

Video Article

From Molecules to Materials: Engineering New Ionic Liquid Crystals Through Halogen Bonding

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Abstract

Herein, we demonstrate that a bottom-up approach, based on halogen bonding (XB), can be successfully applied for the design of a new type of ionic liquid crystals (ILCs). Taking advantages of the high specificity of XB for haloperfluorocarbons and the ability of anions to act as XB-acceptors, we obtained supramolecular complexes based on 1-alkyl-3-methylimidazolium iodides and iodoperfluorocarbons, overcoming the well-known immiscibility between hydrocarbons (HCs) and perfluorocarbons (PFCs). The high directionality of the XB combined with the fluorophobic effect, allowed us to obtain enantiotropic liquid crystals where a rigid, non-aromatic, XB supramolecular anion acts as mesogenic core.

X-ray structure analysis of the complex between 1-ethyl-3-methylimidazolium iodide and iodoperfluorooctane showed the presence of a layered structure, which is a manifestation of the well-known tendency to segregation of perfluoroalkyl chains. This is consistent with the observation of smectic mesophases. Moreover, all the reported complexes melt below 100 °C, and most are mesomorphic even at room temperature, despite that the starting materials were non-mesomorphic in nature.

The supramolecular strategy reported here provides new design principles for mesogen design allowing a totally new class of functional materials.

Video Link

The video component of this article can be found at <https://www.jove.com/video/55636/>

Introduction

Intermolecular interactions play a very important role in determining physical and chemical properties of bulk materials. When a new interaction becomes available, new structures, namely, new functions, become available. Therefore, exploring novel, specific non-covalent interactions underlying an intermolecular recognition process may open new perspectives in different fields such as materials sciences, catalysis, drug design, supramolecular chemistry, and crystal engineering. This was the case for the XB that recently became a routine tool for controlling aggregation and self-assembly phenomena^{1,2,3,4,5}.

According to the IUPAC definition⁶: "A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity." A schematic representation of the XB is given in **Figure 1**, where X is the electrophilic halogen atom (Lewis acid, XB donor) and Y is a donor of electron density (Lewis base, XB acceptor).

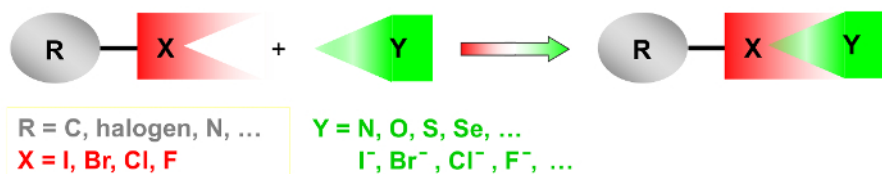


Figure 1: Schematic representation of the halogen bond.

The electrophilic halogen atoms (XB-donors) are covalently linked to a wide variety of molecular scaffolds (R), while the XB-acceptors (Y) can be neutral or anionic species. This figure has been reprinted from reference². [Please click here to view a larger version of this figure.](#)

At first sight, it may seem that this definition tackles somewhat puzzling aspects, since halogen atoms, because of their high electronegativity, are typically considered as sites of high electron density. However, the behavior of halogen atoms as electrophiles is quite general and has been elegantly rationalized by Politzer *et al.* with the introduction of the " σ -hole" concept⁷.

When a halogen atom is involved in a covalent bond, an electron redistribution occurs and the electronic density becomes anisotropic^{8,9,10,11}. The shape of the atom becomes oblate and a region of positive electrostatic potential (the so-called σ -hole) develops along the extension of the covalent bond, on the outermost surface of the halogen atom (Figure 2A). This positive region is surrounded by a belt of negative electrostatic potential, orthogonal to the covalent bond. This model seems to solve the "enigma" of the XB since it explains the non-covalent interaction pattern of covalently-bonded halogen atoms, and the associated directional preferences, *i.e.*, linear interactions with nucleophiles and lateral interactions with electrophiles.

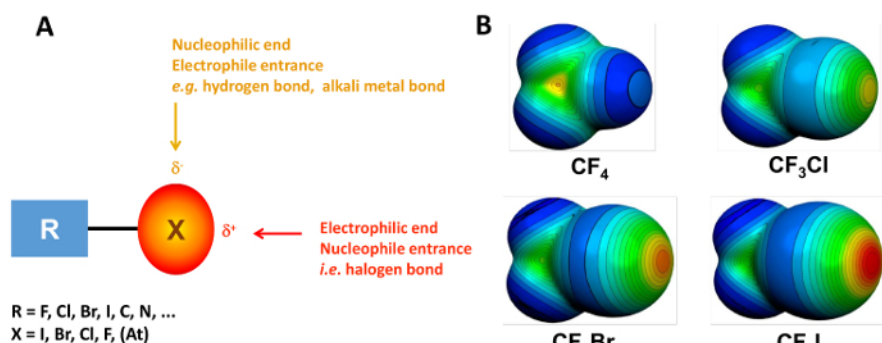


Figure 2: Anisotropic distribution of electron density around halogen atoms. (A) Schematic representation of the anisotropic distribution of the electron density around covalently bound halogen atoms and the pattern of the resulting interactions. (B) Molecular electrostatic potential maps at the isodensity surface with 0.001 au for CF_4 , CF_3Cl , CF_3Br , and CF_3I . Color ranges: red, greater than 27 kcal/mol; yellow, between 20 and 14 kcal/mol; green, between 12 and 6 kcal/mol; blue, negative. This figure has been modified from reference². [Please click here to view a larger version of this figure.](#)

XB has rapidly grown from a scientific curiosity to one of the most interesting noncovalent interactions in designing functional supramolecular materials^{12,13,14,15,16}, thanks to its unique features, *i.e.*, high directionality, tunable interaction strength, hydrophobicity, and donor atom dimensions¹. The high directionality of XB can be easily understood by considering the focused nature of the σ -hole, while the interaction strength frequently correlates to the magnitude of the σ -hole. Both the size (the spatial range) and the magnitude (the value of the maximum electrostatic potential $V_{S,\text{max}}$) of the σ -hole are affected by the polarizability and electronegativity of the halogen atom and the electron-withdrawing ability of the substituents in the neighborhood of the halogen¹⁷ (Figure 2B). As a general trend, as the halogen atom becomes more polarizable and the substituents on the molecule become more electron-withdrawing, the halogen σ -hole becomes more positive. Therefore, for a given R, $V_{S,\text{max}}$ increases in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$, namely it increases with the halogen atom polarizability and decreases with its electronegativity. For a given halogen, $V_{S,\text{max}}$ becomes more positive when the electron-withdrawing ability of R is increased. Therefore, haloperfluorocarbons, specifically iodo-perfluoroalkanes and arenes, can act as powerful XB-donors forming particularly strong interactions^{18,19,20} and particularly hydrophobic adducts.

A case of PFC-HC self-assembly to give cocrystals has been reported in the late 1990s²¹. Upon mixing equimolar amounts of 1,2-diiodotetrafluoroethane and *N,N,N',N'*-tetramethyl-ethylenediamine in chloroform, a supramolecular complex was isolated as white crystals stable in air at room temperature. Single crystal X-ray analysis revealed that the two components alternate in a 1-dimensional (1D) infinite chain and the interaction between the nitrogen and iodine atoms is largely responsible for keeping the perfluorinated bis-iodide in place. This proved that the nitrogen-iodine XB interaction is strong enough to overcome the low affinity existing between PFC and HC compounds and suggested that XB can be successfully exploited as an easy route to introduce fluorinated moieties into any new supramolecular materials^{22,23,24}, including liquid crystalline materials.

Fluorinated substituents, in fact, have been successfully incorporated into liquid crystalline molecules because of the excellent stability that is offered by the C-F bond as well as the small size and the low polarizability of the fluorine atom, which gives rise to very low intermolecular dispersion interactions^{25,26,27}. Moreover the segregation occurring between PFC and HC chains allowed control over supramolecular liquid-crystalline phases, enhancing the smectic character of a mesomorphic material^{28,29,30}. It is generally understood that both the physical/chemical properties and the mesomorphism are strongly affected by the molecular architecture^{29,31}. Thus, an appropriate molecular design is essential to generate new supramolecular liquid crystals with tailored properties. The basic motif of these soft materials lies in a fairly rigid, rod-like moiety linked to one or two flexible aliphatic chains^{32,33,34}. The conventional design of mesomorphic compounds was mainly performed with neutral

species but studies have shown that also ionic pairs can exhibit a mesomorphic behavior, yielding materials with properties at the interface between ionic liquids and liquid crystals^{35,36,37}.

Taking into account recent results on XB liquid crystals^{24,38,39}, and the specific ability of anions to act as XB-acceptors, it seemed particularly interesting to exploit this non-covalent interaction in designing new types of ILCs.

1-Alkyl-3-methylimidazolium iodides (**1-m**) of various chain-length, which are known as ionic liquids⁴⁰, were used for the synthesis of the complexes (**Figure 3**)^{41,42}. Note that only **1-12**, bearing a C12 alkyl chain, exhibits liquid crystallinity with smectic A (Sm A) phase (crystal (Cr) to SmA transition temperature = 27 °C; Sm A to isotropic liquid (ISO) transition temperature = 80 °C; Cr • 27 • SmA • 80 • Iso)⁴³. Imidazolium salts were reacted with iodoperfluorooctane (**2-8**) and iodoperfluorodecane (**2-10**), which are well-known XB-donors^{44,45}.

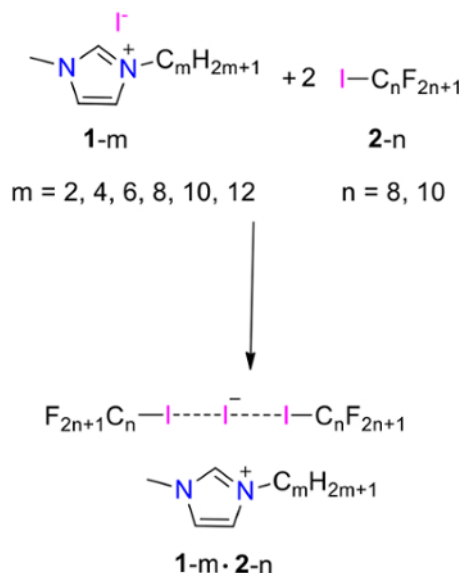


Figure 3: Synthetic scheme. Chemical formulae of starting ionic liquids (**1-m**), iodoperfluoroalkanes (**2-n**), and related XB-complexes **1-m·2-n**. Please click here to view a larger version of this figure.

The iodide anions are expected to participate readily as XB-acceptor in the formation of supramolecular structures with haloperfluoroalkanes⁴⁴. However, it remains challenging to anticipate the number and topology of the coordinated XB-donor species. In fact, halide anions typically are involved in two or three XBs^{46,47,48}, but higher coordination numbers were also observed^{49,50}.

Herein, we describe a procedure for obtaining highly fluorinated XB ILCs and a detailed procedure for the identification and characterization of the occurrence of XB. The sequence of analysis reported here and utilized to identify the XB can be considered as a general procedure and can be applied to the characterization of any type of XB system.

Protocol

Note: Reactions were carried out in oven-dried glassware under nitrogen atmosphere. Please follow the safety measures described in the MSDS of each chemical.

1. Synthesis of 1-Alkyl-3-methylimidazolium Iodide Salts (**1-m**, Figure 3)

- In a three-necked, round-bottomed flask equipped with a reflux condenser fitted with a nitrogen inlet, a thermometer, a magnetic stirring bar, and a heating oil bath, dissolve 1.5 g (0.018 mol, 1 equiv) of freshly distilled 1-methyl-imidazole and 1.3 equiv of the 1-iodoalkane (chain length from C2 to C12) in 10 mL of acetonitrile.
- Heat the reaction mixture to reflux (75 - 80 °C internal temperature) overnight under nitrogen atmosphere and then cool the mixture down to room temperature.
- Remove the volatile materials from the resulting mixture under reduced pressure at 50 °C, using a rotatory evaporator.
NOTE: Imidazolium salts are highly hygroscopic and they quickly absorb water from the air. Thus, it is recommended to store them in a desiccator until use.

2. Synthesis of **1-m · 2-n** XB Complexes

- Procedure 1: From solution (only for 1-2 · 2-8 in Figure 1)**
 - Prepare a solution of the 1-ethyl-3-methylimidazolium iodide (**1-2**, MW = 238.07 g/mol) by dissolving 50 mg (0.21 mmol, 1 equiv) of **1-2** in 0.5 mL of acetonitrile.
 - Prepare a solution of the perfluorooctyl iodide (**2-8**, MW = 545.96 g/mol) by dissolving 229 mg (0.42 mmol, 2 equiv) of **2-8** in 0.5 mL of acetonitrile.

- Mix the two solutions in a vial and keep the vial in a jar filled with paraffin oil.
- Let the solvent diffuse slowly in the paraffin oil at room temperature. After a period ranging from 3 to 7 days, good-quality single crystals suitable for X-ray diffraction analysis were obtained.

2. Procedure 2: Melt methodology

NOTE: This methodology requires an air-sealed system to mitigate against the volatility of the iodoperfluoroalkanes.

- Mix each 1-alkyl-3-methylimidazolium iodide (1-m) with the appropriate iodoperfluoroalkanes (2-n) in a 1:2 molar ratio in a clear borosilicate glass vial equipped with a magnetic stirring bar.
- Close the vial and put it into an oil bath under vigorous stirring.
- Heat at 70 °C using a hot plate for 15 min then cool the mixture down to room temperature.

3. ¹H and ¹⁹F NMR Experiments

NOTE: ¹H NMR and ¹⁹F NMR spectra were recorded at 25 °C on a NMR spectrometer operating at 499.78 MHz for ¹H and 470.21 MHz for ¹⁹F, and using CDCl₃ as the solvent. TMS and CFC₃ were used as internal standards for calibrating the chemical shifts in ¹H NMR and ¹⁹F NMR, respectively. Bis-(2,2,2-trifluoroethyl) ether that contains both hydrogen and fluorine nuclei, was used as internal standard for establishing the ratio between 1-m and 2-n in the cocrystals.

1. Preparation of the sample for NMR analysis and spectra calibration

- Dissolve about 10 mg of each complex 1-m • 2-n in 0.5 mL of CDCl₃.
- Add 1 μL of 2,2,2-trifluoroethyl ether using a micropipette.
- Lock the sample, set the acquisition parameters as reported in **Table 1**, and record ¹H and ¹⁹F NMR consecutive spectra, without removing the NMR tube from the magnet, in order to operate under the same operating conditions.
- Calibrate the integration parameters so that in the ¹H NMR spectra the CH₂O quartet of bis(2,2,2-trifluoroethyl) ether ($\delta = 4.3$ ppm) corresponds to four, and in the ¹⁹F NMR spectra the CF₃ triplet ($\delta = -74.5$ ppm) of 2,2,2-trifluoroethyl ether corresponds to six.
- Calculate the ratio of the -CF₂-I signal area deriving from 2-n ($\delta = -61.2$ ppm in the ¹⁹F NMR spectra) and the -CH₃ signal area deriving from 1-m ($\delta \approx 4.0$ ppm in the ¹H NMR spectra), in order to evaluate the ratio between 2-n and 1-m in each complex.

4. Preparation of the Sample for Hot Stage Polarized Optical Microscopy (POM)

- Prepare a thin layer of the sample by placing a spatula tip amount of the supramolecular complex 1-m • 2-n between two micro cover glasses (18 mm x 18 mm).
- Place the sample in the hot stage between two crossed polarizers, and heat the sample to melt.
- Submit the sample to repeated heating/cooling cycles in order to promote phase transitions. Crystalline and liquid crystalline phases will interact with polarized light leading to brightness and color gradient, while the isotropic phase will appear dark.

Representative Results

Differential scanning calorimetry (DSC), POM, and thermogravimetric analysis (TGA), as well as ¹H and ¹⁹F NMR were used to characterize the obtained complexes. Good-quality single crystals of 1-2•2-8 were obtained from a 1:2 solution of the starting components in acetonitrile by slow evaporation of the solvent at room temperature.

DSC analyses on mixtures of 1-2 and 2-8 with different stoichiometric ratios, allowed us to derive that the right coordination stoichiometry between the imidazolium salt and the iodoperfluoroalkane is 1:2. In fact, the DSC thermogram of the 1:1 complex in **Figure 4A** shows the presence of the uncomplexed imidazolium salt 1-2 (peak at 57 °C), while in the 1:3 complex there is an excess pure 2-8 (melting point 24 °C). On the other hand, the thermogram of the 1:2 complex shows a single peak distinct from those of the starting compounds, demonstrating that a new pure crystalline species was formed.

TGA analyses confirmed this result. In fact, only upon mixing 1-12 and 2-10 in 1:2 ratio, a homogenous sample was obtained, which released quantitatively the fluorinated building block at a temperature higher than the uncomplexed iodoperfluorodecane (**Figure 5A and 5B**).

¹⁹F NMR has been applied as a simple, effective, and sensitive tool to detect the formation of XB adducts. The XB between the electron deficient iodine of the iodoperfluoroalkanes and the I⁻ anion strongly influences the signals of the -CF₂-I group ($\delta = -60.0$ ppm) and gives rise to detectable upfield shifts of the ¹⁹F NMR resonances. A $\Delta\delta$ value of 1.2 ppm was measured for complex 1-2•2-8, confirming the occurrence of attractive noncovalent interactions involving halogen atoms as electrophilic species (**Figure 6**). Moreover, by recording consecutive ¹H and ¹⁹F NMR analyses in the presence of 2,2,2-trifluoroethyl ether as the internal standard for signal integration, the 1:2 stoichiometry between the XB-acceptor and donor modules has been further confirmed.

Single crystal X-ray analysis of 1-2•2-8 confirmed that the XB drives the formation of a trimeric supramolecular complex where the iodide anion acts as a bidentate XB-acceptor, binding two fluorinated chains. The I...I distances are almost the same [3.4582(9) Å and 3.4625(10) Å] and roughly correspond to 27% shortening with respect to the sum of the vdW and Pauling radii of the iodine atom and iodide anion, respectively⁵¹. The high directionality of XB is confirmed by the C-I...I angles of 174.1(1)° and 175.4(2)°, respectively (**Figure 7A**). Two equally-populated conformations are observed for the imidazolium cations, which lie approximately on the same plane and are related by a non-crystallographic twofold axis. **Figure 7B** shows the separation between the ionic and neutral parts, as well as between the HC and PFC chains, within the crystal (disorder removed).

DSC and POM studies revealed that all complexes melted at temperatures lower than 100 °C (**Figure 8A**), as typical for ionic liquids. Furthermore, they all show an enantiotropic liquid crystalline behavior, some at room temperature, with SmB and SmA phases (**Figure 8A**). On cooling, the SmA-SmB transition was identified by the characteristic striations across the back of the fans (**Figure 8B**,left). The striations disappeared on cooling further below the transition.

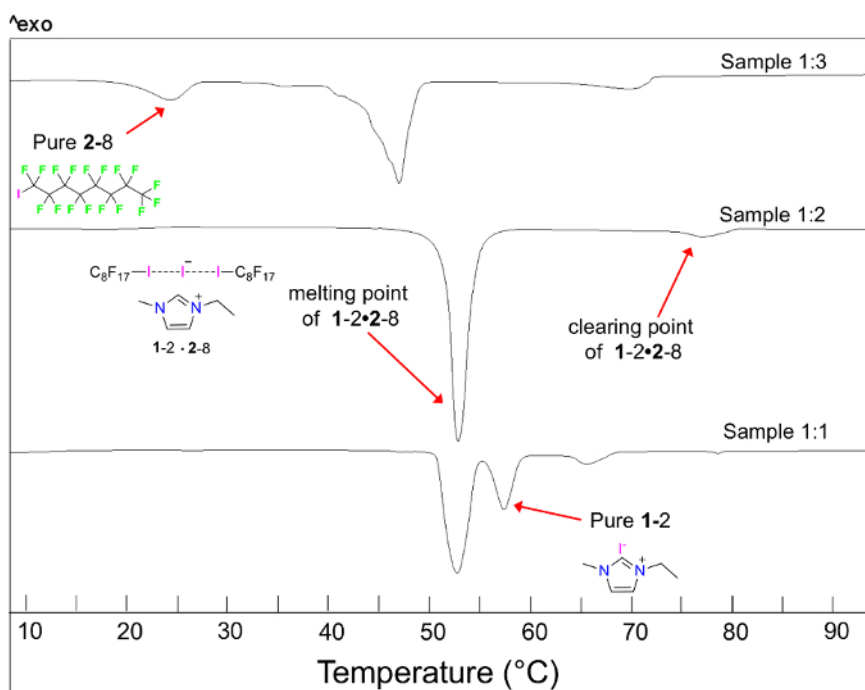


Figure 4: Differential Scanning Calorimetry. DSC thermograms of samples prepared by mixing 1-2 and 2-8 in different stoichiometric ratios: 1:3 sample (top), 1:2 sample (mid), and 1:1 sample (bottom). [Please click here to view a larger version of this figure.](#)

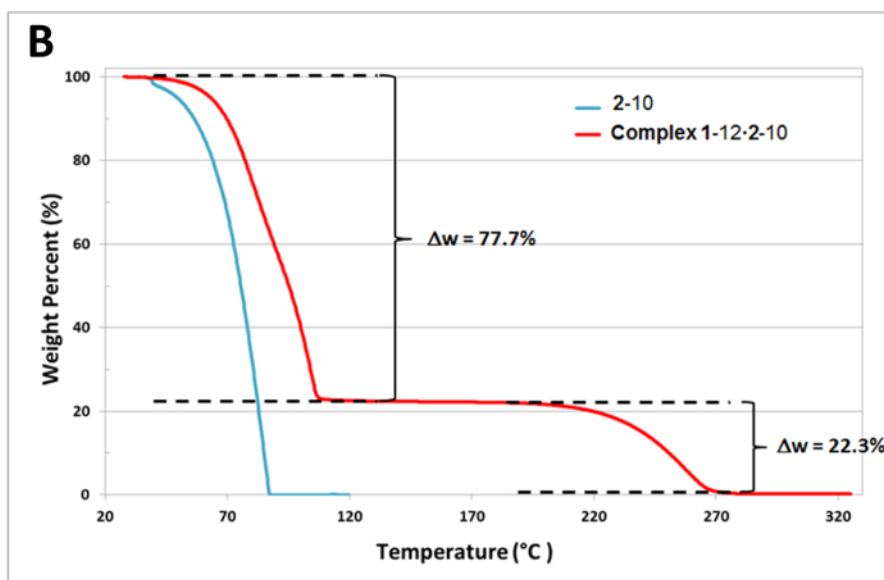
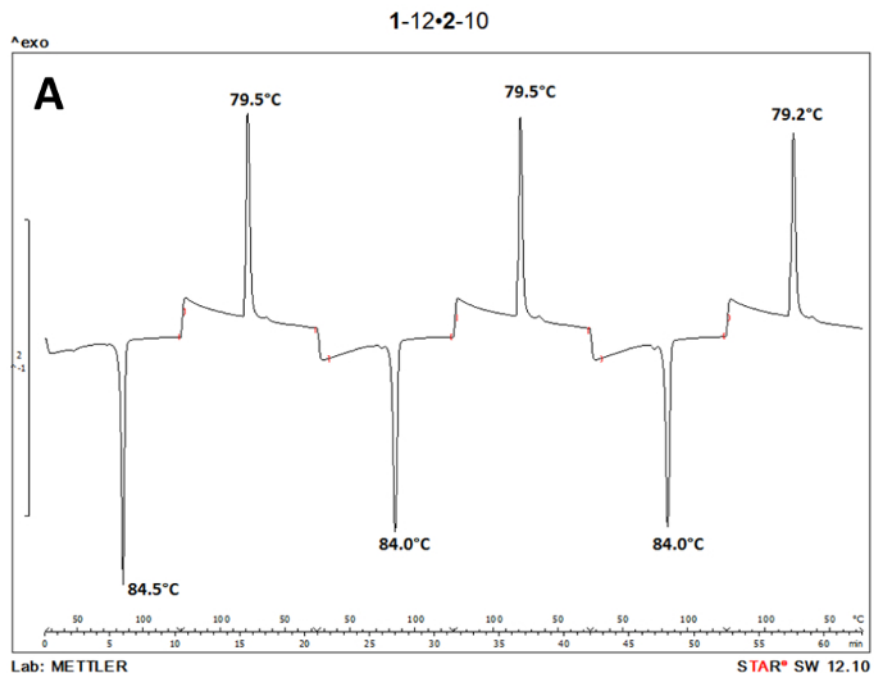


Figure 5: Thermal Analysis. DSC heating/cooling cycles (A) and TGA analysis (B) on a sample prepared by mixing 1-12 and 2-10 in a 1:2 molar ratio. This figure has been modified from reference³⁷. Please click here to view a larger version of this figure.

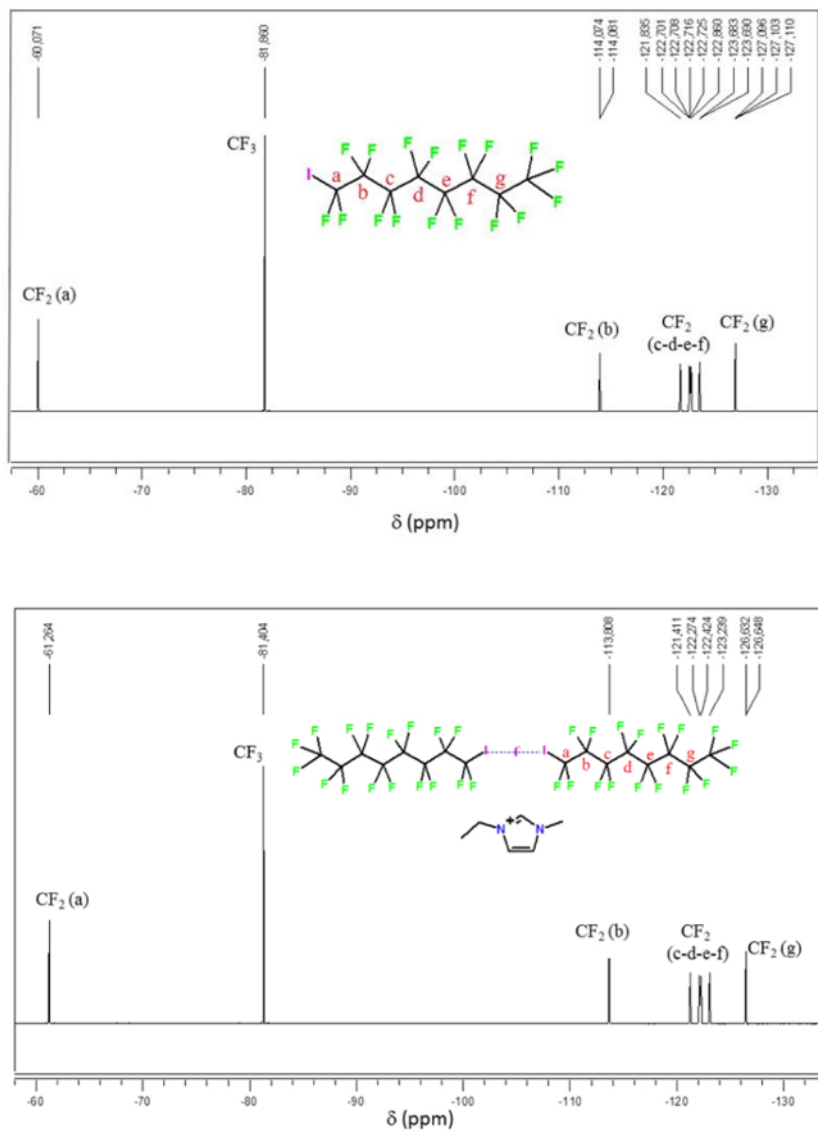


Figure 6: ^{19}F NMR Analysis. ^{19}F NMR spectra in CDCl_3 of **2-8** (top) and related halogen-bonded complex **1-2•2-8** (bottom). [Please click here to view a larger version of this figure.](#)

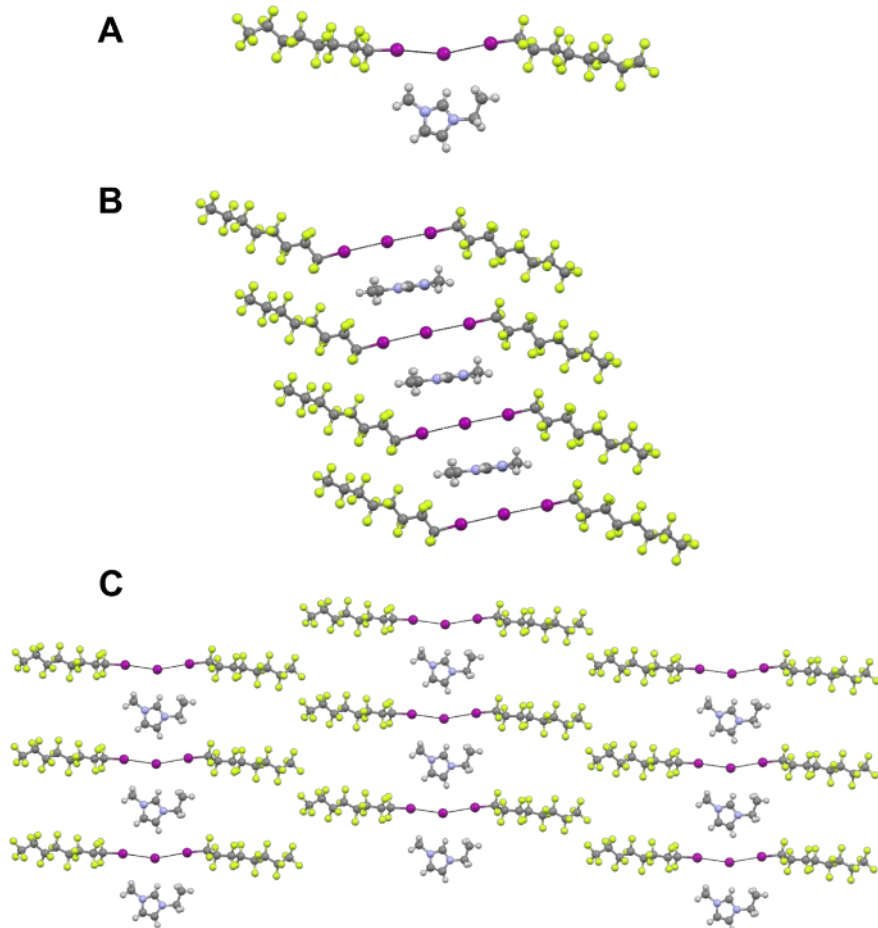


Figure 7: X-ray single crystal analysis. (A) The asymmetric unit of the complex 1-2·2-8 showing the formation of a trimeric superanion where two fluorinated chains are bonded to the central I⁻ anion (a single conformer of the disordered cation is reported); (B) The imidazolium salt 1-2 and the iodoperfluorooctane 2-8 segregate along the crystallographic *b*-axis; (C) Side view showing ionic and fluorocarbon areas of the structure. Color code: grey, carbon; blue, nitrogen; magenta, iodine; green, fluorine; white, hydrogen. Halogen bonds depicted as grey lines. [Please click here to view a larger version of this figure.](#)

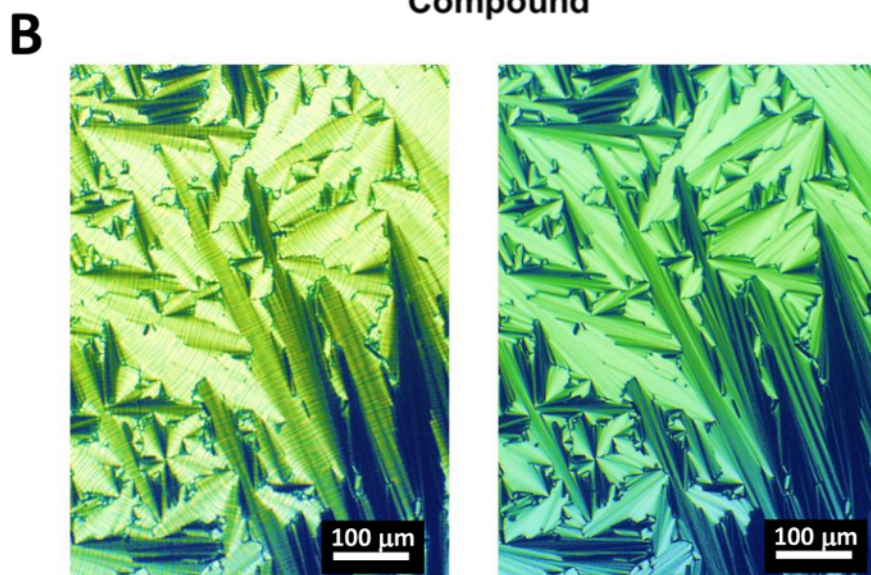
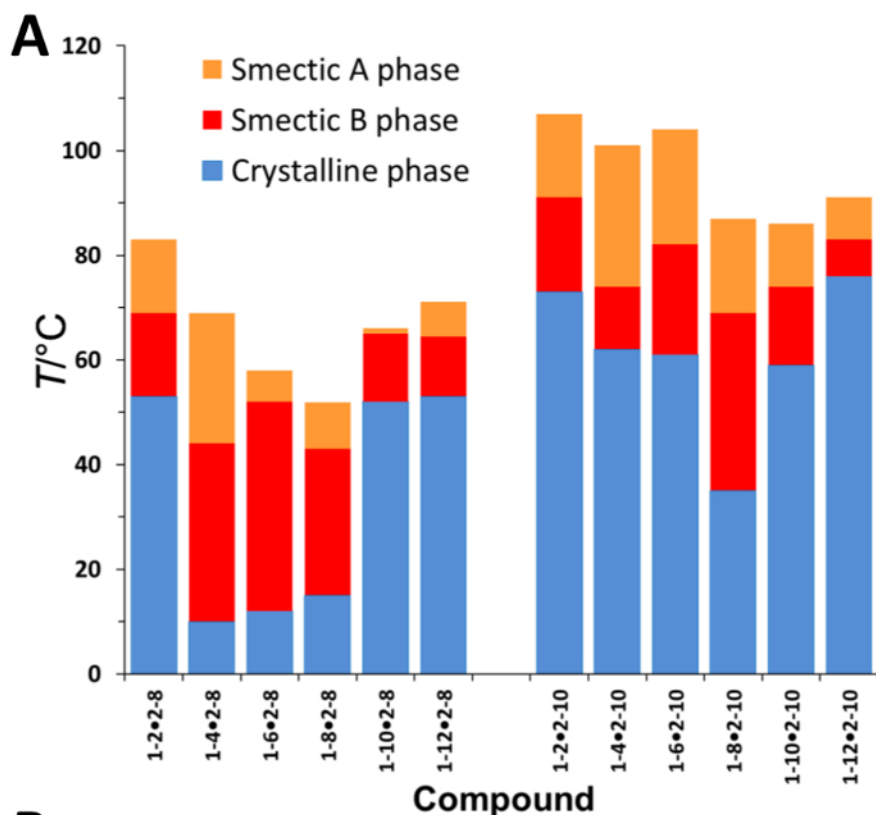


Figure 8: Polarized Optical Microscopy. (A) Chart of the thermal transitions of halogen-bonded complexes $1\text{-}m\cdot 2\text{-}n$ measured by hot-stage POM (blue is solid, red is SmB, and orange is SmA phases). (B) Optical textures of the smectic phases observed for $1\text{-}12\cdot 2\text{-}10$ on cooling from the isotropic state. Left: SmB phase at $77\text{ }^{\circ}\text{C}$; Right: SmA phase at $83\text{ }^{\circ}\text{C}$. Scale bar: $100\text{ }\mu\text{m}$. This figure has been modified from reference³⁷. Please click here to view a larger version of this figure.

	Spectral width (KHz)	Scans number	Pulse delay (s)
^1H	7	16	1
^{19}F	95	16	1

Table 1: Acquisition parameters for ^1H and ^{19}F NMR experiments

Discussion

We have reported an easy and versatile protocol for the synthesis of XB fluorinated ILCs in which mesomorphism is driven by the supramolecular anions $[C_nF_{2n+1}I \cdots I \cdots I-C_nF_{2n+1}]^-$.

It is well-established that ionic liquids based on 1-alkyl-3-methylimidazolium salts can exhibit liquid crystalline behavior. However, whatever the anion, no mesophases were observed for compounds with alkyl chains shorter than 12 carbon atoms. Therefore, the most striking aspect of the reported materials is that it is the anisotropy of the XB anion that determines mesophase formation. In fact, the strict geometrical constraints of XB impose that the intermolecular interaction occurs along the extension of the C-I bond, at the sigma hole, with angles close to 180° . The iodide anions act as bidentate XB acceptors, binding two perfluorinated modules that show linear arrangement around the central iodide anion. Moreover, the fact that perfluoroalkyl chains are stiffer than equivalent HC chains, and adopt a twisted helical structure due to repulsion between 1,3-disposed CF_2 groups^{9,52}, further contributes to the generation of rigid, rod-like superanions.

This perfectly agrees with the observation that complexes containing the iodoperfluorodecane (**2-10**) show transition temperatures higher than those containing the iodoperfluorooctane (**2-8**) as the former is more anisotropic. Furthermore, the known tendency^{45,53} of fluoroalkanes to pack into lamellar phases determines the obtainment of SmB and SmA phases.

The superfluorinated ILCs reported in this paper demonstrate for the first time the application of the XB in the construction of ILCs based on imidazolium salts. Thanks to an accurate supramolecular design based on the high directionality of the XB and the fluorophobic effect, it is possible to obtain enantiotropic liquid crystals based on a rigid, non-aromatic, XB supramolecular synthon as the mesogenic core. The liquid crystalline behavior is independent from the length of the alkyl chains.

The supramolecular approach presented here represents an attractive platform for the design of new liquid crystalline materials and can provide new opportunities for the development of sophisticated functional materials such as room temperature ionic conductors, photoresponsive ILCs, and liquid crystalline electrolytes for application in energy devices.

Disclosures

The authors have nothing to disclose.

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References

1. Priimagi, A., Cavallo, G., Metrangolo, P., & Resnati, G. The Halogen Bond in the Design of Functional Supramolecular Materials: Recent Advances. *Acc. Chem. Res.* **46** (11), 2686-2695 (2013).
2. Cavallo, G., Metrangolo, P., *et al.* The Halogen Bond. *Chem. Rev.* **116** (4), 2478-2601 (2016).
3. Meyer, F., & Dubois, P. Halogen bonding at work: recent applications in synthetic chemistry and materials science. *CrystEngComm.* **15**, 3058-3071 (2013).
4. Berger, G., Soubhye, J., & Meyer, F. Halogen bonding in polymer science: from crystal engineering to functional supramolecular polymers and materials. *Polym. Chem.* **6** (19), 3559-3580 (2015).
5. Bulfield, D., & Huber, S. M. Halogen Bonding in Organic Synthesis and Organocatalysis. *Chem. Eur. J.* **22** (41), 14434-14450 (2016).
6. Desiraju, G. R., Ho, P. S., *et al.* Definition of the halogen bond (IUPAC recommendations 2013). *Pure Appl. Chem.* **85** (8), 1711-1713 (2013).
7. Clark, T., Hennemann, M., Murray, J. S., & Politzer, P. Halogen bonding: The sigma-hole. *J. Mol. Model.* **13**, 291-296 (2007).
8. Palusiak, M., & Grabowski, S. J. Do intramolecular halogen bonds exist? Ab initio calculations and crystal structures' evidences. *Struct. Chem.* **19** (1), 5-11 (2007).
9. Awwadi, F. F., Willett, R. D., Peterson, K. a., & Twamley, B. The nature of halogen...halogen synthons: crystallographic and theoretical studies. *Chemistry.* **12**, 8952-8960 (2006).
10. Politzer, P., & Murray, J. S. Halogen Bonding: An Interim Discussion. *ChemPhysChem.* **14** (2), 278-294 (2013).
11. Politzer, P., Riley, K. E., Bulat, F. A., & Murray, J. S. Perspectives on halogen bonding and other sigma-hole interactions: Lex parsimoniae (Occam's Razor). *Comput. Theor. Chem.* **998**, 2-8 (2012).
12. Priimagi, A., Cavallo, G., *et al.* Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly and Performance of Light-Responsive Supramolecular Polymers. *Adv. Funct. Mater.* **22** (12), 2572-2579 (2012).
13. Priimagi, A., Saccone, M., *et al.* Photoalignment and Surface-Relief-Grating Formation are Efficiently Combined in Low-Molecular-Weight Halogen-Bonded Complexes. *Adv. Mater.* **24** (44), OP345-OP352 (2012).
14. Abate, A., Petrozza, A., *et al.* Anisotropic ionic conductivity in fluorinated ionic liquid crystals suitable for optoelectronic applications. *J. Mater. Chem. A: Energy Sustain.* **1** (22), 6572-6578 (2013).
15. Baldrighi, M., Cavallo, G., *et al.* Halogen Bonding and Pharmaceutical Cocrystals: The Case of a Widely Used Preservative. *Mol. Pharm.* **10** (5), 1760-1772 (2013).
16. Cariati, E., Cavallo, G., *et al.* Self-Complementary Nonlinear Optical-Phores Targeted to Halogen Bond-Driven Self-Assembly of Electro-Optic Materials. *Cryst. Growth Des.* **11** (12), 5642-5648 (2011).
17. Murray, J. S., Macaveiu, L., & Politzer, P. Factors affecting the strengths of σ -hole electrostatic potentials. *J. Comput. Sci.* **5** (4), 590-596 (2014).

18. Resnati, G., Metrangolo, P., Stevenazzi, A., & Ursini, M. Haloperfluorocarbons: Effective tectons in supramolecular synthesis. *Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003.*, FLUO-026 (2003).
19. Metrangolo, P., Meyer, F., Resnati, G., & Ursini, M. Haloperfluorocarbons: versatile tectons in halogen bonding based crystal engineering. *ACS Symposium Series*. **911** (Fluorine-Containing Synthons), 514-542 (2005).
20. Aakeröy, C. B., Wijethunga, T. K., & Desper, J. Practical crystal engineering using halogen bonding: A hierarchy based on calculated molecular electrostatic potential surfaces. *J. Mol. Struct.* **1072**, 20-27 (2014).
21. Amico, V., Meille, S. V., Corradi, E., Messina, M. T., & Resnati, G. Infinite Chain Formation Driven by Nitrogen...Iodine Interactions. *J. Am. Chem. Soc.*, **7863** (16), 8261-8262 (1998).
22. Tschierske, C. Development of Structural Complexity by Liquid-Crystal Self-assembly. *Angew. Chem. Int. Ed.* **52** (34), 8828-8878 (2013).
23. Bruce, D. W., Prasang, C., et al. Halogen bonding in liquid crystals: Opportunities and challenges. *Abstract of Papers, 238th ACS National Meeting, Washington, DC, United States, August 16-20, 2009.*, ORGN-053 (2009).
24. Bruce, D. W., Metrangolo, P., et al. Structure-Function Relationships in Liquid-Crystalline Halogen-Bonded Complexes. *Chem. Eur. J.* **16** (31), 9511-9524 (2010).
25. Kirsch, P., Lenges, M., Ruhl, A., Huber, F., Chambers, R. D., & Sandford, G. Liquid crystals with partially fluorinated side chains: Highly polar materials with very low birefringence. *J. Fluor. Chem.* **128** (10), 1221-1226 (2007).
26. Kirsch, P., Binder, W., et al. Super-fluorinated liquid crystals: Towards the limits of polarity. *European J. Org. Chem.* (20), 3479-3487 (2008).
27. Kirsch, P., Huber, F., Lenges, M., & Taugerbeck, A. Liquid crystals with multiple fluorinated bridges in the mesogenic core structure. *J. Fluor. Chem.* **112** (8), 69-72 (2001).
28. Jeannin, O., & Fourmigué, M. Fluorine segregation in crystalline materials: Structural control and solid-state [2+2] cycloaddition in CF₃-substituted tetrathiafulvalene derivatives. *Chem. Eur. J.* **12**, 2994-3005 (2006).
29. Tschierske, C. Non-conventional liquid crystals-the importance of micro-segregation for self-organisation. *J. Mater. Chem.* **8** (7), 1485-1508 (1998).
30. Kato, T., Mizoshita, N., & Kishimoto, K. Functional liquid-crystalline assemblies: Self-organized soft materials. *Angew. Chem. Int. Ed.* **45** (1), 38-68 (2005).
31. Cheng, X., Su, F., Huang, R., Gao, H., Prehm, M., & Tschierske, C. Effect of central linkages on mesophase behavior of imidazolium-based rod-like ionic liquid crystals. *Soft Matter*. **8** (7), 2274 (2012).
32. Guittard, F., Taffin de Givenchy, E., Geribaldi, S., & Cambon, A. Highly fluorinated thermotropic liquid crystals: an update. *J. Fluor. Chem.* **100** (1-2), 85-96 (1999).
33. *Springer Handbook of Condensed Matter and Materials Data*. Springer-Verlag Berlin Heidelberg: (2005).
34. Kiliç, M., & Çinar, Z. Structures and mesomorphic properties of cyano-containing calamitic liquid crystal molecules. *J. Mol. Struct.: THEOCHEM.* **808** (1-3), 53-61 (2007).
35. Chiou, J. Y. Z., Chen, J. N., Lei, J. S., & Lin, I. J. B. Ionic liquid crystals of imidazolium salts with a pendant hydroxyl group. *J. Mater. Chem.* **16** (29), 2972 (2006).
36. Luo, S.-C., Sun, S., Deorukhkar, A. R., Lu, J.-T., Bhattacharyya, A., & Lin, I. J. B. Ionic liquids and ionic liquid crystals of vinyl functionalized imidazolium salts. *J. Mater. Chem.* **21** (6), 1866 (2011).
37. Axenov, K. V., & Laschat, S. Thermotropic Ionic Liquid Crystals. *Materials*. **4** (1), 206-259 (2011).
38. Bruce, D. W. Halogen-bonded Liquid Crystals. *Halogen Bonding. Fundamentals and Applications.* **126**, 161-180 (2008).
39. Metrangolo, P., Präsang, C., Resnati, G., Liantonio, R., Whitwood, A. C., & Bruce, D. W. Fluorinated liquid crystals formed by halogen bonding. *Chem. Commun. (Camb.)*. 3290-3292 (2006).
40. Cavallo, G., Terraneo, G., et al. Superfluorinated Ionic Liquid Crystals Based on Supramolecular, Halogen-Bonded Anions. *Angew. Chem. Int. Ed.* 6300-6304 (2016).
41. Xu, F., Matsumoto, K., & Hagiwara, R. Effects of alkyl chain length on properties of 1-alkyl-3-methylimidazolium fluorohydrogenate ionic liquid crystals. *Chem. Eur. J.* **16** (43), 12970-12976 (2010).
42. Getsis, a., & Mudring, a. V. Imidazolium based ionic liquid crystals: Structure, photophysical and thermal behaviour of [C_nmim]Br·xH₂O (n = 12, 14; x=0, 1). *Crys. Res. Technol.* **43** (11), 1187-1196 (2008).
43. Yamanaka, N., Kawano, R., et al. Dye-sensitized TiO₂ solar cells using imidazolium-type ionic liquid crystal systems as effective electrolytes. *J. Phys. Chem. B.* **111** (18), 4763-4769 (2007).
44. Metrangolo, P., Carcenac, Y., et al. Nonporous organic solids capable of dynamically resolving mixtures of diiodoperfluoroalkanes. *Science (New York, N.Y.)*. **323** (5920), 1461-1464 (2009).
45. Houbenov, N., Milani, R., et al. Halogen-bonded mesogens direct polymer self-assemblies up to millimetre length scale. *Nat. Commun.* **5**, 4043 (2014).
46. Mele, A., Metrangolo, P., Neukirch, H., Pilati, T., & Resnati, G. A halogen-bonding-based heteroditopic receptor for alkali metal halides. *J. Am. Chem. Soc.* **127** (43), 14972-14973 (2005).
47. Casnati, A., Liantonio, R., Metrangolo, P., Resnati, G., Ungaro, R., & Ugozzoli, F. Molecular and supramolecular homochirality: enantiopure perfluorocarbon rotamers and halogen-bonded fluorinated double helices. *Angew. Chem. Int. Ed.* **45** (12), 1915-1918 (2006).
48. Terraneo, G., Bruce, D. W., et al. Halogen bonding drives the assembly of fluorocarbons into supramolecular liquid crystals. *Abstracts, Joint 66th Southwest and 62nd Southeast Regional Meeting of the American Chemical Society, New Orleans, LA, United States, December 1-4.*, SESW-995 (2010).
49. Rosokha, S. V., Naretin, I. S., Rosokha, T. Y., Hecht, J., & Kochi, J. K. Charge-transfer character of halogen bonding: Molecular structures and electronic spectroscopy of carbon tetrabromide and bromoform complexes with organic σ- and π-donors. *Heteroat. Chem.* **17** (5), 449-459 (2006).
50. Bock, H., & Holl, S. Interaction in molecular crystals. 179. sigma-donor/acceptor complexes {I₂C=Cl₂... X} (X = Cl⁻, Br⁻, I⁻, SCN⁻ of tetraiodoethene in tetra(n-butyl)ammonium halide salts. *Naturforsch. B, J. Chem Sci.* **57**, 713-725 (2002).
51. Bondi, A. van der Waals Volumes and Radii. *J. Phys. Chem.* **68** (3), 441-451 (1964).
52. Riley, K. E., Murray, J. S., et al. Halogen bond tunability I: The effects of aromatic fluorine substitution on the strengths of halogen-bonding interactions involving chlorine, bromine, and iodine. *J. Mol. Model.* **17**, 3309-3318 (2011).
53. Walsh, R. B., Padgett, C. W., Metrangolo, P., Resnati, G., Hanks, T. W., & Pennington, W. T. Crystal Engineering through Halogen Bonding: Complexes of Nitrogen Heterocycles with Organic Iodides. *Cryst. Growth Des.* **1** (2), 165-175 (2001).