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Spontaneous resolution in a halogen bonded supramolecular architecture†

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The halogen bonding driven self-assembly of 1,8-diiodoperfluorooctane and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine induces the formation of a chiral and enantiopure co-crystal wherein the fluorinated chains adopt an unusual *gauche* arrangement.

Perfluorocarbons (PFCs) exhibit unique properties,[1] among others very low surface energies and refractive indexes, with high dielectric constants. Generally, aliphatic PFCs show immiscibility with water and have very low affinity also for hydrocarbons (HCs). Halogen bonding is the non-covalent interaction wherein halogens work as electron density acceptors. The halogen bonding mediated self-assembly of halo-PFCs and HCs possessing electron donor sites has revealed to be an efficient strategy in affording numerous new and structurally different hybrid materials.[2] Useful applications in the topochemically controlled stereoselective photocyclization of olefins,[3] in the synthesis of liquid crystalline materials,[4] and in the non-covalent fluorous coating of polymers[5] have been recently reported.

The rational design of 3D crystal structures in general and of chiral supramolecular structures in particular is, in most instances, not yet possible due to their unpredictability.[6] Minute structural changes at the molecular level may induce dramatic changes beyond the molecule resulting in either a racemic compound or a conglomerate. A deeper understanding of the symmetry-breaking process would be helpful for future crystal structure prediction with implications for areas as diverse as advanced material design[7] or the origin of homochirality in life.[8]

In this contribution we describe the spontaneous resolution occurring when 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro-1,8-diiodooctane (**1**) is halogen bonded to *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (**2**) and the conglomerate **3** is formed (Fig. 1). This is the first case of spontaneous resolution involving a PFC derivative. The structural details of the enantiopure co-crystal **3** will be presented and its unusual features will be discussed, most notably the *gauche* conformation of the perfluorooctyl chain and the lack of segregation.

Adduct **3** precipitates as yellowish crystals stable in air at room temperature on isothermal evaporation of a chloroform solution of **1** and **2** under diffusion conditions. Similar to other co-crystals

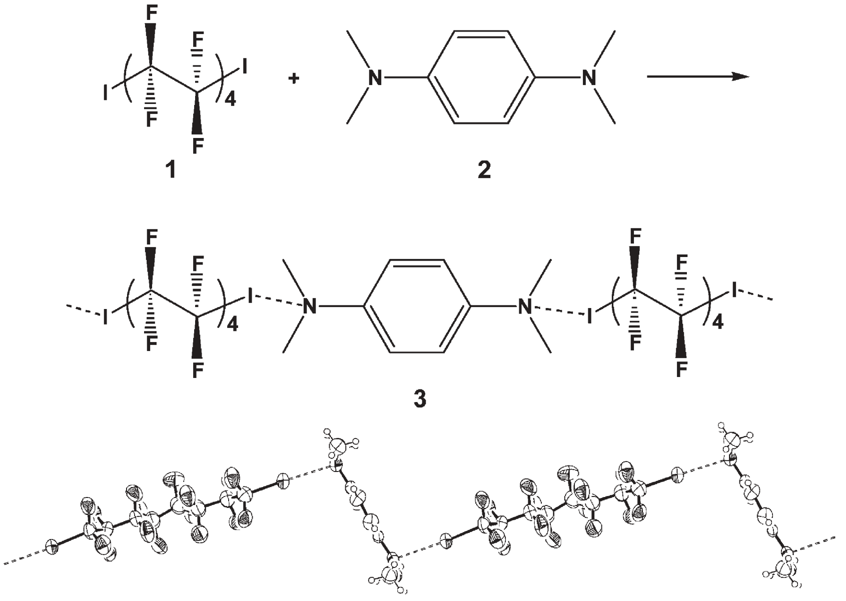

Fig. 1 Formation of 1D infinite networks **3** through halogen bonding driven self-assembly of starting modules **1** with **2** and, at the bottom, a chain of **3** from single crystal X-ray analysis.

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† Electronic supplementary information (ESI) available: Experimental methods and figure for **3**. See http://www.rsc.org/suppdata/cc/b4/b417771a/

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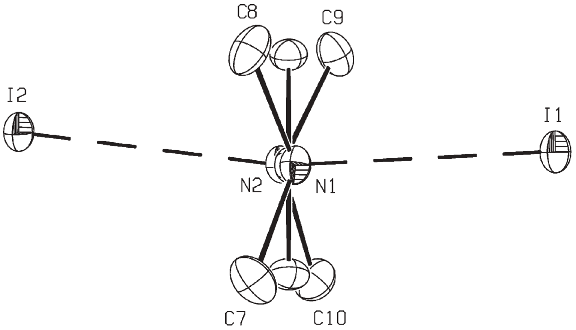

Fig. 2 Perspective view along the N1PhN2 axis of **2** in the cocrystal **3**. Also the halogen bonded iodine atoms are reported.

involving diiodo-PFCs and dinitrogen-HCs, the self-assembly is driven by N···I halogen bonding, which present the usual geometric features (N···I distance 2.847 Å, N···I–C angle 169.94°). Both modules showing telechelic behaviour, **3** consists of 1D infinite chains where PFC and HC components alternate. Most notable, **3** crystallizes as a conglomerate in the chiral space group $P2_12_12_1$. Examples of spontaneous resolution in co-crystal formation have occurred under control of ionic interactions, hydrogen bonding, metal coordination, and $\pi\cdots\pi$ interactions.[7] This is the first example realized under the control of halogen bonding.

The element of chirality in **3** is the propeller conformation adopted by the dimethyl amino groups in **2** resulting in four different distances between the methyls and the phenyl least square plane (C(7) 0.380(6) Å, C(8) 0.415(5) Å, C(9) −0.504(5) Å, C(10) −0.282(5) Å, Fig. 2). Data for both enantiomorphous co-crystals of **3** were collected and the structures refined; here we give the data for only the *M* enantiomer.‡

As already shown by similar iodo-PFCs,[9] the PFC chain of **1** is affected, in **3**, by strong rotational disorder corresponding to distinct and enantiomeric conformers [the torsion angles along the octane chains are 164.7(11), 165.3(10), 49.4(14), 165.3(11), 173.4(12) and 169.1(9), −162.4(9), −51.8(13), −160.4(11), −177.5(12)° for the A and B enantiomorphous rotamers, respectively].

The chiral and enantiopure co-crystal **3** is thus comprised of conformationally chiral and enantiopure HC modules and conformationally chiral and racemic PFC modules (Fig. 3).

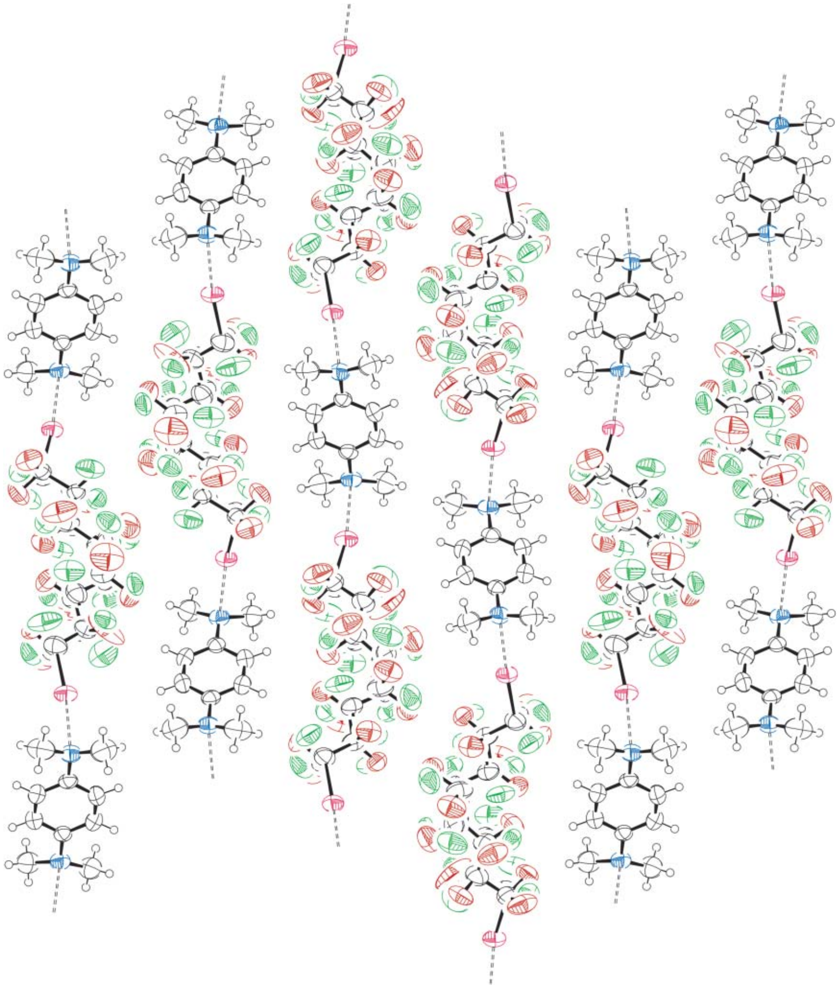

Fig. 3 X-Ray packing of co-crystal **3** viewed down the *a* crystallographic axis. Dashed lines represent the halogen bonding. The disorder is modelled by splitting the fluorocarbon chain over two equally populated rotamers. Colors are as follows: black, carbon and hydrogen; blue, nitrogen; violet, iodine; fluorine, green (rotamer A) and brick-red (rotamer B).

Other features of **1** are quite unusual. Perfluoroalkyl chains typically adopt a distorted *all-trans* conformation[10] due to electrostatic intramolecular repulsions between adjacent fluorine atoms.[11] When halogen bonded in co-crystal **3**, **1** presents an energetically disfavoured *gauche* arrangement (see the central torsion angles reported above). The contact area between adjacent PFC chains is reduced by the formation of kinks and, even more, by the remarkably poor segregation.[12] PFC columns but not layers are in fact present in **3**. As a result, attractive residual forces among PFC chains are smaller than usual and forces between PFC and HC modules are correspondingly larger.

The density of the chiral structure **3** may be greater than alternative racemic or pseudoracemic structures due to the network of F···F and H···F intermolecular contacts (which is different for the two enantiomorphous rotamers of the PFC chain). This net may thus play a role in the spontaneous resolution.

Three other co-crystals are known where **2** works as an *n* electron donor. They are the infinite chain formed with 1,8-dibromoperfluorooctane,[13] the infinite chain formed with 1,4-diiodotetrafluorobenzene[14] and the trimer given with sulfur dioxide.[15] They crystallize in the centrosymmetric space groups $P\bar{1}$, $P\bar{1}$, and $P2_1/c$, respectively. Clearly, the electrons' accepting module plays a crucial role in the possible spontaneous resolution processes involving **2**. Moreover, differently from the other known co-crystals involving **2**, in **3** there are no contacts between the HC modules.

In the pure form, **2** crystallizes in the chiral space group $P2_12_12_1$ as it assumes a homochiral propeller conformation close to that present in **3**.[16] Different from the other electrons acceptors, **1** does not suppress the inherent tendency of **2** to undergo spontaneous resolution.

An explanation as to why this is the case is awaited, but this behaviour may be related to some peculiar features shown by **1**, namely the *gauche* conformation and its consequences, the poor segregation and the net of H···F hydrogen bonding[17] and F···F intermolecular contacts.

In conclusion, we have described the co-crystal **3**, which represents the first case of spontaneous resolution involving a PFC derivative. It is also the first time spontaneous resolution has occured in a halogen bonded supramolecular architecture. Optical activity may impart useful properties to co-crystals. In fact, one of the most efficient approaches to NLO materials is to ensure molecular crystallization in a noncentrosymmetric group.[18] Our findings thus widen the range of applicative perspectives accessible to hybrid PFC–HC crystalline materials. Preliminary results have already shown that the ability of long-chain PFC iodides to be involved in spontaneous resolution processes under supramolecular control could be general.

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Notes and references

‡ *Crystal data for* **3**: $C_{10}H_{16}N_2{\cdot}C_8F_{16}I_2$, M = 818.13, orthorhombic, $P2_12_12_1$, a = 6.1959(10), b = 19.168(3), c = 21.858(4) Å, V = 2595.9(8) Å^3, $Z = 4$, ρ(calc) = 2.093 g cm^{-3}. Data collected by a Bruker SMART APEX diffractometer Mo-Kα radiation, λ = 0.71073 Å, μ = 2.549 mm^{-1}, T = 291 K; 70753 reflection collected, 8973 independent, 6727 with $I_o > 2\sigma(I_o)$, absorption corrections T_{min}/T_{max} = 0.822 R_{ave} = 0.0293, $2\theta_{max}$ = 64.04°. Structure solved by SIR92,[19] refined by SHELX-97,[20] full-matrix least squares, 559 parameters, 1378 restraints, Flack parameters $g = -0.017(18)$. Final R = 0.0476 (0.0349 on observed reflections), wR = 0.0827, $-0.44 < \Delta\rho < 1.11$ e Å^{-3}. CCDC 256351 (*M*) and 259450 (*P*). See http://www.rsc.org/suppdata/cc/b4/b417771a/ for crystallographic data in .cif or other electronic format.

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