building unit of the $(\mathbf{ML})_3$ net is **AgL** while that of $(\mathbf{ML})_6$ net is $\mathbf{AgL}_{2/3}$, corresponding to metal-to-ligand ratios of 1 : 1 and 3 : 2, respectively. In both networks, the ligands display *syn*,*syn*,*syn*-conformation with three Bim pendants locating in the same side of the basal plane defined by Ag^+ ions as shown in Fig. 1(a)–(d). Such arrangements of ligands play important roles to direct interweaving, handedness and packing manners of two networks (*vide infra*).

Formation of these two different networks in one single crystal demonstrates an interesting structure diversity phenomenon which is distinctive in comparison with the supramolecular isomerism



Scheme 1 Schematic representation of two types of (6,3) nets and formation of three-fold interlocking network *via* Borromean links.

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[a] *MOE Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, China. E-mail: cesscy@mail.sysu.edu.cn; Fax: (+86) 20-8411-5178*
[b] *State Key Laboratory of Applied Organic Chemistry Lanzhou University, Lanzhou, 730000, China*

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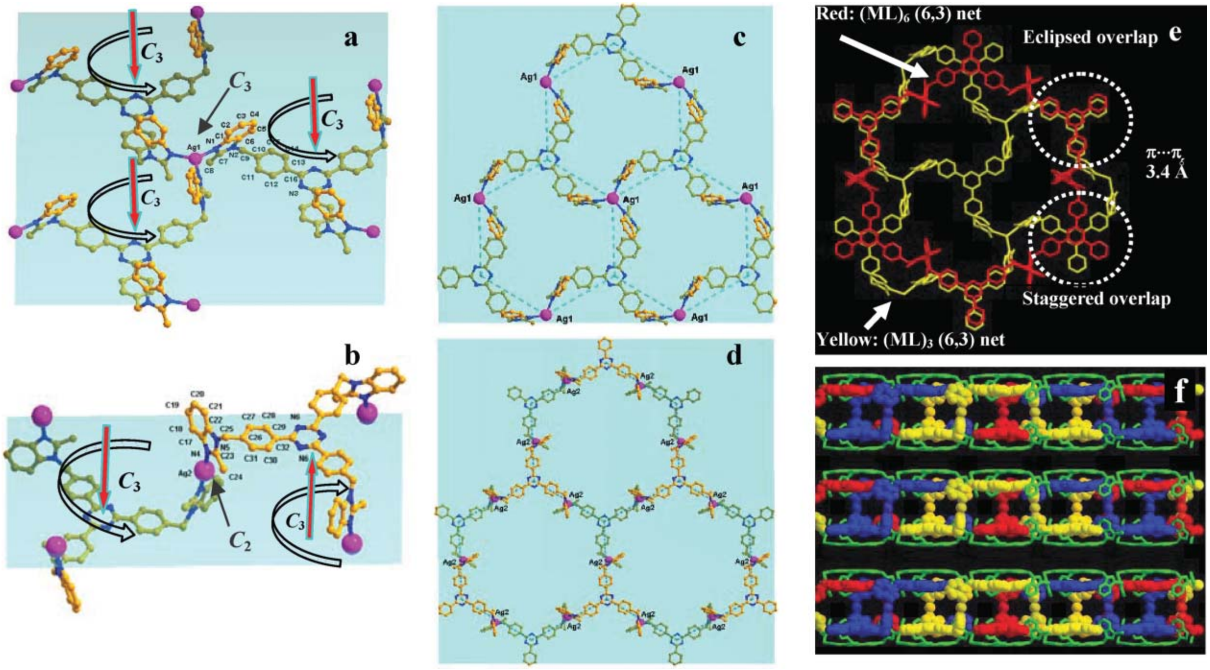

Fig. 1 (a) Left-handed arrangement of three Bim arms around the C_3 axis in each **AgL** subunit and C_3 symmetry relationship between every three neighbouring **AgL** subunits in $(\mathbf{ML})_3$ network in **1** (propeller fashion shown by pink arrows and C_3 axis shown by red arrows); (b) the same left-handed propeller conformation in each $\mathbf{AgL}_{2/3}$ subunit and two C_2 symmetry related $\mathbf{AgL}_{2/3}$ subunits in $(\mathbf{ML})_6$ network in **1**; (c) the $(\mathbf{ML})_3$ type (6,3) network; (d) the $(\mathbf{ML})_6$ type (6,3) network (net topology simplified as the dashed lines); (e) close packing of the $(\mathbf{ML})_3$ and $(\mathbf{ML})_6$ networks showing $\pi\cdots\pi$ interactions; and (f) sandwiched Borromean interlayers packing along the *c*-axis (the $(\mathbf{ML})_3$ networks in stick modes and $(\mathbf{ML})_6$ networks in space-filling modes. Anions and solvent molecules are omitted for clarity).

occurring in the same crystal.[6b] Although structural isomerism has been observed in varied 0D + 1D, 2D + 2D and 2D + 3D fashions, coexistence of two types of (6,3) networks in the same crystal is unprecedented. Since these two networks are topologically identical but chemically different, we can identify them as a 2D + 2D coexistent structural diversity, comparable to previously observed 3D + 3D type coexistent diversity in diamond networks.[6c]

Further topological analysis revealed that the $(\mathbf{ML})_3$ network is independent, but the $(\mathbf{ML})_6$ networks display Borromean linking as depicted in Scheme 1, offering an interesting example showing co-occurrence of interweaving and non-interweaving polymeric networks in the same crystal. Occurring of interweaving or not in these two networks is apparently related to the size of the ligand *vs.* the ring size of the (6,3) net, which is determined by the connecting fashion between the ligand and the Ag^+ ions. It is clear from Fig. 1 that, in $(\mathbf{ML})_3$ network, the hexagonal ring has edges of 10 Å and two types of vertices, resulting in two types of trigonal-prismatic voids: a large one above the ligand and a small one above the Ag^+ ion. By contrast, the hexagonal ring of the $(\mathbf{ML})_6$ network has longer edges of 20 Å and uniform vertices, offering homogeneous large voids above the ligands. In consequence, mutual interlocking of $(\mathbf{ML})_3$ nets is physically hindered due to shape and size mismatch, but the $(\mathbf{ML})_6$ net provides a modular interlocking fashion in favor of Borromean links. Such coexistent networks showing distinct interweaving behaviors are rare. Known examples may be the two-fold entangled (4,4) layers alternated to simple (4,4) layers.[6d,e] The present cases can be simplified as the three-fold entangled (6,3) layers alternated to simple (6,3) layers.

As illustrated in Fig. 2, formation of Borromean topological interweaving with $(\mathbf{ML})_6$ networks is simply driven by a void filling process to achieve close-packing. Due to the *syn,syn,syn*-conformation of three Bim pendants and a large four-ring center of the ligand, the $(\mathbf{ML})_6$ (6,3) networks display hollow character to form a thick concavo-convex "egg tray".[7] The existence of intrinsic large ring cavities and uniform voids induces them to mutually interlock to satisfy close-packing. As seen in Fig. 2, any two of three parallelly interlocked networks are actually

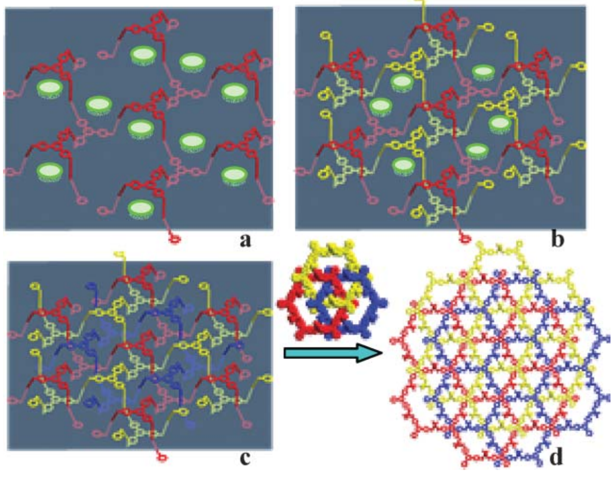

Fig. 2 Formation of Borromean layer *via* mutually interlocking of $(\mathbf{ML})_6$ (6,3) networks through filling of the trigonal-prismatic voids (highlighted as green dishes).

non-interweaving, but filling of the third network causes an inseparable interweaving of three networks, which is characteristic of Borromean topology.[2b] 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. This was confirmed by using the two closely related ligands, $\mathbf{L^1}$ and $\mathbf{L^2}$, both offering the same Borromean structures.

Such formation of three-fold Borromean networks without any intermolecular interaction assistance presents a contrast to a similar Borromean networks formed by a rigid tripodal ligand, where the Borromean interlocking took place by the aid of $\pi\cdots\pi$ stacking.[4b] All other Borromean structures were assembled from linear ditopic organic connectors. Borromean interlocking was found to require high net undulation as well as appropriate intermolecular interactions, which can be hydrogen bonds, $I^-\cdots I$ halogen bonding and Au···Au or $\pi\cdots\pi$ interactions.[4,5]

In crystal packing, the three-fold Borromean $(\mathbf{ML})_6$ networks are intercalated by two non-interweaving $(\mathbf{ML})_3$ networks which lie face-to-face on two sides of the Borromean layers as shown in Fig. 1(f), thus resulting in sandwiched Borromean sheets stacking along the *c* axis. This is due to strong $\pi\cdots\pi$ interactions formed between the interweaving and non-interweaving networks as depicted in Fig. 1(e), where the central four rings of the ligands belonging to interweaving and non-interweaving networks exhibit either eclipsed or staggered overlapping. The counter anions and solvent molecules are located in between the sheets or inside the Borromean layers as shown in Fig. S3, ESI.†

It is also noticeable that two networks crystallized in a chiral space group *P*6(3)22. This means that both networks are chiral, and show the same handedness in the same crystal. Detailed structural analysis revealed that the chirality of the networks is originated from the homogeneous propeller-like conformation of all the ligands.[8] Although the ligands themselves are achiral due to free rotation of three Bim arms, however, once they display *syn*,*syn*,*syn*-conformation with three arms wrapping around the center in a propeller fashion, a C_3 symmetry is imposed, thus causing intrinsic conformational chirality[8a] as shown in Fig. 1(a), (b) and S1, ESI† The same handed propeller conformation of the ligands is fixed during assembly of the networks. Moreover, the handedness is transferred between the networks probably due to close intercalation of two types of network as discussed above. Therefore, the same absolute conformation was propagated between the networks, giving rise to crystallization of the chiral single crystals.

The XRD patterns were recorded for complexes **1** and **2**, which are comparable with the simulated ones as shown in Fig. S4, ESI,† indicating a pure phase of the bulky samples. The thermostability of complex **1** was estimated by thermogravimetric analysis (TGA), which showed a gradual weight loss before 300 °C, suggesting escape of the solvated molecules (Fig. S5, ESI†). A major weight loss occurred in the range 300–500 °C, corresponding to decomposition of the networks. To further confirm structural permanency upon heating, XRD patterns were recorded for complex **1** after heating crystalline samples to different temperatures. As shown in Fig. S6, ESI,†the patterns undergo little change until heating to 290 °C, where some additional peaks appeared. These observations clearly denote that the Borromean sandwich structure is well kept up to 290 °C, and around this temperature, structural transformation starts. This result accords with the TGA analysis, indicating that the clathrate molecules are not essential to sustain the overall architecture.

The photoluminescence property of the ligand $\mathbf{L^1}$ and complex **1** was investigated in the solid state. As shown in Fig. S7, ESI,† the ligand displayed two weak emission peaks around 420 and 460 nm. After coordination, both emission peaks increased but did not significantly shift compared with those of the ligand, indicating that emission of the complex is ligand-based but slightly enhanced.

In summary, two bulky semi-rigid tripodal pendant ligands were prepared and self-assembly with Ag(I) ions were investigated. Two sandwiched Borromean structures were obtained, which display the following features in one single crystal: (a) structural diversity showing co-occurrence of two types of (6,3) networks; (b) Borromean topology showing coexistence of interweaving and non-interweaving coordination polymers; and (c) conformational chirality showing chiral transfer between the networks.

Notes and references

‡ *Crystal data* for **1**: $C_{194}H_{160}Ag_5Cl_6F_{30}N_{36}OSb_5$, M_r = 4942.38, hexagonal, space group *P*6(3)22, a = 17.791(4), c = 37.231(15) Å, V = 10206(5) Å^3, Z = 2, D_c = 1.608 g cm^{-3}, μ(Mo-Kα) = 1.285 mm^{-1}, T = 173(2) K, 6784 unique reflections out of 65372 with $I > 2\sigma(I)$ (R_{int} = 0.1056), final $R1$ = 0.0721, $wR2$ = 0.1818, F = −0.03(7). **2**: $C_{204}H_{171}Ag_5F_{30}N_{24}O_{1.5}Sb_5$, M_r = 4700.75, hexagonal, space group *P*6(3)22, a = 17.9271(6), c = 37.530(3) Å, V = 10445.5(9) Å^3, Z = 2, D_c = 1.495 g cm^{-3}, μ(Mo-Kα) = 1.176 mm^{-1}, T = 150 (2) K, 6347 unique reflections out of 56368 $I > 2\sigma(I)$ (R_{int} = 0.0643), final $R1$ = 0.0811, $wR2$ = 0.1836, F = 0.03(6). CCDC 297861 and 650423. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709118d

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