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Perfluorocarbon–hydrocarbon self-assembly. Part 16: Anilines as new electron donor modules for halogen bonded infinite chain formation☆

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Abstract—*N,N,N′,N′*-tetramethyldianilines are well known donor modules tailored to π,π-interaction driven self-assembly processes. When *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (**1a**) and bis[4-(*N,N*-dimethylaminophenyl)]methane (**1c**) interact with 1,4-diiodotetrafluorobenzene (**2**), the halogen bonding organises the perfluorocarbon and hydrocarbon modules into the one dimensional linear networks **3a,c** overcoming the low affinity between the perfluorocarbon and hydrocarbon modules and their tendency to give π,π stacks. The general effectiveness of *N,N,N′,N′*-tetramethyldianilines as specifically tailored *telechelic* modules in the *exo*-recognition of dihaloperfluorocarbons has been demonstrated. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Perfluorocarbon derivatives are characterised by a unique set of chemical and physical properties. For instance, due to the high ionisation energy of fluorine atom and its low polarisability, perfluorocarbon residues are characterised by weak intermolecular interactions and low surface energies. Heats of solution and cohesive pressures of perfluorocarbons (PFCs) are quite different from those of corresponding hydrocarbons (HCs) and enthalpies of interaction between PFCs and HCs are smaller than interaction enthalpies between HCs. Perfluorinated alkanes, ethers, and tertiary amines are practically insoluble in water and their miscibility with many organic solvents is limited.[1] Consequently, supramolecular architectures compounded by PFC and HC modules are hardly accessible and their structure, reactivity, and functional properties are scarcely explored. The best-studied PFC–HC systems are the di- and triblock derivatives where the PFC and HC chains are bound through a covalent bond (R_F–R_H and R_F–R_H–R_F, respectively, R_F: perfluoroalkyl, R_H: alkyl). These derivatives are endowed with very specific and useful properties, for instance they form micelles, inverse micelles, artificial liposomes.[2]

We are investigating a different approach to PFC–HC supramolecular systems where the PFC and HC parts are not bound each other through a covalent bond, as in the above discussed di- and triblock derivatives, but through the halogen bonding which is an attractive, non-covalent interaction occurring between electron poor halogen atoms and lone pair possessing heteroatoms.[3] The interaction is specific, directional and strong enough to overcome the low affinity existing between PFC and HC derivatives and to drive their self-assembly into supramolecular architectures. The effectiveness and reliability of the halogen bonding in forming one-dimensional (1D) infinite networks starting from PFC–dihalides and dinitrogen substituted HCs has been demonstrated.[4] The formed solids are crystalline materials stable in the air at room temperature.

Until now dibromoperfluoroalkanes and -arenes,[4f,g] as well as mono-[5] or diiodoperfluoroalkanes and -arenes[4a–e] have been used as electron–acceptor modules and aliphatic amines or pyridine derivates[3a,4,5] have been employed as electron–donor modules. To generalise the use of the halogen bonding as a versatile tool in crystal engineering new and convenient donor modules have to be identified. In this paper we describe the results achieved using aniline derivatives. Specifically, the interaction between *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (**1a**, TMPDA) or bis[4-(*N,N*-dimethylaminophenyl)]methane (**1c**) and 1,4-diiodotetrafluorobenzene (**2**) is described in solution and in the solid state.

☆ For part 15 see Ref. 4a.

Keywords: donor–acceptor interactions; iodine; halogen bonding; perfluorocarbon compounds; supramolecular chemistry.

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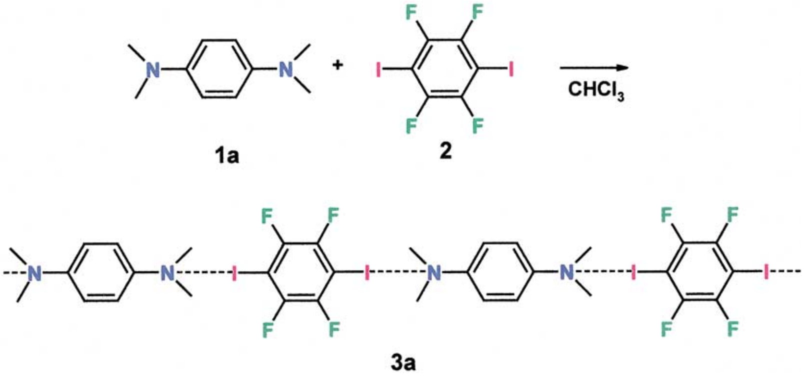


Scheme 1. 1D infinite chain **3a** formed by *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (**1a**) and 1,4-diiodotetrafluorobenzene (**2**).

2. Results and discussion

On evaporation of a chloroform solution of **1a** and **2**, the infinite chain **3a** precipitates in the form of yellowish co-crystals (Scheme 1).

The crystals are stable at room temperature for months in the dark and become green on prolonged standing in the light. This behaviour can be due to a photoinduced single electron-transfer (SET) reaction between **1a**, which is known to work as electron-donor in photochemical reactions,[6] and **2**, which could work as electron-acceptor. Indeed, the single crystal X-ray diffraction of **3a** (Fig. 1, Table 1) proves that the halogen bonding pre-organises the PFC and HC modules towards an electron transfer from nitrogen to iodine, consistent with the suggestion of the halogen bonding as a pre-reactive state.[7] In fact, in the infinite chain **3a** where the PFC and HC module alternate, the N···I distance is 2.935(2) Å, definitively shorter than the sum of nitrogen and iodine van der Waals radii[8] and strictly similar to distances observed in analogous systems formed by diiodo-PFCs and other dinitrogen substituted HCs.[3a,4,5] As required by the n→σ* character of the halogen bonding,[9] the C–I bond lengthens on co-crystal formation (2.091 Å in **3a** and 2.075 Å in pure **2**[10]) and the N···I interaction develops on the extension of the C–I bond (C–I···N angle 174.04(7)°). Moreover, on halogen bonding formation the nitrogen atoms undergo a clear pyramidalisation as shown by the fact that if a tetrahedron is built where three edges are the carbon–nitrogen bonds and are 1 Å long, the nitrogen

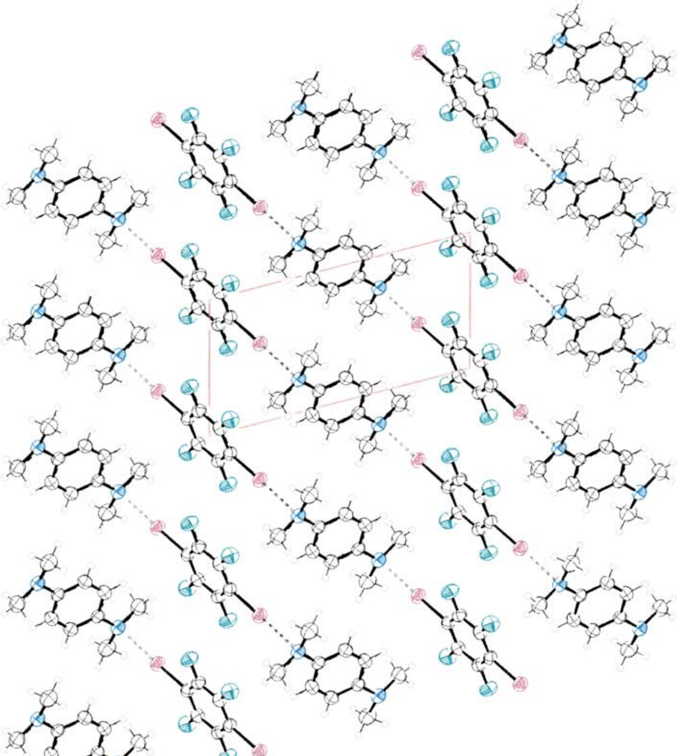


Figure 1. ORTEP view of co-crystal **3a**; dashed lines represent the halogen bonding between the PFC and HC modules. Colours are as follows: black, carbon; grey, hydrogen; blue, nitrogen; violet, iodine; green, fluorine.

Table 1. Details of data collection and of structure refinement for **3a** and **3c**

Compound	**3a**	**3c**
Formula	$C_{10}H_{16}N_2–C_6F_4I_2$	$C_{17}H_{22}N_2–C_6F_4I_2$
M_r	566.01	656.23
Crystal dimensions (mm^3)	0.44×0.20×0.16	0.36×0.12×0.11
System, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$
a (Å)	6.1250(5)	7.968(2)
b (Å)	6.4081(5)	9.203(2)
c (Å)	12.4018(11)	32.409(6)
α (°)	103.516(7)	
β (°)	94.355(6)	91.470(8)
γ (°)	101.427(6)	
V (Å^3)	460.07(7)	2375.8(9)
Z, D_c (gcm^{-3}), μ(Mo Kα) (mm^{-1})	1, 2.043, 3.456	4, 1.835, 2.691
N. refl. collected, independent, observed [$I_0>2\sigma(I_0)$]	4489, 2653, 2477	15656, 2715, 2501
R_{ave}	0.0154	0.239
Refined parameters, goodness-of-fit	141, 1.143	162, 1.283
$R(F)$ on all reflections, $R(F)$ on observed	0.0211, 0.0233	0.401,0.468
$wR(F^2)$ on all reflections, $wR(F^2)$ on observed	0.0529,0.0518	0.0633, 0.0659
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.59, 0.44	−0.83, 0.63

atom distance from the opposite face is 0.222 Å in donor–acceptor network **3a** and 0.163 Å in pure donor **1a**.[11,12]

A careful survey of the literature (Cambridge Structural Database included; CSD, version 5.1.10, 1 October 2000, 224000 crystal structures having atomic co-ordinates available) revealed that TMPDA **1a** has been widely studied for its tendency to form complexes with various partners.[13] The structural characterisation[12,14] of adducts formed by **1a** confirms the indications resulting from studies in the liquid and gas phases that the module **1a** has a strong preference to work as a π rather than an n electron donor.

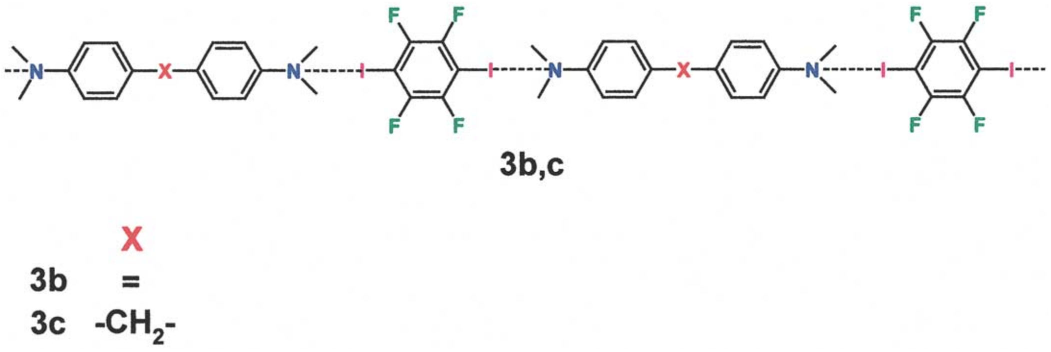
The X-ray structure of the 1:1 co-crystal between TMPDA **1a** and hexafluorobenzene[15] is particularly interesting. It consists of infinite columns stacking alternately PFC and HC modules. The rings of these modules are held in a nearly coplanar arrangement by their large quadrupolar moments which are similar in magnitude yet opposite in sign.[16] TMPDA **1a** is thus a reliable and convenient module if the intermolecular recognition through π–π stacking interaction is pursued. Also 1,4-diiodotetrafluorobenzene **2** can self-assemble with electron rich benzene derivatives through π–π interactions.[17]

In the co-crystal **3a** the halogen bonding prevails over the π–π interaction and drives the self-assembly of **1a** and **2**. The PFC and HC modules are not co-planar (the angle between the two least square planes through the two phenyl rings is 109.9°) and they alternate in a linear rather than stacked fashion. The module segregate into separate PFC and HC layers held together by the N···I interaction. The low affinity existing between PFC and HC derivatives[1] may favour this crystal packing where segregation is allowed.

The halogen-bonding markedly affects the IR and Raman absorptions of pure HC and PFC modules **1a** and **2** in co-crystal **3a**. Most of the vibrations of the acidic and basic modules, **1a** and **2**, respectively, are present in co-crystal **3a** and the expected[18] modifications with respect to the pure modules are also observed. In IR spectra the most noticeable changes are associated with the C–H and C–F stretching modes in the 2700–3100 and 1550–1400 cm^{-1} regions which are shifted to higher and lower frequencies, respectively. Raman spectra of **3a** also showed a high frequency shift of the C–H absorptions (3000–3100 cm^{-1} region) compared to pure **1a** along with a lower frequency shift of the C–I stretching ($\Delta\nu$=4 cm^{-1}) compared to pure **2**.

The thermal characterisation by differential scanning calorimetry (DSC) of infinite network **3a** indicates the presence in the co-crystal of well defined molecular aggregates and thus reveals that the halogen bonding between **1a** and **2** is a strong intermolecular interaction. Theoretical calculations[4g,19] and experimental results[20] have shown that a medium strength halogen bonding between a PFC iodide and an HC nitrogen donor is approximately 30 kJ/mol. Melting endotherms of pure components **1a** and **2** (49–51 and 108–110°C, respectively) are missing in the heating curves of co-crystals **3a** which melts at 128–130°C, higher than the starting materials as expected for the formation of new crystal species.

^{1}H and ^{19}F NMR spectra of co-crystal **3a** in solution reveal the halogen bonding is present in the liquid phase too. In $CDCl_3$ both the aromatic and aliphatic ^{1}H signals of TMPDA **1a** are not detected and in d_6-DMSO particularly broad peaks are observed near the shifts of pure **1a**. This may be related with the charge-transfer character of the



Scheme 2. 1D infinite chains **3b**,**c** formed by 1,4-diiodotetrafluorobenzene (**2**) and *N*,*N*,*N*′,*N*′-tetramethylbenzidine (**1b**) or bis[4-(*N*,*N*-dimethylaminophenyl)]methane (**1c**), respectively.

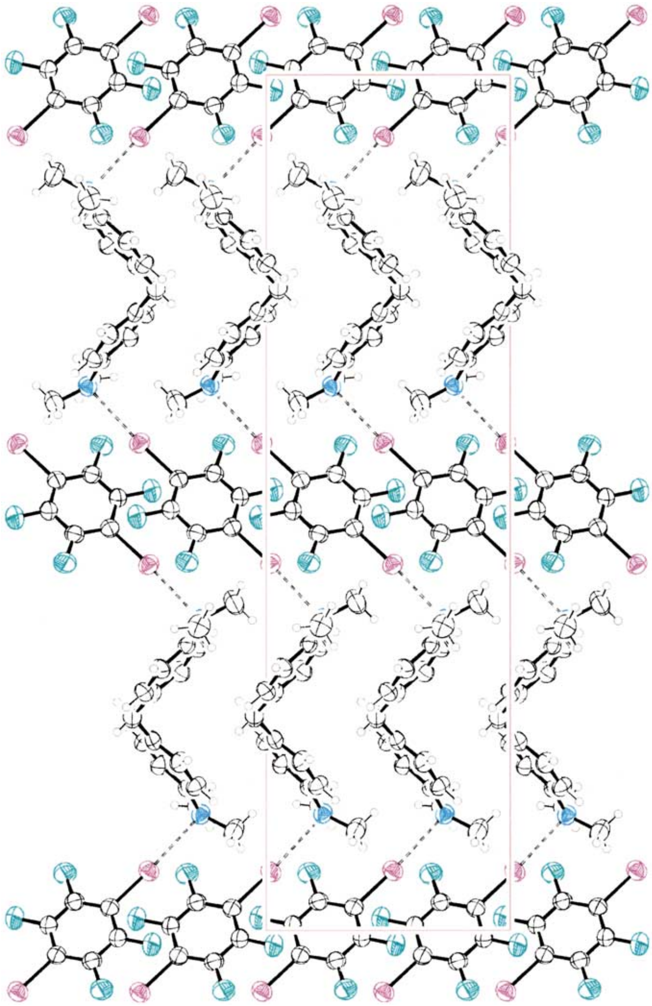


Figure 2. ORTEP view of co-crystal **3c**; dashed lines represent the halogen bonding between the PFC and HC modules. Colours are as follows: black, carbon; grey, hydrogen; blue, nitrogen; violet, iodine; green, fluorine.

interaction which forms paramagnetic species. DMSO effectively works as electron-donor towards dihaloperfluoroarenes[21] and so in this solvent the concentration of N···I bonded complexes, and related paramagnetic species, is smaller than in $CDCl_3$ and ^1H NMR signals become at least detectable. The ^{19}F NMR spectrum of **3a** in $CDCl_3$ shows the expected resonance of 1,4-diiodotetrafluorobenzene with the high field shift, with respect to pure **1a**, typical for halogen bonded PFC iodides.[21]

In order to assess the general usefulness of aniline derivatives in the intermolecular recognition of dihaloperfluoroarenes, *N*,*N*,*N*′,*N*′-tetramethylbenzidine (**1b**) and bis[4-(*N*,*N*-dimethylaminophenyl)]methane (**1c**) have also been reacted with 1,4-diiodotetrafluorobenzene (**2**) (Scheme 2).

The slow evaporation of the solvent from a 1:1 chloroform mixture containing both the electron-donor and -acceptor modules afforded pale yellow crystals of complexes **3b** and **c**. The 1:1 ratio of the PFC and HC modules was established by microanalyses (in **3b**,**c**) and by NMR in the presence of bis(2,2,2-trifluoroethyl)ether (in **3c**).

Compared to pure starting modules **1b**,**c** and **2**, the co-crystals **3b**,**c** showed, in the IR/Raman spectra, shifts of the C–H, C–F, and C–I stretching modes similar to those given by the complex **3a** and, in the ^{19}F NMR spectra, the usual[21] highfield shift of the CF resonance. The presence of the halogen bonding in **3b**,**c** in the solid phase and in solution was thus proven.

Single crystal X-ray analysis of the co-crystal **3c** (Table 1) showed that the intermolecular interaction pattern governing the module self-assembly is strictly similar to that operating in the co-crystal **3a**. The shortest contact is the N···I interaction [2.954(2) Å] which develops roughly on the extension of the C–I bond [N···I–C angle 172.3(1)°] and forms 1D infinite chains where the HC modules alternate with the PFC modules (Fig. 2).

The packing of these infinite chains in the supramolecular architecture forms layers of segregated PFC and HC modules where the phenyl rings are piled in columns developing in nearly perpendicular directions [the angles between the two least square planes through the aniline phenyl rings is 92.2(4)°[22] and between the least square planes through the two aniline rings and the diiodophenyl ring are 95.2(2) and 103.6(2)°]. The complexes reported in the literature for the bis-aniline **1c** typically involve π-acceptor species[23] (e.g. 7,7,8,8-tetracyano-*p*-quinodimethane, tetrachloro-*p*-benzoquinine, trinitrobenzene). Differently, in **3c** no π–π attractive interaction exist as the bis-aniline **1c** and the diiodide **2** are connected exclusively by the n→σ* donation from nitrogen to iodine.[24]

3. Conclusions

In conclusions, the results described in this paper definitely show how *N*,*N*,*N*′,*N*′-tetramethyldianilines **1** are new and well tailored *telechelic*[25] modules to be involved in halogen bonding driven *exo*-recognition processes. The N···I halogen bonding described here is strong enough to overcome both the low affinity existing between PFC and HC modules and their tendency to self-assemble giving rise to π–π interactions.

The self-assembly of dihaloperfluoroarenes with secondary or tertiary alkyl amines and with pyridine derivatives is quite similar to the self-assembly of dihaloperfluoroalkanes.[3a,4,5] 1D infinite networks have been obtained also through interaction of *N*,*N*,*N*′,*N*′-tetramethyldianilines **1** with dibromo- and diiodoperfluoroalkanes and presently we are trying to perform the crystallographic characterisation of these adducts.

These results offer new opportunities in the design and manipulation of molecular aggregation processes and may be useful in many fields. For instance, stoichiometric and catalytic chemical transformations in perfluorinated solvents have recently attracted the interest of several groups.[26] This approach requires reagents and catalysts which are soluble in fluorinated solvents. The preparation of these new reagents/catalysts is sometimes a challenging task as is the case, for instance, of the synthesis of porphyrins bearing a covalently bound ‘perfluorinated ponytail’.[27] The nitrogen–iodine interaction discussed in this paper offers an alternative as it can promote the solubility of hydrocarbon reagents/catalysts in PFC solvents by appending the perfluorinated ponytail in situ through a non-covalent interaction rather than a covalent bond. 5,10,15,20-Tetrakis[4-dimethylaminophenyl]-21*H*,23*H*-porphine is not soluble in *n*-perfluorohexane but the addition of 8 equiv. of 1-iodoperfluoroheptane allows 0.002 M solutions to be obtained. A similar behaviour is shown by 5,10,15,20-tetrakis[4-pyridyl]-21*H*, 23*H*-porphine revealing that motifs other than dimethylaniline can allow the solubilisation induced by non-covalent perfluoroalkylation. In general, perfluoroalkyl iodides, and bromides, may be proposed as a new class of phase transfer catalysts tailored to fluorous/solid, fluorous/aqueous, fluorous/organic two phase systems.

4. Experimental

4.1. General methods

All materials were obtained from commercial suppliers and were used without further purification. ^{19}F NMR and ^{1}H NMR spectra were recorded with a Bruker AV 500 spectrometer; $CFCl_3$ and tetramethylsilane were used as internal standard, respectively. IR and Raman spectra were recorded with a Perkin–Elmer 2000 FT-IR and a Bruker FRA 106 spectrophotometer, respectively. Selected spectral data of starting modules are reported to show the changes occurring on PFC–HC adduct formation. X-Ray crystal structures were determined using a Bruker P4 or a Bruker APEX CCD diffractometer.

4.1.1. Formation of non-covalent co-crystal 3a compounded by *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPDA, 1a) and 1,4-diiodotetrafluorobenzene (2). In a vial of clear borosilicate glass at room temperature and in the darkness, equimolar amount of TMPDA (**1a**) and of the diiodoarene **2** were dissolved. Chloroform was used as solvent. The open vial was closed in a cylindrical wide mouth bottle containing carbon tetrachloride. Volatile solvents were allowed to diffuse at room temperature. After 1 day yellow crystals of **3a** were isolated. Mp (chloroform) 130–135°C; FT-IR (KBr pellet, cm^{-1}): pure **1a**: 3049, 2943, 2785, 1521, 1323, 1216, 1057, 952, 813; pure **2**: 1465, 1214, 943, 760; co-crystal **3a**: 3051, 2960, 2809, 1518, 1455, 1304, 937, 816, 756; ^{19}F NMR ($CDCl_3$, 298 K, 0.16 M in co-crystal **3a**, ppm) δ: −118.67 (s), $\Delta\delta_F=\delta_{\text{pure }\mathbf{2}}-\delta_{\mathbf{3a}}=\Delta\delta_{IC_6F_4I}=0.13$; ^{1}H NMR ($d_6$-DMSO, 298 K, 0.16 M in co-crystal **3a**, ppm) δ: 6.68 (brs, 4H), 2.75 (brs, 12H); Raman (neat, cm^{-1}): pure **1a**: 3081, 2788, 1618, 1455, 1219, 1157, 778, 193, 87; pure **2**: 1610, 1386, 500, 443, 404, 157, 83; co-crystal **3a**: 3083, 2803, 1613, 1444, 1210, 1141, 777, 499, 151, 109.

4.1.2. Formation of non-covalent co-crystal 3b compounded by *N*,*N*,*N*′,*N*′-tetramethylbenzidine (1a) and 1,4-diiodotetrafluorobenzene (2). Co-crystals **3b** were obtained by using the procedure described above and starting from equimolar amounts of *N*,*N*,*N*′,*N*′-tetramethylbenzidine (**1b**) and the diiodoarene **2**. Acetone and carbon tetrachloride were used as solvents in the vial and in the cylindrical wide mouth bottle, respectively. Elemental analyses: (%): Calcd for $C_{22}H_{20}F_4I_2N_2$: C, 41.12; H, 3.11; F, 11.84; I, 39.56; N, 4.36; found: C, 40.90; H, 3.28; F, 11.51; I, 39.51; N, 4.80. Mp (acetone) 130–134°C; FT-IR (KBr pellet, cm^{-1}): pure **1b**: 3032, 2887, 2798, 1611, 1509, 1351, 1226, 1195, 943, 807; co-crystal **3b**: 3038, 2891, 2813, 1611, 1506, 1455, 938, 811, 758; ^{19}F NMR ($CDCl_3$, 298 K, 0.16 M in co-crystal **3b**, ppm) δ: −118.61 (s), $\Delta\delta_F=\delta_{\text{pure }\mathbf{2}}-\delta_{\mathbf{3b}}=\Delta\delta_{IC_6F_4I}=0.07$; ^{1}H NMR ($CDCl_3$, 298 K, 0.16 M in co-crystal **3b**, ppm) δ: 7.44 (d, 2H, *J*=8.8 Hz), 6.78 (d, 2H, *J*=8.8 Hz), 2.96 (s, 12H); Raman (neat, cm^{-1}): pure **1b**: 1605, 1542, 1290, 1220, 787; co-crystal **3b**: 1608, 1292, 1220, 1141, 791, 501, 155.

4.1.3. Formation of non-covalent co-crystal 3c compounded bis[4-(*N*,*N*-dimethylaminophenyl)]methane and 1,4-diiodotetrafluorobenzene (2). Co-crystals **3c** were obtained by using the procedure described above and starting from equimolar amounts of bis[4-(*N*,*N*-dimethylaminophenyl)]methane (**1c**) and the diiodoarene **2**. Chloroform and vaseline oil were used as solvents in the vial and in the cylindrical wide mouth bottle, respectively. Elemental analyses (%): Calcd for $C_{23}H_{22}F_4I_2N_2$: C, 42.07; H, 3.35; F, 11.58; I, 38.72; N, 4.27. Found: C, 41.71; H, 3.79; F, 11.22; I, 39.05; N, 4.23. Mp (chloroform) 99–103°C; FT-IR (KBr pellet, cm^{-1}): pure **1c**: 3092, 2883, 2803, 1615, 1521, 1342, 1231, 942, 795; co-crystal **3c**: 3096, 2895, 2817, 1611, 1516, 1463, 1319, 941, 757; ^{19}F NMR ($CDCl_3$, 298 K, 0.16 M in co-crystal **3c**, ppm) δ: −118.61 (s), $\Delta\delta_F=\delta_{pure\ \mathbf{2}}-\delta_{\mathbf{3b}}=\Delta\delta_{IC_6}F_4I=0.07$; ^{1}H NMR ($CDCl_3$, 298 K, 0.16 M in co-crystal **3c**, ppm) δ: 7.05 (d, 2H, J=8.8 Hz), 6.68 (d, 2H, J=8.8 Hz), 3.80 (s, 2H), 2.89 (s, 12H); ^{1}H NMR of **3c** ($CDCl_3$, 298 K) was registered in the presence of bis(2,2,2-trifluoroethyl)ether as internal standard: On calibrating the integration parameters so that the CH_2O quartet of the ether was corresponding to two and in the ^{19}F NMR spectrum the CF_3 triplet of the ether was corresponding to three, the ratio of the $-CF{=}CI$ signal area (deriving from **2**) and the $-CH_2-$ signal area (deriving from **1c**) is 2:1 revealing that the **1c/2** ratio in **3c** is 1:1; Raman (neat, cm^{-1}): pure **1c**: 3077, 2806, 1617, 1447, 1192, 1165, 834, 741, 796, 741, 89; co-crystal **3c**: 3078, 2811, 1613, 1446, 1192, 1142, 798, 499, 153, 101.

4.1.4. X-Ray crystallographic study of 3a and c. Single crystal data of **3a** and **c** were collected on a Bruker P4 (for **3a**) and on a Bruker APEX CCD (for **3c**) diffractometer with graphite monochromatised Mo Kα radiation (λ=0.71073 Å). Absorption correction was based on ψ-scans.[28] The structures were solved by *SIR*-92,[29] and refined on F^2 by SHELX-97.[30] Details of data collection and refinement are reported in Table 1. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 172272 (**3a**) and CCDC 172935 (**3c**). Copies of the data can be obtained, free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk].

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