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The N···I Intermolecular Interaction as a General Protocol for the Formation of Perfluorocarbon–Hydrocarbon Supramolecular Architectures[1]

Paolo Cardillo,[a] Eleonora Corradi,[b] Angelo Lunghi,[a] Stefano Valdo Meille,[b]
Maria Teresa Messina,[b] Pierangelo Metrangolo[b] and Giuseppe Resnati[b,*]

[a]*Stazione sperimentale combustibili, 3, via De Gasperi, I-20097 San Donato Milanese, Milan, Italy*
[b]*Dipartimento Chimica, Politecnico di Milano, 7, via Mancinelli, I-20131 Milan, Italy*

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Abstract—The formation of infinite 1D networks where diiodoperfluorocarbons are halogen bonded to di-nitrogen substituted hydrocarbons is described. The N···I non-covalent interaction is specific, directional, and strong enough to effectively overcome the low affinity between perfluorocarbon and hydrocarbon modules and to drive their self-assembly in the solid and liquid phase. Several analytical techniques are used to identify and characterise the electron donation from nitrogen to iodine atoms. The effectiveness of the interaction is largely independent from the overall structure of the involved modules. Indeed, supramolecular architectures have been obtained starting from diiodoperfluoroalkanes and -arenes (electron poor motifs) as well as from pyridine derivatives and di- or trialkylamines (electron rich motifs). The halogen bonding can thus begin to be considered as a first choice intermolecular interaction in crystal engineering. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Supramolecular architectures are identified by the covalent structure of their molecular modules and by the non-covalent interactions between the modules.[2] The rational design of supramolecular architectures consequently relies on a double analysis. One analysis is at a molecular level and pertains to the covalent binding of atoms to give molecules where the functional groups are positioned according to precise geometrical features. The other is at a supramolecular level and deals with the nature, strength, and directionality of the non-covalent interactions between modules, which generate the networks of the supramolecular architectures. The latter level is obviously more subtle. Any crystal structure, as well as any organised aggregate in the liquid phase, is the result of a non-covalent interaction pattern which maximises the attractive forces between single molecular modules within the framework of the geometrical constraints deriving from the covalent structure of the modules. This interaction pattern may be dominated by one kind of non-covalent binding and this is often the case of the 'strong' interactions (hydrogen bonds such as O···H–N and N···H–N[3,4] or metal co-ordinations such as pyridine···transition metal[5]). In other cases the interaction pattern is the result of a balanced co-operation of different types of 'weak' interactions (e.g. van-der-Waals attractions, π–π stacking, hydrogen bonds such as O···H–C and π···H–C).[6]

Perfluorocarbon (PFC) compounds have physical properties and chemical reactivities quite different from those of their corresponding hydrocarbon (HC) parents.[7] Saturated PFCs are dense, highly inert liquids, with greater compressibilities and viscosities but lower internal pressure, refractive indexes, and surface tensions than their HC parents. All these characteristics are responsible for the low affinity existing between PFCs and HCs, which results in the non-miscibility of most PFC derivatives with HCs and water. A specifically tailored and particularly strong interaction pattern therefore has to be developed if the self-assembly of PFCs and HCs is pursued. Ideally, the interaction has to be strong enough so that the effective self-assembly of the two types of modules becomes largely independent from their overall structures.

In this paper we describe how the N···I–R_f (R_f=perfluoroalkyl chain) intermolecular interaction occurring between diiodo-PFCs and dinitrogen-HCs fulfils the requirements discussed above and allows the low affinity existing between PFCs and HCs to be effectively overcome. The attractive N···I–R_f intermolecular interaction is specific, directional and strong enough to drive the self-assembly of PFC and HC modules into 1D infinite networks which

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* Corresponding author. Tel.: +390-2-23993032; fax: +390-2-23993080; e-mail: resnati@dept.chem.polimi.it

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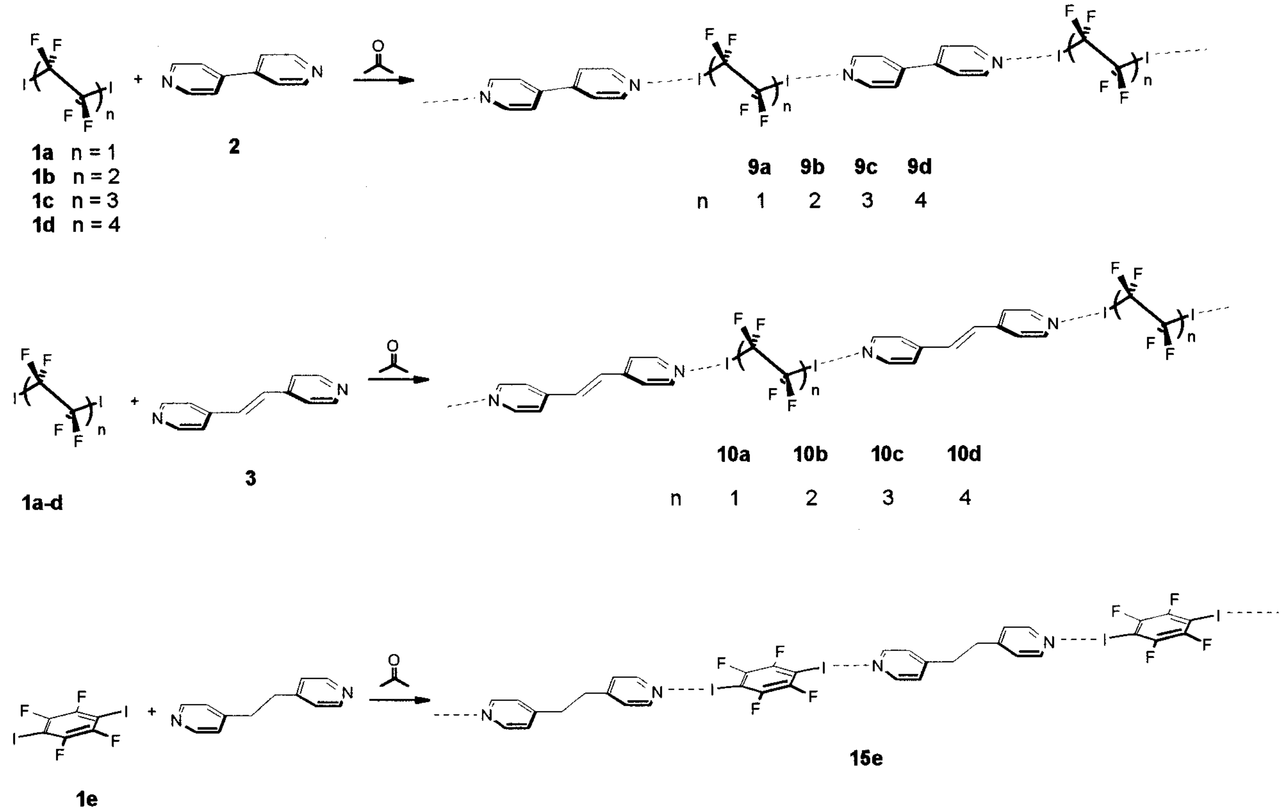


Scheme 1. Synthesis of 1D infinite networks **9a–d**, **10a–d**, and **15e** starting from pyridine modules **2**, **3**, and **8**.

are stable, solid, and crystalline at room temperature and in the air. Although overpowered, the low affinity between PFC and HC manifests itself in the co-crystals formed through the segregation of the two types of modules. The N···I interaction pattern can involve structurally different diiodo-PFCs and dinitrogen-HCs and can be reliably employed as a first choice intermolecular interaction in the rational design of supramolecular architectures.

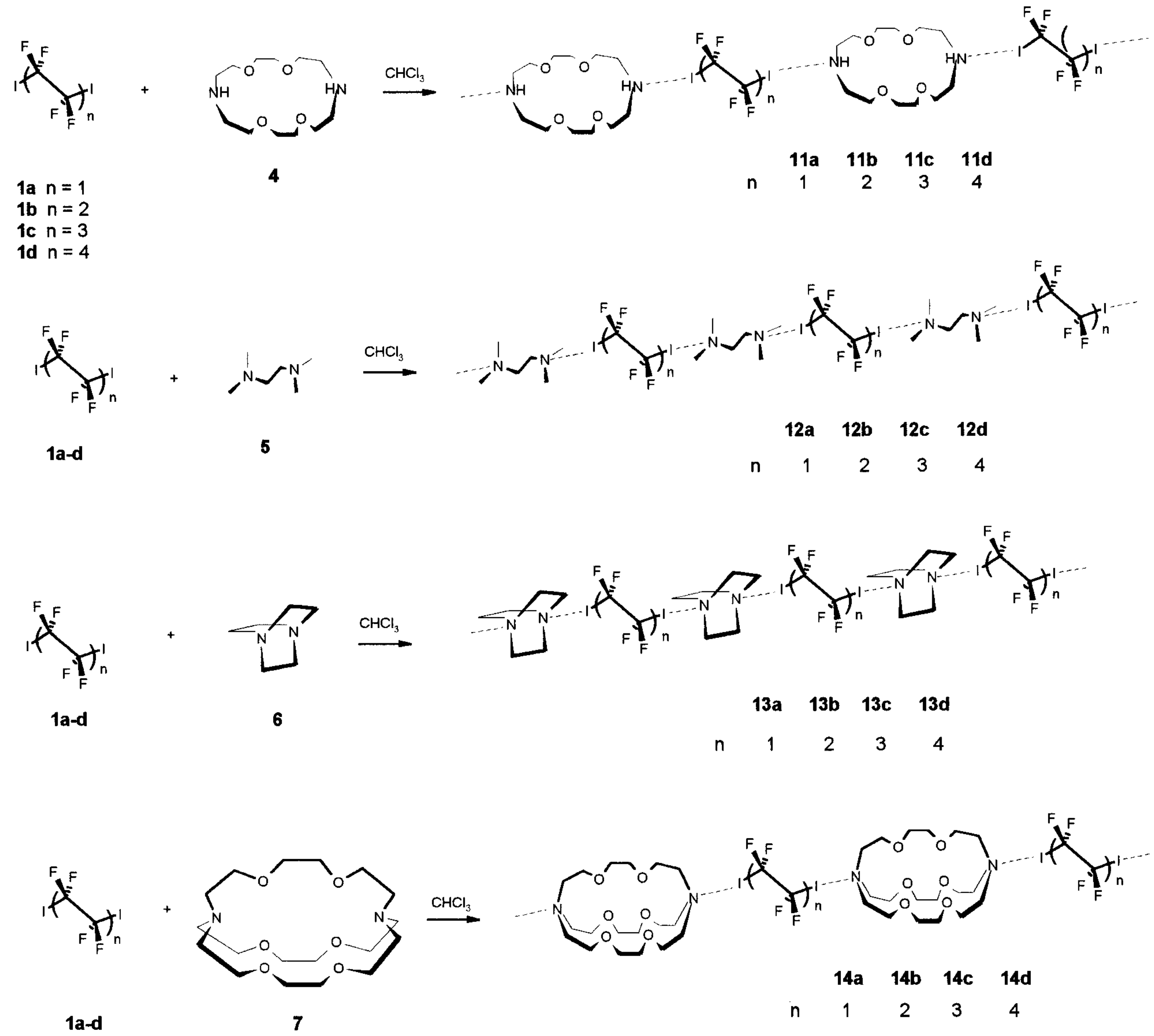
Results and Discussion

The attractive intermolecular interaction between fluorocarbon iodides (working as Lewis acids) and heteroatom substituted hydrocarbons (working as Lewis bases) was first observed in the early 1950s by Haszeldine who also emphasised the effectiveness of fluorine in strengthening this interaction.[8] The general ability[9] of carbon-bound iodine, bromine, and chlorine atoms C–X (X=Cl, Br, I) to work as electron acceptor motifs and to give donor–acceptor complexes C–X···B (X=Cl, Br, I; B=O, S, Se, N,...) with a wide variety of neutral basic motifs was rapidly recognised and documented in the 1950s and 1960s. More recently, also the fluorine atoms of perfluoroalkanes were reported to work as electron acceptors in charge transfer complexes formed with amines.[10] So, it has become apparent that the tendency to form strong complexes (I>Br>Cl>[F]) usually parallels the order of halogen atom polarisabilities, consistent with a key-role of halogen polarisation (and/or charge transfer energies) in the interaction.[11] Similar to other C–X···B interactions, the non-covalent bonding R_f–I···B (R_f=perfluoroalkyl chain, B=N, O, S,...) between perfluoroalkyl iodides and variously functionalised organic bases has been rationalised as a $n \rightarrow \sigma^*$ donation[12] and has been called 'halogen bonding'[9b,13] to stress the similarity with the hydrogen bonding. Despite its strength,[10a,14] the R_f–I···B interaction has received only occasional attention.[15,16]

We reasoned that by using bidentate acceptors and bidentate donors, for instance by using diiodo-PFCs and dinitrogen-HCs, the donor–acceptor interaction would be doubled at either ends of the two self-assembling modules. The resulting reiteration was expected to allow PFCs and HCs to self-assemble in a particularly effective way. Indeed, when an acetone solution of 1,2-diiodotetrafluoroethane (**1a**) and 4,4′-dipyridyl (**2**) was slowly evaporated, the infinite 1D chain **9a** was isolated as a white crystalline solid, which was stable in the air at room temperature (Scheme 1).

A similar behaviour was shown by the α,ω-diiodoperfluoroalkanes **1b–d**, which gave the corresponding 1D infinite networks **9b–d**. The general ability of the pyridine moiety to work as an effective donor motif was shown by the formation of the solid co-crystals **10a–d** starting from the α,ω-diiodoperfluoroalkanes **1a–d** and (*E*)-1,2-bis(4-pyridyl)-ethylene **3** (Scheme 1).

Not only heteroaromatic nitrogen bases, but also the dialkyl- and trialkylamine motifs proved effective in producing 1D infinite networks. When 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Kryptofix® 2.2., K.2.2., **4**) was mixed with diiodoperfluoroalkanes **1a–d** in chloroform, or carbon tetrachloride solution, the co-crystals **11a–d** were obtained



Scheme 2. Synthesis of 1D infinite networks **11a–d**, **12a–d**, **13a–d**, and **14a–d** starting from di- and trialkyl amine modules **4–7**.

(Scheme 2). Analogously, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, **5**),[17] 1,8-diazabicyclooctane (DABCO, **6**),[18] and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]-hexacosane (Kryptofix 2.2.2., K.2.2.2., **7**)[17,19] gave 1D infinite chains **12a–d**, **13a–d**, and **14a–d**, respectively (Scheme 2).

Both perfluoroalkyl- and perfluoroaryliodides gave co-crystals.[20] When an acetone solution of 1,2-bis-(4-dipyridyl)-ethane (**8**) and 1,4-diiodotetrafluorobenzene **1e** was slowly evaporated, the corresponding non-covalent co-crystal **15e** was formed (Scheme 1).

In all cases, 1D infinite chains **9–15** were isolated as white and crystalline solids which are stable at room temperature and can be handled in air. The 1:1 ratio of the PFC and HC modules **1** and **2–8**, respectively, in co-crystals **9–15** was proven by microanalyses (H, C, N, I, F) and by ^1H and ^{19}F NMR spectra in the presence of $(CF_2CH_2)_2O$ as internal standard. A structural study of these architectures with different analytical techniques (X-ray analyses, IR and Raman spectroscopies, DSC, ^{19}F NMR) was undertaken to define the nature of the R_f–I···N intermolecular interaction both in the solid and in the liquid phase and to identify simple, effective, and sensitive analytical tools to detect the formation of the halogen bonding.

X-Ray crystal structure analyses

Single crystal X-ray analyses of the 1D infinite networks **9c** and **11a** compounded by dipyridine/1,6-diiodoperfluorohexane and by Kryptofix® 2.2./1,2-diiodotetrafluoroethane, respectively, clearly revealed some general characteristics of the PFC-HC self-assembly processes driven by the R_f–I···N interaction.

The reluctance of PFC and HC derivatives to mix survives in the two co-crystals (Figs. 1 and 2) where the PFC and HC modules segregate into layers which are joined by the I···N intermolecular interaction. In the infinite network **11a** the PFC-diiodide is arranged in isolated columns parallel to the crystallographic *c*-axis and these columns are

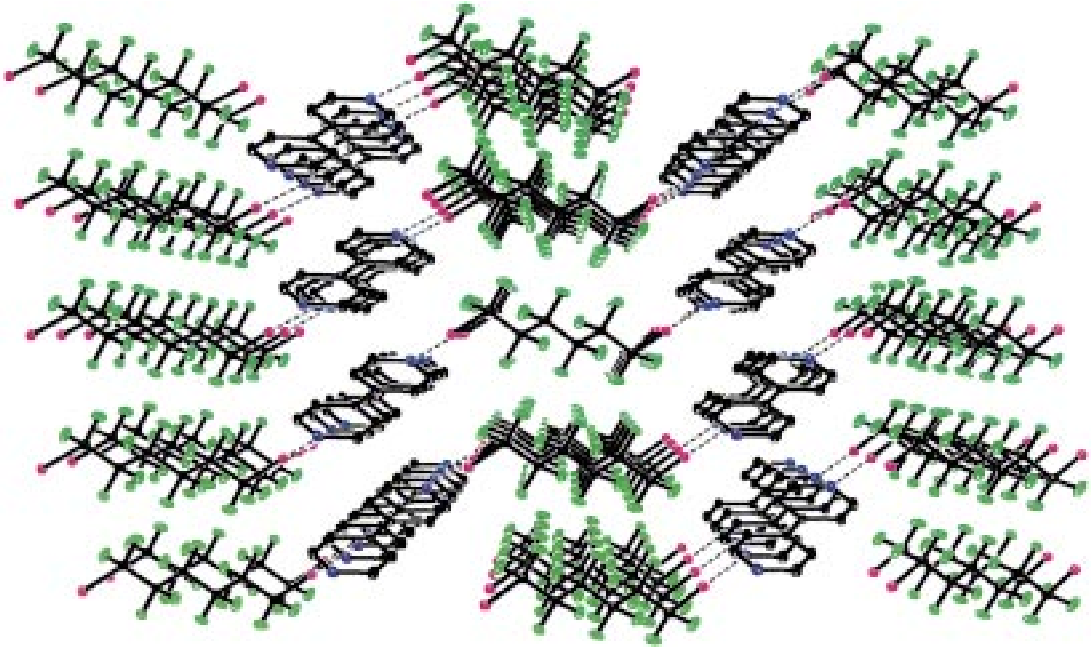


Figure 1. Packing diagram of co-crystal **9c**. Dotted lines evidence N···I interactions.

microsegregated from the bicontinous matrix of the hydrocarbon crown ether.[21]

Analogously, the HC electron donors and the PFC acceptors segregate into layers perpendicular to the crystallographic *c*-axis both in the co-crystal **12a** (Fig. 3A) and in the co-crystal **9d**.[22] The low affinity between PFC and HC moieties is apparent also from the structure of **14a** which is not characterised by layers due to the different steric requirements of the two co-crystallising species. In fact the diamine **7** forms in the co-crystal a 3D network of ordered molecules interacting through dispersive forces, and the disordered perfluorinated diiodide **1a** gives rise to pairs of segregated and parallel columns linked to the diamine by the N···I–R_f interactions (Fig. 3 B). In co-crystal **15e**, the aromatic rings stack parallel to each other, about 5 Å apart, forming distinct columns of perfluorinated and hydrocarbon compounds.[20] This arrangement is probably imposed by van der Waals interactions involving iodine atoms and the 1,2-bis(4-pyridyl)ethane molecules. In co-crystals **9c**, **9d**, and **15e** where the diiodides self-assemble with different dipyridyl systems, the iodine atom is nearly coplanar with the aromatic system, deviations from the pyridinyl least-squares plane being around 0.2 Å. The two C–N···I angles differ in all three cases significantly from each other, quite probably for reasons related to the packing. The close similarities in the packing of **9c** and **9d** are made apparent by the *quasi* identical *ab* lattice

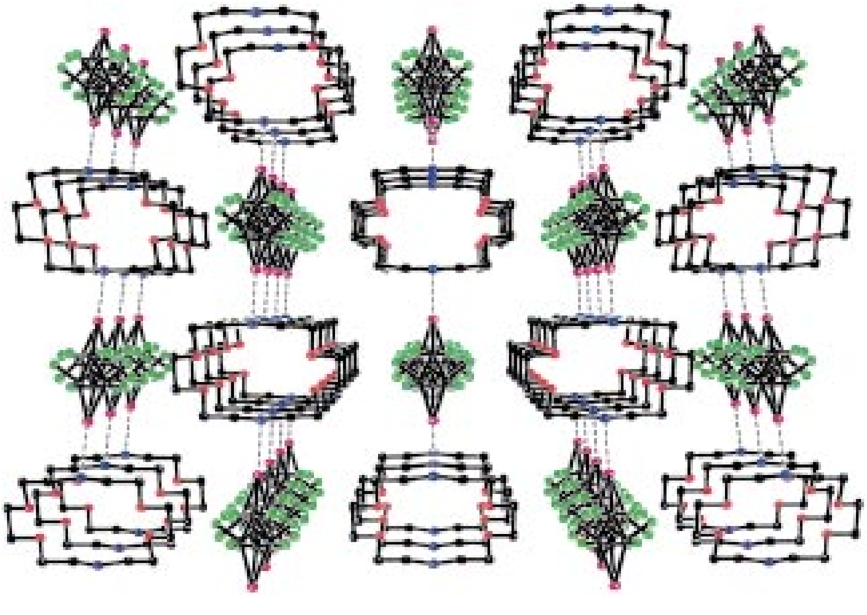


Figure 2. Packing diagram of co-crystal **11a**. Dotted lines evidence N···I interactions.

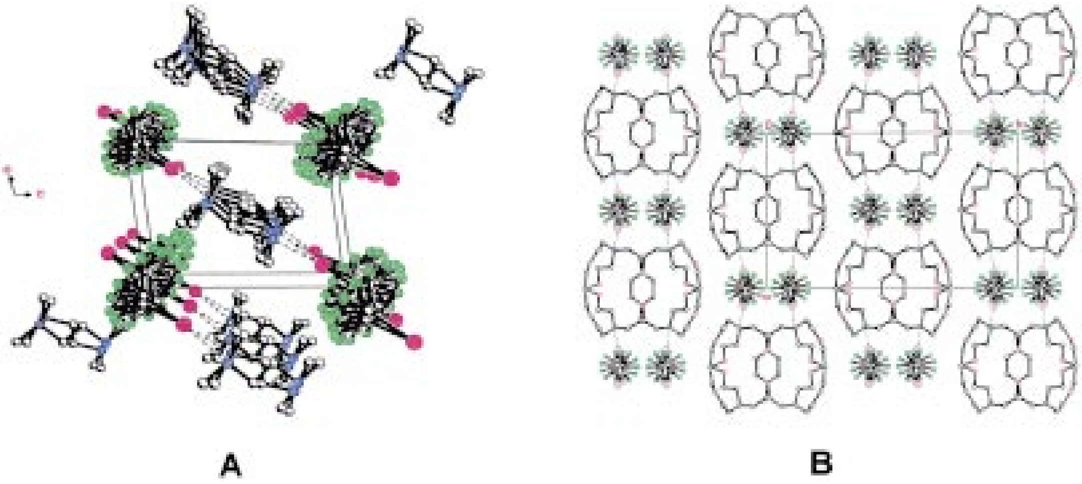


Figure 3. Crystal packing of: **A**, co-crystal **12a** viewed down the *b*-axis, and **B** co-crystal **14a** viewed down the *b*-axis. Dotted lines evidence N···I interactions.

projection of the two crystals, which differ with respect to the third lattice dimension along which the perhaloalkyl chain is oriented. This behaviour confirms a somewhat loose self-packing of the perfluoroalkyl layers, consistent with their limited propensity to crystallisation.

In all the established structures the length of the N···I–R_f non-covalent bonding spans from 2.79 to 2.84 Å as detailed in Table 1 where other key parameters of the structures are also reported. These values are longer than the average N–I covalent bond (2.07 Å), approximately 0.8 times the sum of the van der Waals radii for nitrogen (1.55 Å) and iodine (1.98 Å),[23] and closely comparable to the N···I distances observed in the complexes that I_2 forms with heteroaromatic containing nitrogen atoms as electron donors[24] (e.g. 2.817(1), 2.982(1)–3.092(1), 3.072(1), 2.724(1)–2.95(1) Å for pyrazine,[25] phenazine,[26] tetramethylpyrazine,[25] and quinoxaline[27] complexes with I_2, respectively). The somewhat large standard errors associated with the molecular dimension reported in Table 1 are clearly related to the disorder which characterises all the co-crystals discussed in this paper. Specifically, the C–I bond distance appears to be marginally affected by the halogen bond interaction in the more ordered systems **9c**, **9d** and **15e** as expected values are 2.162(15) and 2.095(15) Å for aliphatic and aromatic carbons, respectively. Some lengthening is on the other hand suggested for **11a**, **12a** and **14a** but all these lengths are less reliable because they involve highly disordered diiodotetrafluoroethane molecules. The values of the more reliable N···I distances in **9c** and **9d** on the one hand, and in **15e** on the other, could be suggestive of a somewhat more efficient halogen bonding for the co-crystal where both the donor and the acceptor modules are aromatic. A more complete disorder treatment may be required to further improve our understanding of these systems, since even relatively ordered co-crystals **9c** and **9d**, give rise to reflections which remain unaccounted by the adopted packing. The relatively large anisotropic thermal factors of the fluorine atoms in **9c** and **9d** may well be indicative of limited conformational disorder, which is indeed expected for the PFC chains at room temperature.

The N···I–R_f interaction is largely responsible for keeping the PFC-diiodides in place. For instance, in **11a** the iodine atoms are pinned in a *trans* arrangement as a consequence of the halogen bonds to the nitrogen atoms of adjacent K.2.2. molecules but all the other atoms in the perhalogenated module are heavily affected by disorder which has been modelled effectively refining the perfluorodiiodide with rigid body constraints over three roughly equally populated locations, two of them symmetry related. Similarly, the pure modules **1a** and **5** are both liquid at room temperature and they both exhibit disorder in the corresponding co-crystal **12a**. All the atoms of the diamine, including the nitrogens, exhibit disorder over two equally populated positions corresponding to different molecular orientations or to distinct conformers. The two iodine atoms of **1a** are the only non-disordered atoms of the infinite network **12a** as the perfluorinated diiodoethane moiety exhibits dramatic rotational disorder around the axis joining the two iodine atoms and this disorder has been described by splitting the carbon and the fluorine atoms over four locations. The

Table 1. Selected and relevant bond lengths (Å) and angles (°) of co-crystals **9c**, **9d**, **11d**, **12a**, **14a**, and **15e**

Property	9c	9d	11a	12a	14a	15e
N···I (Å)	2.840(11)	2.842(12)	2.806(14)	2.820(13)[b]	2.802(10)	2.792(9)
C–I (Å)	2.152(13)	2.161(14)	2.204(13)[b]	2.192(15)[b]	2.177(15)[b]	2.101(9)
C–I···N (°)	177.4(6)	176.7(4)	165.5(8)[b]	166(3)[b]	167.7(13)[b]	175.8(3)
C–N···I (°)	112.7(8)[a]	113.0(1.0)[a]	111.0(8)	118.6(11)[a]	116.6(7)[a]	117.2(9)[a]
	131.6(11)[a]	129.5(1.0)[a]		104.6(14)[a]	102.6(7)[a]	128.6(7)[a]
				102.3(13)[a]	100.2(7)[a]	

[b] Average values determined over different disordered molecular images.

[a] Values referred to the different nitrogen bound carbon atoms.

Table 2. Selected infrared bands of single components **1**–**8** and corresponding co-crystals **9**–**15**

Compound	Infrared absorptions[a]
1a	1159 (s), 1108 (s), 709 (s)
1b	1196 (s), 1136 (s), 637 (s)
1c	1149 (s), 1122 (s), 1090 (s)
1d	1150 (s), 1113 (s), 1091 (m), 641 (s)
1e	1468 (s), 1431 (m), 944 (s), 761(s)
2	3027 (m), 2895 (m)
3	3020 (m)
4	3336 (m), 2919 (s), 2884 (s)
5	2945 (s), 2767 (s)
6	2942 (s), 2875 (s), 1459 (s)
7	2878 (s), 2814 (s)
8	3067 (m), 3031 (m), 2860 (m)
9a	3029 (w), 1118 (s), 1086 (s), 698 (s)
9b	3033 (w), 1182 (s), 1130 (s), 360 (s), 613 (s)
9c	3059 (w), 3036 (w), 1135 (s)
9d	3059 (w),3036 (w), 1142 (s)
10a	3038 (w), 1123 (s), 1084 (s), 699 (s)
10b	3030 (w), 1197 (s), 1187 (s), 1120 (s), 1109 (s), 628 (s)
10c	3031 (w), 1134 (s), 1117 (s)
10d	3042 (w), 1141 (s), 1096 (s)
11a	3312, 2949 (w), 2881 (s), 699 (s)
11b	3293, 2892 (w), 1183 (s), 632 (s)
12a	2964 (m), 2786 (m), 1121 (s), 1088 (s), 695 (s)
12b	2967 (m), 2786 (m), 1190 (s), 1128 (s), 650 (s), 631 (s)
12c	2966 (w), 2789 (m), 1140 (s), 1110 (s), 1084 (s)
12d	2835 (m), 2786 (w), 1150 (s), 1109 (s), 1084 (m), 637 (s)
13a	2948 (m) 2879 (m), 1116 (s), 1086 (s), 692 (s)
13b	2951 (m), 2882 (m), 1186 (s), 1124 (s), 648 (s), 631 (s)
13c	2951 (m), 2882 (m), 1138 (s), 1107 (s), 1083 (s)
14b	2887 (m), 2825 (w), 1183 (s), 618 (s)
14d	2887 (m), 2823 (w), 634 (m)
15e	3075 (w), 3036 (w), 2872 (w),1456 (s), 1422 (m), 940 (s), 749 (s)

[a] Absorbance intensity: s=strong, m=medium, w=weak.

disorder of both the PFC and the HC modules was modelled by using rigid body restraints. A qualitative measure of the effectiveness of the N···I interaction in binding the modules **1a** and **5** results from the fact that the molar volume of the liquids **1a** and **5** is reduced by 21% in the co-crystallisation process to give **12a**. These data seem particularly significant since in the co-crystals the PFC and the HC components segregate and volume reduction must result at the interface between the two components. Differently, in the crystal structure of **9c** and **9d** not only the diheteroaromatic modules but also the perfluoroalkyl chains are substantially ordered at ambient conditions. In these cases the N···I–R_f interactions and the dipyridyl packing requirements are responsible for locking the perfluoroalkyl chains in an ordered state. To minimise intramolecular 1–3 fluorine repulsion, the perfluoroalkyl chains deviate from the exact *trans* planar conformation, as is the case not only in poly-(tetrafluoroethylene)[29] but also in the case of other short chain perfluorinated compounds.[27,30]

The similarity between perfluoroalkyliodides and iodine in co-crystal formation holds not only for the N···I bond length, but also for the N···I–C angle, which, in our structures, spans from the value of **9c** (7.4(2)°) to the value of **11a** (165(2)°). The linearity of the N···I–C moiety is consistent with the $n\rightarrow\sigma^*$ character of the interaction.

While in infinite networks **9**, **10**, **12**–**15** the halogen bonding is the only strong intermolecular interaction, in the co-crystal **11a** both hydrogen bonding and halogen bonding contribute to determine the overall structure of the supramolecular architecture. In fact, Kryptofix® 2.2. module **4** shows, both in the pure compound[31] and in the co-crystal **11a**, weak but significant bifurcated intramolecular hydrogen bonds between the hydrogens bound to the nitrogen atoms and the two nearby oxygen atoms. These hydrogen bonds stabilise, both in the pure compound[31] and in the co-crystal **11a**, the *exo*–*exo* conformation, which outwardly orients the lone pairs of the tetrahedral nitrogens. A similar conformation where the lone pairs of nitrogen atoms are outwardly oriented is obviously adopted also by cryptand **7** in co-crystal **14a** (Fig. 3B) despite the fact that the preferred conformation of the cryptand alone inwardly orients both the nitrogen lone pairs.[32] While the *exo*–*exo* conformation of module **7** in co-crystals **14** is the result of a conformational induced fit experienced by the cryptand in the divergent self-assembly with the PFC-diiodides **1**, the *exo*–*exo* conformation of crown ether **4** in co-crystals **11** is secured by the above discussed intramolecular hydrogen bonds.

Infrared spectra

Most of the bands shown by the single acid and basic modules **1a**–**e** and **2**–**8**, respectively, are present in the spectra (KBr pellets) of corresponding co-crystals **9**–**15**. However, systematic modifications of some of the absorptions of pure modules occur on co-crystal formation. The principal differences between the spectra of the starting modules **1**–**8** and those of the electron donor–acceptor adducts **9**–**15** are the shifts of some vibrational frequencies and the change in some band intensities.

The N···I–R_f intermolecular interaction is weaker than covalent or ionic bonds[14] and, being specific, it directly involves only some of the acid and basic module atoms. It is thus reasonable to discuss the vibrational spectra of the infinite networks **9**–**15** in terms of modified modes of starting diiodo and dinitrogen components **1**–**8**. The validity of this approach is supported by the similarity of the changes shown by the diiodo-PFCs and dinitrogen-HCs when interacting with different dinitrogen-HCs and diiodo-PFCs, respectively. The analyses of the frequency shifts of single module absorptions has already been employed as an analytical probe for non-covalent adduct formation.[15e,33]

The C–H stretching modes of pure HC donors **2**–**8**, either aliphatic or aromatic, occur in the 2700–3100 cm^{-1} region and shifts to higher frequencies in co-crystals **9**–**15** due to the halogen bonding formation with the aliphatic or aromatic PFC acceptors **1a**–**e**. Similar upward shifts have been described for structurally related donor–acceptor complexes,[34] for instance the dimers given by trimethylamine with I_2, Br_2, and IBr[35] or the trimers formed by 1,4-diazabicyclo[2.2.2.]octane with boron trihalides.[33c] Moreover, the intensities of the C–H bands in the complexes **9**–**15** are reduced compared to in pure nitrogen donors **2**–**8**, thus following the well documented rule that the higher the ν_{C-H} frequency, the lower its IR intensity is. For instance, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**5**) shows C–H absorption bands at 2945, 2767 cm^{-1} and the complex **12a**, formed with 1,2-diiodotetrafluoroethane (**1a**)

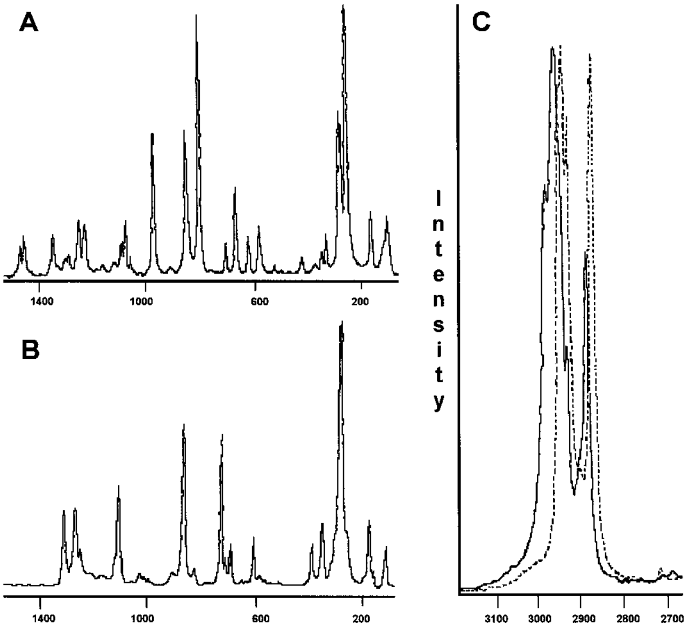


Figure 4. Raman spectra of: **A**: co-crystal **13b** formed by DABCO **6** and 1,4-diiodoperfluorbutane (**1b**); **B**: pure diiodoperfluorobutane (**1b**); **C**: continuous line, co-crystal **13b**, dotted line, pure diiodoperfluorobutane (**1b**).

gives the corresponding C–H absorptions at 2964, 2786 cm^{-1} with pronounced decreased intensities. Other selected absorptions of starting modules and corresponding co-crystals are summarised in Table 2 and full data are reported in the Experimental section. The upward shift and intensity decrease observed for the C–H absorption bands may be correlated with a higher positive charge on, namely, a more acidic character for the H atoms in co-crystals **9–15** than in pure nitrogen donors **2–8**, consistent with the PFC and HC modules being bound through an $n \rightarrow \sigma^*$ electron donation from the nitrogen to the iodine atoms. Moreover, the CH_2 scissoring (δ_{CH2}) motion frequently undergoes a splitting and an intensity decrease on co-crystal formation. For instance, the relative absorbance of the ν_{CH} ($\sim$3000 cm^{-1}) with respect to the δ_{CH2} ($\sim$1460 cm^{-1}) is 9.2 in dinitrogen HC **6** and 4.6, 3.8 and 4.2 in **13a**, **13b**, and **13c**, respectively.

To conclude the discussion of the spectral changes induced by the halogen bonding formation on the HC donor absorbances, it is interesting to observe that when the HC donor is a secondary amine its ν_{N-H} band appears at lower frequencies in the co-crystal than in the pure donor. For instance, the stretching shown by pure K.2.2. **4** at 3336 cm^{-1} is shifted to 3312 cm^{-1} with increased intensity in co-crystal **11a**, consistent with a more positive character of the nitrogen atom due to the $n \rightarrow \sigma^*$ electron donation from nitrogen to iodine. This behaviour parallels the shift observed for the amine ν_{N-H} band when nitrogen is involved in hydrogen bonding.

The formation of halogen bonding interactions also affects the absorption bands of the diiodo-PFCs **1**. Specifically, the frequencies and the intensities of the C–F stretching vibrations in the 1200–1000 cm^{-1} region should decrease and increase, respectively, due to the $n \rightarrow \sigma^*$ donation and indeed this is the case for all the 1D networks **9–14**. For instance, the free diiodotetrafluoroethane **1a** shows the C–F absorption bands at 1159, 1108 cm^{-1} and the corresponding absorptions appear with increased intensity at 1117, 1087 cm^{-1} in the complex **9a** formed with **2**. Other selected examples are reported in Table 2. The observed intensity enhancement may be due to the change in dipole moment.[36] In addition, the lower frequency shift of the C–F stretchings shown by the electron donor–acceptor complexes **9a–14a**, which are compounded by 1,2-diiodotetrafluoroethane (**1a**) and different bases, are larger than those shown by the complexes **9b,c,d–14b,c,d** derived by longer chain diiodoperfluoroalkanes **1b–d**. This is consistent with the specificity of the N···I interaction which involves the iodine atom so that the α-CF_2 group is heavily perturbed but the internal difluoromethylene groups, which are present in α,ω-diiodoperfluoroalkanes **1b–d** but are missing in **1a**, are nearly unaffected. It is finally interesting to note that, with a given diiodo-PFC, DABCO **6** gives larger shifts than tetramethylethylenediamine **5** and, in fact, the former base is known to be a better electron donor than the latter base.

Raman spectra

Raman spectroscopy is also a powerful tool to detect the formation of halogen bonded adducts. Similar to IR spectra, the attention will be focussed on the observed systematic changes in frequency and intensity of the bands of the single modules **1–8** when they interact to form 1D networks **9–15**. For a given diiodo-PFC electron acceptor the direction of frequency changes is independent from the structure of the complementary basic module and the values of the changes reflect the strength of the interaction. A quite parallel behaviour is observed when a given HC base is halogen bonded to PFC acids having different chain lengths.

The frequency and the intensity of C–H stretching modes are very powerful probes for studying intra- and intermolecular interactions. They have given fundamental contributions to the understanding of physical–chemical

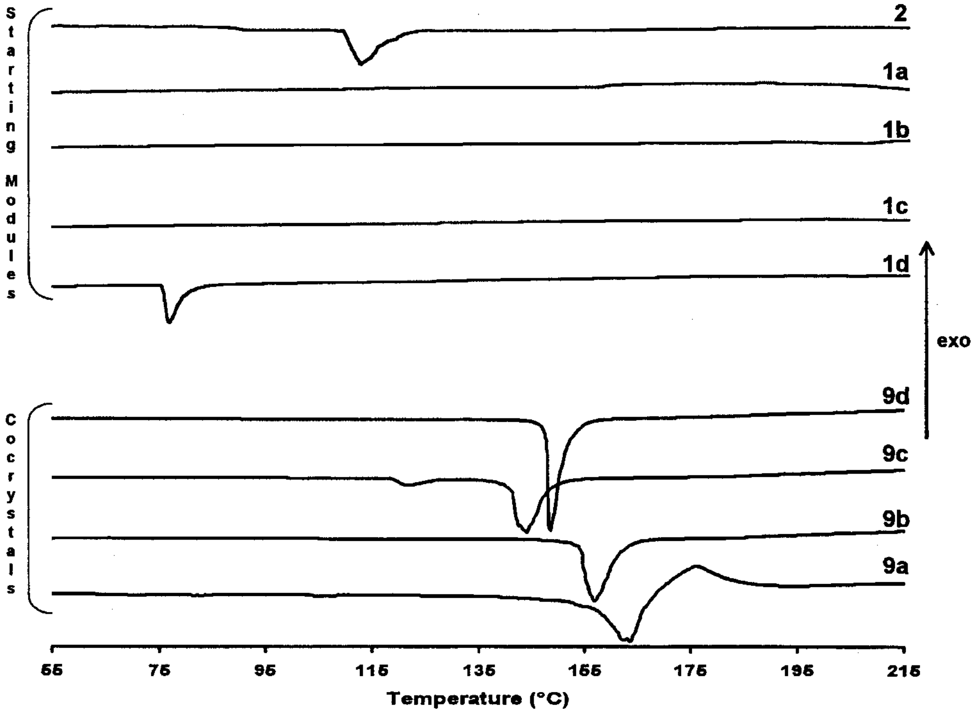


Figure 5. Heating curves of starting modules **1a–d**, **2** and corresponding 1D infinite networks **9a–d**.

properties, such as bond strength, equilibrium distance, and electron distribution, of both molecules and polymers.[37] Similar to in the IR spectra, the C–H stretching modes deriving from the dinitrogen-HCs are at lower frequencies and exhibit a greater intensity in the spectra of the pure basic modules than of corresponding co-crystals (Fig. 4).[18] For instance, the C–H stretching modes of the free amine **6** are at 2935, 2925, 2914, 2861 cm^{-1} and shift to 2970, 2948, 2922, 2875 cm^{-1} in the adduct **13a**. Similar to IR spectra, this is consistent with the single HC and PFC components being bound through an $n\rightarrow\sigma^*$ electron donation from the nitrogen to the iodine atoms. Such an interaction in the co-crystals decreases the electron density on the nitrogen atoms, which thus behave as more electronegative groups. Indeed, more electronegative groups are known to raise the C–H stretching frequency by the inductive effect.[37] Alternatively, the C–H stretching shifts could also be rationalised by suggesting a through space electron withdrawal by the difluoromethylene groups of the diiodo derivatives when they are near to the methylene groups of the diamine. However, this hypothesis contrasts with the frequently encountered segregation of the aliphatic PFC and HC components in the co-crystals which has been revealed by single crystal X-ray analyses (see above).

On complex formation other interesting changes were observed. For instance, when diiodotetrafluoroethane (**1a**) is halogen bonded with DABCO and K.2.2.2 in co-crystals **13a** and **14a**, a Raman band at 1216 and 1217 cm^{-1}, respectively, is activated. The 1200 cm^{-1} region is characteristic of both C–F and C–C stretching and this behaviour can be understood in terms of local symmetry variation passing from the pure diiodoperfluoroalkane to the co-crystal. Specifically, on the formation of halogen bonding interactions, the normal vibration mode corresponding to this frequency is a totally symmetric one. Usually, when this symmetry situation occurs, the selection rules for Raman and IR activity are mutually exclusive. As a result the 1216 cm^{-1} band can be assigned to a totally symmetric motion like the C–C stretching (*trans* conformation) or to an in phase CF_2 symmetric stretching motion with both iodine atoms involved in an interaction with nitrogen atoms of basic modules.

Another diagnostic probe of the donor–acceptor interaction is the shift to lower frequencies of the band due to the C–I stretching in complexes **12a**, **13a** (261, 254 cm^{-1}, respectively) and **12b** (263 cm^{-1}) with respect to the pure iodides **1a** (268 cm^{-1}) and **1b** (279 cm^{-1}). Usually, the lower the frequency, the longer the bond equilibrium distance (r_0) and the smaller the bond dissociation energies (BDE) are. If this is the case, the shift observed for the C–I stretching on co-crystal formation **12a,b** and **13a** implies a weaker C–I bond force constant and is consistent with the $n\rightarrow\sigma^*$ nature of the N···I interaction. It is also consistent with the lengthening of the C–I bond, which has been revealed by X-ray analyses. Analogous shifts to lower frequencies of the ICF_2 deformation motion were observed in the liquid systems formed by a 1:1 mixture of **1a** with piperidine, its 1-methyl and 1,2,2,5,5-pentamethyl derivatives, tetrahydrofuran, tetrahydrothiophene, and triethylphosphite (666.2, 666.5, 669.7, 669.0, 668.0 and 668.5 cm^{-1}, respectively). The magnitude of the shift depends on the strength of the interaction, namely stronger donors[38] give larger shifts. Heteroatoms other than nitrogen have already been shown to be able to act as electron donor motifs to iodoperfluoroalkanes[38,39] if they have unshared lone pairs, and these Raman shifts further confirm this ability.

Table 3. ^{19}F chemical shift changes observed in deuterochloroform solutions of **9–13**. All spectra have been obtained in $CDCl_3$. The diiodide chemical shifts do not change with the concentration in the range 0.05–1.6 M. $\Delta\delta=\delta_{\text{pure dioiodide }\mathbf{1}}-\delta_{\text{co-crystals }\mathbf{9-13}}$. $\delta_{\mathrm{ICF2CF2I}}=-53.89$, $\delta_{(\mathrm{CF2C}F\mathrm{2I})}=-60.07$, $\delta_{(\mathrm{C}F\mathrm{2CF2I})2}=-113.39$, $\delta_{(\mathrm{CF2CF2C}F\mathrm{2I})2}=-60.24$, $\delta_{(\mathrm{CF2C}F\mathrm{2CF2I})2}=-114.27$, $\delta_{(\mathrm{C}F\mathrm{2CF2CF2I})2}=-122.13$, $\delta_{(\mathrm{CF2CF2CF2C}F\mathrm{2I})2}=-60.23$, $\delta_{(\mathrm{CF2CF2C}F\mathrm{2CF2I})2}=-114.28$, $\delta_{(\mathrm{CF2C}F\mathrm{2CF2C}F\mathrm{2I})2}=-122.10$, $\delta_{(\mathrm{C}F\mathrm{2CF2CF2CF2I})2}=-122.91$

Compound (molar conc.)	$\Delta\delta_{\mathrm{IC}F\mathrm{2-}}$ (ppm)	$\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}$ (ppm)	$\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2-}}$ (ppm)	$\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}$ (ppm)
9a (0.12 M)	0.30	–	–	–
9b (0.07 M)	0.23	0.02	–	–
9c (0.05 M)	0.22	0.02	0.01	–
9d (0.05 M)	0.19	0.04	0.04	0.03
10a (0.12 M)	0.38	–	–	–
10b (0.07 M)	0.26	0.01	–	–
10c (0.05 M)	0.19	0.01	0.01	–
10d (0.05 M)	0.21	0.04	0.04	0.03
11a (0.13 M)	1.24	–	–	–
11b (0.07 M)	1.05	0.13	–	–
11c (0.05 M)	0.71	0.07	0.02	–
11d (0.05 M)	0.74	0.10	0.04	0.03
12a (0.12 M)	1.20	–	–	–
12b (0.07 M)	0.92	0.09	–	–
12c (0.05 M)	0.79	0.07	0.01	–
12d (0.05 M)	0.84	0.10	0.04	0.04
13a (sat. soln.)	1.06	–	–	–
13b (sat. soln.)	0.89	0.09	–	–
13c (sat. soln.)	1.01	0.08	0.03	–
13d (sat. soln.)	1.29	0.13	0.06	0.03

Thermal analyses

A comparison of the differential scanning calorimetry behaviour of the pure modules **1–8** and corresponding co-crystals **9–15** gave useful information. Heating curves of pure diiodo-PFCs **1a–d**, of 4,4′-dipyridyl (**2**), and of co-crystals **9a–d** (temperature range 33–280°C, heating rate 10°C/min) are reported in Fig. 5.

The melting temperatures of **9a–c** decrease with increased length of the fluorinated chain and the same holds for **14a–c**.[19] The endotherm melting peak at 113°C in the curve of the pure dipyridyl **2** is not present in any of the co-crystals **9a–d**. Similarly, the melting peak of diiodoperfluorooctane **1d** at 77°C is missing in the curve of the complex **9d**, the melting peaks of dipyridylethane **8** (111°C) and of diiodotetrafluorobenzene **1e** (109°C) are missing in the curve of the corresponding co-crystal **15e**, and the melting peaks of K.2.2.2. **7** (73°C) and diiodoperfluorooctane **1d** are missing in the curves of **14a–d**. All the above-discussed co-crystals show specific melting temperatures, which are higher than those of pure dinitrogen-HC and diiodo-PFC modules. These thermal behaviours prove that the R_F–I···N interaction produces well defined molecular aggregates. It also proves that the effectiveness of the halogen bonding in driving the self-assembly of diiodo-PFC and dinitrogen-HC modules is general and quite independent of the structural features of the single modules. Well ordered co-crystals, as revealed by melting points higher than those of the single components, are formed starting from short or long chain diiodoperfluoroalkanes (**1a** and **1d**, respectively) and from diiodoperfluoroaromatics as well as starting from structurally different HC donors having either an aliphatic or aromatic carbon framework. The strength of the R_f–I···N interaction and its role in determining the melting point of the formed co-crystals is emblematically revealed by a comparison between mps of the co-crystals **12a** and **14a** (105 and 119°C, respectively) and mps of starting modules **1a**, **5**, and **7** (−28, −55 and 73°C, respectively).

Other factors obviously determine the melting temperatures of the PFC–HC aggregates, for instance the packing energies of the single components, which become influential via the segregation present in the crystal lattices of the complexes. Diiodoperfluorooctane co-crystals melt at higher temperatures than those of diiodoperfluorohexane (e.g. mps of **9d** and **9c**, of **14d** and **14c** are 152, 146, 83, 76°C, respectively) and this contrasts with the decrease of melting temperatures on increasing the difluoromethylene chain length observed in the ethane, butane, hexane series, but reflects the fact that **1d** melts at higher temperature than **1c** (mp 77 and 29°C, respectively). As a further example it can be observed that pure dipyridine modules **2** and **3** melt at higher temperatures than pure TMEDA and DABCO **5** and **7**. Correspondingly, co-crystals **9a–d** and **10a–d**, formed by **2** and **3**, melt at higher temperatures than co-crystals **12a–d** and **13a–d**, formed by **5** and **6**, if the comparison is made among co-crystals containing the same diiodo-PFC component. These differences contrast with the stronger donor ability of the trialkylamine motif compared to the pyridyl motif.[38a]

On heating the co-crystals given by diiodotetrafluoroethane **1a** with both aromatic and aliphatic donors, e.g. **9a**, **10a**, and **13a**, **14a**, the initially observed melting endotherm is rapidly followed by an exotherm associated with a reaction/decomposition which forms tetrafluoroethylene as revealed by ^{19}F NMR.[16b] Longer chain α,ω-diiodoperfluoroalkanes **1b–d** give co-crystals which melt then decompose when the electron donor is an amine (e.g. **12b–d** and **14b–d**) while no decomposition occurs when the donor is a pyridine motif (e.g. **9b–d** and **10b–d**).

^{19}F NMR

Most of the analytical studies discussed above deal with halogen bonded aggregates in the solid state. NMR studies allowed useful information to be obtained for the solution state of these systems. ^{1}H, ^{13}C, and ^{19}F NMR spectra of highly diluted solutions of co-crystals **9–15** are identical to those shown by pure modules **1–8**. At higher concentrations substantial differences in chemical shifts (mainly in ^{19}F and ^{1}H spectra) are observed and the changes were proportional to the co-crystal concentration in solution. No signal doubling or changes in linewidth were ever observed. On evaporating the solvent, the starting co-crystals were re-formed. These observations prove that the R_f–I···N interaction also exists in solution, that it is reversible (non-covalent) and that the association equilibrium between the PFC and HC modules is rapid at room temperature in the NMR timescale.

^{19}F NMR spectra were particularly interesting. High field shifts of the $-CF_2I$ signals of the diiodide modules **1a–d** were observed for co-crystals **9–14**[15g,16b] and the chemical shifts changed up to values larger than 1 ppm (see Table 3) when reasonably concentrated solutions (0.05–0.12 M) could be obtained (as is the case for co-crystals generated from trialkylamines). A similar behaviour was observed also for the –CF signal of aromatic compound **1e** when interacting with dipyridylethane **8** to give solutions containing co-crystal **15e**.

The signals given by the internal difluoromethylene groups in longer chain diodides **1b–d** were affected by the N···I interaction, but decreasing shifts were observed with increasing distance from the iodine atom. For example, the adduct **12d** (0.05 M solution) shows the following shifts: $\Delta\delta_{\mathrm{ICF2-}}=0.84$, $\Delta\delta_{\mathrm{ICF2}\mathit{CF2}-}=0.10$, $\Delta\delta_{\mathrm{ICF2CF2}\mathit{CF2}-}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2CF2}\mathit{CF2}-}=0.04$ ($\Delta\delta_{\mathrm{F}}$ (ppm)$=\delta_{\text{pure iodide }\mathbf{1d}}-\delta_{\text{adduct }\mathbf{12d}}$). Other selected shifts are reported in Table 3 and full data are given in the Experimental section. This behaviour confirms the specific and directional nature of the halogen bonding and that the changes of spectral properties of the single PFC and HC modules **1–8** in co-crystal solutions are not due to 'generic' effects (e.g. those which may be explained in term of non-specific solute–solute interactions) but can be ascribed to specific, directional, and selective N···I–R_f intermolecular interactions. Indeed, *n*-perfluorohexane and *n*-perfluorooctane, which can be involved only in 'generic' solute–solute interactions, showed no chemical shift difference when in the presence of up to 20 equiv. of donors **2**, **4**, or **5**.

The basic character of different nitrogen moieties towards iodine acceptors in iodoperfluoroalkanes can be partly anticipated from the basic character towards proton acceptors so that the magnitude of the interaction induced shift of the $-CF_2I$ signals can be partly anticipated considering the strength of the base as proton acceptor. The higher the hybridisation state of a given basic heteroaton is, the larger the $-CF_2I$ shift it induces is.[38a] Consistent with this generalisation, infinite networks **9** and **10**, containing the pyridine donor motif, give $\Delta\delta$ values which are smaller than those observed for equimolar solutions of infinite networks **11–14** which contain di- or trialkylamine donor motifs. For instance, adduct **9a** (0.12 M solution) shows $\Delta\delta_{\mathrm{ICF2-}}=0.30$ and at the same molar concentration, adducts **11a** and **12a** give rise to $\Delta\delta_{\mathrm{ICF2-}}=1.24$ and 1.20, respectively. The different sensitivity of the hydrogen bonding and the halogen bonding to the steric hindrance around the lone pair of the donor has been tested on specifically tailored basic motifs and will be discussed in the future.

Conclusions

The attractive intermolecular N···I–R_f interaction, namely 'halogen bonding', can be successfully employed as a general protocol to overcome the low affinity existing between PFCs and HCs in the solid and in the liquid phase. This interaction is specific, directional, and strong enough to drive the self-assembly of different diiodo-PFCs and dinitrogen-HCs into supramolecular architectures. The recognition pattern involves structurally different PFC and HC modules, being largely independent from the overall structure of them. The reiteration of this donor–acceptor interaction at either ends of the two modules allows them to self-assemble into 1D infinite chains.

IR and Raman spectroscopies provide powerful tools to detect the formation of 'halogen bonded' adducts and to elucidate the $n\rightarrow\sigma^*$ nature of the N···I non-covalent interaction which has been interpreted in terms of charge-transfer complexes. The changes shown by the vibrational spectra of the single HC and PFC components when involved in the formation of the co-crystal, can be used as diagnostic probes for the existence of the interaction and as sensitive parameters to rank their electron-donor or electron-acceptor ability, respectively.

Single crystal X-ray analyses confirmed the $n\rightarrow\sigma^*$ nature of the N···I–R_f interaction being the N···I bonding on the elongation of the C–I bond with the value of the N···I–C angle near to 180°. The structural features of these infinite chains, studied with various analytical techniques, strictly parallel to those of analogous co-crystals given by halogens, interhalogens, and pseudohalogens so that an analogy between α,ω-diiodo-PFCs and those compounds can be identified. The relevance of the N···I–R_f interaction in driving the self-assembly of the PFC and HC moieties and its substantial stabilising contribution in the packing of the resulting infinite chains is shown by their differential scanning analyses. The strength of this non-covalent binding plays a key role in controlling the melting points of the formed co-crystals which all melt at higher temperatures than starting materials. The ability of the 'halogen bonding' to overpower the low affinity existing between PFCs and HCs is also confirmed by the crystal structure of the complexes in which reminiscences of the low affinity between HC and PFC modules are clearly shown by their microsegregation into layers joined only by N···I–R_f interactions.

The importance of the N···I–R_f interactions in solution was proven through NMR spectroscopy. ^{19}F NMR revealed as a simple, sensitive, and convenient tool to establish the occurrence of the interaction and to rank the ability of PFC and HC modules to be involved in this electron donor–acceptor interaction also in the liquid phase. So both aliphatic and aromatic diiodo-PFCs as well as aliphatic and aromatic dinitrogen-HC are involved in this non-covalent bonding. ^{19}F NMR studies show how sp^3 hybridised N is a better donor than sp^2 hybridised N and how secondary amines are better donors than tertiary amines. A wide variety of electron donors give rise in the liquid phase to strong attractive contacts with perfluoroalkyliodides, but the specificity and the strength of the $\mathrm{N}\cdots\mathrm{I{-}R_f}$ intermolecular interaction exclusively drive the recognition pattern even in the presence of other competitive heteroatomic donor sites in the HC module. Indeed, in co-crystals **11a–d** and **14a–d** the nitrogen atoms but not the oxygen atoms are involved in halogen bonds with iodine atoms of PFC components.

In conclusion, the results described in this paper offer new opportunities in the design and manipulation of molecular aggregation processes. The halogen bonding may begin to be considered as a first choice intermolecular interaction in crystal engineering.[2,40] The importance of having such interactions of substantial strength and stability that can drive intermolecular recognition processes is particularly high when they involve a class of molecules of great technological relevance, such as PFC compounds,[41] and this importance extends to quite different fields such as supramolecular chemistry and drug design.[42]

Experimental

^{19}F NMR spectra were recorded on a Bruker AC 250 spectrometer at 25°C and at 235.3 MHz, chemical shifts (δ) are given in ppm, unless otherwise stated $CDCl_3$ was used as solvent and $CFCl_3$ as internal standard. The IR and Raman spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrophotometer and a Nicolet 905 FT-Raman system, respectively. Thermal analyses were recorded with a heat flux calorimeter DSC 820 Mettler (silver furnace, ceramic sensor, with 14 Au–AuPd thermocouples). Elemental analyses were performed by Redox Snc, Cologno Monzese, Milano, Italy. X-Ray crystal structures were determined using a Siemens P4 diffractometer. Analytical data of pure modules **1–8** are also reported, when necessary, in order to show the differences with respect to the data for the corresponding co-crystals **9–15** due to the presence of the $\mathrm{N}\cdots\mathrm{I}$ interaction.

General procedure for the synthesis of co-crystals 9a–d

The 1D infinite networks **9a–d** were obtained by dissolving, at room temperature and in a vial, equimolar amounts of 4,4′-dipyridyl (**2**) and α,ω-diiodoperfluoroalkanes **1a–d**. Acetone, or chloroform, was used as solvent. The open vial was closed in a cylindrical bottle containing vaseline oil or *n*-pentane. Volatile solvents were allowed to diffuse at room temperature and after one day the formed white crystals were filtered and washed with *n*-pentane.

Co-crystal 9a formed by 4,4′-dipyridyl (2) and 1,2-diiodotetrafluoroethane (1a). Elemental analyses (%): calcd for $C_{12}H_8N_2I_2F_4$: C 28.26, H 1.58, N 5.49, I 49.76, F 14.9; found C 27.72, H 1.48, N 5.45, I 49.51, F 15.52. Mp **2** (chloroform) 111–114°C; mp **9a** (acetone) 164–170°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): diamine **2**: 3027, 1591, 1407, 1219, 807, 608; diiodoperfluoroalkane **1a**: 1159, 1108, 975, 835, 709; co-crystal **9a**: 3029, 1591, 1406, 1118, 1086, 1061, 801, 698, 611. ^{19}F NMR: diiodoperfluoroalkane **1a**: $\delta_\mathrm{F}=-53.89$; co-crystal **9a**: $\Delta\delta_\mathrm{F}=\delta_{\text{pure }\mathbf{1a}}-\delta_{\mathbf{9a}\ (0.12\ \mathrm{M})}=0.30$.

Co-crystal 9b formed by 4,4′-dipyridyl (2) and 1,4-diiodoperfluorobutane (1b). Elemental analyses (%): calcd for $C_{14}H_8N_2I_2F_8$: C 27.54, H 1.31, N 4.59, I 41.64, F 24.92; found C 27.16, H 1.61, N 4.19, I 41.04, F 25.49. Mp (acetone) 158–163°C. IR (KBr/ν/cm^{-1}, selected bands): diiodoperfluoroalkane **1b**: 1196, 1136, 1042, 889, 764, 718, 637; co-crystal **9b**: 3033, 1590, 1407, 1182, 1130, 1045, 803, 630, 613. ^{19}F NMR: diiodoperfluoroalkane **1b**: $\delta_{\mathrm{(IC}F\mathrm{2CF2)2}}=-60.07$, $\delta_{\mathrm{(ICF2C}F\mathrm{2)2}}=-113.39$; co-crystal **9b**: $\Delta\delta_\mathrm{F}=\delta_{\text{pure }\mathbf{1b}}-\delta_{\mathbf{9b}\ (0.07\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2-}}=0.23$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}=0.02$.

Co-crystal 9c formed by 4,4′-dipyridyl (2) and 1,6-diiodoperfluorohexane (1c). Elemental analyses (%): calcd for $C_{16}H_8N_2I_2F_{12}$: C 27.04, H 1.13, N 3.94, I 35.77, F 32.11; found C 27.23, H 1.07, N 3.88, I 35.87, F 31.91. Mp **9c** (acetone) 146–150°C. IR (KBr/ν/cm^{-1}, selected bands): diiodoperfluoroalkane **1c**: 1211, 1149, 1122, 1090, 926, 632, 554; co-crystal **9c**: 3036, 1593, 1407, 1230, 1135, 1078, 805, 614. Raman (ν/cm^{-1}/selected bands): diamine **2**: 3043, 1620, 1600, 1294, 1000; co-crystal **9c**: 3075, 1600, 1288, 1055, 1000, 750, 256. ^{19}F NMR: diiodoperfluoroalkane **1c**: $\delta_{\mathrm{(IC}F\mathrm{2CF2CF2)2}}=-60.24$, $\delta_{\mathrm{(ICF2C}F\mathrm{2CF2)2}}=-114.27$, $\delta_{\mathrm{(ICF2CF2C}F\mathrm{2)2}}=-122.13$; co-crystal **9c**: $\Delta\delta_\mathrm{F}=\delta_{\text{pure }\mathbf{1c}}-\delta_{\mathbf{9c}\ (0.05\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2)2}}=0.22$, $\Delta\delta_{\mathrm{(ICF2C}F\mathrm{2CF2)2}}=0.02$, $\Delta\delta_{\mathrm{(ICF2CF2C}F\mathrm{2)2}}=0.01$.

Co-crystal 9d formed by 4,4′-dipyridyl (2) and 1,8-diiodoperfluorooctane (1d). Elemental analyses (%): calcd for $C_{18}H_8N_2I_2F_{16}$: C 26.67, H 0.99, N 3.46, I 31.36, F 37.53; found C 27.07, H 1.29, N 3.86, I 30.76, F 36.93. Mp (acetone) **9d** 152–158°C. IR (KBr/ν/cm^{-1}, selected bands): diiodoperfluoroalkane **1d**: 1207, 1150, 1113, 836, 641, 556; co-crystal **9d**: 3036, 1593, 1234, 1142, 1101, 1056, 805, 614, 548. ^{19}F NMR: diiodoperfluoroalkane **1d**: $\delta_{\mathrm{(IC}F\mathrm{2CF2CF2CF2)2}}=-60.33$, $\delta_{\mathrm{(ICF2C}F\mathrm{2CF2CF2)2}}=-114.28$, $\delta_{\mathrm{(ICF2CF2C}F\mathrm{2CF2)2}}=-122.10$, $\delta_{\mathrm{(ICF2CF2CF2C}F\mathrm{2)2}}=-122.91$; co-crystal **9d**: $\Delta\delta_\mathrm{F}$ (ppm)$=\delta_{\text{pure }\mathbf{1d}}-\delta_{\mathbf{9d}\ (0.05\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2CF2-}}=0.19$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2CF2-}}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2CF2-}}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}=0.03$.

General procedure for the synthesis of co-crystals 10a–d

The infinite networks **10a–d** were obtained through crystallisation, at room temperature, of equimolar solutions of (*E*)-1,2-bis(4-pyridyl)ethylene (**3**) and α,ω-diiodoperfluoroalkanes **1a–d** in acetone through the diffusion technique described above. The obtained co-crystals were separated and washed with *n*-pentane.

Co-crystal 10a formed by (*E*)-1,2-bis(4-pyridyl)ethylene (3) and 1,2-diiodotetrafluoroethane (1a). Elemental analyses (%): calcd for $C_{14}H_{10}N_2I_2F_4$: C 31.34, H 1.87, N 5.22, I 47.39, F 14.18; found C 31.74, H 2.17, N 4.82, I 46.79, F 13.68. Mp (acetone) 177–181°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): diamine **3**: 3020; co-crystal **10a**:

3038, 1123, 1084, 699. ^{19}F NMR: co-crystal **10a**: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1a}}-\delta_{\mathbf{10a}\ (0.12\ \mathrm{M})}=0.38$.

Co-crystal 10b formed by (*E*)-1,2-bis(4-pyridyl)ethylene (3) and 1,4-diiodoperfluorobutane (1b). Elemental analyses (%): calcd for $C_{16}H_{10}N_2I_2F_8$: C 30.19, H 1.57, N 4.4, I 39.94, F 23.89; found C 30.55, H 2.07, N 4.0, I 39.34, F 23.35. Mp (acetone) 185–190°C. IR (KBr/ν/cm^{-1}, selected bands): 3030, 1197, 1187, 1120, 1109, 628. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1b}}-\delta_{\mathbf{10b}\ (0.07\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2-}}=0.26$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}=0.01$.

Co-crystal 10c formed by (*E*)-1,2-bis(4-pyridyl)ethylene (3) and 1,6-diiodoperfluorohexane (1c). Elemental analyses (%): calcd for $C_{18}H_{10}N_2I_2F_{12}$: C 29.35, H 1.36, N 3.80, I 34.51, F 30.98; found C 29.75, H 1.66, N 4.25, I 33.91, F 30.39. Mp (acetone) 170–176°C. IR (KBr/ν/cm^{-1}, selected bands): 3031, 1134, 1117,1077. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1c}}-\delta_{\mathbf{10c}\ (0.05\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2-}}=0.19$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2-}}=0.01$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2-}}=0.01$.

Co-crystal 10d formed by (*E*)-1,2-bis(4-pyridyl)ethylene (3) and 1,8-diiodoperfluorooctane (1d). Elemental analyses (%): calcd for $C_{20}H_{10}N_2I_2F_{16}$: C 28.71, H 1.19, N 3.35, I 30.38, F 36.36; found C 29.11, H 1.49, N 2.95, I 29.83, F 35.76. Mp (acetone) 160–165°C IR (KBr/ν/cm^{-1}, selected bands): 3042, 1141, 1096. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1d}}-\delta_{\mathbf{10d}\ (0.05\ \mathrm{M})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2CF2-}}=0.21$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2CF2-}}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2CF2-}}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}=0.03$.

General procedure for the synthesis of co-crystals 11a–d

The complexes **11a–d** were obtained by dissolving, at room temperature and in a vial, equimolar amounts of kryptofix 2.2. **4** and α,ω-diiodoperfluoroalkanes **1a–d** in chloroform (carbon tetrachloride can also be used as solvent). The open vial was closed in a cylindrical bottle containing vaseline oil or *n*-pentane. Volatiles were allowed to diffuse at room temperature. After 1 day white crystals were isolated, filtered and washed with *n*-pentane.

Co-crystal 11a formed by K.2.2. 4 and 1,2-diiodotetrafluoroethane (1a). Elemental analyses (%): calcd for $C_{14}H_{26}N_2O_4I_2F_4$: C 27.29, H 4.25, N 4.54, I 41.19; found C 27.01, H 4.48, N 4.71, I 41.56. Mp **4** (chloroform) 111–114°C; mp **11a** (chloroform) 115–121°C (dec.). IR (KBr/ν/cm^{-1}; selected bands): diamine **4**: 2884, 2821, 1094, 961, 781; co-crystal **11a**: 2881, 1114, 1085, 699. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}$ (ppm)$=\delta_{\text{pure }\mathbf{1a}}-\delta_{\mathbf{11a}\ (0.13\ \mathrm{M})}=1.24$.

Co-crystal 11b formed by K.2.2. 4 and 1,4-diiodoperfluorobutane (1b). Elemental analyses (%): calcd for $C_{16}H_{26}N_2O_4I_2F_8$: C 26.83, H 3.66, N 3.91, I 35.44; found C 26.52, H 3.97, N 4.11, I 35.14. Mp (chloroform) 91–97°C (dec.). IR (KBr/ν/cm^{-1}; selected bands): 2892, 1183, 1124, 1104, 1043, 954, 764, 632. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}$ (ppm)$=\delta_{\text{pure }\mathbf{1b}}-\delta_{\mathbf{11b}\ (0.07\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2-}}=1.05$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}=0.13$.

Co-crystal 11c formed by K.2.2. 4 and 1,6-diiodoperfluorohexane (1c). Elemental analyses (%): calcd for $C_{18}H_{26}N_2O_4I_2F_{12}$: C 26.48, H 3.21, N 3.43, I 31.09; found C 26.22, H 3.37, N 3.51, I 30.86. Mp (chloroform) 112–118°C (dec.). IR (KBr/ν/cm^{-1}; selected bands): 2903, 2875, 1192, 1162, 1150, 1110, 986, 591. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1c}}-\delta_{\mathbf{11c}\ (0.05\ \mathrm{M})}$, $\delta_{\mathrm{IC}F\mathrm{2CF2CF2-}}=0.71$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2-}}0.07$, $\Delta_{\delta\mathrm{ICF2CF2C}F\mathrm{2-}}=0.02$.

Co-crystal 11d formed K.2.2. 4 and 1,8-diiodoperfluorooctane (1d). Elemental analyses (%): calcd for $C_{20}H_{26}N_2O_4I_2F_{16}$: C 26.22, H 2.86, N 3.06, I 27.70; found C 25.89, H 3.08, N 3.21, I 28.00. Mp (chloroform) 103–110°C (dec.). IR (KBr/ν/cm^{-1}; selected bands): 2909, 2877, 1199, 1105, 628, 547. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{iodide }\mathbf{1d}}-\delta_{\mathbf{11d}\ (0.05\ \mathrm{M})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2CF2-}}=0.74$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2CF2-}}0.10$, $\Delta_{\delta\mathrm{ICF2CF2C}F\mathrm{2CF2-}}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}=0.03$.

General procedure for the synthesis of co-crystals 12a–d

The infinite networks **12a–d** were isolated through crystallisation, at room temperature and in a vial, of equimolar solutions of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (**5**) and α,ω-diiodoperfluoroalkanes **1a–d** in chloroform (dichloromethane can also be used as solvent). The open vial was closed in a cylindrical, wide mouth bottle containing vaseline oil or *n*-pentane. Volatiles were allowed to diffuse at room temperature. After 1 day white crystals were isolated, filtered and washed with *n*-pentane.

Co-crystal 12a formed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5) and 1,2-diiodotetrafluoroethane (1a). Elemental analyses (%): calcd for $C_8H_{16}N_2I_2F_4$: C 20.43, H 3.40, N 5.96, I 54.04; found C 20.78, H 3.58, N 6.24, I 53.44. Mp(chloroform) 116–121°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): diamine **5**: 2945, 2817, 2767, 1460, 1033; co-crystal **12a**: 2964, 2786, 1465, 1121, 1088, 1019, 834, 791, 695. Raman (ν/cm^{-1}/selected bands): diamine **5**: 2947, 2818, 2764; diiodoperfluoroalkane **1a**: 998, 977, 670, 363, 268; co-crystal **12a**: 2960, 2835, 2790, 1216, 1171, 1000, 659, 261. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure}\mathbf{1a}}-\delta_{\mathbf{12a}(0.12\ \mathrm{M})}=1.20$.

Co-crystal 12b formed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5) and 1,4-diiodoperfluorobutane (1b). Elemental analyses (%): calcd for $C_{10}H_{16}N_2I_2F_8$: C 21.06, H 2.81, N 4.91, I 44.54, F 26.68; found C 21.66, H 2.93, N 5.32, I 43.96, F 26.10. Mp (chloroform) 189–194°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2967, 2786, 1467, 1190, 1128, 1041, 1020, 835, 764, 650, 631. Raman (ν/cm^{-1}/selected bands): diiodoperfluoroalkane **1b**: 1286, 1250, 1090, 850, 775, 594, 279; co-crystal **12b**: 2957, 2835, 2789, 1175, 1080, 856, 809, 675, 588, 263. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1b}}-\delta_{\mathbf{12b}\ (0.07\ \mathrm{M})}$, $\delta_{\mathrm{IC}F\mathrm{2CF2-}}=0.92$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}=0.09$.

Co-crystal 12c formed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5) and 1,6-diiodoperfluorohexane (1c). Elemental analyses (%): calcd for $C_{12}H_{16}N_2I_2F_{12}$: C 21.5, H 2.39, N 4.18, I 37.89, F 34.04; found C 22.10, H 2.52, N 4.29, I 37.41, F 33.47. Mp (chloroform) 196–200°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2966, 2789, 1467, 1200, 1140, 1084, 834, 765, 695. Raman (ν/cm^{-1}/selected bands): 2955, 2840, 2789, 1180, 1052, 785, 269. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\text{pure }\mathbf{1c}}-\delta_{\mathbf{12c}\ (0.05\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2-}}=0.79$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2-}}=0.07$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2-}}=0.01$.

Co-crystal 12d formed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (5) and 1,8-diiodoperfluorooctane (1d). Elemental analyses (%): calcd for $C_{14}H_{16}N_2I_2F_{16}$: C 21.82 H 2.08, N 3.64, I 32.98, F 39.48; found C 22.39, H 2.68, N 4.13, I 31.84, F 38.88. Mp (chloroform) 78–84°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2835, 2786, 1467, 1214, 1150, 835, 776, 637, 556. Raman (ν/cm^{-1}/selected bands): 2955, 2834, 2786, 1175, 1081, 780, 275. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{iodide}\ \mathbf{1d}}-\delta_{\mathbf{12d}\ (0.05\ \mathrm{M})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2CF2-}}=0.84$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2CF2-}}=0.10$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2CF2-}}=0.04$, $\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}=0.04$.

General procedure for the synthesis of co-crystals 13a–d

The 1D infinite networks **13a–d** were obtained by dissolving, at room temperature and in a vial, equimolar amounts of DABCO (**6**) and α,ω-diiodoperfluoroalkanes **1a–d**. Chloroform was used as solvent. The open vial was closed in a cylindrical, wide mouth bottle containing vaseline oil or *n*-pentane. Volatile solvents were allowed to diffuse at room temperature and after one day the formed white crystals were filtered and washed with *n*-pentane.

Co-crystal 13a formed by diazabicyclooctane (6) and 1,2-diiodotetrafluoroethane (1a). Elemental analyses (%): calcd for $C_8H_{12}N_2I_2F_4$: C 20.62, H 2.60, N 6.01, I 54.47, F 16.31; found C 20.30 H, 2.92, N 6.94, I 54.91, F 16.06. Mp (chloroform) 140–146°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): diamine **6**: 2942, 2875; co-crystal **13a**: 2948, 2879, 1116, 1086, 692. Raman: (ν/cm^{-1}/selected bands): diamine **6**: 2944, 2935, 2923, 2868; diiodoperfluoroalkane **1a**: 998, 977, 670, 363, 268; co-crystal **13a**: 2973, 2951, 2925, 2878, 997, 972, 661, 363, 254. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\ \mathbf{1a}}-\delta_{\mathbf{13a}\ (\mathrm{sat.\ soln})}=1.06$.

Co-crystal 13b formed by diazabicyclooctane (6) and 1,4-diiodoperfluorobutane (1b). Elemental analyses (%): calcd for $C_{10}H_{12}N_2I_2F_8$: C 21.22, H 2.14, N 4.95, I 44.84, F 26.85; found C 20.92, H, 2.44, N 5.02, I 45.34, F 26.08. Mp (chloroform) 193–200°C(dec.). IR (KBr/ν/cm^{-1}, selected bands): 2951, 2882, 1186, 1124, 648, 631. Raman (ν/cm^{-1}/selected bands): 2973, 2951, 2925, 2881, 975, 853, 806, 681, 288, 269. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\ \mathbf{1b}}-\delta_{\mathbf{13b}(\mathrm{sat.\ soln.})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2-}}=0.89$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}=0.09$.

Co-crystal 13c formed by diazabicyclooctane (6) and 1,6-diiodoperfluorohexane (1c). Elemental analyses (%): calcd for $C_{12}H_{12}N_2I_2F_{12}$: C 21.64, H 1.82, N 4.21, I 38.11, F 34.23; found C 21.95, H 2.12, N 4.51, I 37.61, F 33.63. Mp (chloroform) 175–182°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2951, 2882, 1138, 1107, 1083. Raman (ν/cm^{-1}/selected bands): 2973, 2951, 2925, 2881, 1050, 975, 800, 788, 267. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\mathbf{1c}}-\delta_{\mathbf{13c}(\mathrm{sat.\ soln.})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2-}}=1.01$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2-}}=0.08$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2-}}=0.03$.

Co-crystal 13d formed by diazabicyclooctane (6) and 1,8-diiodoperfluorohexane (1d). Elemental analyses (%): calcd for $C_{14}H_{12}N_2I_2F_{16}$: C 21.93, H 1.57, N 3.66, I 33.16, F 39.69; found C 21.96, H 1.97, N 3.62, I 32.99, F 39.29. Mp (chloroform) 150–158°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2952, 2883, 1150, 1106, 1082, 637. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\mathbf{1d}}-\delta_{\mathbf{13d}(\mathrm{sat.\ soln.})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2CF2-}}=1.29$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2CF2-}}=0.13$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2CF2-}}=0.06$, $\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}=0.03$.

General procedure for the synthesis of co-crystals 14a–d

The infinite networks **14a–d** were obtained by dissolving, at room temperature and in a vial, equimolar amounts of kryptofix 2.2.2. **7** and α,ω-diiodoperfluoroalkanes **1a–d** in chloroform (carbon tetrachloride can also be used as solvent). The open vial was closed in a cylindrical, wide mouth bottle containing vaseline oil or *n*-pentane. Volatile were allowed to diffuse at room temperature. After one day white crystals were isolated, filtered and washed with *n*-pentane.

Co-crystal 14a formed by K.2.2.2. 7 and 1,2-diiodotetrafluoroethane (1a). Elemental analyses (%): calcd for $C_{20}H_{36}N_2O_6I_2F_4$: C 32.89, H 4.97, N 3.84, I 34.75; found C 32.96, H 5.09, N 3.99, I 34.40. Mp (chloroform) 118–123°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): diamine **7**: 2878, 2814, 1102, 950; co-crystal **14a**: 2884, 1104, 1080, 951, 694. Raman (ν/cm^{-1}/selected bands): 1220, 997, 662, 254, 132. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\mathbf{1a}}-\delta_{\mathbf{14a}(0.13\ \mathrm{M})}=0.11$.

Co-crystal 14b formed by K.2.2.2. 7 and 1,4-diiodoperfluorobuthane (1b). Elemental analyses (%): calcd for $C_{22}H_{36}N_2O_6I_2F_8$: C 31.82, H 4.37, N 3.37, I 30.57; found C 31.53, H 4.59, N 3.60, I 30.24. Mp (chloroform) 92–98°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2887, 2825, 1183, 1107, 1042, 951, 618. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\mathbf{1b}}-\delta_{\mathbf{14b}(0.08\ \mathrm{M})}$, $\delta_{\mathrm{IC}F\mathrm{2CF2-}}=0.27$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2-}}=0.03$.

Co-crystal 14c formed by K.2.2.2. 7 and 1,6-diiodoperfluorohexane (1c). Elemental analyses (%): for **14c**: calcd for $C_{24}H_{36}N_2O_6I_2F_{12}$: C 30.98, H 3.90, N 3.01, I 27.28; found C 30.68, H 4.03, N 2.76, I 27.52. Mp (chloroform) 76–80°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2886, 2817, 1206, 1106, 1081, 951, 933, 631. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{pure}\mathbf{1c}}-\delta_{\mathbf{14c}(0.05\ \mathrm{M})}$, $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2-}}=0.18$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2-}}=0.01$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2-}}=0.01$.

Co-crystal 14d formed by K.2.2.2. 7 and 1,8-diiodoperfluorooctane (1d). Elemental analyses (%): calcd for $C_{26}H_{36}N_2O_6I_2F_{16}$ C 30.31, H 3.52, N 2.72, I 24.63; found C 30.01, H 3.72, N 2.48, I 24.95. Mp (chloroform) 83–88°C (dec.). IR (KBr/ν/cm^{-1}, selected bands): 2887, 2823, 1215, 1152, 1133, 1106, 950, 556. ^{19}F NMR: $\Delta\delta_{\mathrm{F}}=\delta_{\mathrm{iodide}\mathbf{1d}}-\delta_{\mathbf{14d}(0.03\ \mathrm{M})}$: $\Delta\delta_{\mathrm{IC}F\mathrm{2CF2CF2CF2-}}=0.10$, $\Delta\delta_{\mathrm{ICF2C}F\mathrm{2CF2CF2-}}=0.01$, $\Delta\delta_{\mathrm{ICF2CF2C}F\mathrm{2CF2-}}=\Delta\delta_{\mathrm{ICF2CF2CF2C}F\mathrm{2-}}=0.00$.

Synthesis of co-crystal 15e formed by 1,2-bis-(4-pyridyl)ethane (8) and 1,4-diiodotetrafluorobenzene (1e). Following the procedure described above, equimolar amounts of 1,2-bis-(4-pyridyl)ethane (**8**) and 1,4-diiodotetrafluorobenzene (**1e**) were crystallised from acetone to give the co-crystal **15e**. Elemental analyses (%): calcd for $C_{18}H_{32}N_2I_2F_4$: C 36.86, H 2.05, N 4.78, I 43.34, F 12.97; found C 36.46, H 2.35, N 4.38, I 42.94, F 13.17. Mp **15e** (acetone) >205. IR (KBr/ν/cm^{-1}, selected bands): 2887, 2823, 1215, 1152, 1133, 1106, 950, 556.

General procedure for X-ray crystal structure determination

X-Ray diffraction data were collected from a colourless crystal with graphite monochromatic Cu K_α radiation (1.54178 Å). Lorentz and polarisation but no absorption correction were applied. The structure was solved by direct methods with SIR92[45] and refined by full-matrix least-squares against F^2, using SHELXL97.[46]

X-Ray structure determination of the co-crystal 9c formed by 4,4′-dipyridyl (2) and 1,6-diiodoperfluorohexane (1c). $C_8H_4F_6IN$; f.w. 355.02 triclinic, space group P-1, a=5.418(1) Å, b=7.332(1) Å, c=14.112(3) Å, α=92.81(3)°, β=95.44(3)°, γ=107.56(3)°; Z=2, D_c=2.223 Mg/m^{-3}; μ=24.358 mm^{-1}; F(000)=332, final R_1 (I>2.0 $\sigma(I)$)=0.0810, $wR2$ (all data)=0.2260, S=1.023; extinction coefficient=0.0055 (3); largest peak and hole=1.875 and −1.893 eÅ^{-3}. The independent unit is half of both molecules forming the co-crystal. Some conformational disorder of the perfluorodiiodide molecule is made apparent by the very large thermal factors of some fluorine atoms. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined in the riding mode.

X-Ray structure determination of the co-crystal 9d formed by 4,4′-dipyridyl (2) and 1,8-diiodoperfluorooctane (1d). $C_9H_4F_8IN$; f.w. 405.03 triclinic, space group P-1, a=5.464(1) Å, b=7.292(1) Å, c=16.142(3) Å, α=99.90(2)°, β=95.16(2)°, γ=106.89(2)°; Z=2, D_c=2.244 Mg/m^{-3}; μ=21.907 mm^{-1}; F(000)=380, final R_1 (I>2.0 $\sigma(I)$)=0.1033, $wR2$ (all data)=0.2730, S=1.293; extinction coefficient=0.021 (3); largest peak and hole=1.875 and −1.893 eÅ^{-3}. The independent unit is half of both molecules forming the co-crystal. Conformational disorder of the perfluorodiiodide molecule is made apparent by the very large thermal factors of some fluorine atoms. More detailed modelling of disorder could be attempted. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined in the riding mode.

X-Ray structure determination of the co-crystal 11a formed by K.2.2. 4 and 1,2-diiodotetrafluoroethane (1a). $C_7H_{13}F_2INO_2$; f.w. 308.08, monoclinic, space group $C2/m$, a=13.806(1) Å, b=14.783(1) Å, c=5.906(1) Å, β=106.61(1); Z=4, D_c=1.772 Mg/m^{-3}; μ=21.856 mm^{-1}; F(000)=596, final R_1 (I>2.0 $\sigma(I)$)=0.0636, $wR2$ (all data)=0.1832, S=1.038; extinction coefficient=0.0011 (3); largest peak and hole=0.769 and −0.764 eÅ^{-3}. The molecules are both located in special positions. Bond lengths, angles and torsion angles of the perhaloethane molecule were constrained according to a *quasi*-rigid-body model. The iodine atom and the cryptand non-hydrogen atoms were refined anisotropically while disordered atoms of the perfluorodihalide and hydrogens were treated isotropically; hydrogen atoms were located at calculated positions and refined in the riding mode. Ordered K2.2. molecules are placed with the N atoms on the mirror plane and the midpoint of the C3–C3A bond on the twofold axis, fully exploiting the fact that the molecular symmetry coincides with the 2/*m* space group symmetry. The diiodotetrafluoroethane species has the iodine atoms on the *m* plane, the twofold axis running through the inversion centre at the midpoint of the C1′–C1′B bond, and shows rotational disorder around the I1···I1A intramolecular vector.

X-Ray structure determination of the co-crystal 12a formed by *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (5) and 1,2-diiodotetrafluoroethane (1a). $C_4H_8F_2IN$; f.w. 235.02 monoclinic, triclinic, space group P-1, a=6.380(1) Å, b=6.808(1) Å, c=9.242(1) Å, α=109.20(2)°, β=96.86(1)°, γ=94.95(1)°; Z=2, D_c=2.093 Mg/m^{-3}; μ=33.370 mm^{-1}; F(000)=220, final R_1 (I>2.0 $\sigma(I)$)=0.0650, $wR2$ (all data)=0.2047, S=1.373; largest peak and hole=0.769 and −0.764 eÅ^{-3}. The independent unit is half of both molecules forming the co-crystal. Bond lengths, angles and torsion angles of the perhaloethane molecule were constrained according to a *quasi*-rigid-body model. Only the iodine atom was refined anisotropically while disordered atoms of the diamine, of the perfluorodihalide and hydrogens were treated isotropically. Hydrogen atoms were located at calculated positions and refined in the riding mode.

X-Ray structure determination of the co-crystal 14a formed by K.2.2.2. 7 and 1,2-diiodoteterafluoroethane (1a). $C_{20}H_{36}F_4I_2N_2O_6$; f.w. 308.08, monoclinic, space group $C2/c$, a=15.917(2) Å, b=23.778(2) Å, c=8.714(1) Å, β=123.17(1); Z=4, D_c=1.757 Mg/m^{-3}; μ=18.457 mm^{-1}; F(000)=1440,: final R_1 (I>2.0 $\sigma(I)$)=0.0803, $wR2$ (all data)=0.2362, S=1.041; extinction coefficient=0.0012 (2); largest peak and hole=2.502 and −1.621 eÅ^{-3}. Bond lengths, angles and torsion angles of the perhaloethane molecule were constrained according to a simple *quasi*-rigid-body model involving two equally populated molecular orientations. The iodine atom and the cryptand non-hydrogen atoms were refined anisotropically while disordered atoms of the perfluorodihalide and hydrogens were treated isotropically; hydrogen atoms were located at calculated positions and refined in the riding mode.

X-Ray structure determination of the co-crystal 15e formed by 1,2-bis-(4-pyridyl)ethane (8) and 1,4-diiodotetrafluorobenzene (1e). Data were collected using $\lambda_{\text{Cu-K}_\alpha}$=1.54178 Å, $\theta/2\theta$ scan mode (3.5≤θ≤70.0°, at 293(2) K and corrected for Lorentz, polarisation and absorption; the structure was solved by direct methods using SIR97[45] and refined using SHELX 97[46] against F^2, with hydrogen atoms at calculated positions in the riding mode. Crystal data are as follows: 0.65×0.50×0.35 mm^3, triclinic, space group P-1, a=5.032(2) Å, b=9.902(4), 10.598(5) Å, α=64.70(3)°, β=82.24(4)°, γ=87.94(4)°; V=472.9(5) Å^3; Z=1; ρ_c=2.058 g cm^{-3}, μ=26.5 mm^{-1}; 2151 collected reflections, 1588 independent, 119 refined parameters, R_1=0.067 (for 1573 data with I≥2$\sigma(I)$). Further crystallographic details of the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 137462. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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