Superfluorinated ionic liquid crystals through mesomorphic, halogen-bonded anions

Gabriella Cavallo, Giancarlo Terraneo, Alessandro Monfredini, Marco Saccone, Arri Priimagi, Giuseppe Resnati,* Pierangelo Metrangolo,* and Duncan W. Bruce*

Abstract: Unconventional liquid crystalline ionic liquids in which the liquid crystallinity is driven by halogen-bonded supramolecular anion $[C_nF_{2n+1}–I\cdots I\cdots I–C_nF_{2n+1}]^-$ that acts as the mesogenic unit are reported. The material system is unique in many ways, demonstrating for the first time (i) ionic, halogen-bonded liquid crystals, and (ii) imidazolium-based ionic liquid crystals in which the liquid crystallinity is not driven by the alkyl chains of the cation.

Ionic liquids are defined as salts with melting points below 100 °C. They bear several unique characteristics such as high ionic conductivity, low volatility, and lack of flammability, on account of which they are investigated extensively as new materials for electrochemical devices, and as green solvents for materials synthesis and characterization.[1–5]

The properties of ionic liquids are highly sensitive to the choice of counter-anion, and can be tailored further through chemical modification of the organic cation. In particular, upon substituting the cation with long alkyl chain(s), some ionic liquids may exhibit liquid-crystalline properties, combining the attractive properties of liquid crystals and ionic liquids.[6–9] Of particular interest is the anisotropic conductivity of liquid-crystalline ionic liquids (LC-ILs), which can find applications in molecular electronics[10,11] or in dye-sensitized solar cells.[12–14]

In order to realize the potential of LC-ILs, there is high demand for developing novel types of ionic mesogens with tailored physical and/or chemical properties. Herein, we present a strategy for obtaining new types of LC-ILs, in which the liquid crystallinity is driven by formation of supramolecular, halogen-bonded trimeric anions based on perfluorinated iodoalkanes. Use of perfluorinated chains promotes the self-organization of LC-ILs because of the segregation of the perfluorocarbon chains (fluorophobic effect),[15–17] while the supramolecular, anisotropic C–I⋯I ⋯I–C synthon acts here as a mesogenic unit, so that the mesophase formation is driven by the anion and is to some extent independent of the nature of the organic cation. These unconventional superfluorinated LC-ILs (Scheme 1) exhibit liquid-crystallinity even at room temperature.[18]

In the conventional design, calamitic liquid crystals consist of a fairly rigid core functionalized with one or more flexible alkyl or alkoxy chains.[19,20] An archetype LC-IL comprises 1-alkyl-3-methylimidazolium cation as a mesogenic core[6] and for mesophase formation to occur, the length of the alkyl chain attached to the imidazolium core is of critical importance; it has been claimed that at least a dodecyl chain is required for the system to exhibit liquid crystallinity.[21,22] Typically, lamellar mesophases are formed, driven largely by attractive, electrostatic interactions between charged species, which separate naturally from the apolar alkyl tails.[23] However, while the imidazolium cation plays a key role in defining the mesomorphism, the counter-anion is also important in influencing both the phase behaviour and physical properties of the material.[6,8] For example, with the perchloroborate cluster anions $[B_{10}Cl_{10}]^{2-}$ and $[B_{12}Cl_{12}]^{2-}$, imidazolium salts with C16 and C18 alkyl chains exhibit smectic phases with very high melting and clearing temperatures,[24] whereas using the very polar fluorohydrogenate anion $[FHF]^-$, a smectic A phase was observed even for a C10 chain.[25] It is also generally known that while mesophases are commonly observed with, for example, small fluorinated anions such as $[BF_4]^-$ and $[PF_6]^-$, larger anions such as $[Tf_2N]^-$ do not normally support liquid crystal phase formation. Incorporation of Eu-containing counter-anions can give mesophases that show the luminescence of the anion,[26] while iodide appears promising when using the LC-ILs as a hole-transporting layer in dye-sensitized solar cells.[12–14] Halide-containing anions are encountered rather frequently in ionic liquids and importantly, they can serve also as electron-donating moieties to participate in halogen bonding.[27–29]

Halogen bonding refers to the non-covalent interaction involving a halogen atom as electrophilic species.[30] It has proven to be a viable tool in crystal engineering,[31–34] and is also emerging as a noncovalent interaction of choice in designing functional supramolecular materials.[35,36] Thanks to its directionality,[37] halogen bonding is an effective tool in constructing supramolecular liquid crystals from non mesogenic starting compounds,[38–40] yet no halogen-bonded LC-ILs have been demonstrated up to date. The strength of the halogen bond can be tuned by the choice of halogen atom taking part in the noncovalent interaction[41] and fluorination of the chemical

[*]   Dr. G. Cavallo, Prof. Dr. G. Terraneo, A. Monfredini, Prof. Dr. G.
        Resnati, Prof. Dr. P. Metrangolo
        NFMLab, Department of Chemistry, Materials, and Chemical
        Engineering "Giulio Natta", Politecnico di Milano
        Via L. Mancinelli 7, 20131 Milan, Italy
        E-mail: pierangelo.metrangolo@polimi.it; giuseppe.resnati@polimi.it

        Prof. Dr. P. Metrangolo
        VTT-Technical Research Centre of Finland
        Biologinkuja 7, 02150 Espoo, Finland
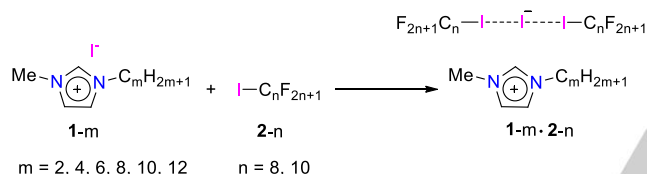
        Dr. M. Saccone, Prof. Dr. A. Priimagi
        Chemistry and Bioengineering Unit
        Tampere University of Technology
        P.O. Box 541, FI-33101 Tampere, Finland

        Prof. Dr. D. W. Bruce
        Department of Chemistry,
        University of York,
        Heslington, York, YO10 5DD, United Kingdom
        E-mail: duncan.bruce@york.ac.uk

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groups at the vicinity of the bond-donor atoms enhances their ability to be involved into strong intermolecular interactions.[42,43] The electron-donating halogen bond acceptors can be neutral Lewis bases such as pyridine groups,[44] or charged species such as mono- to tetra-dentate iodide anions.[27] In the latter case, the number of halogen bonds in which the anion is involved depends both on the shape and the valence of the partner.[28] Taking into account: (i) the potential of halogen bonding in constructing supramolecular liquid crystals, and (ii) the ability of the commonly used halide counter-anions of LC-ILs to act as halogen-bond acceptors, it seems feasible to utilise halogen bonding in designing novel types of LC-ILs with potentially unprecedented properties and tunability.

The complexes under investigation are derived from 1-alkyl-3-methylimidazolium iodides (**1**-m) of varying alkyl chain length (Scheme 1). Note that from these only **1**-12, bearing a C12 chain, exhibits liquid crystallinity (Cr • 27 • SmA • 80 • Iso)[12], the others being isotropic ionic liquids. The imidazolium compounds were complexed with iodoperfluorooctane (**2**-8) and iodoperfluorodecane (**2**-10), which have already proven themselves as viable tectons in crystal engineering.[45]

Scheme 1. Chemical structures of the used imidazolium salts (**1**-m) and iodoperfluorocarbons (**2**-n) and their halogen-bonded complexes **1**-m•**2**-n.

All complexes were characterized by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and polarized optical microscopy (POM). DSC analysis of complex **1**-2•**2**-8 was consistent with the preferred 1:2 stoichiometry between the salt and the iodoperfluoroalkane. Thus, as shown in Figure 1, the DSC thermogram of the 1:1 complex shows the presence of excess pure **1**-2 (melting point 57 °C) while the endothermic peak at 24 °C present in the 1:3 complex corresponds to melting of uncomplexed **2**-8. Hence, only the thermogram of the 1:2 complex is consistent with the presence of a single species with thermal properties distinct from those of the starting compounds.

In order to investigate the supramolecular organisation of **1**-2•**2**-8 in the solid state, single crystals were grown by slow, isothermal evaporation of a solution of the imidazolium salt and the iodoperfluoroalkane in acetonitrile in a 1:2 molar ratio. Single crystal X-ray analysis (Figure 2 and Table S1) confirmed that two fluorinated chains are bound to one iodide anion; the I···I$^-$ distances are almost identical (3.458(1) Å and 3.462(1) Å) corresponding to approximately 83% of the sum of the van der Waals and Pauling radii of the iodine atom and iodide anion, respectively. The C–I···I$^-$ angles are 174.12(1)° and 175.40(2)°, consistent with the expected high directionality of halogen bonding, and the I···I$^-$···I angle is 162.38(1)°. The imidazolium

cations are disordered over two positions that are occupied equally. The two cation sites are related by what appears to be a reflection (not a property of the crystal as the space group is P-1) and the two positions are shown in the ESI (Figure S1). With disorder removed, Figure 2B shows the separation between the ionic and neutral species, as well as between hydrocarbon and perfluorocarbon chains, within the crystal.

The perfluorinated chains are arranged in layers, giving rise to a stepped organization with the iodide anion. The imidazolium rings are located in between the fluorinated units, developing a stack parallel to the fluorinated columns. The overall crystal
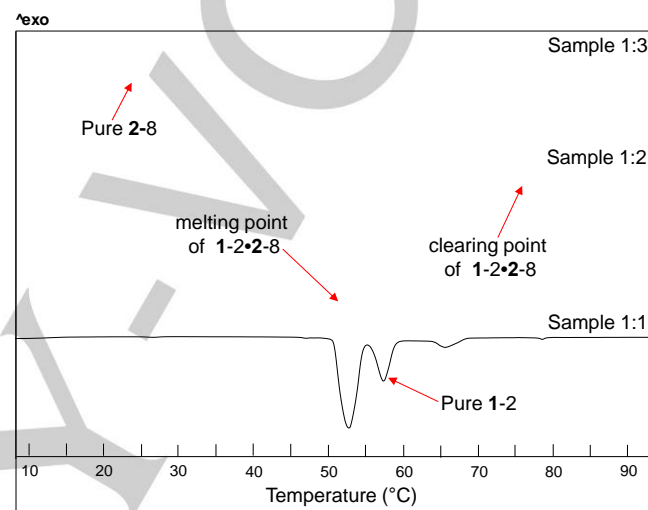

Figure 1. Thermal analysis of the **1**-2•**2**-8 complex, prepared using 1:1, 1:2, and 1:3 mixing ratios of **1**-2 and **2**-8, respectively.

packing shows a clear separation between the ionic and neutral species, which acts also to segregate the perfluorinated chains from the cation.

The liquid crystal properties of the new complex were characterised using a combination of polarised optical microscopy and DSC, with characteristic optical textures being obtained on cooling. The halogen-bonded complex **1**-2•**2**-8 exhibited enantiotropic LC phases and the mesomorphism was characterised as crystal-to-SmB transition at 52.9 °C, a SmB-to-SmA transition at 68.8 °C with a clearing point of 72.8 °C. When the material was subjected to repeated heating and cooling cycles, the liquid-crystalline properties disappeared suggesting that in this halogen-bonded system, partial and irreversible rupture of C–I···I$^-$ interactions may accompany isotropisation. Similar observations of lability have been made previously in 2:1 halogen-bonded complexes of 4-alkoxystilbazoles with 1,4-[39] and 1,3-diiodotetrafluorobenzenes.[40] Nevertheless, the supramolecular complex **1**-2•**2**-8 is stable at room temperature at least for a period of one month.

Taking into account these data, we synthetized all the complexes presented in Scheme 1 using a 1:2 complexation ratio between the imidazolium salts and the iodoperfluorocarbons. Thermogravimetric analysis on samples containing the imidazolium salt **1**-12 and either **2**-8 or **2**-10 in

ratios 1:1, 1:2, and 1:3 confirmed the preferred 1:2 stoichiometric ratio. The TGA thermograms (Figures S3 and S4) show that the complexes release the perfluorocarbon in a single step. For the 1:1 and 1:2 complexes there is no weight loss in the temperature range where unbound **2**-8 and **2**-10 are expected to be released (30-50°C for **2**-8 and 40–60°C for **2**-10). For the 1:3 samples the weight loss starts at a temperature lower than the other complexes and the slope of the curve reproduces well the behaviour of pure **2**-8 and **2**-10. Therefore we can conclude that in the 1:3 samples part of the perfluorocarbon is not bound, while in the 1:1 and 1:2 samples, all the perfluorocarbon interacts with I⁻ and the maximum complexation ratio is 1:2. (Figures S3 and S4).
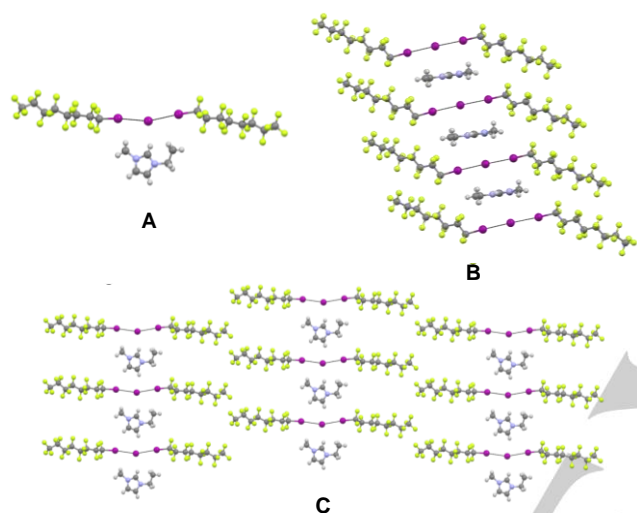

Figure 3. Thermal behaviour of halogen-bonded complexes **1**-m•**2**-n as measured upon heating by hot-stage polarised optical microscopy. Blue represents the crystal phase, red the SmB, and orange the SmA phases.

Figure 2. A) Halogen bonding drives the self-assembly of the imidazolium salt **1**-2 and the iodoperfluorooctane **2**-8 into trimeric supramolecular complex **1**-2•**2**-8; **B**) Top view of the crystallographic *b*-axis showing the segregation between the imidazolium salt **1**-2 and the iodoperfluorooctane **2**-8; **C**) Side view showing ionic and fluorocarbon lamellae of the structure of complex **1**-2•**2**-8. Color code: grey, carbon; blue, nitrogen; magenta, iodine; green, fluorine; white, hydrogen. Halogen bonds depicted as grey lines.

Figure 4. Optical textures of the smectic phases observed for **1**-12•**2**-10 on cooling from the isotropic state. Left: SmB phase at 77 °C; Right: SmA phase at 83 °C.

Optical microscopy studies revealed that all complexes were liquid-crystalline, some even at room temperature, with SmB and SmA phases (Figures 3 and 4). The SmA-SmB transition was identified by the appearance of characteristic striations across the back of the fans (Figure 4, left), which disappear on cooling further below the transition. Table S2 reports the phase transition temperatures for all of the complexes presented in Scheme 1.
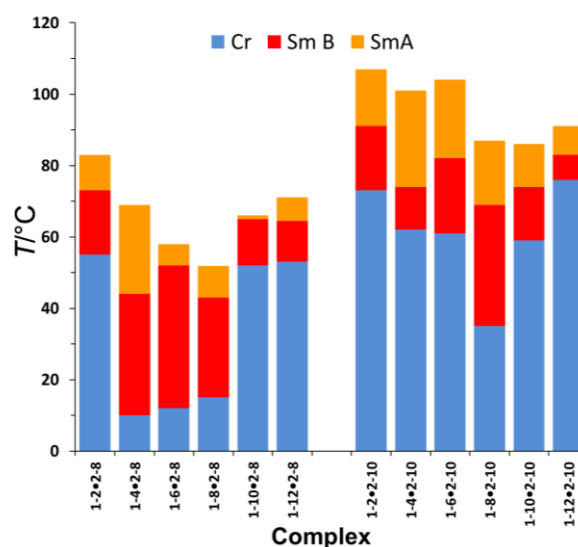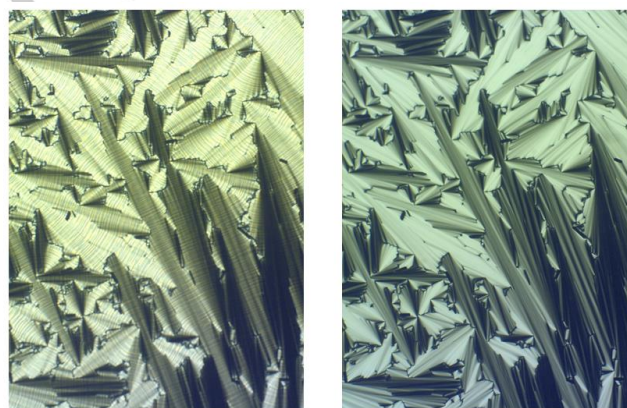
Given that 1-alkyl-3-methylimidazolium cations with alkyl chains as short as ethyl are not known to induce liquid crystallinity, then the remarkable thing about these new materials is that the mesomorphism is driven by the anisotropy of the anion. With the exception of simple salts of carboxylic acids,[41] such an observation is at best rare. Thus, the mesomorphism evidently arises as the anion is highly anisotropic owing to the effectively linear disposition of the iodoperfluoroalkanes about the central iodide anion (found in the crystal structure and assumed to persist into the mesophase) and the fact that perfluoroalkyl chains are very much 'stiffer' than analogous hydrocarbon chains, adopting a sterically induced helical structure due to repulsion between 1,3-disposed CF_2 groups.[42,43] This is then consistent with the observation that the transition temperatures for complexes with the anion prepared from iodoperfluorodecane (**2**-10) are generally higher than those

with anion **2**-8 as the former is more anisotropic. Furthermore, the known tendency[44,45] for perfluorinated chains to give rise to lamellar phases, which is a manifestation of nanophase segregation, is consistent with the observation of SmB and SmA phases. These phases are also those seen most commonly for ionic liquid crystals.[5]

In considering the study of the liquid crystal properties of these complexes in more detail, it is important first to recall lessons from some previous work. Thus, previously we reported on a large and systematic study [46] of liquid-crystalline halogen-bonded complexes between five different 4-alkoxystilbazole and five different 4-alkoxytetrafluorostilbene compounds. It was possible to obtain most of the 25 combinations as crystalline materials and in these cases, melting points and transition temperatures were sharp. However, for a few examples it was necessary to prepare the complexes in the melt (crystallisation did not work) and here it was found that there was a small amount of biphasic behaviour at melting and clearing points, indicative of slightly incomplete complex formation. However, comparison of the phase behaviour of samples prepared by both crystallisation and in the melt showed that the phase behaviour was the same in each case.

In the present study, a melt methodology was used again with a sealed system mitigating against the volatility of the iodoperfluoroalkanes. The materials clearly have the correct overall composition, but with two halogen bonds to form there is a slightly greater chance that the molecular integrity is not perfect, which would account for the slightly uneven pattern in the thermal behaviour of some of the complexes of **2**-10.

Consideration of the mesophase behaviour of the complexes **1**-m•**2**-8 shows a monotonic decrease in clearing point as the chain length in **1**-m increases from m = 2 to m = 8. The next homologue, **1**-10•**2**-8, shows a much enhanced melting point compared to **1**-8•**2**-8 and greater stability for both the SmA and SmB phases. The behaviour of **1**-12•**2**-8 is similar. A not dissimilar pattern of monotonic decrease in clearing point is also found for complexes **1**-m•**2**-10, with a minimum in the crystal phase stability for cation **1**-8 that recovers with longer cation chain length. The observation that the clearing points for the materials with anion **2**-n (which is longer and, therefore, more anisotropic) are higher than those with anion **1**-n is totally consistent with the proposition that the mesomorphic behaviour is driven by the anion.

So how might the thermal behaviour of these complex salts be understood? The salts with anion **2**-8 show a clear progression with a significant destabilisation of the crystal phase as the cation chain length extends beyond two carbons, then recovering with increasing m until for m = 10 and 12, it becomes much more stable again. A similar overall pattern is seen with anion **2**-10. In the absence of solid-state structural data it is not possible to rationalise these data, but it is interesting that when both hydrocarbon and fluorocarbon chains are longest the crystal phase is at its most stable, which is perhaps a little surprising as this is when hydrocarbon/fluorocarbon immiscibility would be expected to be greatest. This last comment is made in the light of the parallel observation that conventional SmA and SmB phases are seen when both anion and cation chains are long. The existence of these phases requires that the mesomorphic species is calamitic but self-evidently, this is the

anion yet it would be very surprising to find the long fluorocarbon chains parallel with long hydrocarbon chains. One possibility would be that they somehow extended perpendicular to the long axis of the anion giving a sort of T-shaped arrangement. This would both preserve the stronger electrostatic cation-anion interaction and would not act to destabilise a lamellar, fluorous arrangement. This could, in principle, be also consistent with a more stable crystal phase and, if the electrostatic interactions dominate phase stability, then it would be consistent with higher clearing points. What is perhaps a little less clear is how this arrangement would form a hexagonal next (SmB phase) and also the fact that such an arrangement might imply a weak biaxiality, although this would depend strongly on the correlation between alkyl chains, which may well be rather low (certainly there is no evidence whatsoever of anything other than a conventional optical texture).

To summarise, we report on unconventional liquid crystalline ionic liquids in which the liquid crystallinity is driven by halogen-bonded supramolecular anion $[C_nF_{2n+1}–I\cdots I\cdots I–C_nF_{2n+1}]^-$ that acts as the mesogenic unit. The material system is unique in many ways, demonstrating for the first time (i) ionic, halogen-bonded liquid crystals, and (ii) imidazolium-based ionic liquid crystals in which the liquid crystallinity is not driven by the alkyl chains of the cation – indeed with our supramolecular design, even salts of the 1-ethyl-3-methylimidazolium cation exhibit smectic mesophases. The results reported in this paper may pave the way towards totally new design principles in liquid crystalline materials.

The use of fluorocarbon-based materials as ordered, quasi-solid electrolytes in dye-sensitised solar cells may be beneficial for improving their performance and extending their long-term intrinsic stability.[47] In this regard, the order offered by a liquid-crystalline system could provide for preferential conduction pathways, improving conductivity.[48] It is also important that some of the complexes reported here are mesomorphic even at room temperature. We foresee that the reported superfluorinated ionic liquid crystals might develop as an attractive new functional materials platform.

Experimental Section

The starting materials were purchased from Sigma-Aldrich, and they were used as received. Commercial HPLC-grade solvents were used without further purification. The LC textures were studied with an Olympus BX51 polarized optical microscope equipped with a Linkam Scientific LTS 350 heating stage and a Sony CCD-IRIS/RGB video camera. DSC analysis were performed with a Mettler Toledo DSC823e instrument, using aluminium light 20 µL sample pans and Mettler STARe software for calculation. Thermogravimetric analysis (TGA) were performed on a TGA Q500 (TA Instruments) at a heating rate of 5°C/min, from 25 °C to 250 °C under nitrogen atmosphere (flow rate 45 ml/min). The single crystal X-ray structure was determined on a Bruker Kappa Apex II diffractometer. Experimental details about the crystal structure determination can be found in the Supporting Information.

Synthetic procedures: All the 1-alkyl-3-methyl imidazolium iodides were prepared as previously reported.[49] The supramolecular complexes were synthetized as follows: The 1-methyl-3-alkyl-substituted imidazolium iodides and the appropriate iodoperfluoroalkanes were mixed in a 1:2 ratio in a clear borosilicate glass vial. The vial was closed and put into an oil bath under vigorous stirring. The temperature was then raised to 70°C. After 15 min stirring the mixture was allowed to cool

to room temperature. Single crystals of **1**-2•**2**-8 were prepared by dissolving separately 1-methyl-3-ethylimidazolium iodide and 1-iodoperfluorooctane, in acetonitrile at room temperature in a 1:2 ratio, under saturated conditions. The two saturated solutions were then mixed in a clear borosilicate glass vial, which was left open in a closed cylindrical wide-mouth bottle containing paraffin oil. Solvent was allowed to slowly evaporate at room temperature until yellow crystals, suitable for X-ray analysis, were formed. Both the crystallization and melt methodologies afforded the same complexes as confirmed by DSC and POM analysis.

Single-crystal XRD data for **1**-2•**2**-8: $C_{22}H_{11}F_{34}I_3N_2$, $M_r = 1329.995$, triclinic, $P\text{-}1$, $a = 7.662(2)$ Å, $b = 9.723(2)$ Å, $c = 26.220(6)$ Å, $\alpha = 99.83°$, $\beta = 91.33(2)°$, $\gamma = 91.03(2)°$, $V = 1923.65$ Å^3, $T = 220(2)$ K, $Z = 2$, 41341 reflns measured, 11564 indep. reflns, 622 parameters, 235 restraints, $\theta_{max} = 30.57°$, R[$F^2 > 2\sigma(F^2)$] = 0.0414 wR(F^2) = 0.0910.
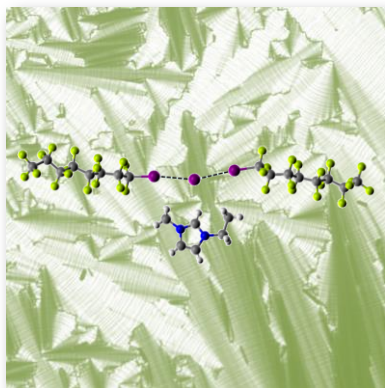
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Layout 1:

COMMUNICATION

Unconventional liquid crystal design: An accurate molecular design based on the high directionality of the halogen bond and the fluorophobic effect, allows to obtain a new family of superfluorinated ionic liquid crystals where the liquid crystallinity is driven by halogen-bonded supramolecular anions.

Gabriella Cavallo, Giancarlo Terraneo, Alessandro Monfredini, Marco Saccone, Arri Priimagi, Giuseppe Resnati,* Pierangelo Metrangolo* and Duncan W Bruce*

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Superfluorinated ionic liquid crystals through mesomorphic, halogen-bonded anions