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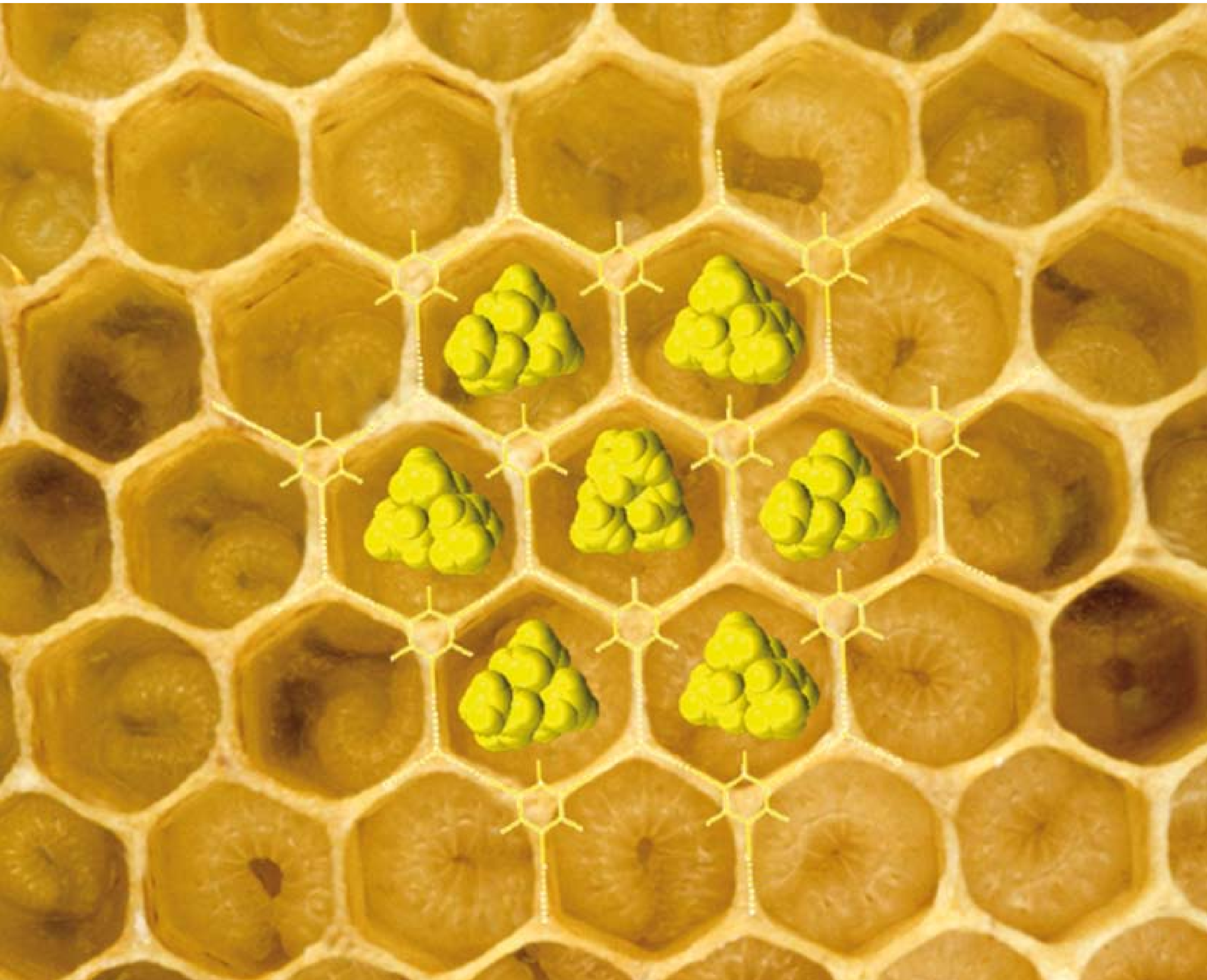

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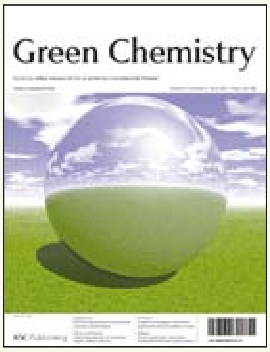

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# Mutual induced coordination in halogen-bonded anionic assemblies with (6,3) cation-templated topologies†

**Pierangelo Metrangolo,*[a] Frank Meyer,[a] Tullio Pilati,[b] Giuseppe Resnati*[ab] and Giancarlo Terraneo[a]**

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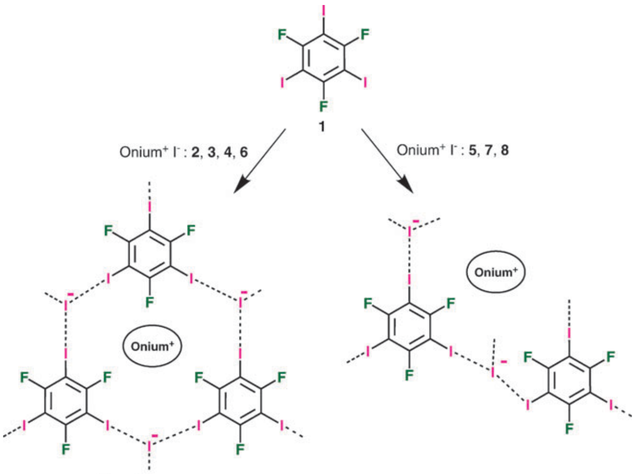
**We describe the use of halogen bonding for the deliberate construction of cation-templated anionic (6,3) networks thanks to a strategy based on the mutual induced fitting of the valences of the building blocks.**

Anion coordination chemistry has only recently been systematically investigated and our understanding of the processes involved is still relatively under-developed.[1] Some analogies are emerging with transition-metal coordination chemistry. For instance, anions have a primary valence, their negative charge, and a secondary valence, provided by intermolecular interactions to the anion. Hydrogen bonding (HB) is a major structure-defining aspect of the secondary valence in anion coordination.[2] On the other hand, halogen bonding (XB),[3] any noncovalent interaction involving halogens as the electrophilic species, is emerging as a new entry in the field of crystal engineering, and proving its remarkable efficiency and reliability in the construction of supramolecular architectures.[4] However, there are few reports in the literature on the use of XB to direct the self-assembly of anionic coordination networks.[5] Nevertheless, thanks to its high interaction energy, which has been calculated to be as high as $-153$ kJ $\mathrm{mol}^{-1}$ for the HCC–I···$F^-$ system,[6] XB could be considered a first-choice tool for driving anions' recognition processes.

In this communication we show the use of the XB between various naked iodide anions and 1,3,5-trifluoro-2,4,6-triiodobenzene[7] (**1**, Scheme 1) for the deliberate construction of anionic honeycomb-like networks with a degree of precision and accuracy that is unusual for crystal engineering. (6,3) Networks are common in supramolecular and coordination chemistry and a variety of self-assembly protocols have been employed for their construction.[8] Most of these protocols require a trigonal tecton[9] as network node, the threefold symmetry of the starting module being reflected in the hexagonal network structure. 1,3,5-Benzenetricarboxylic acid (trimesic acid) or its cyclohexane analogue[10] and 2,4,6-trisubstituted-1,3,5-triazines (*e.g.* melamine, cyanuric acid, and their derivatives)[11] are the most frequently tridentate and trigonal modules used when HB is employed.

In analogy with trimesic acid and melamine, we reasoned that 1,3,5-trifluoro-2,4,6-triiodobenzene (**1**), thanks to its threefold symmetry, could be effectively used in analogous self-assembly processes under XB-control. Following this same rationale, van der Boom *et al.*[12] recently challenged **1** with various bipyridyl XB-acceptors, which were expected to work as bidentate spacers and afford (6,3) networks. However, **1** was invariably functioning as a bidentate XB-donor and infinite chains, rather than honeycomb-like networks, were obtained. DFT calculations revealed a weakening of N···I interactions as more electron-donor moieties coordinate to **1** and the authors concluded that there are limitations to the number of halogen bonds that can be formed with a single aromatic XB-donor. They also argued that 1D rather than 2D networks were formed to bypass the problems related to filling the potential empty space inside the hexagonal framework.

We reasoned that a judicious choice of the XB-acceptor could overcome both the electronic and the steric problems described above and allow **1** to show its potential as a trigonal node for the formation of (6,3) networks. Spherical anions, such as halides, are known to undergo multidentate binding, with coordination numbers from 1 to 9.[2] In particular, when



| Complexes | Onium+ I− |
|---|---|
| 9 | 2 $SMe_3^+$ $I^-$ |
| 10 | 3 $NEt_4^+$ $I^-$ |
| 11 | 4 $NPr_4^+$ $I^-$ |
| 13 | 6 $PEt_4^+$ $I^-$ |

| Complexes | Onium+ I− |
|---|---|
| 12 | 5 $NBu_4^+$ $I^-$ |
| 14 | 7 $PPh_4^+$ $I^-$ |
| 15 | 8 K.2.2.2. KI |

**Scheme 1** Formation of anionic networks **9–15** by self-assembly of trifluorotriiodobenzene **1** with onium salts **2–8**.

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involved in XB, $I^-$ can function as a mono-,[5a] bi-,[5b,e] tri-,[5c,d] and even tetradentate electron-donor.[13] We expected that, on interaction with the threefold symmetry module **1**, the three-coordinate profile of $I^-$ would be preferred thanks to a kind of mutual induced fitting process of the valences of interacting partners. The tridentate and trigonal potential of **1** and iodide anion being elicited, (6,3) networks could form if the empty space inside the hexagonal framework is conveniently filled by selecting a counterion of the right size.

In this paper we show how both **1** and naked $I^-$ ions **2**–**8** typically work as tridentate XB-donor and acceptor modules in their heteromeric crystals. (6,3) Anionic networks characterize the complexes **9**–**11**, and **13**, which are obtained from onium iodides **2**–**4**, and **6**, wherein cations sit in the hexagonal cavities, filling the potential voids and stabilizing these 2D networks. When the cations are too large to fit in the hexagonal voids, as is the case for iodides **5**, **7**, and **8**, the tridentate character of **1** and $I^-$ is maintained in the formed adducts **12**, **14**, and **15**, but topologies markedly different from the honeycomb-like one are adopted to accommodate the counterions.

Specifically, when an equimolar solution of trifluorotriiodobenzene **1** and trimethylsulfonium iodide **2** is slowly evaporated, the colourless heteromeric crystal **9** is obtained wherein the triiodobenzene and iodide salt are present in a 1 : 1 ratio (as revealed by NMR analysis in the presence of $(CF_3CH_2)_2O$ as a standard, see ESI†). Single crystal X-ray analysis‡ revealed that both **1** and $I^-$ are tridentate and the $I\cdots I^-$ contacts, which span the range 3.385–3.508 Å, are 15–18% shorter than the sum of the van der Waals and Pauling radii for I and $I^-$.[14] The trigonal coordination profile of starting modules leads to the formation of the designed honeycomb-like supramolecular anionic network. The small trimethylsulfonium cation sits perfectly in the centre of the formed hexagonal frame where it is pinned by electrostatic interactions and weak $H\cdots F$ contacts (which slightly deform the hexagonal symmetry of the network, $-I\cdots I^-\cdots I-$ angles spanning the range 110.25–139.41°). The overall crystal packing thus consists of electrically neutral and perfectly planar honeycomb-like 2D layers, which are 3.608 Å apart from each other[15] (Fig. 1a).

In order to identify the critical cation size in relation to the ability of the **1**–$I^-$system to form (6,3) networks, we challenged **1** with various onium iodides having larger and larger cations, namely tetraethylammonium iodide **3**, and its tetra-*n*-propyl and tetra-*n*-butyl analogues **4** and **5**. In the heteromeric crystals formed, **10**, **11**, and **12**, the starting triiodobenzene **1** and the onium salts **3**–**5** are present in a 1 : 1 ratio. Single crystal X-ray analysis shows that, in all of the three cases, both **1** and $I^-$ are tridentate and give rise to three short $I\cdots I^-$ contacts (Table S1, ESI†) forming 2D supramolecular anionic networks. Interestingly, both **10** and **11**, obtained from tetraethyl- and tetra-*n*-propylammonium iodides, respectively, present the (6,3) network topology, while **12**, obtained from tetra-*n*-butyl ammonium iodide, shows a different network. While tetraethylammonium cations still sit perfectly in the centre of the hexagonal frames formed (Fig. 1b), tetra-*n*-propyl ammonium cations are moved slightly out of the hexagonal frames (Fig. 1d), and tetra-*n*-butyl cations are moved even further out of the 2D layer, so that the overall crystal packing of **12** consists of alternating anionic and cationic layers (Fig. 1e). On increasing the cation size, the anionic networks become more and more corrugated and the distance between two of them increases, moving from 4.529, to 5.549, and 7.986 Å in **10**, **11**, and **12**, respectively.[15] Clearly, the upper limit to the cation size for preventing the **1**–$I^-$ system from forming (6,3) networks seems to lie between the dimensions of tetra-*n*-propylammonium and tetra-*n*-butylammonium cations.

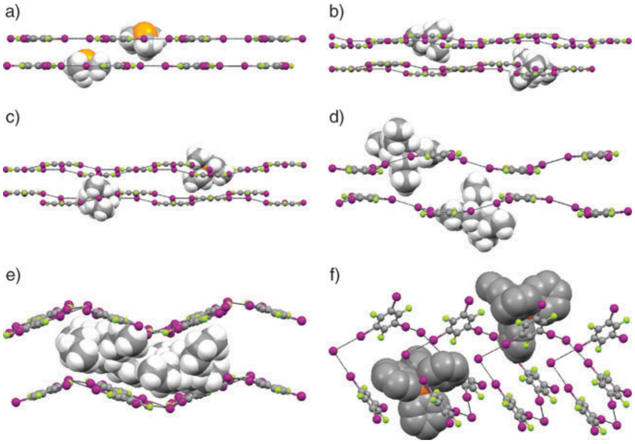

**Fig. 1** Overall packing of heteromeric crystals **9**–**14**. The adopted view evidences the layers and their corrugation. Anionic networks are in ball-and-stick style while cations are in spacefill style. **9** (a); **10** (b); **13** (c); **11** (d); **12** (e); **14** (f). Colours are as follows: C, grey; I, purple; F, green.

We also established the structural properties of heteromeric crystal **13** obtained starting from tetraethylphosphonium iodide **6** and **1**. The coordination pattern and overall topology of **13** is strikingly similar to the one of the ammonium analogue **10**. Both **1** and $I^-$ are tridentate and form a supramolecular anionic network with the (6,3) topology. The centres of the hexagonal frames are occupied by the phosphonium cations (Fig. 1c and Fig. 2), which here support the (6,3) anionic network construction from within their cavities as was the case for trimethylsulfonium, tetraethylammonium, and tetra-*n*-propylammonium cations in **9**, **10**, and **11**, respectively. As the phosphonium cation is larger than the ammonium cation, the separation between network layers is slightly greater in **13** than in **10** (4.601 *vs.* 4.529 Å, respectively[15]).

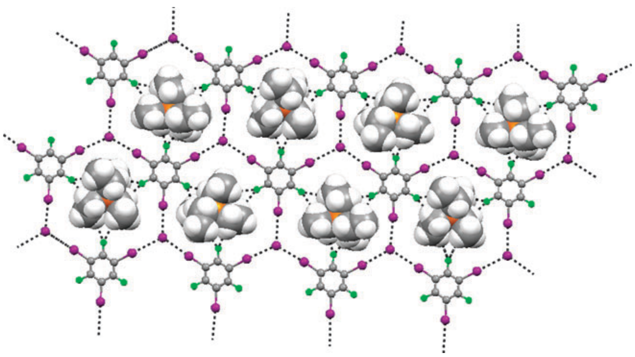

**Fig. 2** The $Et_4P^+$ cations are accommodated in the hexagonal frames of the (6,3) networks defined by the connectivity of $I\cdots I^-$ XB in the crystal structure of **13**. Colours are as in Fig. 1. Halogen and hydrogen bonds as dotted black lines.

Another interesting observation was that the mixed crystals (solid solutions) **16**, **17**, and **18**, obtained on evaporation of solutions containing $C_6F_3I_3$, $Et_4N^+I^-$, and $Et_4P^+I^-$ in 1 : 0.5 : 0.5, 1.0 : 0.7 : 0.3, and 1.0 : 0.3 : 0.7 molar ratios, were isostructural with **10** and **13**. They consist of 2D hexagonal networks and both $Et_4N^+$ and $Et_4P^+$ cations statistically occupy the centres of the hexagonal frames. The $Et_4N^+I^-$ : $Et_4P^+I^-$ molar ratios in the crystals, established *via* single crystal X-ray analysis, were nicely close to the solution ratios (0.42 : 0.58; 0.64 : 0.36; 0.27 : 0.73 in **16**, **17**, and **18**, respectively), finally confirming that the main structural role of cations is here to template the (6,3) anionic network construction.

In addition to tetra-*n*-alkyl onium salts, we have also been challenged with tetraphenylphosphonium **7**, yielding the heteromeric crystal **14**. **1** and $I^-$ are tridentate also in **14**, but the size of the cation prevents the translation of the starting modules' trigonal symmetry into the formation of a honeycomb-like supramolecular network. The (6,3) topology is thus opened up into a hexagonal helical network that continues to mimic the structure of the honeycomb and wherein the bulky tetraphenylphosphonium cations can be accommodated (Fig. 1f). Finally, non-onium iodides were also used, the heteromeric crystal **15** being prepared starting from the cryptate K.2.2.2.$\subset$KI **8** as a source of naked iodide anions. Single crystal X-ray analysis showed that, in **15**, both **1** and $I^-$ are engaged once again in the formation of three short $I\cdots I^-$ contacts yielding a supramolecular anionic network with the same topology observed in the tetra-*n*-butylammonium adduct **12**. Here too the large cations form a layer separated from the supramolecular anionic layer (Fig. S1g, ESI†) and the interlayer distance is 12.209 Å,[15] even larger that in **12**. Clearly, the tridentate coordination of both the XB-donor ($C_6F_3I_3$) and acceptor ($I^-$) building blocks remains very conservative in all of the examined heteromeric crystals and variations in the size of the "supporting" cations modify, or even break, the honeycomb-like connectivity of the donor/acceptor moieties in the $C_6F_3I_3$–iodide formed networks.

In conclusion, we have successfully demonstrated that 1,3,5-trifluoro-2,4,6-triiodobenzene (**1**) can behave as tridentate planar ligand when involved in iodide ions' recognition processes. Three ligands arrange according to a trigonal topology about the anion centre, promoting selective binding through topological complementarity. This complementarity elicits the three-coordinate character of $I^-$ thanks to a mutual induced fitting process. Only occasional examples of this strategy are reported in the literature and all use pyramidal XB-donors (iodoform or carbon tetrabromide).[13,16] In heteromeric adducts **9**–**15**, only the combined matching, at both the electronic and steric level, of all the components allows **1** to work as a structurally simple, compact, threefold (Table S2, ESI†), and planar tecton in the XB-directed self-assembly of supramolecular networks, mimicking the trimesic acid or triazine derivatives used in HB-based self-assembly protocols. Honeycomb-like anionic networks are thus obtained if the cation template nicely fits in the hexagonal frames;[17] if not, supramolecular networks with different topologies are formed, the trivalent character of XB-donors and acceptors being maintained.

The cation-exchange properties[18] of networks **9**–**13** and the interaction of **1** with other spherical anions (*e.g.* bromide and chloride anions) are under current investigation.

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‡ CCDC 665593–665602. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716879a

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