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## **Chemical Communications**

### COMMUNICATION



### A three-dimensional cubic halogen-bonded network

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The rational, deliberate design of supramolecular architectures is of great importance for the discovery of complex materials. A three-dimensional cubic halogenbonded network has been prepared by combination of an octahedral metal-containing halogen bond acceptor and a linear ditopic donor. This material displays α-Po pcu topology and is seven-fold interpenetrated. This is the first neutral, metal-containing three-dimensional halogen-bonded network to be reported.

The controlled arrangement of molecules in a predictable fashion is a fundamental step in the development of stimuliresponsive functional materials and underpins many biological functions.<sup>1-4</sup> Network materials in particular often respond to the application of light, magnetic fields and temperature or pressure in unusual ways leading to properties such as flexibility, extreme positive or negative thermal expansion and compressibility.<sup>5-8</sup> Complex materials of this type have a wide range of applications including sensing, selective guest uptake/release and aero-space engineering.5, 9-11

The complexity of such networks provides synthetic challenges particularly where a desired architecture and specific properties are required. One of the most successful approaches to the controlled synthesis of these systems is the net-based approach which was proposed by Robson<sup>12, 13</sup> and later developed into a reticular approach.<sup>14</sup> These approaches have yielded a plethora of metal-containing networks. Rationally controlling the formation of three-dimensional assemblies relying on intermolecular interactions such as hydrogen bonds or halogen bonds, which are weaker and more labile than coordinate bonds, are far less explored.<sup>15-20</sup> While a number of metal-containing halogen-bonded systems have been reported,<sup>21-23</sup> the predictable design of complex

network architectures comprised of these components is yet to be achieved.<sup>24-27</sup> Here we present the first example of a charge neutral, three-dimensional cubic halogen-bonded network.

We reasoned that co-crystallisation of a combination of octahedral and linear topological components in the appropriate ratio required to form saturated halogen bonds (i.e. donor : acceptor) would produce a halogen-bonded network with an  $\alpha$ -Po (primitive cubic, pcu) topology (Figure 1). <sup>4,5</sup>

We selected  $[Fe(bppd)_3]$ ,<sup>24, 25, 28</sup> **1**, to act as the six-fold halogen bond acceptor as it contains six divergent pyridyl nitrogens arranged approximately octahedrally and chose 1,4diiodotetrafluorobenzene (1,4-DITFB, 2) as a linear halogen bond donor. The combination of 4-pyridyl-substituted organic ligands (including bppdH) and 2 has been previously shown to reliably form linear halogen bonds (i.e. the average of the C<sub>4</sub>-N…I and N…I-C angles approximate 180 °).  $^{29,\;30}$ 

Figure 1. The combination of an octahedral and a linear component should lead to the



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 $I, [Fe(bppd)_3]$ 

By combining 1 and 2 in 1:3 molar ratio (that is, a 1:1 N to I ratio) in a 10:1 acetone/water solution and allowing slow evaporation of the acetone, red block-like crystals suitable for X-ray analysis were retrieved with quantitative yield. The  $[Fe(bppd)_3](1,4-DITFB)_3\cdot 0.5H_2O,$ material resulting 3. crystallises in the space group  $P2_1/c$  (Figure S1 in the ESI<sup>+</sup>). As expected, each of the six pyridyl nitrogen atoms of 1 forms a single halogen bond with iodine atoms from six different molecules of 2 (average N···I distance 2.81(4) Å) such that all nitrogen and iodine atoms are involved in halogen bonding interactions. The result is that each molecule of 2 acts as a linear di(halogen bond) bridge between adjacent octahedral [Fe(bppd)<sub>3</sub>] complexes. An infinite cubic network with a  $\alpha$ -Po pcu topology (point symbol 4<sup>12</sup>.6<sup>3</sup>) results (Figure 2). The iron(III) centres are separated by 25.25 - 25.96 Å and are located on the corners of the cubic array with the 1,4-DITFB molecules arranged along the edges. The network is not perfectly cubic, but instead has a rhombohedral distortion



with Fe-Fe-Fe angles of between 43 and 113 °. Figure 2. Repeating rhombohedral subunit in the three-dimensional halogen bonded pcu network of 3 (water molecules not shown).

Each rhombohedral  $[Fe(bppd)_3]_8(1,4-DITFB)_{12}$  subunit encapsulates a volume of approximately 16600 Å<sup>3</sup> which is occupied by six other identical networks resulting in a sevenfold (class Ia) interpenetrated structure<sup>31</sup> (Figure 3 and Figure S2 in the ESI<sup>+</sup>). Each of the interpenetrated frameworks undergo a combination of  $\pi$ - $\pi$  and CH- $\pi$  interactions with adjacent networks. We infer that the high degree of interpenetration arises from the large aspect ratio of the 1,4-DITFB linkers relative to that of the [Fe(bppd)<sub>3</sub>] units producing an "open" network.



Figure 3. Schematic representation of the seven-interpenetrated networks in 3. One rhombohedral sub-unit of each network is shown in a different colour.

We have reported the first rational, deliberate design of a cubic coordination compound-based halogen bonded network, which was achieved by a symmetry interaction or reticular synthesis approach similar to that used for coordination polymer design. This material represents the first example of a new class of three-dimensional, charge neutral metal-containing architectures formed using supramolecular interactions. One advantage of these systems over those relying on coordination-bonds for network assembly may stem from the improved inherent error checking capabilities of the labile halogen bond and the resulting potential for isolation of these complex products in quantitative yields under mild reaction conditions.

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#### **Conflicts of interest**

There are no conflicts to declare.

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