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Metric engineering of perfluorocarbon–hydrocarbon layered solids driven by the halogen bonding†

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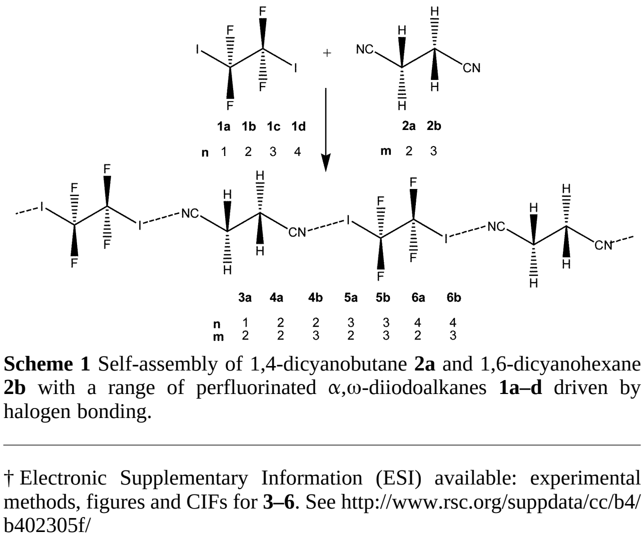
The halogen bonding driven self-assembly of 1,4-dicyanobutane and 1,6-dicyanohexane with a range of perfluorinated telechelic diiodoalkanes yields layered 1D, infinite chain co-crystals. The structure and metrics of these co-crystals are remarkably predictable.

One of the most important issues in crystal engineering is the structural control of the formation of supramolecular aggregates.[1] In fact, the weak nature of the intermolecular interactions driving the self-assembly processes makes the prediction of the resulting architectures quite hard. This is the case also when even the slightest change is introduced in the assembling modules. The concept of metric engineering has been adopted for describing the prediction of the overall structural pattern of crystalline aggregates, independently of the size and nature of the single starting modules.[2] Examples of a successful prediction and control of the metrics of a crystal lattice have been presented recently by Fujita who employed metal coordination-driven self-assembly processes,[3] and Ward *et al.*, who used hydrogen bonding-driven self-assembly processes.[1]

Halogen bonding is the charge-transfer interaction that occurs between Lewis bases and halogen atoms. It has recently proven to be a useful tool in dictating the self-assembling processes and in giving rise to sophisticated supramolecular architectures. This is due, especially, to the high strength and directionality of the N$\cdots$I halogen bonding, which are ideal features for the rational design of crystal structures.[4]

Following our interest in perfluorocarbon–hydrocarbon (PFC–HC) self-assembly processes,[5] we report here on the design and synthesis of a new class of halogen-bonded PFC–HC layered solids **3–6**. We describe how the organization and metrics of these layered materials may be programmed with great accuracy, starting from the geometric properties of the halogen bonding and the metrics of the source tectons[6] **1** and **2** (Scheme 1).



Scheme 1 Self-assembly of 1,4-dicyanobutane **2a** and 1,6-dicyanohexane **2b** with a range of perfluorinated α,ω-diiodoalkanes **1a–d** driven by halogen bonding.

In detail, 1,4-dicyanobutane **2a** and 1,6-dicyanohexane **2b** were mixed with a range of α,ω-diiodoperfluoralkanes **1a–d**. Even though all the materials, except for **1d**, are liquid at room temperature, crystalline solids **3–6** grew under isothermal conditions (T = 298 K). The thermal analysis (DSC) of these crystals gave some very interesting information. All the crystals melt above room temperature, and the melting endotherms of the source compounds were missing in the thermographs of **3–6**. This behaviour is consistent with the formation of new well-defined crystalline species.[7] A 1 : 1 ratio between the fluorinated and hydrogenated modules was determined for co-crystals **3–6** by integrating their ^{1}H and ^{19}F NMR spectra in the presence of 2,2,2-trifluoroethylether as the internal standard.

Obtaining single crystals of **5a** and **6b**, suitable for X-ray analysis, was easy. Their overall structures are impressively similar (Figs. 1 and 2). Both iodoperfluoroalkanes **1c,d** and cyanoalkanes **2a,b** behave as telechelic[8] modules. Consequently, 1-dimensional (1D) infinite chains with alternating PFC and HC tectons are formed. These tectons are connected to each other at both ends through N$\cdots$I halogen bondings. These bondings are the only

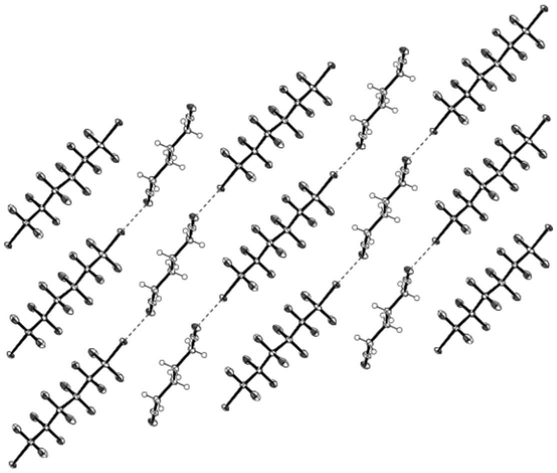


Fig. 1 Crystal packing of **5a** viewed down the *a* crystallographic axis.

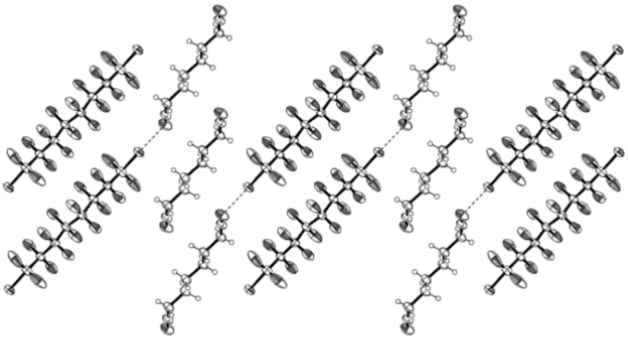


Fig. 2 Crystal packing of **6b** viewed down the *a* crystallographic axis.

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† Electronic Supplementary Information (ESI) available: experimental methods, figures and CIFs for **3–6**. See http://www.rsc.org/suppdata/cc/b4/b402305f/

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strong interactions present in the two co-crystals and dominate the intermolecular recognition processes.[9] The N$\cdots$I distances are 3.046 (**5a**) and 3.023 Å (**6b**), which coincides with the data reported in the literature for similar kinds of structures.[10]

These distances are 14% shorter than the sum of the van der Waals radii for N and I.[11] The N$\cdots$I–C angles are 176.63 (**5a**) and 177.54° (**6b**), in good agreement with the $n \rightarrow \sigma^*$character of the halogen bonding and its high directionality.[4]

The low affinity between HCs and PFCs[5] induces a remarkable segregation of the two modules giving rise to alternating layers. Tectons **1d** and **2b**, which form **6b**, are bis homologues of **1c** and **2a**, which give **5a**. The layers in **6b** are thus thicker than in **5a**. Considering this type of behaviour as the norm, the molecular metrics could be predictably translated into supramolecular metrics. The mesogenic character of the perfluorocarbon and hydrocarbon chains, along with the high directionality of the halogen bonding, may allow chains and/or metrics of the layers to be anticipated from one of the tectons.

In order to test this hypothesis, we strived, successfully, to obtain co-crystals suitable for X-ray analysis from all hybrid materials **3–6**.‡ Indeed, in all of them the tectons of the PFCs and HCs behave as mesogens and the halogen bonding maintains its geometrical preferences. Layered structures comparable to those of co-crystals **5a** and **6b** are present. The 1D chain pitch-length (*d*)[12] correlates linearly with the numbers of the methylene groups (*i.e.* 2*n*) in HC modules **1** and with the numbers of the difluoromethylene groups (*i.e.* 2*m*) in PFC modules **2** (Table 1). This linear correlation is good and it is independent of the size of the PFC and HC tectons used. An understanding of the differences in the packing of co-crystals **3–6** of PFC–HC chains is possible by analyzing this correlation.[13] A quantitative representation of the interdependence of the metric parameters is reported in Fig. 3. Considering $n > m$, the thickness of alternating PFC and HC layers is a function of the lengths of the perfluoroalkyl and alkyl chains. On the other hand, for $n = m$ or $n = m + 1$, the thickness of the layers is roughly constant.

In conclusion, the concept of metric engineering has been applied for the first time in the field of PFC–HC layered systems. We have synthesized the novel 2D perfluoroorganic–organic layered structures **3–6** *via* halogen bonding-driven self-assembly of telechelic dicyano- and diiodoperfluoroalkanes. The high strength, specificity, and directionality of the halogen bonding together with the mesogenic character of perfluoro compounds allow an accurate prediction of the metrics and topologies of the obtained hybrid materials. In recent years, diblock semifluorinated *n*-alkanes $F(CF_2)_n(CH_2)_mH$ have been studied for their useful peculiarities.[14] The co-crystals **3–6** may be considered as a non-covalent version of this peculiar class of compounds. Evaluations of the physical properties of these new, non-covalent R_F–R_H di-block compounds are in progress. Other telechelic HC modules (*e.g.* α,ω-diaminoalkanes) are under study in order to establish whether the correlations described above are independent of the nature of the HC tectons.

Table 1 The 1D chain pitch-length (*d*) in Å for co-crystals **3–6**.

	$m = 2$		$m = 3$	
n	Co-crystal	*d*	Co-crystal	*d*
1	**3a**	19.35	—	—
2	**4a**	21.31	**4b**	24.03
3	**5a**	23.67	**5b**	26.16
4	**6a**	25.84	**6b**	28.35

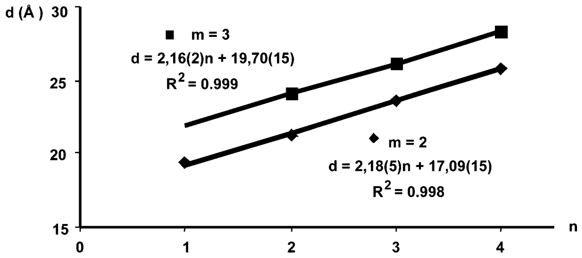

Fig. 3 The 1D chain pitch-length *d* for co-crystals **3–6** as a function of *n* and *m*.

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Notes and references

‡ Single crystal X-ray diffraction data were collected on a Bruker diffractometer using a Mo–Kα radiation [$\lambda = 0.71073$ Å]: **5a**) $M = 662.00$, triclinic, $P\bar{1}$, No. 2, $a = 5.3183(8)$, $b = 7.0369(11)$, $c = 13.415(2)$ Å, $\alpha = 75.865(8)$, $\beta = 86.012(12)$, $\gamma = 71.855(9)°$, $U = 462.63(12)$ Å^3, $Z = 1$, $T = 90(2)$ K, μ(Mo–Kα) = 3.515 mm^{-1}, 143 parameters, $R = 0.0446$ (4056 reflections); **6b**) $C_{16}H_{12}F_{16}I_2N_2$, $M = 790.08$, triclinic, $P\bar{1}$, $a = 5.4008(16)$, $b = 7.214(2)$, $c = 16.065(4)$ Å, $\alpha = 88.713(8)$, $\beta = 87.854(8)$, $\gamma = 72.453(10)°$, $U = 596.3(3)$ Å^3, $T = 200(2)$ K, $Z = 1$, μ(Mo–Kα) = 2.769 mm^{-1}. 187 parameters, $R = 0.0431$ (2756 reflections). CCDC numbers: (**3a**) CCDC 230372, **6a**) CCDC 230373, **4a**) CCDC 230374, **5a**) CCDC 230375; **4b**) CCDC 230376, **5b**) CCDC 230377, **6b**) CCDC 230378. See http://www.rsc.org/suppdata/cc/b4/b402305f/ for crystallographic data in .cif or other electronic format.

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12 *d* is here the length of the repeating linear unit of the co-crystals' 1D infinite chains.
13 The two linear equations in Fig. 3 can be combined in the following equation: $d(n,m) = 12.00(17) + 2.18(3)n + 2.55(7)m$. Interesting information can be drawn by analyzing this equation. The increase of *d* when a CF_2CF_2 group is added is 0.37 Å higher than the increase resulting from the addition of a CH_2CH_2 group. This is consistent with the fact that the C–C–C angle of modules **1** is wider than that of modules **2** due to the repulsion of the vicinal fluorines. Both these increases are smaller than those of single molecules **1** and **2** as the single molecules axes are not parallel to the 1D infinite chains axes (Figs. 1 and 2).
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