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Perfluorocarbon–hydrocarbon self-assembly. Part 6:[1] α,ω-Diiodoperfluoroalkanes as pseudohalogens in supramolecular synthesis

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Abstract

4,4′-Bipyridine **1** works as an electron donor to α,ω-diiodoperfluoroalkanes **2a–d** and gives infinite chains **3a–d** as white, crystalline solids which are stable at room temperature and in air. The structural features of these non-covalent co-polymers have been studied using various techniques (IR, Raman, ^{19}F NMR, DSC, X-ray) and parallel strictly those of analogous co-crystals given by halogens, interhalogens, and pseudohalogens. The close analogy between α,ω-diiodoperfluoroalkanes and halogens and pseudohalogens allows the use of the literature data on aggregation abilities of the latter compounds to anticipate those of the former ones. © 1999 Elsevier Science Ltd. All rights reserved.

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Molecular iodine is well known[2] to work as an effective electron acceptor (Lewis acid) when interacting with an assortment of atoms (either neutral or negatively charged) containing lone-pairs of electrons (Lewis bases). Also Br_2 molecules[2] as well as interhalogens (e.g. ICl and IBr)[3] and pseudohalogens (mainly ICN)[4] can be involved in the formation of similar acid/base complexes. Particular attention has been devoted to the adducts formed by nitrogen-based donor molecules. For instance, complexes of the $n \rightarrow \sigma^*$ type given by 4,4′-bipyridine **1** with I_2, ICl, IBr, ICN have been prepared and the N···I–X interaction (N of the pyridine moiety, X=I, Cl, Br, CN) has been characterised with a variety of analytical techniques.[5] Here we describe how 4,4′-bipyridine **1** works as a donor also to α,ω-diiodoperfluoroalkanes **2a–d** and gives infinite chains **3a–d** as white, crystalline solids which are stable at room temperature and in air (Scheme 1).[6] These chains, locked by the non-covalent N···I–X interactions (N of the pyridine moiety, X=perfluoroalkyl residue, R_f), and the related systems reported in previous papers of this series,[7] (N of a trialkyl or dialkyl amine, X=R_f) show how the iodine atom of iodoperfluoroalkanes behaves similarly to the iodine atom of interhalogens and pseudohalogens discussed

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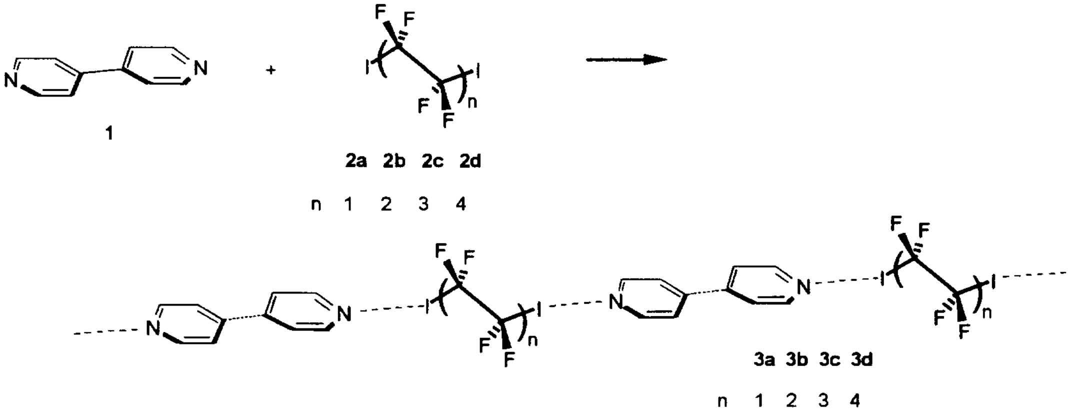
above. The results reported in the literature on the complex forming ability of halogens, interhalogens, and pseudohalogens can thus be used to anticipate the aggregation features of perfluoroalkylhalides, a class of compounds which have been recognised only recently as useful motifs for the construction of supramolecular architectures.[1,7]



Scheme 1.

The importance of the N···I–R_f interactions in solution was proven through NMR spectroscopy. The signal observed in ^{19}F NMR spectra of equimolar chloroform solutions of bipyridine **1** and 1,2-diiodotetrafluoroethane **2a** is at higher fields than that given by pure **2a**.[8] The observed signal shifts increase on increasing the solution concentrations and the **1**:**2a** ratio.

Similar shifts at higher fields[7] with respect to the pure perfluorocarbon motifs were also observed for **2b–d** in the presence of **1**. Moreover, in these longer chain diiodo compounds the highest shift was given by the -CF_2I group and the shifts of the other difluoromethylene groups progressively decreased with distance from the iodine atoms.[8] This proves how the observed spectral changes are not due to 'generic' solvent effects (e.g. non specific solute–solute interactions) but they can be ascribed to specific N···I–R_f intermolecular interactions that occur in solution and lead to the formation of dimeric, trimeric, etc. adducts through rapid association equilibria.[9] Slow evaporation of equimolar chloroform solutions of **1** and **2a–d** afforded white crystalline solids **3a–d** in which both pyridine nitrogen atoms of **1** act as electron donors to both iodine atoms of α,ω-diiodoperfluoroalkanes **2a–d**. The 1:1 ratio of the hydrocarbon and perfluorocarbon modules in non-covalent co-polymers **3a–d** was proven by microanalyses (H, C, N, I) and by ^1H and ^{19}F NMR spectra of the non-covalent co-polymers in the presence of $(CF_2CH_2)_2O$. ^1H and ^{19}F NMR spectra of highly diluted solutions of **3a–d** were identical to those of single pure hydrocarbon and fluorocarbon modules **1** and **2**, respectively, thus proving that, similar to corresponding complexes formed by **1** with halogens, interhalogens, and pseudohalogens, the N···I interaction is non-covalent and reversible.

The electron donor–acceptor character of the N···I–R_f interaction was revealed by vibrational spectroscopies. In IR (KBr pellets) and Raman (neat) spectra of **3a–d** the C-H stretching modes (3000 cm^{-1} region) of the hydrocarbon module **1** were shifted to higher frequencies and appeared with weaker intensity than in pure heteroaromatic **1**.[10] The N···I–R_f intermolecular interaction also induced changes in the band frequencies and intensities of the electron acceptor modules **2a–d**. Stretching absorptions in the 1200–1050 cm^{-1} region ($\nu_{C\text{-}F}$ and $\nu_{C\text{-}C}$) of IR spectra of **3a–d** were at lower frequencies than in pure diiodoperfluoroalkanes **2a–d**. These spectral changes are consistent with the hydrocarbon and fluorocarbon components, **1** and **2a–d**, respectively, being bonded in co-polymers **3a–d** through an $n \rightarrow \sigma^*$ electron donation from nitrogen (donor site) to iodine (acceptor site).

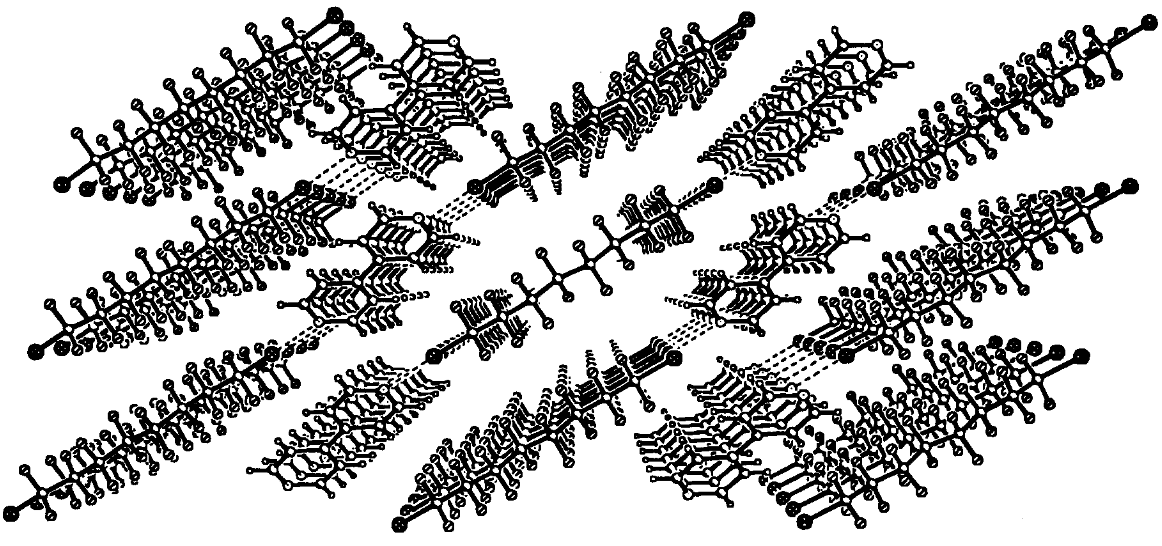


Figure 1. Packing diagram of co-crystals **3d** viewed down *a* axis. Dotted lines evidence N···I interactions

The relevance of the N···I–R_f interaction in driving the self-assembly of the perfluorocarbon and hydrocarbon moieties and its substantial stabilising contribution[11] in the packing of the resulting co-polymers is shown by the differential scanning calorimetry analyses of **3a–d** and by the single crystal X-ray analyses of bipyridine/1,8-diiodoperfluorooctane co-polymer **3d** (Fig. 1).[12–14] We recall that perfluorocarbon and hydrocarbon derivatives have usually a very low affinity[15] to the point of being hardly miscible. However, while perfluorooctane is only sparingly soluble, 1,8-diiodoperfluorooctane is miscible in all proportions with pyridine. In the co-crystal **3d**, reminiscences of the incompatibility of the hydrocarbon and the fluorocarbon species are clearly apparent in the microsegregation into layers perpendicular to the crystallographic *c* axis.

As already found in analogous co-polymers[7] such layers are joined only by N···I interactions running roughly along the (111) direction. The value of these intermolecular interactions (2.84(3) Å) is shorter than the sum of Van der Waals radii of N (1.55 Å) and I (1.98 Å)[16] but clearly longer than the average covalent bond (2.07 Å).[17] It is closely comparable to the values we observed in analogous co-polymers derived from diiodides **2** and diamines[7] (2.80–2.84 Å) and with the N···I bond distance in the co-crystals between iodine and various dinitrogen heteroaromatic compounds (2.817(1), 2.982(1)–3.092(1), 3.072(1), 2.724(1)–2.95(1) for pyrazine,[18] phenazine,[19] tetramethylpyrazine,[18] quinoxaline,[5a] respectively). The similarity between perfluoroalkyl iodides[1,7] and iodine[5a,18,19] in co-crystal formation is also evident by the value of N···I–C angle (177.5(4)°) which is consistent with a possible $n \rightarrow \sigma^*$ character of the interaction. A surprising feature in co-crystal **3d** is that not only the diheteroaromatic modules but also the perfluoroalkyl chains adopt substantially ordered structures at ambient conditions. It seems plausible that the perfluoroalkyl chains are effectively locked in an ordered state by N···I interactions and dipyridyl packing requirements. To minimise intramolecular 1–3 fluorine repulsion, the perfluoroalkyl chain deviates from the exact *trans* planar conformation as it does not only in poly(tetrafluoroethylene),[20] but also in the case of other short perfluorinated chain compounds.[21,22]

The results here described show that not only hydrocarbon aliphatic diamines[7] but also hydrocarbon diheteroaromatic compounds can undergo a self-assembly process with diiodoperfluoroalkanes. The pseudohalogen character of perfluoroalkyliodides was first recognised by Haszeldine in the early fifties[23] and it has been used by Prakash and Olah[24] in the late eighties to rationalise the behaviour of these compounds in molecular synthesis. Here we report how the pseudohalogen analogy for perfluoroalkyl iodides also allows the behaviour of iodoperfluoroalkanes in supramolecular synthesis to be understood. Specific heuristic principles concerning the non-covalent binding between complementary modules have to be developed if supramolecular synthesis has to succeed in the assembly of rationally designed architectures. The use of perfluoroalkyl halides in supramolecular chemistry is just starting to emerge[1,7] so that no such principles are available to predict their behaviour in this context. The parallel sketched above exemplifies that the same principles useful in understanding the molecular reactivity of iodoperfluoroalkanes can be used to anticipate their supramolecular reactivity.

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