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Metric engineering of supramolecular Borromean rings†

Rosalba Liantonio,[a] Pierangelo Metrangolo,*[a] Franck Meyer,[a] Tullio Pilati,[b] Walter Navarrini[a] and Giuseppe Resnati*[a]

Received (in Cambridge, UK) 25th November 2005, Accepted 13th January 2006
First published as an Advance Article on the web 1st February 2006
DOI: 10.1039/b516730b

Two homologues of supramolecular Borromean rings were obtained based on the halogen-bonding-driven self-assembly of iodide ions with telechelic diiodoperfluoroalkanes.

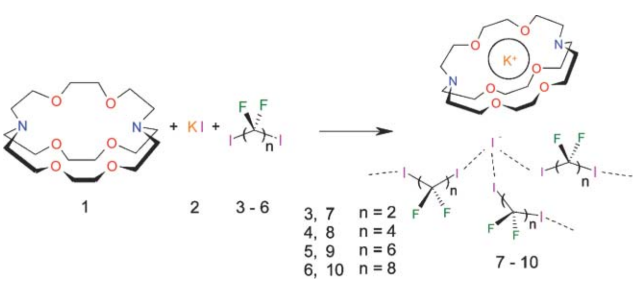
The Borromean system represents one of the most intriguing patterns of entanglement because of its complexity, structural integrity and aesthetic beauty.[1] The three rings taken together are inseparable, but remove any one ring and the other two fall apart. Because of this property, Borromean rings have been used as a symbol of "strength in unity" in many fields. In chemistry, the Borromean linking of three rings is one of the most challenging synthetic targets generated from molecular graphs of complex topology. Since the 1960s, chemists have made considerable efforts towards realizing Borromean links in molecular form. Seeman *et al.*'s manipulation of DNA sequences resulted in the first example of molecular Borromean rings in 1997,[2] while the smallest molecular Borromean link recently resulted from an all-in-one classical synthetic strategy.[3]

To the best of our knowledge, only a handful of supramolecular architectures comprising of three-fold entangled (6,3) layers and exhibiting Borromean links have been reported.[4,5] These architectures have been assembled by means of a variety of building blocks and non-covalent interactions, including, among others, metal coordination,[5a–d] halogen bonding (XB),[5e] and argentophilic interactions.[5f] However, none of these structures were programmed in terms of their Borromean-type connectivity. We report now the first case of applying tools of metric engineering to the prediction, design and synthesis of this fascinating class of interwoven supramolecular architectures.

The concept of metric engineering has been adopted in the literature for describing the prediction of the overall structural pattern of crystalline aggregates, independently of the size and nature of their single starting modules.[6] The weak nature of the intermolecular interactions, which drive self-assembly processes, makes the prediction of the resulting architectures in general, and their topology more specifically, quite hard. Nevertheless, several examples of successful prediction and control of the metrics of supramolecular crystal lattices have been reported by employing metal coordination-,[7] hydrogen bonding-,[6,8] and XB-driven[9] self-assembly processes.

The term XB defines any non-covalent interaction that involves halogens as acceptors of electron density.[10] Thanks to its high strength and directionality, which are ideal features for the rational design of crystal structures, XB has recently proved to be an effective tool for dictating self-assembly processes and given rise to sophisticated supramolecular architectures. Moreover, XB is particularly tailored to haloperfluoroalkane (haloPFA) self-assembly. The carbon frameworks of these molecules typically adopt distorted, all-*trans*, rigid, rod-like conformations that account for their stiffness and propensity to align as parallel bars. This allows the engineering of XB-based crystal structures whose metrics can be carefully tuned, simply by choosing perfluoroalkyl chains of different lengths.[9] We report here a successful application of this strategy to the design and synthesis of supramolecular architectures as complex as Borromean rings. XB drives the self-assembly of naked iodide ions with α,ω-diiodoPFAs to give infinite honeycomb-like (6,3) sheets whose metric sizes are tuned by varying the lengths of the diiodoPFAs used. In two of the four homologue structures reported, three different (6,3) sheets are entangled through *n*-Borromean links.

We reported[5e] how K.2.2.2. (**1**) and potassium iodide (KI, **2**) self-assemble 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**) and give rise to the three-component supramolecular complexes **8** and **10** (Scheme 1) thanks to the synergic metal *endo*-coordination by K.2.2.2. (**1**) and anion *exo*-coordination by the diiodoPFAs **4** and **6**. In both structures **8** and **10**, iodide ions behave as pyramidal tridentate XB acceptors, bridging three different iodine atoms belonging to three distinct perfluoroalkyl chains, which, in turn, act as bidentate and telechelic XB donors. This connectivity around the iodine atoms translates in both structures into infinite and highly undulating 2D honeycomb-like sheets, topologically equivalent to (6,3) networks. Each hexagon is defined by six I^- ions (vertexes) and six diiodoPFAs (sides). The six I^- ions are non-coplanar as the hexagon adopts approximately a chair conformation.



Scheme 1 Formation of the three component supramolecular complexes **7–10** through synergic K^+ cryptation by K.2.2.2. and $I^- \cdots I–C$ XB.

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[a] *NFMLab - DCMIC "G. Natta" Polytechnic of Milan, Via L. Mancinelli 7, 20131 Milan, Italy. Campus of Como, Via Castelnuovo 7, 22100 Como, Italy. E-mail: pierangelo.metrangolo@polimi.it; giuseppe.resnati@polimi.it; http://nfmlab.chem.polimi.it; Fax: (+39) 02 2399 3080; Tel: (+39) 02 2399 3041 (P. M.) Tel: (+39) 02 2399 3032 (G. R.)*
[b] *CNR-ISTM, University of Milan, Via C. Golgi 19, 20133 Milan, Italy*

† Electronic supplementary information (ESI) available: Methods and figures for **7** and **9**. See DOI: 10.1039/b516730b

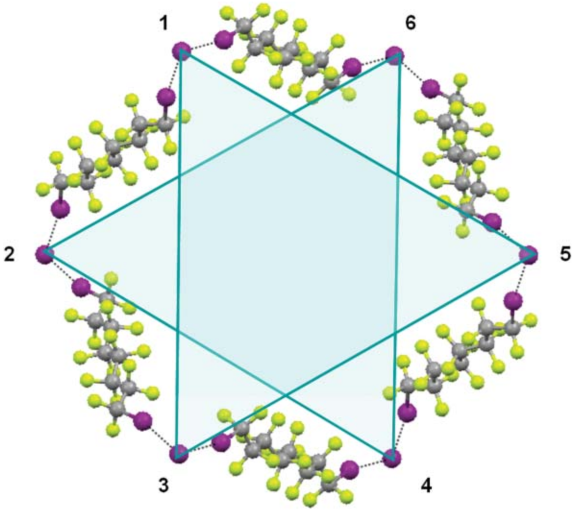

Fig. 1 A view down the crystallographic c-axis of a hexagonal ring of **10**, consisting of six I^- ions and six diiodoPFA **6**; C: grey, F: green, I: purple, XBs: dotted lines. Semi-transparent sky blue triangles indicate that alternate I^- ions are non-coplanar.

It is more useful to describe the six I^- ions as forming the vertexes of two triangles:[5f] one triangle is defined by the I^- anions at positions 1, 3 and 5, while the second triangle is defined by the I^- ions at positions 2, 4 and 6 (Fig. 1). These two triangles are parallel to one another and, as a function of the PFA chain length, their relative distance is 11.618 and 15.529 Å in **8** and **10**, respectively.

In the packing of **8**, some voids are present (see ESI, Fig. S2†) and neither interpenetration nor Borromean link formation is observed. Complex **10**, which is comprised of the longer PFA **6** and consequently has a larger separation between the two triangles defined by the alternating I^-, also shows some voids and presents fluorinated layers wherein three separate honeycomb-like sheets entangle to give *n*-Borromean links (Fig. 2b). It is, in fact, well-known that when coordination polymeric complexes form large 3D holes, the structures usually interpenetrate to satisfy close packing. We reasoned that, thanks to the stiffness of haloPFAs and the robustness of XB, the architecture formed upon self-assembly of a diiodoPFA shorter than **4** should show the same (6,3) network as **8**. More interestingly, the architecture formed upon self-assembly of a diiodoPFA shorter than **6** should preserve both the (6,3) network topology and the Borromean entanglement of **10**. The modulation of the voids would contribute to the anticipated maintenance of topologies.

To test these hypotheses, the supramolecular complexes **7** and **9** were investigated. They were obtained by reacting K.2.2.2. (**1**) and potassium iodide (KI, **2**) with 1,1,2,2-tetrafluoro-1,2-diiodoethane (**3**) and 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1,6-diiodohexane (**5**), respectively, in ethanol (see ESI†) in a 1 : 1 : 1.5 molar ratio. The structures of **7** and **9** were established through single-crystal X-ray analyses of samples deposited over periods ranging from three to five days.‡ As in the larger analogues **8** and **10**, in both **7** and **9**, I^- ions behave as pyramidal tridentate electron donors and bridge three different iodine atoms belonging to three distinct perfluoroalkyl chains (which act as bidentate and telechelic acceptors). The values of the $I^-\cdots I$–PFA XB distances are 3.456 Å (**7**) and 3.513 Å (**9**) (which correspond to reductions of about 17% (**7**) and 15% (**9**) with respect to the sum of the van der Waals and ionic radii for I (4.14 Å)). The $I^-\cdots I$–C and $-I\cdots I^-\cdots I-$ angles are 166.12, 176.66 and 72.43° for **7**, and 167.30 and 72.24° for **9**. Concerning the PFA modules **3** and **5**, they behave as stiff connectors between two I^- ions, both adopting all-*trans* conformations. This coordination mode around the I^- ions translates into infinite 2D honeycomb-like (6,3) networks also found in **7** and **9**. Once again, each chair-shaped hexagon is defined by six non-coplanar I^- ions and six diiodoPFAs, the separation between the triangles defined by the co-planar I^- ions being 9.638 and 12.384 Å in **7** and **9**, respectively. Thus, the (6,3) supramolecular networks of **7**–**10** are homologues, differing in the chain length of the diiodoPFA used, which is translated into the thickness of the hexagonal rings and the sheets they form.

While in covalent chemistry homology is a well-established concept and practice, in supramolecular chemistry, as a consequence of the subtle interplay of weak interactions determining the arrangement of modules, even the slightest change in the assembling modules affects their overall supramolecular organization. It is therefore particularly noticeable that in the fluorinated layers of **9**, three separate honeycomb-like networks are present and entangle to form *n*-Borromean links, as in the case of **10** (Fig. 2a and Fig. 3). The chain of 1,6-diiodoperfluorohexane **5**, being shorter than the chain of the 1,8-diiodo analogue **6**, means that the weave of the Borromean rings in **9** is less thick (Fig. 4) than in **10**.

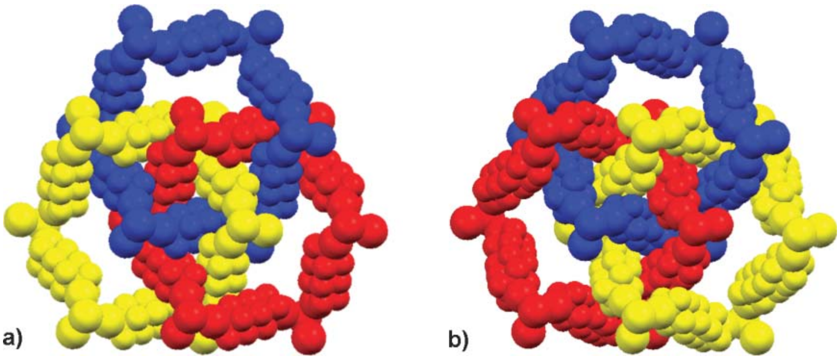

Fig. 2 Space-filling representation (down the crystallographic c-axis) of one of the Borromean links of the honeycomb-like sheets defined by the $\cdots I^-\cdots I$–$(CF_2CF_2)_n$–$I\cdots$ connectivity in the crystal structures of (a) **9** starting from 1,6-diiodoperfluorohexane **5** and (b) **10** starting from 1,8-diiodoperfluorooctane **6**. Three different colours have been used for highlighting the Borromean ring topology.

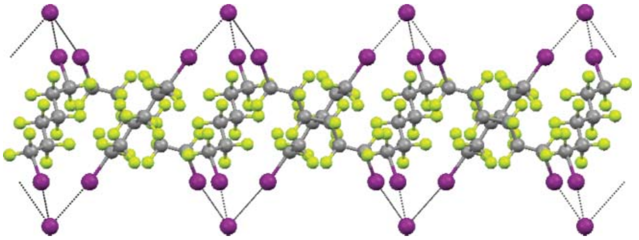

Fig. 3 A ball-and-stick view down the crystallographic *a*-axis of one of the Borromean weaves in complex **9**. Colours are as applied in Fig. 1.

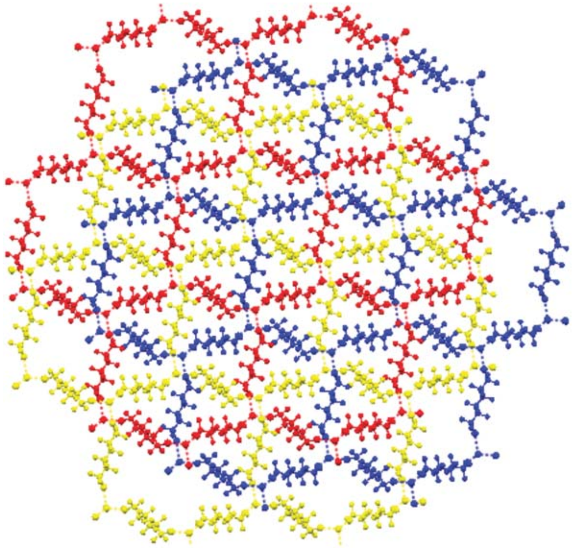

Fig. 4 A ball-and-stick view down the crystallographic *c*-axis of an infinite Borromean weave in the supramolecular complex **9**.

A remarkable segregation of modules characterizes the overall crystal packing of the ternary complexes **7** and **9**, as in their homologues **8** and **10**. The low affinity existing between PFAs and hydrocarbons results in the formation of alternating supercation (K.2.2.2. $\subset$ K$^+$) and superanion (I$^-\cdots$I–PFA–I$\cdots$I$^-$) nanometric layers (Fig. 3), which in all the cases extend in the (001) crystallographic plane. The cation layers' thickness in **7–10** is in the range 4.136–4.935 Å. The thickness of the fluorinated layers, measured as the separation between the two triangles defined by the alternating I$^-$ (Fig. 1), depends on the chain's length and increases from 9.638 (**7**) to 11.618 (**8**), 12.384 (**9**) and 15.579 Å (**10**). Obviously, Borromean entanglement forms only when the length of the diiodoperfluoroalkanes used reaches an optimum value (corresponding to **5**), allowing the required undulation of the (6,3) network obtained. In all of the structures **7–10**, the **1** $\subset$ K$^+$ supercations are located in order to fill lattice interstices and accommodate trigonal prisms (distorted in the case of **8**), wherein the vertexes are the iodide anions. The basal edges of the trigonal prism in **7–10** are nearly constant (varying in the range 11.740–11.861 Å) and depend only on the dimensions of the supercation. The heights of the trigonal prisms correspond to the thicknesses of the cations' layers, as discussed above.

In conclusion, XB drives the self-assembly of naked iodide ions with α,ω-diiodoPFAs into *n*-Borromean rings whose metric size can be tuned carefully by varying the length of the diiodoPFAs used. We have presented the first case of the metric engineering concept being applied to achieving control over the structures of molecular graphs with topologies as complex as that of Borromean rings. For the first time, two homologues of supramolecular Borromean rings have been reported. The high strength and directionality of XB, along with the stiffness of haloPFAs, may represent a general, reliable and valuable strategy for the prediction, design and realization of supramolecular networks of complex topology.

This work was partially supported by grants from Fondazione Cariplo and the EU (COST D29/0011/03 and D31/0017/05).

Notes and references

‡ *Crystal data:* **7**: $C_{42}H_{72}F_{12}I_8K_2N_4O_{12}$, M = 2134.44, tablets, 0.32 × 0.14 × 0.05 mm, trigonal, space group R-3c, a = 11.7478(15), c = 85.034(10) Å, V = 10163(2) Å^3, Z = 6, D_c = 2.104 g cm^{-3}, F_{000} = 6108, Mo-K$_\alpha$ radiation, λ = 0.71073 Å, μ = 3.870 mm^{-1}, T = 90(2) K, $2\theta_{max}$ = 73.52°, 91069 reflections collected, 5274 unique (R_{int} = 0.0278), 4536 with $I_o > 2\sigma(I_o)$, absorption corrections T_{min}/T_{max} = 0.627. Solved using SIR92[11] and refined with SHELX-97,[12] full-matrix least-squares on F^2, 178 parameters, 107 restraints for the disordered PFA, GoF = 1.048, R_1 = 0.0354, wR_2 = 0.0690 (all reflections), $-0.81 < \Delta\rho < 2.39$ eÅ^{-3}; **9**: $C_{54}H_{72}F_{36}I_8K_2N_4O_{12}$, M = 2746.56, tablets, 0.24 × 0.21 × 0.03 mm, trigonal, space group P-3, a = 11.861(2), c = 17.319(3) Å, V = 2110.1(6) Å^3, Z = 1, D_c = 2.161 g cm^{-3}, F_{000} = 1306, Mo-K$_\alpha$ radiation, λ = 0.71073 Å, μ = 3.172 mm^{-1}, T = 90(2) K, $2\theta_{max}$ = 62.00°, 38631 reflections collected, 4493 unique (R_{int} = 0.0356), 4459 with $I_o > 2\sigma(I_o)$, no absorption corrections. Solved using SIR92[11] and refined with SHELX-97,[12] full-matrix least-squares on F^2, 223 parameters, 177 restraints for the disordered PFA, GoF = 1.356, R_1 = 0.0404, wR_2 = 0.1069 (all reflections), $-0.80 < \Delta\rho < 2.64$ eÅ^{-3}. CCDC 290598 (**7**) and 290599 (**9**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516730b

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