DOI: 10.1002/anie.200806198

Organic Crystals

Rational Construction of 2D and 3D Borromean Arrayed Organic Crystals by Hydrogen-Bond-Directed Self-Assembly**

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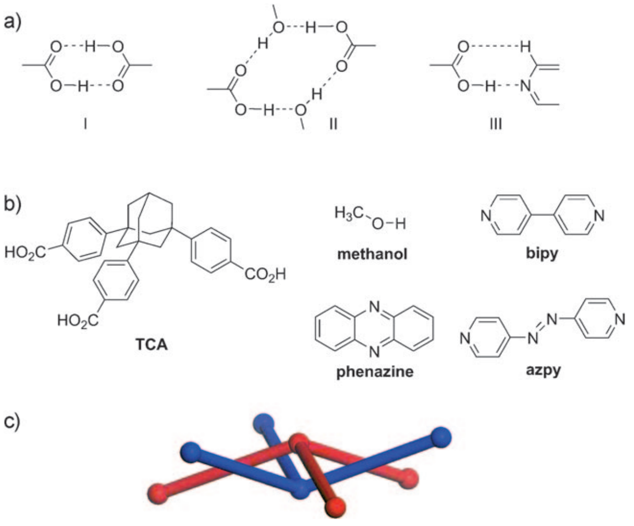
Crystal engineering, which relies on intermolecular interactions to prepare the crystalline organic solids and coordination polymers with desired properties, has become an important field of chemistry and material science.[1] The construction of large networks with appropriate packing geometries and topologies from well-designed building blocks is one of the main goals in crystal engineering. This field has thus become important, as the properties of materials depend on the overall crystal structures.[2] To date, crystal structures are not entirely predictable owing to the numbers of noncovalent interactions with little energy difference.[3] There are only a few cases for which the actual crystal structure was deduced ahead of knowledge of the chemical composition.[4] Especially for the entanglement of molecular crystals, which are expected to be 2D or 3D networks, the rationalization and prediction of the structures are more difficult. One way to understand the topologies of crystals is to compare the known phase diagram of very large systems, in which the vagaries of individual energetic terms are often averaged away.[5] On the other hand, the design and construction of molecular networks in the crystalline phase may be realized by using the supramolecular synthon approach[6] or the reticular synthesis method;[7] however, the desired final frameworks can not be absolutely guaranteed.[8]

The Borromean system, which contains nontrivial three-ring links (no ring is interlocked to another without the help of the third one), is a very intriguing pattern of crystal entanglements, because of the topological complexity, structural integrity, and aesthetic beauty. Molecular Borromean rings have been realized by Stoddart et al. with an all-in-one assembly strategy.[9] As far as we know, only a handful of structures have been reported that consist of three-fold entangled 6^3 nets with Borromean links.[10,11] These structures were prepared by the connection of inorganic metal ions, metal clusters, or anions.[10,11] Predictable construction of Borromean networks, however, still remains a challenge. Herein we report the rational construction of Borromean three-fold 2D→2D entangled layers and n-Borromean 2D→3D entangled infinite layers with pure organic supramolecular synthons based on hydrogen-bond-directed self assembly.



Scheme 1. a) Hydrogen bond synthons of carboxylic acid (I), acid–alcohol/water (II), and acid–base (III). b) The structures of TCA and of four linkers. c) The topology of a six-fold phenyl embrace in a TCA dimer.

To build a Borromean structure, the 6^3 honeycomb net (hcb net) is essential. Our synthetic strategy was to construct the 2D large honeycomb-like networks based on the assembly of Y-shaped building blocks through the supramolecular synthons I, II, and III (Scheme 1 a). Pure trimesic acid (TMA) facilitates assembly into a prototypal hcb net through carboxylic acid dimer synthon I,[12] and is solvated with water or methanol to form a pseudohexagonal net with mixed synthon I and II.[13] Cocrystallization of TMA with 4,4′-bipyridine (bipy) or 1,2-bis(4-pyridyl)ethane (bpea) results in the formation of honeycomb grids with even larger channels or cavities by the heterosynthon III.[14] However, it is impossible to form a Borromean topology with fully planar networks. Furthermore, the honeycomb cavities should be large enough to ensure that three hexagonal rings can penetrate each other.[15] Therefore, the rigid and trigonal pyramidal molecule 1,3,5-tris(4-carboxyphenyl)adamantane (TCA)[16] was taken into the main skeleton for the construction of Borromean linked organic crystals, which plays an

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[**] This work was supported by the National Natural Science Foundation of China (No. 20672118), the Major State Basic Research Development Program of China (No. 2007CB8008005, 2008CB617501), and the Chinese Academy of Sciences.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806198.

important role in directing the interweaving and the packing of the crystals. Furthermore, linear or approximately linear linkers, such as methanol, phenazine, bipy, and 4,4′-azopyridine (azpy), were chosen as the guiding skeletons for larger and more complicate entangled frameworks (Scheme 1b).

Five structures, namely TCA, [TCA·methanol], [2TCA·3-phenazine], [2TCA·bipy], and [2TCA·azpy] were determined by single crystal X-ray diffraction.[17] They all possess 2D hexagonal or pseudohexagonal networks (Figure 1; Supporting Information, Figure S5–S9). In TCA, the molecule predictably self-assembles into an infinite 2D hcb net with 30 × 30 Å cavities through synthon I. In [TCA·methanol], there are two kinds of hcb nets, and in each unit cell, six nets consist of TCA molecules, whereas the other three (30 × 30 Å cavities) consist of both TCA and methanol molecules assembled through synthon II. Unlike the 2:3 cocrystal of trimesic acid with bipy reported by Zaworotko and Sharma,[14a] only the hcb nets with 2:1 stoichiometry were observed in cocrystals of TCA with phenazine, bipy, and azpy, even upon dissolving a 2:3 ratio of TCA and the linkers in the solvent. Owing to two additional phenazine molecules in the residual volume, the stoichiometry of the entire structure is 2:3 in [2TCA·3phenazine]. In these three structures, corresponding linkers were only inserted at one third of hcb edges by the supramolecular synthon III as shown in Figure 1c–e, and the final pseudohexagonal nets have larger internal dimensions of 30 × 33, 30 × 40, and 30 × 37 Å, respectively. In all these five kinds of rings shown in Figure 1, the six apexes are non-coplanar owing to the trigonal pyramidal structure, which form the vertexes of two triangles. The triangle formed by apexes at positions 1, 3, and 5 is parallel to the other triangle formed by apexes at positions 2, 4, and 6, with relative distance of 5.7, 6.0, 7.7, 7.2, and 8.4 Å, respectively.

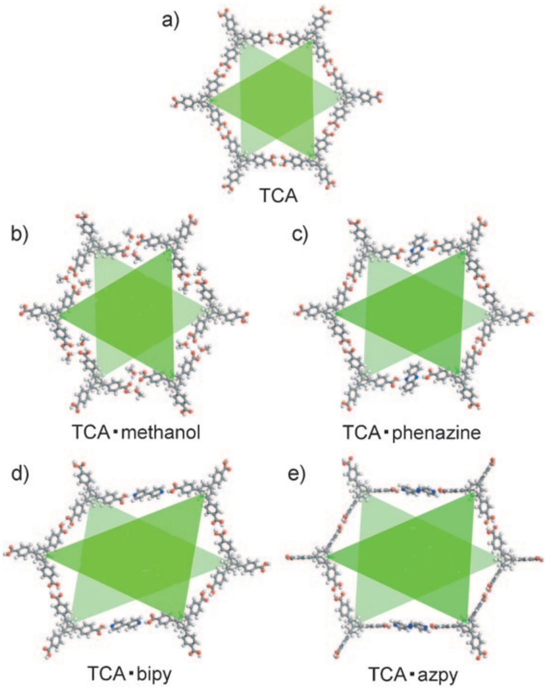

Figure 1. Ball- and stick models showing five kinds of hexagonal or pseudohexagonal nets found in a) TCA, b) [TCA·methanol] (which also contains TCA hexagonal nets), c) [2TCA·3phenazine], d) [2TCA·bipy], and e) [2TCA·azpy]. C gray, N blue, O red, H white. Semitransparent green triangles indicate that alternative apexes of TCAs are situated at different levels with respect to the mean plane of the hexagon.

Self-inclusion or entanglement is facilitated by such a trigonal pyramidal structure of TCA and the chair conformation of these hexagonal nets, resulting in closed-packed structures.[18] In fact, in the crystal structures of TCA, [TCA·methanol], [2TCA·3phenazine], and [2TCA·bipy], all adjacent TCA pairs form a well-known supramolecular motif called a six-fold phenyl embrace (Scheme 1c),[19] which is stabilized by multiple edge-to-face $\text{C-H}\cdots\pi$ interactions between phenyl rings from both TCA molecules. Similar to argentophilic, aurophilic, hydrogen-bonding, halogen-bonding, or π–π interactions found in reported Borromean links,[10,11] this motif could be considered as a key supramolecular synthon, which further connects the 6^3 net into more complicated layers or even 3D polycatenated structures (see below).

As expected, for TCA alone, three hcb nets of TCA are interpenetrated to form a Borromean weave through multiple $\text{C-H}\cdots\pi$ interactions. Three hcb nets lie on top of another, as shown in Figure 2a in green→red→blue→green, which repeats in a cyclic fashion. Thus, three nets in the Borromean system are linked in such a way that none of them is bonded to another, but they are not separable. These layered Borromean weaves are further stacked with a small shift along the layer. As shown in Figure 2c, every third Borromean weave goes back to the original position, which is similar to the ABCABC stacking in cubic close packing. In [TCA·methanol], the only difference is that every third Borromean weave is replaced by a new Borromean weave (Figure 2b), which consists of three [TCA·methanol] hcb nets in Figure 1b (see

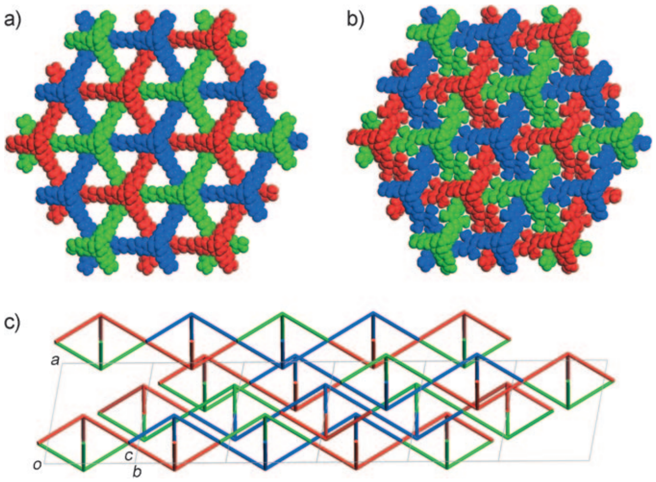

Figure 2. a) Space-filling model of one Borromean weave consisting of three TCA hcb nets in TCA. b) Space-filling model of one Borromean weave consisting of three TCA·methanol hcb nets in [TCA·methanol]. c) Topological view of four separable TCA Borromean weaves in TCA. Three hcb nets in the same Borromean weave are shown as red, blue and green.

also Supporting Information, Figure S10). To the best of our knowledge, [TCA·methanol] is the only reported structure containing two different Borromean weaves.

Similar Borromean weaves were formed in [2TCA·3phenazine] and [2TCA·bipy] (Figure 3a,b). However, owing to the non-equivalent edge lengths of hcb nets (Figure 1c,d), half of the TCA molecules in the blue and green hcb nets do not form TCA dimers (six-fold phenyl embraces) inside this Borromean weave. Instead, these TCAs form dimers with TCAs from either up or down Borromean weaves (Figure 3c). Thus, all Borromean weaves are locked together through this kind of TCA dimer, resulting in a 3D polycatenated net. A particularly interesting aspect in this entire 3D network is the entanglement of three adjacent hcb networks as a Borromean weave, as shown using the thick red, thick green, and thin blue net in Figure 3c. This new type of network is a so-called *n*-Borromean link, and only two examples have been reported to date.[10,11a,c] Figure 3c shows a simple illustration of *n*-Borromean links, where the absolute heights are in order of thin green→thin red→thin blue→thick green→thick red→thick blue, but the adjacent lower network is always above the higher one (see also the Supporting Information, Figure S11).

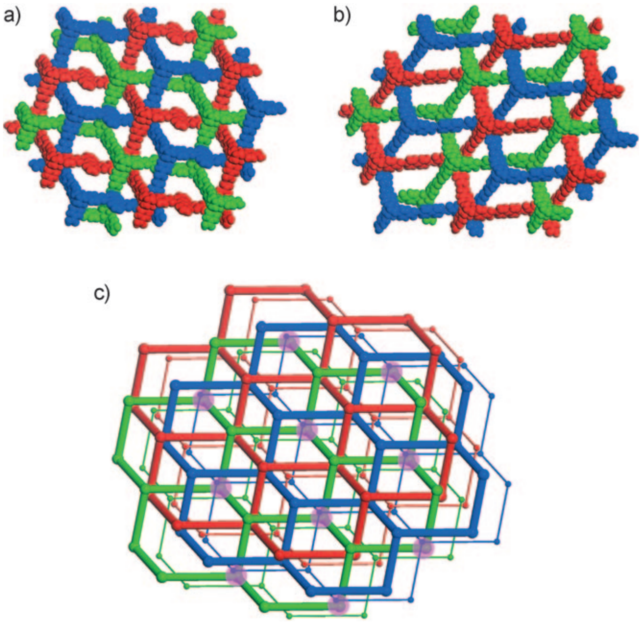

Figure 3. a) Space-filling model of one Borromean weave consisting of three TCA·phenazine hcb nets in [2TCA·3phenazine]. b) Space-filling view of one Borromean weave consisting of three TCA·bipy hcb nets in [2TCA·bipy]. c) Topological view of six adjacent hcb nets in [2TCA·phenazine], which is similar to [2TCA·bipy]. Three thick hcb nets and three thin hcb nets form two Borromean weaves, which further interlock each other by the TCA dimers between thick green and thin blue nets around pink circles. Three hcb nets in the same Borromean weave are shown as red, blue, and green.

In the above four structures, TCA molecules always form a six-fold phenyl embrace with each other, whereas such a dimer was not found in [2TCA·azpy], although the hcb nets of [2TCA·azpy] are similar to those of the above four structures (Figure 4a). In contrast to the 2D Borromean and *n*-Borromean links above, [2TCA·azpy] has an inclined polycatenation: twelve identically orientated hydrogen-bonded hcb nets thread through the same void of the thirteenth hcb net resulting in a 3D inclined polycatenated network (Figure 4b). The formation of these two inclined hcb nets, might be due to the small parallel shift of 1.1 Å between two pyridine moieties of azpy, which results in two orientated azpy linkers, as well as two inclined hcb nets in [2TCA·azpy].

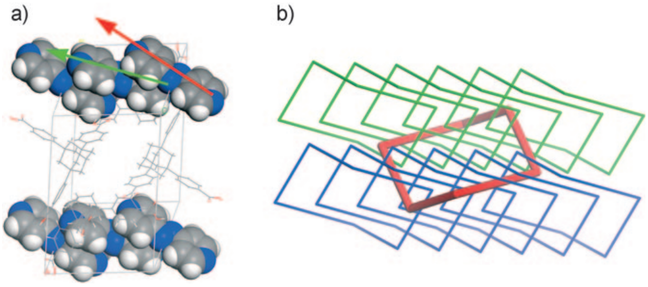

Figure 4. a) One unit cell of [2TCA·azpy]; azpy molecules are shown using a space-filling model and TCA is shown with lines. b) The topology of inclined polycatenated networks in [2TCA·azpy]; the main hexagonal ring is shown red, and the twelve hexagonal rings interlocked with it are shown green and blue.

In conclusion, we have successfully constructed five hydrogen-bonded 6^3 honeycomb nets. Although the topologies of the 2D networks are same, they are different in the way they entangle. 2D→2D Borromean entangled layers, mixed 2D→2D Borromean entangled layers, and 2D→3D *n*-Borromean entangled infinite layers have been obtained by the crystallization of TCA and cocrystallization of TCA with methanol, phenazine, and 4,4′-bipyridine. However, the cocrystalliation of TCA and 4,4′-azopyridine formed a 3D inclined polycatenation network owing to two orientated azpy linkers. It is the first time that Borromean linked organic crystals have been constructed systematically based on hydrogen-bonding directed self-assembly.

Received: December 19, 2008

Keywords: Borromean rings · crystal engineering · hydrogen bonds · self-assembly · topology

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[17] Crystal data for TCA: triclinic, $P\bar{1}$, $a = 17.1909(3)$, $b = 17.5114(3)$, $c = 17.5337(3)$ Å, $\alpha = 60.1413(4)$, $\beta = 77.3032(6)$, $\gamma = 84.4332(3)^\circ$, $V = 4465.21(13)$ Å^3, $Z = 6$, $T = 173$ K, $F(000) = 1572$, $\rho_{calcd} = 1.108\ \mathrm{g\,cm^{-3}}$. $\mu(\mathrm{Mo_{K\alpha}}) = 0.076\ \mathrm{mm^{-1}}$ ($\lambda = 0.71069$ Å), 30154 measured reflections, 16882 independent reflections ($R_{int} = 0.0341$), 1000 refined parameters, $R_1 = 0.0691$, $wR_2 = 0.1868$ for 8941 reflections with $I > 2\sigma(I)$, GOF = 1.030. The diffuse electron density due to the disordered and unidentified moieties was treated with SQUEEZE routine within the PLATON software package (A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34). The void volume is listed at the end of each of the crystal information files. [TCA·methanol]: trigonal, $P\bar{3}$, $a = 17.598(3)$, $c = 15.334(3)$ Å, $V = 4112.8(12)$ Å^3, $Z = 6$, $T = 173$ K, $F(000) = 1680$, $\rho_{calcd} = 1.280\ \mathrm{g\,cm^{-3}}$. $\mu(\mathrm{Mo_{K\alpha}}) = 0.090\ \mathrm{mm^{-1}}$ ($\lambda = 0.71073$ Å), 9617 measured reflections, 4838 independent reflections ($R_{int} = 0.0284$), 353 refined parameters, $R_1 = 0.0856$, $wR_2 = 0.2058$ for 3253 reflections with $I > 2\sigma(I)$, GOF = 1.001. The diffuse electron density due to the disordered and unidentified moieties was treated with SQUEEZE routine within the PLATON software package. [2TCA·3phenazine]: triclinic, $P\bar{1}$, $a = 9.805(2)$, $b = 13.971(3)$, $c = 14.357(3)$ Å, $\alpha = 75.84(3)$, $\beta = 84.43(3)$, $\gamma = 84.14(3)^\circ$, $V = 1891.8(7)$ Å^3, $Z = 2$, $T = 173$ K, $F(000) = 806$, $\rho_{calcd} = 1.346\ \mathrm{g\,cm^{-3}}$. $\mu(\mathrm{Mo_{K\alpha}}) = 0.089\ \mathrm{mm^{-1}}$ ($\lambda = 0.71073$ Å), 12451 measured reflections, 6660 independent reflections ($R_{int} = 0.0262$), 524 refined parameters, $R_1 = 0.0778$, $wR_2 = 0.1861$ for 5337 reflections with $I > 2\sigma(I)$, GOF = 1.011. [2TCA·bipy]: triclinic, $P\bar{1}$, $a = 10.4648(6)$, $b = 11.5920(8)$, $c = 13.3415(11)$ Å, $\alpha = 88.298(6)$, $\beta = 85.013(5)$, $\gamma = 78.412(4)^\circ$, $V = 1579.32(19)$ Å^3, $Z = 2$, $T = 113$ K, $F(000) = 606$, $\rho_{calcd} = 1.208\ \mathrm{g\,cm^{-3}}$. $\mu(\mathrm{Mo_{K\alpha}}) = 0.082\ \mathrm{mm^{-1}}$ ($\lambda = 0.71070$ Å), 19846 measured reflections, 7477 independent reflections ($R_{int} = 0.0270$), 392 refined parameters, $R_1 = 0.0481$, $wR_2 = 0.149$ for 5461 reflections with $I > 2\sigma(I)$, GOF = 1.098. The diffuse electron density due to the disordered and unidentified moieties was treated with SQUEEZE routine within the PLATON software package. [2TCA·azpy]: monoclinic, $P2/c$, $a = 22.228(4)$, $b = 11.809(2)$, $c = 12.144(2)$ Å, $\beta = 105.17(3)^\circ$, $V = 3076.8(11)$ Å^3, $Z = 4$, $T = 173$ K, $F(000) = 1240$, $\rho_{calcd} = 1.271\ \mathrm{g\,cm^{-3}}$. $\mu(\mathrm{Mo_{K\alpha}}) = 0.087\ \mathrm{mm^{-1}}$ ($\lambda = 0.71069$ Å), 9918 measured reflections, 5401 independent reflections ($R_{int} = 0.0378$), 397 refined parameters, $R_1 = 0.0836$, $wR_2 = 0.1909$ for 4391 reflections with $I > 2\sigma(I)$, GOF = 1.011. CCDC 713783, 713784, 713785, 713786 and 713787 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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