



Halogen bonding driven self-assembly of (*E*)-1,2-diiodo-1,2-difluoroethene with nitrogen substituted hydrocarbons[☆]

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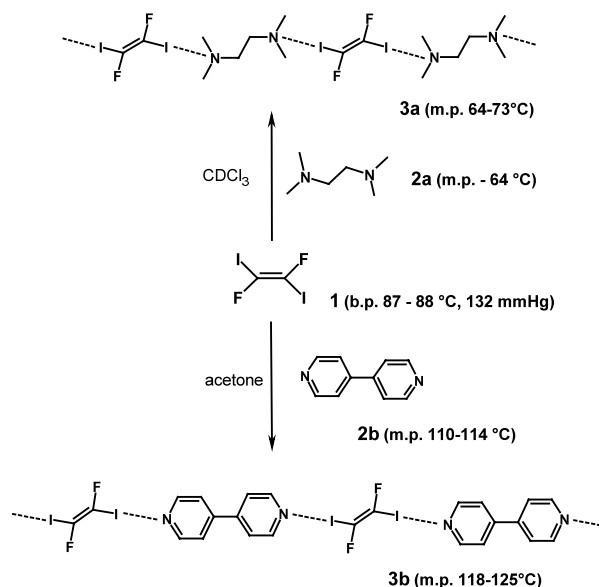
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Abstract—N⋯I halogen bondings drive the intermolecular recognition between (*E*)-1,2-diiodo-1,2-difluoroethene, which work as bidentate electron acceptor, and TMEDA or 4,4'-dipyridyl, which work as bidentate electron donors. The presence of 1D infinite chains in both co-crystals has been established through X-ray analyses. © 2003 Elsevier Science Ltd. All rights reserved.

The halogen bonding is the attractive interaction between lone pair possessing heteroatoms, which work as electron donor sites, and halogen atoms, which work as electron acceptor sites.¹ When iodo- or bromo-perfluorocarbons are used, the interaction is strong enough to overcome the low affinity existing between perfluorocarbon (PFC) and hydrocarbon (HC) derivatives and to drive their self-assembly into adducts which are stable and solid at room temperature.² Several co-crystals have been reported in which nitrogen and oxygen substituted HCs (secondary and tertiary amines,³ pyridine derivatives and their *N*-oxides,⁴ ethers⁵) are halogen-bonded to perfluoroalkyl and perfluoroaryl iodides.

In this paper the first examples are presented where an iodo-perfluoroalkene is used as electron acceptor module. We describe the structure of the one dimensional (1D) infinite networks **3a,b** obtained through the halogen bonding driven self-assembly of (*E*)-1,2-

difluoroethene (**1**) with amine and pyridine derivatives **2a,b**.



Scheme 1. Formation of 1D infinite networks **3a,b** through halogen bonding driven self-assembly of starting modules **1** and **2a,b**.

Keywords: halogen bonding; halo-perfluoroalkenes; self-assembly; co-crystals.

[☆] Perfluorocarbon–hydrocarbon self-assembly. Part 19; for Part 18 see Ref. 4e.

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Slow evaporation of a chloroform solution of **1**⁶ and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, **2a**) (ratio spanning in the range 0.5–2.0) affords the white crystalline solid **3a** where the two starting modules are present in a 1:1 ratio independent of their stoichiometry in solution⁷ (Scheme 1). Similarly, the co-crystal **3b** is obtained from an acetone solution of **1** and 4,4'-dipyridyl (**2b**).

The co-crystal **3a** melts in the range 64–73°C while both starting modules are liquid at room temperature (**1**, bp 87–88°C at 132 mmHg; **2a**, mp –64°C). Likewise, **3b** melts higher than the pure precursors (**2b**, mp 110–114°C; **3b**, mp 118–125°C). While hard to be quantified, a strict correlation exists between intermolecular interactions strength and melting point. The dramatic mp increase in halogen-bonded co-crystal **3a**, with respect to the pure starting modules, is a meaningful indication of the strength of the halogen bonding and of its ability to form well-defined chemical species.

Compared with the IR spectra of the single modules **1** and **2a**, the IR spectrum of the co-crystal **3** showed the band shifts and the band intensity variations typical for the presence of halogen bonding.^{8,3c}

Specifically, the $\nu_{\text{C-H}}$ absorptions appear at 2972 and 2766 cm^{-1} in pure **2a** and are shifted to 2981 and 2783 cm^{-1} in the co-crystal **3a** where they show a reduced intensity. These changes may be correlated with a higher positive charge on the H atoms in the adduct **3a** than in pure TMEDA as a result of the $\text{n} \rightarrow \sigma^*$ electron donation from nitrogen to iodine. Similar to what is observed when **2a** self-assembles with iodo-perfluoroalkanes and -arenes, the band appearing at 1033 cm^{-1} in pure **2a** is shifted to 1022 cm^{-1} in **3a** and its intensity decreases. The pyridine ring absorption appearing at 992 cm^{-1} in the pure bipyridine **2b** moves to 995 cm^{-1} in the adduct **3b** and similar blue shifts occur whenever pyridine derivatives function as electron donors in halogen or hydrogen bonds.⁹ As to the IR spectrum of **1**, due to the very high volatility of this molecule, literature data¹⁰ refer to gas- or liquid-phase spectra while the IR spectra of **3a,b** were obtained in the solid phase. The strong bands shown by pure **1** at 1182 and 685 cm^{-1} in the gas phase (1165 and 679 cm^{-1} in the liquid phase) appear at 1131 and 659 cm^{-1} in 1D network **3a** and at 1128 and 661 cm^{-1} in **3b**.

The structures of co-crystals **3a** and **3b** have been established through single crystal X-ray analyses at 90 K (Figs. 1 and 2, Table 1).¹¹ As to the single module arrangement, no disorder affects the HC modules **2a,b** while the PFC module **1** is disordered over two positions, simulating a cross, as sometimes happens for symmetrical ethylenes and azides.¹² In **3a**, both TMEDA and **2a** are on a centre of symmetry; here the populations of disordered **1** are equal. In **3b**, the disorder of **1** is generated through a 180° rotation along the axis connecting the two fluorine atoms; here the disordered group shows different populations, namely 73.2(3) and 26.8(3). In **3a**, the TMEDA module adopts an exact *trans* conformation^{3a} while in solution, or

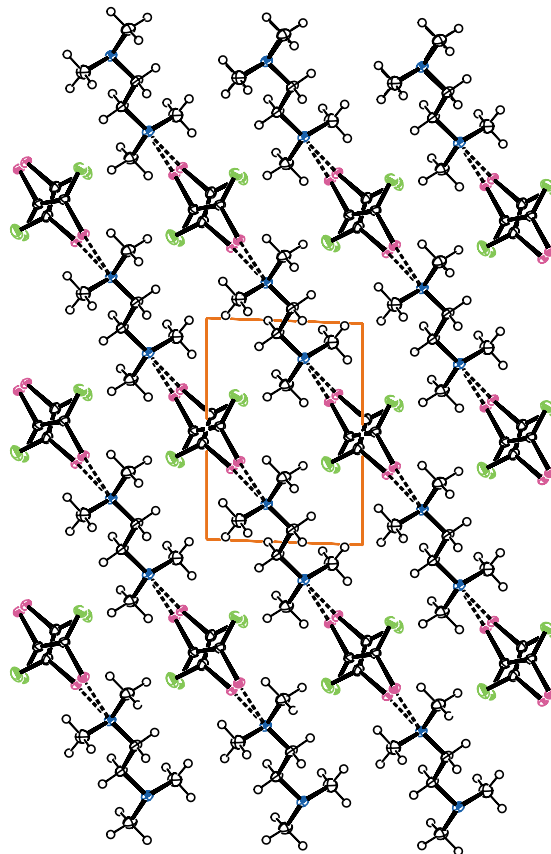


Figure 1. Packing of co-crystal **3a** viewed down the *b*-axis. Dashed lines represent the halogen bonding between the PFC and HC modules. Colours are as follows: Black, carbon and hydrogen; blue, nitrogen; violet, iodine; green, fluorine.

when chelating metal cations, it preferentially adopts a *gauche* conformation.¹³ In **3b**, the two pyridine rings of **2b** are not coplanar and form a dihedral angle of 29.2(2)°; the PFC and HC modules are nearly perpendicular to each other as shown by the angle (86.56(2)°) between the least-square planes of the disordered diiodoethylene module **1** and of the whole dipyrindyl module **2b**.

As to the supramolecular structure, the key features of the packings of **3a** and **3b** are strictly similar. 1D infinite chains are present where the PFC and HC modules, **1** and **2**, respectively, alternate and are pinned in their position by the $\text{N} \cdots \text{I}$ halogen bonding. Similar infinite chains have been observed when the same electron donors **2a,b** self-assemble with perfluoroalkyl- and perfluoroaryliodides.^{3c} The $\text{N} \cdots \text{I}$ distances associated with the disordered iodine atoms of **1** are 2.805(2) Å ($\text{N} \cdots \text{I1}$) and 2.815(2) Å ($\text{N} \cdots \text{I2}$) in **3a**, 2.781(1) Å ($\text{N} \cdots \text{I1A}$) and 2.757(1) Å ($\text{N} \cdots \text{I1B}$) in **3b**. These values are substantially shorter than the sum of van der Waals radii¹⁴ and prove the presence of strong attractive interactions between the atoms involved.

The $\text{N} \cdots \text{I}-\text{C}$ angles are approximately linear (**3a**: $\text{N} \cdots \text{I1}-\text{C}$ is 175.9(1)° and $\text{N} \cdots \text{I2}-\text{C}$ is 175.6(2)°; **3b**: $\text{N} \cdots \text{I1A}-\text{C}$ is 179.2(1)° and $\text{N} \cdots \text{I1B}-\text{C}$ is 171.2(1)°). Then nitrogen atoms meet iodine atoms roughly in line

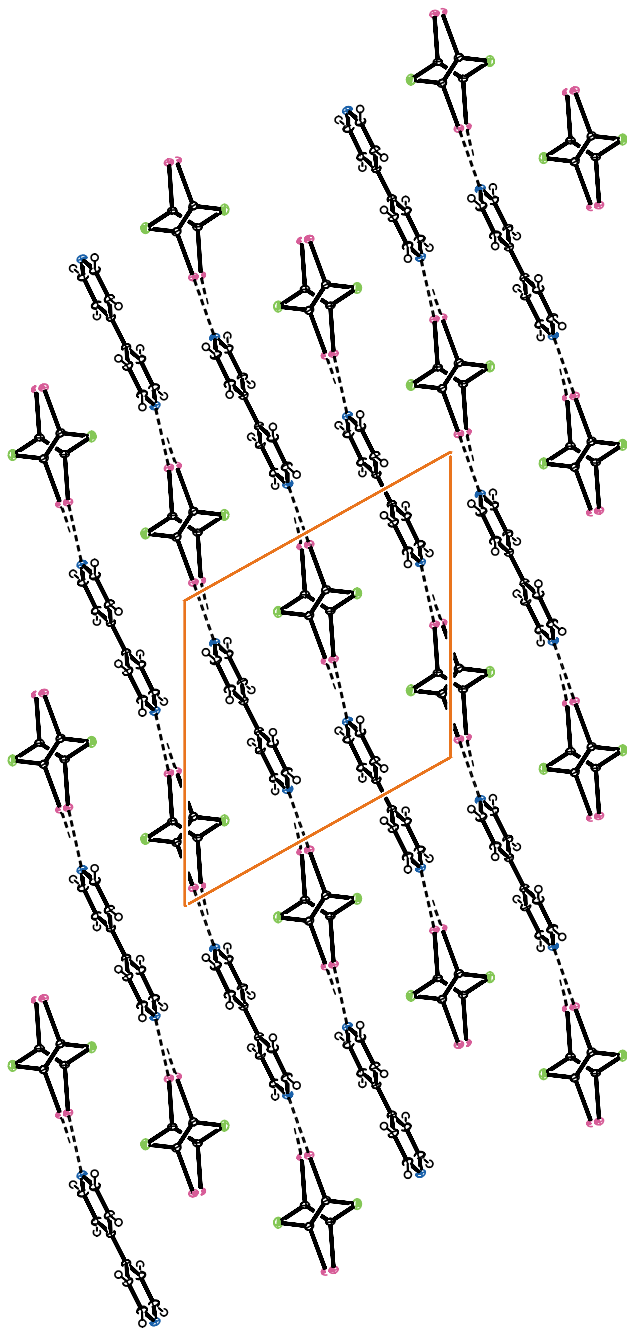


Figure 2. Single layer of the packing of co-crystal **3b** viewed down the *b*-axis. Dashed lines represent the halogen bonding between the PFC and HC modules. Colours are as follows: Black, carbon and hydrogen; blue, nitrogen; violet, iodine; green, fluorine.

with the I–C bond, consistent with an $n \rightarrow \sigma^*$ electron donation from nitrogen to iodine. Fluorinated alkenes are electron-poor species and both organic and inorganic nucleophiles easily attack their carbon atoms¹⁵ leading to the formation of either addition or fluorine substitution products. The rates of nucleophilic addition to the double bond increases from perfluoroalkenes to chloroperfluoroalkenes, to bromoperfluoroalkenes.¹⁶ Iodoperfluoroalkenes are therefore expected to undergo an easy nucleophilic attack at carbon. However, the

Table 1. Variations in ^{19}F NMR chemical shifts values of **1**, **4**, and **5** in the presence of increasing equivalents of TMEDA

Iodo-PFC	δ_{F} (ppm) ^a	$\Delta\delta_{\text{F}}^{\text{a,b}}$ (ppm) on TMEDA addition		
		1 equiv.	5 equiv.	10 equiv.
1	–106.21	0.04	0.89	1.61
4	–53.89	0.05	2.0	3.04
5	–118.55	0.03	0.61	0.98

^a CDCl_3 was used as solvent and CFCl_3 as internal standard.

^b $\delta_{\text{pure I-PFC}} - \delta_{\text{I-PFC}}$ in the presence of TMEDA.

$\text{N} \cdots \text{I} - \text{R}_{\text{f}}$ (R_{f} = PFC residue) halogen bonding is so robust an interaction to control the recognition between **1** and **2a,b**. The nitrogen atoms prefer to function as nucleophiles towards iodine atoms than towards carbon atoms and the resulting self-assembly neglects the reactivity profile of the fluoroalkenyl residue.

Lone pairs possessing heteroatoms and halogen atoms form halogen bonds also in the liquid phase. When perfluorocarbon halides are used as electron acceptors, the ^{19}F NMR spectroscopy is a simple, powerful, and versatile tool to detect the interaction and to rank the electron donors and acceptors according to their tendency to be involved in halogen bonding formation. Specifically, the $-\text{CF}_2\text{X}$ and $-\text{CF}=\text{CX}$ signals of perfluoroalkyl and -aryl derivatives are shifted upfield on interaction and greater electron donor/acceptor abilities of the involved modules result in larger shifts.¹⁷ The $=\text{CFI}$ signal of iodofluoroolefin **1** is also shifted to high fields in the presence of TMEDA (Table 1). These shifts increase on increasing the electron donor concentration and no signal broadening or splitting has been observed for any concentration and ratio of the modules. These observations are consistent with a rapid association equilibrium which gives dimeric, trimeric, ... adducts. The shifts given by **1** are smaller than those given by 1,2-diiodoperfluoroethane (**4**) (both compounds bearing the fluorine probe in a geminal position to the halogen bonded iodine atom), and they are larger than those of 1,4-diiodoperfluorobenzene **5** (fluorine and iodine being in a vicinal relationship in this latter compound).

In conclusion, the ability of PFC iodides to act as acidic motifs in donor–acceptor complexes with nitrogen substituted HC compounds has been extended to the iodofluoroolefin (**1**). The 1:1 cocrystals **3a,b** formed with the tertiary aliphatic diamine **2a** and the nitrogen heteroaromatic **2b** were characterised by X-ray diffraction and IR spectroscopy in the solid ^{19}F NMR in solution.

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References

- (a) Hassel, O. *Science* **1970**, *170*, 497–502; (b) Bent, H. A. *Chem. Rev.* **1968**, *68*, 587–648; (c) Dumas, J. M.; Gomel, L.; Guerin, M. In *The Chemistry of Functional Groups, Supplement D*; Patai, S.; Rappoport, Z., Eds.; John Wiley and Sons: New York, 1983; pp. 985–1020; (d) Legon, A. C. *Chem. Eur. J.* **1998**, *4*, 1890–1897; (e) Legon, A. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2687–2714.
- Metrangolo, P.; Resnati, G. *Chem. Eur. J.* **2001**, *7*, 2511–2519.
- (a) Fontana, F.; Forni, A.; Metrangolo, P.; Panzeri, W.; Pilati, T.; Resnati, G. *Supramolecular Chem.* **2002**, *14*, 47–55; (b) Liantonio, R.; Luzzati, S.; Metrangolo, P.; Pilati, T.; Resnati, G. *Tetrahedron* **2002**, *58*, 4023–4029; (c) Cardillo, P.; Corradi, E.; Lunghi, A.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Tetrahedron* **2000**, *56*, 5535–5550; (d) Amico, V.; Meille, S. V.; Corradi, E.; Messina, M. T.; Resnati, G. *J. Am. Chem. Soc.* **1998**, *120*, 8261–8262; (e) Messina, M. T.; Metrangolo, P.; Pilati, T.; Resnati, G. *New J. Chem.* **2000**, *24*, 777–780.
- (a) Messina, M. T.; Metrangolo, P.; Panzeri, W.; Pilati, T.; Resnati, G. *Tetrahedron* **2001**, *57*, 8543–8550; (b) Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1782–1786; (c) Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Tetrahedron Lett.* **1999**, *40*, 7519–7523; (d) Messina, M. T.; Metrangolo, P.; Pappalardo, S.; Parisi, M. F.; Pilati, T.; Resnati, G. *Chem. Eur. J.* **2000**, *6*, 3495–3500; (e) De Santis, A.; Liantonio, R.; Logothetis, T. A.; Messina, M. T.; Metrangolo, P.; Pilati, T.; Resnati, G. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1373–1382.
- Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. *J. Am. Chem. Soc.* **2001**, *123*, 11069–11070.
- Fontana, S. A.; Davis, C. R.; He, Y.-B.; Burton, D. J. *Tetrahedron* **1996**, *52*, 37–44.
- Chloroform solutions of **1** and **2a** (molar ratio in the range 0.5–2.0) were mixed in a vial at room temperature. The open vial was closed in a cylindrical bottle containing vaseline oil; the volatile solvent was allowed to diffuse at room temperature and after 1 day the white crystals of **3a** were filtered and washed with *n*-pentane. The co-crystal **3b** was prepared by a similar procedure starting from an acetone solution of **1** and **2b**.
- Messina, M. T.; Metrangolo, P.; Navarrini, W.; Radice, S.; Resnati, G.; Zerbi, G. *J. Mol. Struct.* **2000**, *524*, 87–94.
- (a) Bertani, R.; Moiana, A.; Metrangolo, P.; Perez, E.; Pilati, T.; Resnati, G.; Rico-Lattes, I.; Sassi, A. *Adv. Mater.* **2002**, *14*, 1197–1201; (b) Ruokolainen, J.; Tanner, J. R.; ten Brinke, G.; Thomas, E. L.; Ikkala, O. *Macromolecules* **1998**, *31*, 3532–3536; (c) Ruokolainen, J.; Saari-aho, M.; Serimaa, R.; ten Brinke, G.; Thomas, E. L.; Ikkala, O. *Macromolecules* **1999**, *32*, 1152–1158.
- (a) Friedrich, H. B.; Tardy, D. C.; Burton, D. J. *J. Fluorine Chem.* **1993**, *65*, 53–58; (b) Fontana, S.; Davis, C. R.; He, Y.-B.; Burton, D. J. *Tetrahedron* **1996**, *52*, 37–44.
- Crystallographic data for co-crystal **3a**: Formula $C_{10}H_8N_2 \cdot C_2F_2I_2$; $M_r = 472.00$; monoclinic, space group $C2/c$; temperature 90 K, $a = 13.2125(12)$, $b = 8.2129(8)$, $c = 13.1626(16)$ Å, $\beta = 119.217(10)^\circ$; $V = 1337.7(2)$ Å³; $Z = 4$, $D_c = 2.344$ g cm⁻³, $\mu(\text{Mo-K}\alpha) 4.708$ mm⁻¹; data collection: $2\theta_{\text{max}} = 104.96^\circ$, 39025 refl. collected, 7735 independent, 5834 observed [$I_o > 2\sigma(I_o)$], absorption correction: $T_{\text{min}}/T_{\text{max}} = 0.66832$; $R_{\text{ave}} = 0.0257$; 117 refined parameters, goodness-of-fit = 0.925; $R(F) = 0.0358$ on all reflections (0.0231 on observed); $wR(F^2) = 0.0538$ on all reflections (0.0505 on observed); $-0.94 < \Delta\rho < 1.38$ e Å⁻³. Crystallographic data for **3b**: Formula $C_6H_{16}N_2 \cdot C_2F_2I_2$; $M_r = 432.03$; triclinic, space group $P\bar{1}$; temperature 90 K, $a = 6.1187(5)$, $b = 6.5605(7)$, $c = 8.7712(10)$ Å, $\alpha = 76.888(8)$, $\beta = 89.531(8)$, $\gamma = 78.845(8)^\circ$; $V = 336.20(6)$ Å³; $Z = 1$, $D_c = 2.164$ g cm⁻³, $\mu(\text{Mo-K}\alpha) 4.672$ mm⁻¹; data collection: $2\theta_{\text{max}} = 64.98^\circ$, 5411 refl. collected, 2389 independent, 2301 observed [$I_o > 2\sigma(I_o)$], absorption correction: $T_{\text{min}}/T_{\text{max}} = 0.57121$; $R_{\text{ave}} = 0.0232$; 124 refined parameters, goodness-of-fit = 1.092; $R(F) = 0.0206$ on all reflections (0.0193 on observed); $wR(F^2) = 0.0429$ on all reflections (0.0422 on observed); $-0.85 < \Delta\rho < 0.84$ e Å⁻³. Detailed crystallographic data were deposited as CCDC 194241 (**3a**) and CCDC 194242 (**3b**) with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.
- (a) Casalone, G.; Pilati, T.; Simonetta, M. *Tetrahedron Lett.* **1980**, *21*, 2345–2348; (b) Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B* **1982**, *38*, 1649–1652; (c) Decoster, M.; Conan, F.; Kubicki, M.; Le Mest, Y.; Richard, P.; Pala, J. S.; Toupet, L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 265–267.
- (a) Lam, Y.-L.; Huang, H. H. *J. Mol. Struct.* **1997**, *412*, 141–152; (b) Boche, G.; Fraenkel, G.; Cabral, J.; Harms, K.; van Eikema Hommes, N. J. R.; Lohrenz, J.; Marsch, M.; von Ragué Schleyer, P.; Kranz, M.; Dietrich, H.; Mahadi, W.; Müller, G.; Hampel, F.; Clark, T.; Hacker, R.; Neugebauer, W.; Kos, A. J.; von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1993**, *115*, 4698–4704.
- Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.
- (a) Bayliff, A. E.; Bryce, M. R.; Chambers, R. D. *J. Chem. Soc., Perkin Trans. 1* **1987**, 763–767; (b) Cooper, J. A.; Olivares, C. M.; Sandford, G. *J. Org. Chem.* **2001**, *66*, 4887–4891; (c) Chambers, R. D. *Fluorine in Organic Chemistry*; John Wiley and Sons: New York, NY, 1973.
- (a) Chambers, R. D.; Mobbs, R. H. *Adv. Fluorine Chem.* **1965**, *4*, 50; (b) Chambers, R. D.; James, S. R. In *Comprehensive Organic Chemistry*; Burton, D.; Ollis, D., Eds.; Pergamon Press: Oxford, 1979; pp. 537–547; (c) Hine, J.; Burske, N. W.; Hine, M.; Langford, P. B. *J. Am. Chem. Soc.* **1957**, *79*, 1406–1412.
- (a) Messina, M. T.; Metrangolo, P.; Panzeri, W.; Ragg, E.; Resnati, G. *Tetrahedron Lett.* **1998**, *39*, 9069–9072; (b) Metrangolo, P.; Panzeri, W.; Recupero, F.; Resnati, G. *J. Fluorine Chem.* **2002**, *114*, 27–33.