Fluorinated liquid crystals formed by halogen bonding†

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New, halogen-bonded fluorinated mesogens are reported; the expected microphase separation associated with perfluoroalkyl chains is surprisingly absent in the mesophase.

Fluorination has for a long time been a productive strategy for exerting control over both mesomorphism and physical properties in liquid crystals.[1] In particular, lateral fluorination has been used to exert control over melting points, mesomorphism and the sign of properties such as dielectric anisotropy, a particularly fine example being the work undertaken on 4,4″-disubstituted terphenyl derivatives.[1,2] It was also found that liquid crystals can derive their molecular dipole moment from terminal substitution with perfluoroalkyl (R_f) chains. These so-called superfluorinated materials (SFMs) are typically characterised by a strong dielectric anisotropy and high melting temperatures, and also fulfil certain requirements for use in modern liquid crystal displays.[3]

Generally, the introduction of long R_f chains in mesogens enhances the smectic character of a liquid crystal,[4] and the smectic A (SmA) phase can be stabilised even for compounds with a core that consists of a single benzene unit, owing to the stiffness of long R_f chains.[5] Thus, a major feature of the mesomorphism of compounds containing long R_f chains is the dominance of lamellar phases and the effective absence of the nematic phase due to the microphase separation that occurs between these chains and other segments of the molecule (fluorophobic effect).[4] For this reason, the fluorophobic effect could lead to a significant stabilisation and even to modifications of smectic, columnar, and cubic mesophases.

In recent years the number of reports in the literature on the use of R_f chains has risen consistently, perhaps prompted in part by reports of possible symmetry-breaking in the SmA phase of materials containing R_f chain segments.[6] For example, our own work with four-ring imine mesogens containing two, terminal perfluorinated chains revealed a new class of materials showing cubic phases.[7,8] More recently, such general ideas on the self-organisation of fluorinated segments have also found expression in the search for materials showing the biaxial nematic phase.[9,10]

New families of liquid-crystalline materials have been developed by the identification of non-covalent interactions such as hydrogen bonding,[11] quadrupolar[12] and charge-transfer[13] interactions that can lead to new mesomorphic supramolecular species by self-assembly. Most recently, the halogen bond has proven successful in determining the self-assembly of supramolecular mesogens.

The halogen bond[14] is a charge-transfer interaction directly analogous to the hydrogen bond, and major contributions to the development of its scope and chemistry have been driven by the Milan group.[15] Halogen-bonded interactions require the presence of an electron-poor halogen (normally iodine or bromine) and an electron-rich Lewis base (often an amine or pyridine derivative), and a range of structures has been described.[16] Recently, some of us reported[17] that halogen bonding could also be used to induce liquid crystal phase behaviour by combination of a non-mesomorphic alkoxystilbazole with iodopentafluorobenzene (Fig. 1), where for $n = 4$ the complexes showed a monotropic nematic phase, while for $n = 12$, an enantiotropic SmA phase was seen. Subsequently, supramolecular polymeric liquid crystals based on halogen bonding have been reported.[18] Keen to extend this work and having shown examples of dimeric complexes formed by single halogen bonds, we then undertook a low molar mass approach to trimeric systems based on two halogen bonds and investigated the complexation of a range of alkoxystilbazoles to α,ω-diiodoperfluoroalkanes. Reports regarding supramolecular mesogens obtained on combining hydrogen bonding and the fluorophobic effect are very rare in the literature.[19] Here we report the first case of liquid crystals formed by combining halogen bonding and the use of iodoperfluoroalkanes.

Complexes were obtained by crystallising from THF solution a 2:1 mixture of the stilbazole and the diiodoperfluoroalkane to give the products **1**, shown in Fig. 2, which have been fully characterised (see ESI†). The complexes were pale yellow in colour, indicating a degree of charge-transfer to the stilbazole chromophore, whose absorption has been shown to shift on charge-transfer complexation.[20] Fig. 3 shows two views of the structure of the complex **1d** as determined by single crystal X-ray diffraction methods.‡ The ratio of stilbazole to 1,6-diiodoperfluorohexane in the crystal is 2:1 as can be anticipated from the telechelic halogen bond donor behaviour of 1,6-diiodoperfluorohexane. The adduct is characterised by a stepped arrangement between the two stilbazoles, a consequence of the antiperiplanar arrangement of the perfluoromethylene groups of the halogen bond donor. There is an inversion centre about the centre of the central C–C bond of the

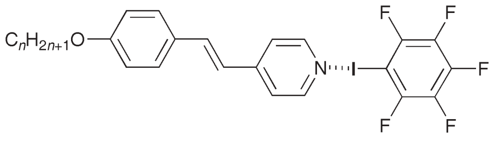

Fig. 1 Halogen-bonded liquid crystals.

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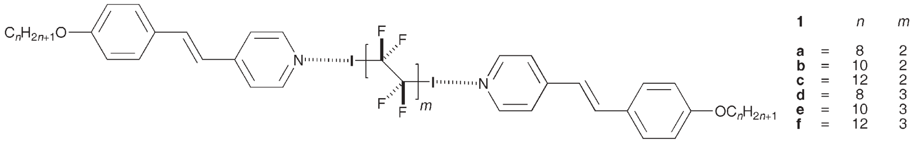

Fig. 2 Structure of the new halogen-bonded complexes **1**.

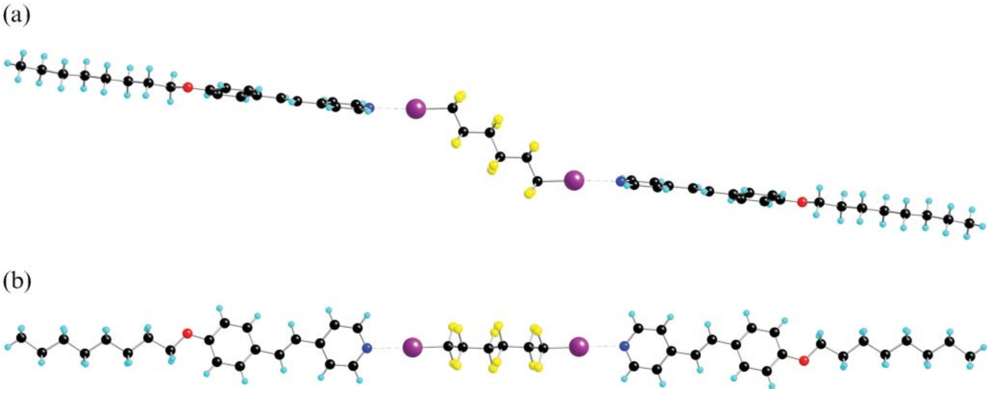

Fig. 3 Two ball-and-stick views of the single crystal X-ray structure of the halogen-bonded trimeric complex **1d**.

diiodoperfluorohexane, and so there is only one N···I distance, found to be 2.805(2) Å, which corresponds to a reduction of about 20% with respect to the sum of van der Waals radii for N and I (3.53 Å),[21] with a N···I–C angle of 176.71(8)°. Such parameters are typical of those found in the literature of halogen-bonded materials.[16] Analysis of the crystal packing of complex **1d** shows how the stilbazole and the perfluorinated modules stack in separated columns parallel to the *a* crystallographic axis (Fig. 4), probably as a consequence of the fluorophobic effect. However, multiple H···F intercolumnar interactions (distances between 2.498–2.659 Å) stabilise the crystal packing.

For all of the complexes **1** the ratio between the stilbazole and the diiodoperfluoroalkane used was established by recording their ^{1}H and ^{19}F NMR spectra, respectively, in the presence of 2,2,2-trifluoroethyl ether as an internal standard. On calibrating integration parameters so that in the ^{1}H NMR spectrum the CH_2O quartet of 2,2,2-trifluoroethyl ether corresponded to four hydrogens and that in the ^{19}F NMR spectrum the CF_3 triplet of 2,2,2-trifluoroethyl ether corresponded to six fluorines, the ratio between the $–CH_3$ signal area (derived from the stilbazole) and the $–CF_2I$ signal area (derived from the diiodide) was 3:2, thus revealing that the stilbazole:diiodide ratio in all of the complexes **1** is 2:1 (see ESI†).[15]

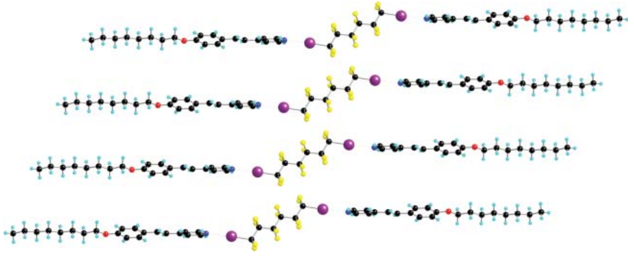

Fig. 4 Partial view of the crystal packing of the complex **1d** showing microphase separation between the R$_f$ chains and the hydrocarbon molecules. The diiodoperfluorohexane and stilbazole modules stack in columns, which run parallel to the *a* crystallographic axis.

The liquid crystal properties (Table 1) of the new complexes were studied by hot stage polarising optical microscopy and differential scanning calorimetry (DSC). On heating, all of the complexes **1a–f** melted directly to the isotropic liquid, yet the process occurred over several degrees and showed apparent biphasic behaviour with the presence of both an isotropic liquid and crystals floating therein. We will return to this point presently, but interestingly, this melting point increased with the chain length of the diiodoperfluoroalkane and decreased with the chain length of the stilbazole used, with the exception of **1e**. The former behaviour is apparently in contrast with previous observations of melting points that are always lower for halogen-bonded complexes of 1,6-diiodoperfluorohexane compared to those of 1,4-diiodoperfluorobutane.[22] Once an apparently homogeneous isotropic state was reached, the samples were cooled, and for the examples shown in Table 1, a monotropic nematic phase was seen, evident from its characteristic schlieren texture (Fig. 5), with the only exception of **1e**. The samples heated were, in each case, single crystal in nature (structures have been obtained for >1 of the materials described in this communication) and so the behaviour on melting can be ascribed to initial breakdown of the halogen-bonded complex followed by its re-formation, probably in the isotropic phase. This is evidenced by the fact that, in the

Table 1 Thermal behaviour of the new complexes

Complex	Transition	*T*/°C
1a	Cr–I	102.8
	(N–I)	(95.2)
1b	Cr–I	99.3
	(N–I)	(91.1)
1c	Cr–I	95.3
	(I–N)	(90.1)
1d	Cr–I	108.4
	(N–I)	(103.5)
1e	Cr–I	110.4
1f	Cr–I	99.7
	(I–N)	(95.8)

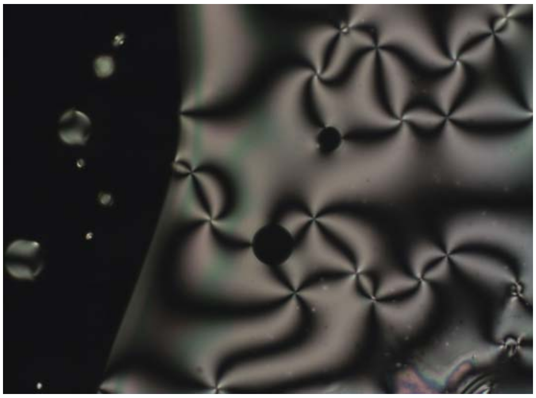

Fig. 5 Optical texture of the monotropic nematic phase of **1b** at 91 °C.

non-mesomorphic materials, crystallisation occurred at temperatures that were well above the clearing points of the related stilbazoles and shows the high thermal stability of the halogen bond. Such behaviour is allowed thermodynamically, simply reflecting the lower Gibbs function for the mixture of crystals and the isotropic phase, than for the single isotropic phase at these temperatures; this behaviour has literature precedent.[23] In most cases, the nematic phase was observed over a range of perhaps 3–5 °C before the material crystallised, after which the thermal behaviour could be reversed (*i.e.* melting to isotropic followed by monotropic N phase). However, for **1c** the nematic phase appeared longer lived and reproducibly existed for some 10 °C before crystallisation occurred.

What is intriguing about these materials is that they all show the nematic phase. The mesomorphism of the halogen-bonded stilbazole complexes reported earlier (Fig. 1)[17] was that of a simple, dipolar mesogen, showing a nematic phase at short chain length and a SmA phase with longer chains. Similar behaviour was found for *cis*-[MCl(CO)$_2$]-functionalised stilbazoles (M = Rh, Ir).[24] However, as suggested earlier, the mesomorphism of mesogens containing perfluoroalkyl chains is dominated by the formation of smectic phases – normally SmA[1,4] – due to an effective microphase separation between fluorocarbon and other segments of the molecule. Here, this is clearly not the case and even the materials containing a diiodoperfluorohexane spacer show a nematic phase. One possible origin might be the flexibility in the N···I link, although we suspect that the size of the stilbazole makes this unlikely and another explanation must be sought in due course.

In conclusion, halogen bonding drives the self-assembly of a range of alkoxystilbazoles with α,ω-diiodoperfluoroalkanes into trimeric complexes. And, despite the non-mesomorphic nature of the starting materials, most of the halogen-bonded complexes show liquid-crystallinity. Thus, we have shown the first case of the use of halogen bonding and iodoperfluoroalkanes in the design of new, supramolecular, fluorinated liquid crystals. The use of shorter and longer chain diiodoperfluoroalkanes than those reported in this communication, as well as the use of mono-iodoperfluoroalkanes are currently under study for the synthesis of new halogen-bonded fluorinated liquid crystals.

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Notes and references

‡ *Crystal data for* **1d**: $C_{24}H_{27}F_6INO$, M = 586.37 g mol^{-1}, yellow blocks, 0.36 × 0.20 × 0.10 mm^3, triclinic, space group $P\bar{1}$, a = 7.9751(4) Å, b =12.3703(6) Å, c = 12.7345(6) Å, α = 105.832(1)°, β = 97.487(1)°, γ = 96.492(1)°, V = 1183.72(10) Å^3, Z = 2, D_c = 1.645 g cm^{-3}, F000 = 586, MoK$_\alpha$ radiation, λ = 0.71073 Å, μ = 1.417 mm^{-1}, T = 110(2) K, $2\theta_{max}$ = 60.02°, 13476 reflections collected, 6656 unique (R_{int} = 0.0165), 6211 with $I_0 > 2\sigma(I_0)$, absorption corrections T_{min}/T_{max} = 0.880. Solved using SHELXS-97[25b] and refined with SHELXL-97[25a] with full-matrix least squares on F^2, 299 parameters, GoF = 1.049, $R_1[I > 2\sigma(I_0)]$ = 0.0236, w$R_2[I > 2\sigma(I_0)]$ = 0.0587, R_1 (all reflections) = 0.0259, wR_2 (all reflections) = 0.0598, $-0.52 < \Delta\rho < 1.17$ eÅ^{-3}. CCDC 604155. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605101d

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