Fluorinated liquid crystals – properties and applications

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This *critical review* begins with a brief, but essential, introduction to the special nature of liquid crystal materials, their peculiar properties, and their commercial applications, followed by an introductory insight into the remarkable nature of the fluoro substituent, and its fascinating influence on the properties of organic compounds. However, the main focus of the review is to discuss the enormous amount of exciting research on fluorinated liquid crystals that has been reported. The small size of the fluoro substituent enables its incorporation into all types of liquid crystal, including calamitic, discotic, banana, lyotropic, and polymers, without ruining the liquid crystalline nature of the material. However the fluoro substituent is larger than hydrogen, and hence causes a significant steric effect, which combined with the high polarity, confers many fascinating, and often remarkable, modifications to melting point, mesophase morphology and transition temperatures, and the many other very important physical properties, such as dielectric anisotropy, optical anisotropy, and visco-elastic properties. There are many different positions within a liquid crystal structure where a fluoro substituent can be located, including (i) a terminal position, (ii) within a terminal chain, as a semi-fluorinated or as a perfluorinated chain, or as one fluoro substituent at a chiral centre, (iii) as part of a linking group, and (iv) a lateral position in the core section. Such variety enables the interesting and advantageous tailoring of properties, both for the fundamental purposes of establishing structure–property relationships, and for materials targeted towards commercially-successful liquid crystal display applications.

Introduction to liquid crystals

Liquid crystals have proved to be truly fascinating materials in terms of their academic fundamental properties, and their tremendous success in commercial applications.[1–5] Liquid crystals are fluid phases of matter where the constituent molecules are sufficiently disordered to be classified as a liquid, and generate flow properties, yet retain varying degrees of ordering depending on the actual type of liquid crystal phase (Fig. 1). Hence, liquid crystals are anisotropic fluids, where the unique combination of flow and molecular ordering confers some exciting and interesting optical, dielectric, and

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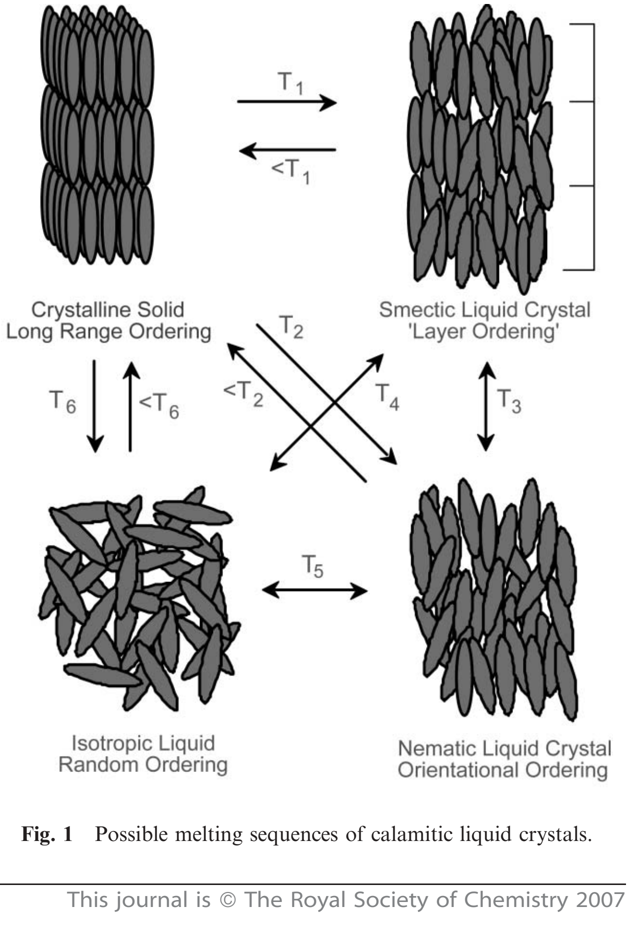


Fig. 1 Possible melting sequences of calamitic liquid crystals.

visco-elastic properties. The constituent molecules in the crystalline solid phase are ordered in a predictable manner throughout the entire three-dimensional structure. Normally, a crystalline solid melts directly, in one distinct step, into the isotropic liquid phase where the constituent molecules are randomly ordered throughout the entire system. However, such a destructive phase transition is not universal for all compounds, some compounds of a particular stylized molecular structure, such as rod-shaped, disc-shaped, and amphiphilic, melt through one or more phases of intermediate molecular ordering, such phases are called mesophases or liquid crystal phases, and the compounds that exhibit such behaviour are called mesogens or liquid crystals.

Fig. 1 shows an example of possible melting sequences of calamitic liquid crystal compounds. At T_1 the compound melts from the crystalline solid to the smectic liquid crystal phase, where the molecules have lost the long range positional ordering, but retain some degree of layer ordering and orientational order. Possible different organization of the molecules within the layers gives rise to several different smectic liquid crystal phases. Alternatively, a calamitic liquid crystal may lose positional and layer ordering in one step (T_2) to generate a nematic liquid crystal phase, which possesses only orientational ordering of the constituent molecules. In other compounds, a smectic liquid crystal phase may lose the layer ordering of the constituent molecules (T_3) to generate the nematic liquid crystal phase. Alternatively, a smectic liquid crystal phase may lose both layer ordering and the orientational ordering of the constituent molecules in one step to generate the isotropic liquid (T_4). The loss of the orientational molecular ordering of the nematic phase will also generate the isotropic liquid phase (T_5). For completeness, the destructive scenario of a compound melting directly from the crystalline solid phase to the isotropic liquid (T_6) is shown. In liquid crystal terminology, any transition to the isotropic liquid is termed the clearing point. All transitions between various liquid crystal phases and between liquid crystal phases and the isotropic liquid phase are reversible. However, supercooling, due to the kinetic nature of crystallization on cooling, allows liquid crystal phases to be generated below the melting point, and these phases are termed monotropic.

The nematic liquid crystal phase is the most commonly encountered liquid crystal phase, and is exhibited by a vast range of compounds; it is the least ordered, and hence the most fluid and the least viscous liquid crystal phase. Accordingly, it is the nematic phase that is employed in the vast majority of liquid crystal display formats developed over the past 40 years. Liquid crystal displays are not the topic of this review, but a brief discussion is important to understand the significance of later discussions of fluoro-substituted liquid crystals, and further details are available in several review articles and books.[1–11] In the most simple terms, rod-like nematic liquid crystals are anisotropic, and have different properties when measured along the molecule and across the molecule. Such direction-dependent properties, combined with the ability to switch the orientation of liquid crystal molecules with a small electric field, facilitate display applications.

Liquid crystal displays consist of a thin (5–6 μm) sandwich of nematic liquid crystal material between two glass plates. The exterior surfaces of the glass are coated with polarizing films (usually crossed at 90° with respect to each other). The interior surfaces of the glass are coated with a transparent electrode, which is etched away in areas that will never be switched. A polymer layer (usually rubbed polyimide) is then applied so as to align the nematic molecules (usually horizontally). A so-called twisted nematic (TN) mode is generated by arranging the rubbing directions at 90° with respect to each surface, and in order to ensure a unidirectional helix throughout the display, a small amount (0.1%) of an enantiopure chiral dopant is incorporated into the nematic liquid crystal material. In this unswitched state, polarized light enters the cell, and the plane of polarized light is rotated through 90° by the twisted nematic material, thus allowing light to pass through the other polarizer (bright, off-state). The application of a small electric field will re-orient the molecules towards the direction of the applied field, and hence the twist structure is destroyed, and so the crossed polarizers block the passage of light (dark, on-state).

Traditionally, simple twisted nematic liquid crystal displays were directly-addressed, meaning each pixel (switching area) is connected by two electrodes. Clearly, this bulky situation is only practical for the most simple, agricultural watch and calculator displays, and the massive number of connections would rule out use in more complex, elegant, high information displays. Multiplex-addressing, which involves the time-sequential addressing of rows and columns, allows 'dot-matrix' displays to show more complex information, but there are severe limitations as the molecules cannot respond fast enough to such addressing, and hence contrast suffers greatly. A further development came in the mid-1980s with super-twisted nematic (STN) displays, which inherently provide a steeper electrooptic characteristic (*i.e.*, a steeper change in contrast with applied field). Hence STN displays enable the addressing of larger numbers of rows and columns, but the same limitations remain, and the inherent generation of interference colours is a further disadvantage.

Solving the above problems came with the development of active matrix (AM) addressing of the twisted nematic device through the use of thin-film transistors (TFTs). Such technology essentially allows the control advantages of a direct connection without the bulky connections, or put another way, allows all the advantages of multiplex addressing with no loss of contrast. Such technology, using arrays of TFTs, is highly complex and expensive, hence in the early days of the late 1980s and early 1990s these displays were rather small, just a few inches diagonal, and the yield of successful devices was very low. Hence, cheaper, more easily constructed multiplex-addressed TN and STN devices still dominated most applications. However, TN active matrix TFT technology developed steadily, eventually became much cheaper and much more reliable and consistent, and is invaluable in satisfying the needs of small portable devices, such as personal organizers, cameras, mobile telephones, lap-top computers, desk-top monitors and some, usually small, televisions.

However, the contrast shown by the twisted nematic display is very dependent on the viewing angle, which can be a problem even for personal viewing displays in mobile phones and lap-top computers, but is a severe limitation for television displays. Additionally, owing to the manner of switching, the speed is rather slow for applications where fast-moving graphics are prevalent. Other display formats based on liquid crystals, notably the in-plane switching (IPS) mode and the multi-domain vertically-aligned (MVA) mode, have been developed to provide a 170° viewing angle and very fast switching speeds of 5 ms. These latter two device formats tend to dominate the larger, higher-value displays for television applications, with typical sizes of between 26 and 42 inches, but displays of around 100 inches are now being made available, however, such displays are becoming increasingly employed in lap-top computer and desk-top monitor displays.

Although it is the nematic liquid crystal phase that completely dominates the LCD market, displays based on the chiral smectic C phase, called ferroelectric liquid crystal displays (FLCDs), are commercially available in the form of microdisplays. Such ferroelectric microdisplays offer much faster switching (a few ms), better contrast and higher resolution than nematic displays, and tend to be used in view-finder displays of cameras, in eye-glasses, goggles, and visors for a variety of leisure and professional activities.

Of course, aspects of molecular structure of the liquid crystal materials are of paramount importance in the operation and quality of any device format. The various device formats require similar essential features of materials, but significant physical property requirements vary quite widely, as will become clear later. The most essential properties such as the melting point, mesophase morphology and transition temperatures, and the many other very important physical properties, such as dielectric anisotropy, optical anisotropy, and visco-elastic properties, all depend strongly on molecular structure, which needs to be optimized through appropriate molecular design and synthesis. Such a task is not easy, out of the massive number of materials that are liquid crystalline only a very small percentage are suitable for use in display applications. It is relatively straightforward to formulate a liquid crystal mixture with a nematic phase between −40 °C and +100 °C (less easy for a chiral smectic C mixture), but to additionally engineer all other optimized physical properties can prove an enormous challenge. Indeed, although LCDs have been around for nearly 40 years, the whole field has developed gradually over that time, and it is only over the last couple of years that large area colour television displays of acceptable quality have been possible. As will be seen later, the development of fluoro-substituted liquid crystals has played an essential role in satisfying the exacting demands of the various types of liquid crystal displays through both fundamental, academic structure–property relationship research and targeted commercial research.

Introduction to the interesting properties of fluoro-substituted organic compounds

In order to provide a background of knowledge and understanding in respect of fluoro-substituted liquid crystals it is essential to first consider the more general fascinating, unusual, and often most beneficial properties of fluoro-substituted organic compounds.[12–20] The fluoro substituent in organic compounds is regarded as so interesting because of the combination of polar and steric effects, and the great strength of the C–F bond which confers stability on fluoro-substituted compounds.

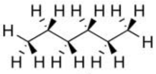
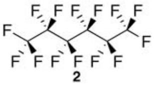
Table 1 Quantified polarity and size parameters for common substituents of organic molecules[21–23]

Property X	H	F	Cl	Br	I	C	N	O
Electronegativity	2.20	3.98	3.16	2.96	2.66	2.55	3	3.5
C–X Dipole Moment/D	0.4	1.41	1.46	1.38	1.19	—	—	—
Polarizability/10^{-25} cm^{-1}	6.67	5.57	21.8	30.5	47	—	—	—
van der Waals Radii/Å	1.20	1.47	1.75	1.85	1.98	1.70	1.55	1.52
C–X Bond Length/Å	1.09	1.38	1.77	1.94	2.13	—	—	—
C–X Bond Strength/ Kcal mol^{-1}	98.0	115.7	77.2	64.3	50.7	—	—	—

Table 1 shows some quantified parameters in respect of polarity and size of various substituents found in organic molecules, and the values for fluorine tend to stand out. Fluorine has the highest electronegativity of all the elements (3.98), and hence as a substituent confers a high dipole moment on the C–F bond. In an aliphatic or alicyclic environment the dipole moment is relatively large, *e.g.*, 1.85 D in fluoromethane, however, in an aromatic environment the mesomeric effect causes a reduction in dipole moment, *e.g.*, 1.50 D for fluorobenzene. Despite the high polarity, the fluoro substituent has a low polarizability which confers low intermolecular dispersion interactions. The fluoro substituent is the smallest, after hydrogen, of all possible substituents, and like hydrogen it is monoatomic. So although a fluoro substituent obviously causes a steric effect, the size influence is not too drastic, which enables it to be usefully incorporated into parent molecules for beneficial modification of properties. Substituents that include carbon, nitrogen and oxygen are also shown in Table 1, but of course they must have other units bonded to them to give various different groups (*e.g.*, CH_3, NH_2, OH, OCH_3) which are much larger than a fluorine.

The interesting influence of fluoro substituents on properties is well exemplified by comparing hydrocarbons with perfluorocarbons, and such a comparison of behaviour and properties is very applicable to liquid crystals, which almost always possess hydrocarbon chains in their molecular structure. Hexane (**1**) is a typical hydrocarbon that finds use as a non-polar solvent, and has a low boiling point and a low dielectric constant (Table 2). Perfluorohexane (**2**) has an even lower boiling point, despite a much higher molecular weight, and is even less polar than hexane with a lower dielectric constant than hexane. These findings are perhaps unexpected considering the highly polar nature of the fluoro substituent. However, the symmetry

Table 2 Some properties of hexane (**1**) and perfluorohexane (**2**)[12,13,16]

Compound Property	 **1**	 **2**
Boiling Point/°C	69	57
Density at 25 °C/g cm^{-3}	0.655	1.672
Viscosity/mPa s	0.29	0.66
Surface Tension/dyn cm^{-1}	17.9	11.4
Refractive Index at 25 °C	1.372	1.252
Dielectric Constant	1.89	1.69

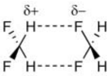
of the perfluoro system (**2**) causes a 'cancellation' of the local dipoles to leave a non-polar system overall, and given the low polarizability of fluorine, a less polar and lower boiling compound results. Of course, not all properties of fluoro-substituted compounds are surprising, for example the bulky nature of the neighbouring fluoro substituents cause steric interactions which tends to limit conformational flexibility, and hence perfluoro chains are often described as stiff; this situation is reflected in the higher density and higher viscosity of perfluorohexane (**2**) compared with hexane (**1**).

The low polarizability of fluorine confers weak intermolecular forces of perfluoro systems which results in very low surface tensions of liquids (see Table 2 for the values of hexane and perfluorohexane). The same phenomenon confers a very low surface energy on perfluorinated solids, for example, poly(tetrafluoroethene), commonly known as PTFE or Teflon, has a surface energy value of 18.5 dyn cm^{-1}, and hence has well-known anti-stick properties for a variety of applications.[16]

Fascinating background to the exceptional way that fluorine confers unusual properties on organic compounds is found in partially fluorinated systems. Interestingly, the highly polar nature of the C–F bond can in turn cause polarization of the C–H bond of the same carbon, thus enabling the hydrogen to be involved in hydrogen bonding with the fluorine of a neighbouring molecule. For example, difluoromethane (**3**) has a significantly higher boiling point (−51.6 °C) than either the hydrocarbon (methane, **4**) or the perfluorocarbon (tetrafluoromethane, **5**), which boil at −161 °C and −128 °C respectively.[24]

Not surprisingly, the monofluoro system (**6**) and the trifluoro system (**7**) have intermediate boiling points of −78.6 °C and −82.2 °C respectively, which reflects the extent of possible hydrogen bonding between the molecules.[24]

Another well-documented, remarkable influence of fluoro substituents is found in the complex resulting from an equimolar mixture of benzene (**8**) and hexafluorobenzene (**9**). Benzene (**8**) melts at 5.5 °C and hexafluorobenzene (**9**) melts at just 3.9 °C, yet an equimolar complex melts at 23.7 °C, clearly demonstrating a high degree of intermolecular attractions, which is in sharp contrast to the large miscibility gaps that are found in mixtures of hydrocarbons (*e.g.*, **1**) and perfluorocarbons (*e.g.*, **2**).[25,26]



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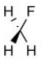

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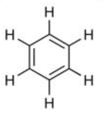

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A greater depth of detail of these exciting introductory aspects of the special nature of fluoro substituents in organic molecules, and indeed examples of further interesting aspects can be found in the excellent texts of Banks, Smart, and Tatlow,[13] Banks,[12] Kirsch,[16] Chambers,[14] and Uneyama.[17]

Introduction to fluorinated liquid crystals

In the brief introductory background to liquid crystals above, the rod-like nature of the molecules was emphasized, and it was also mentioned that the structural nature of the liquid crystal molecules was crucial for both the generation of liquid crystal phases and the physical properties exhibited.

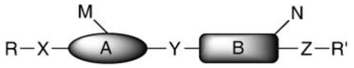


Fig. 2 A typical structural template for a calamitic liquid crystal.

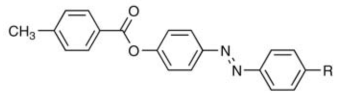
Fig. 2 shows a typical structural template for a liquid crystal molecule of the calamitic variety, where A and B represent core units, R and R′ denote terminal units, X, Y and Z are referred to as linking groups, and M and N are lateral substituents. Clearly there are many possibilities to be selected from the vast array of chemical units, however, the need to retain a broadly linear, rod-like structure, a reasonable length to breath ratio, and an optimum compromise of rigidity and flexibility, tends to restrict those possibilities. Core units are typically 1,4-disubstituted benzene, *trans*-1,4-disubstituted cyclohexane, 2,5-disubstituted pyrimidine, but other common core units include 2,6-disubstituted naphthalene, 2,5-disubstituted thiophene, and 2,5-disubstituted 1,3-dioxinane. Terminal units are most usually moderately long linear hydrocarbon alkyl chains, but branched chains, or small substituents (*e.g.*, fluoro, chloro, bromo, trifluoromethyl and cyano) on the chain are sometimes employed, particularly where a chiral centre is required. Alternatively, a small polar substituent is often used as a terminal unit (*e.g.*, fluoro, chloro, bromo, trifluoromethyl, cyano and nitro). Linking groups are not always present, hence X, Y and Z would simply represent a single bond, however, linking groups that extend the molecular length and maintain linearity of structure (*e.g.*, ester, imine, ethenyl, ethynyl, methyleneoxy and dimethylene) are frequently incorporated into liquid crystal structures. Lateral substituents clearly detract from the ideal linear, rod-like structure of liquid crystals, and hence they tend to be small substituents or groups (*e.g.*, chloro, fluoro, bromo, methyl, cyano and trifluoromethyl). Lateral substituents, particularly fluoro, are frequently employed in liquid crystal structures to modify melting point, liquid crystal transition temperatures and mesophase morphology, and to modify the physical properties of liquid crystals to enable their use in applications.

Fluoro substituents have been so successfully, and usefully incorporated into liquid crystal molecules because of the combination of small size and high polarity, and because the high strength of the C–F bond (see earlier) confers excellent stability. The relatively small size of a fluoro substituent means that it does not unduly alter the necessary stylized structure, which helps to maintain the existing liquid crystalline nature of the compound. However, the important attributes of the fluoro substituent discussed above, ensures that subtle, but significant, modifications are frequently encountered in respect of melting point, mesophase morphology, transitions temperatures, and the many essential physical properties of liquid crystals, such as optical, dielectric, and visco-elastic properties. Such alterations to the attributes of liquid crystals are of great significance in terms of fundamental academic structure–property relationships, and crucial to the development of commercially-successful liquid crystal displays. As is clear from the above structural template (Fig. 2), there are many possible locations for fluoro substituents within the structure of a calamitic liquid crystal.[27,28] Furthermore, fluoro substituents have been incorporated into discotic liquid crystals,[29–31] metal-containing liquid crystals,[32–35] banana liquid crystals,[36–39] liquid crystal polymers[40–44] and lyotropic liquid crystals.[45–49] This review will provide broad coverage, but focus on the fundamental structure–property relationships of fluorinated calamitic liquid crystals with a strong emphasis on the display applications of liquid crystals, which essentially is what has made fluoro substitution of liquid crystals such an important, fascinating, and topical subject.

Fluoro substituents in a terminal location as a single unit and within small groups

The first use of a fluoro substituent in a terminal location of a liquid crystal dates back to 1925.[27,50] Historically, research into the structure–property relationships of liquid crystals focused on determining which structural units promoted good liquid crystal phase stability.[27,28] Table 3 shows the effect of some terminal substituents on liquid crystal phase stability, in the case of the T_{N-I} value.[27] Alkyl chains (compound **11**) were found to be good because, despite being of low polarizability, they enhance the length to breadth ratio of the molecules. Small polar groups such as cyano (compound **16**) and nitro (compound **15**) were also found to be very good because they have a high polarizability, and in the terminal location enhance the overall polarizability anisotropy, and hence provide for high clearing points. Unfortunately, the fluoro substituent (compound **10**) does not enhance the length to breadth ratio, and it is of very low polarizability, and hence it does not promote liquid crystal phase stability particularly well, and accordingly research into such materials was rather limited. Much research centred on liquid crystals with those terminal groups that provided a high degree of liquid crystallinity, in particular terminal alkyl chains, and because of the need for a positive dielectric anisotropy for application in twisted nematic displays (see earlier), liquid crystals with a terminal cyano group were the subject of extensive research. However, the introduction of high technology active matrix (AM) addressing of liquid crystal displays (LCDs) through thin film transistors (TFTs) necessitates the use of liquid crystals of very high resistivity. The cyano group tends to attract ions, and confers a low resistivity to the liquid crystal material due to the high polarity and high polarizability, which significantly impairs the performance of AM-TFT displays based on active matrix (TFT) addressing, and hence such compounds cannot be used.[5,11,51–55]

Table 3 The effect of different terminal units on liquid crystal phase stability



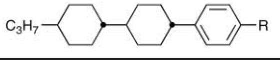
Compound		Transition Temperatures/°C				
Number	R	C		N		I
10	F	•	156.0	•	222.0	•
11	CH_3	•	160.0	•	243.5	•
12	I	•	187.0	•	243.5	•
13	Br	•	178.0	•	251.0	•
14	Cl	•	167.0	•	252.0	•
15	NO_2	•	179.5	•	289.0	•
16	CN	•	169.0	•	312.0	•

Of course, the fluoro substituent has a reasonable polarity to provide positive dielectric anisotropy, and yet has a very low polarizability, and tends to confer a high resistivity. Hence liquid crystals with a terminal fluoro substituent became the subject of extensive research for their use in nematic mixtures for active matrix displays.[5,11,51–55] Furthermore, other similar, and connected fluoro-substituted structural units (*e.g.*, $–CF_3$, $–OCF_3$, $–SF_5$) were incorporated in order to provide higher values of positive dielectric anisotropy, whilst generating a reasonable level of nematic phase stability and low viscosity.

Compounds with a terminal fluoro substituent can exhibit high T_{N-I} values if three-ring structures (Table 4) are employed (*e.g.*, compound **17**).[16,56] However, the dielectric anisotropy is significantly lower than for the terminal cyano-substituted analogue (**22**),[16,57] which also has a much higher T_{N-I} value, indeed illustrating the intrinsic problems of replacing such impressive compounds, where excellent T_{N-I} values are seen in two-ring structures which have the additional advantage of much lower viscosity.

Extension of the terminal group can allow for multiple fluoro substituents. For example compound **18** has two 'terminal' fluoro substituents, which has an advantageous effect on the dielectric anisotropy, and gives a high T_{N-I} value.[16,58] Compound **19** possesses three 'terminal' fluoro substituents which enhance the dielectric anisotropy even further, and confer a low melting point and a high T_{N-I} value.[16,59] However, the disadvantage of such fluoro substitution is the enhancement of the smectic tendency. Compounds **20**[16,60] and **21**[16,54] both have high melting points and are not liquid crystalline, however, the T_{N-I} values have been determined by extrapolation using a commercial nematic mixture, and as expected are in keeping with the bulk of the terminal group. As a single group compatible with AM-TFT technology, the SF_5 provides the highest known positive dielectric anisotropy, however, the viscosity ($\gamma 1$) of compound **21** is very high (612 mPa s), compared with the desired 70 mPa s required for the overall material used in display applications.[16,54] A good alternative manner of modifying a terminal fluoro-substituted compound such as **17** to give lower melting points and higher dielectric anisotropy is to use a lateral fluoro substituent (discussed in detail later) next to the original.

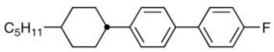
Table 4 The effect of different types of terminal fluoro substituent on transition temperatures and dielectric anisotropy ($\Delta\varepsilon$) in comparison with the cyano group



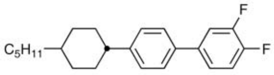
Compound	R	Transition Temperatures/°C	$\Delta\varepsilon$
17	F	C 90.0 N 158.0 I	3.0
18	$OCHF_2$	C 52.0 SmB 69 N 173.6 I	5.2
19	OCF_3	C 39 SmB 70.0 N 154.7 I	6.9
20	CF_3	C 133.0 [N 112.2] I	9.5
21	SF_5	C 121.0 [N 95.5] I	11.6
22	CN	C 75 N 241.7 I	14.8

Compound **23** has a high melting point and a very high T_{N-I} value, and is of relatively low positive dielectric anisotropy ($\Delta\varepsilon$).[16,61] Further fluoro-substitution next to the original fluoro substituent (compound **24**) has dramatically reduced the melting point and the T_{N-I} value, but enhances the positive dielectric anisotropy.[16,51,62]

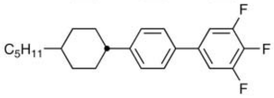
The introduction of a third fluoro substituent (compound **25**), again next to the original, causes a further significant reduction of the melting point and T_{N-I} value.[16,56] The third fluoro substituent tends to cancel the lateral dipole influence of the second fluoro substituent, and hence the longitudinal dipole is increased more substantially to give a very high positive dielectric anisotropy. In compounds **24** and **25**, the lateral fluoro substituents are in effect serving as additional terminal units in enhancing the positive dielectric anisotropy, and could easily be defined as terminal substituents, but the convention in liquid crystals is always to call them lateral positions, and these are discussed in more detail later.



23
C 102.0 N 153.9 I (°C)
$\Delta\varepsilon$ = 4.2

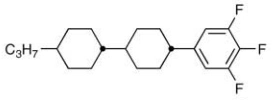


24
C 55.0 N 105.4 I (°C)
$\Delta\varepsilon$ = 6.3

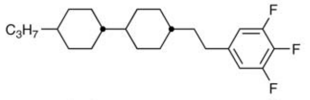


25
C 25.0 N 54.8 I (°C)
$\Delta\varepsilon$ = 11.7

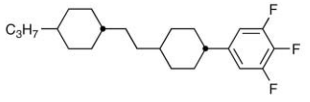
Compounds **26**, **27** and **28** all have the trifluorophenyl unit to provide high values of positive dielectric anisotropy ($\Delta\varepsilon$).[7,16,56] The flexible dimethylene linking group in compounds **27** and **28** has caused a useful reduction in melting point, however, viscosity values have also increased. In comparison with compound **26**, compound **29** has an extended molecular length, which facilitates a higher T_{N-I} value, and the melting point is reasonably low. Compound **29** has a lower viscosity than that of compound **26**, which is most surprising given the additional fluoro substituent and the ether oxygen.[16,63] Commercial liquid crystal mixtures require a wide range of small, two-ring systems to provide for a lower overall viscosity, and compounds **30** and **31** both provide similar dielectric anisotropy values, but compound **31** has the massive advantages of a much higher T_{N-I} value and a much lower viscosity.[7]



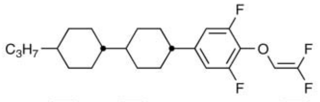
26
C 66.0 N 94.1 I (°C)
$\Delta\varepsilon$ = 9.7
γ1 = 171 mpa s



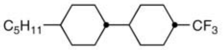
27
C 35.0 SmB 42.0 N 100.8 I (°C
$\Delta\varepsilon$ = 9.3
γ1 = 207 mpa s



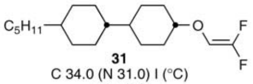
28
C 45.0 N 82.8 I (°C)
$\Delta\varepsilon$ = 9.4
γ1 = 212 mpa s



29
C 49.0 N 135.9 I (°C)
$\Delta\varepsilon$ = 9.8
γ1 = 132 mpa s



30
C 35.0 (SmX 33.0) [N -20.5] I (°C)
$\Delta\varepsilon$ = 5.3
γ1 = 99 mpa s



31
C 34.0 (N 31.0) I (°C)
$\Delta\varepsilon$ = 5.6
γ1 = 65 mpa s

A wide range of other compounds with fluoro substituents in a terminal location have been developed to generate the highest positive dielectric anisotropy and the lowest viscosity. Many of these compounds also have fluoro substituents in a lateral position or on a linking group, and hence will be discussed later under the appropriate headings.

Fluoro substituents in lateral locations

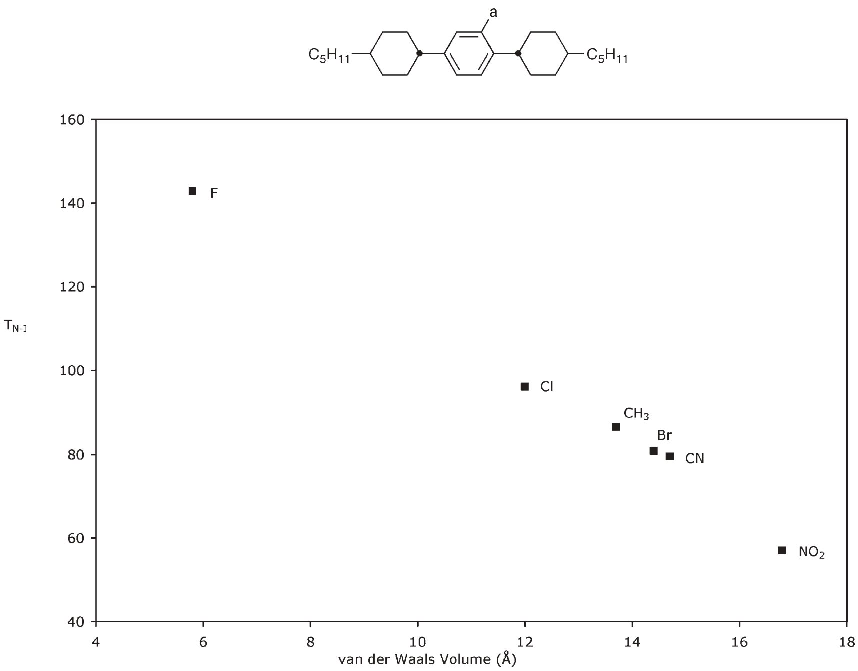
Of all the various possible locations of fluoro substituents in a liquid crystal molecule, the lateral location has certainly been the most widely investigated. As outlined earlier, any unit that protrudes from the side of the mesogenic core will tend to cause a disruption in the intermolecular forces of attraction and molecular packing. However, in general, only the fluoro substituent is sufficiently small so as to preserve reasonable liquid crystallinity, and hence fluoro substitution in the lateral position has received much research attention. Such investigations have centred on various different aims and objectives, but in general they all involved lateral fluoro substitution as a means of making subtle, but significant modifications to the melting point, transition temperatures, mesophase morphology, and various physical properties.

Initial studies involved fundamental research to establish structure–property relationships, then with the explosion in research dedicated to display applications, research became focused on using the subtle increase in size of a fluoro substituent over the parent hydrido system, and the high polarity of the fluoro substituent, to tailor the properties of liquid crystals for the ever-increasing technological complexity of display applications.

Fig. 3 shows a typical example of the reduced liquid crystal phase stability when lateral substituents are present. The use of van der Waals 'volume' instead of radii gives a much more accurate picture of the influence of a substituent on liquid crystal transition temperatures.[64] The parent compound (**32**) shows a smectic phase to high temperature, however, the influence of the larger fluoro substituent (compound **33**) has caused a large reduction in the clearing point. The larger size of the fluoro substituent clearly affects the smectic phase stability much more than the nematic phase stability, a point clarified by the even larger size of the chloro substituent in compound **34** which does not show a smectic phase, despite a very low melting point. The lateral substituents in compounds **35–38** are larger still, and cause a proportionate reduction in the nematic phase stability. Whilst the lowering influence of the lateral substituents on nematic phase stability is nice and linear, the extent to which the smectic phase stability is reduced varies widely depending on the exact location on a core (see later). The effect of lateral substituents on melting point is widely variable, as can be seen from Fig. 3, however, a lateral fluoro substituent does usually reduce the melting point, something not seen in the specific example of Fig. 3.

The first examples of lateral fluoro-substituted liquid crystals were reported by Gray in 1954 with simple 4-alkoxybenzoic acids (compounds **39** and **40**).[65]

Such acids dimerize to enable the generation of mesophases, and a broadening of the molecules by the lateral fluoro substituent causes a reduction in the liquid crystal phase

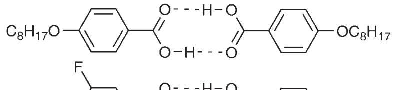


Compound		Transition Temperatures (°C)							van der Waals Volume (Å)
No.	a	C		Sm		N		I	
32	H	•	50.0	•	196.0	-	-	•	3.4
33	F	•	61.0	•	79.2	•	142.8	•	5.8
34	Cl	•	46.1	-	-	•	96.1	•	12.0
35	CH_3	•	55.5	-	-	•	86.5	•	13.7
36	Br	•	40.5	-	-	•	80.6	•	14.4
37	CN	•	62.8	•	(43.1)	•	79.5	•	14.7
38	NO_2	•	51.2	-	-	•	57.0	•	16.8

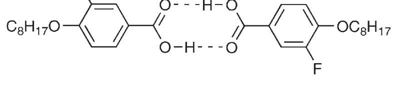
Fig. 3 The effect of lateral substituents of increasing size on melting point, liquid crystal phase stability and mesophase morphology.[64]

stability. The reduction in $T_{N\text{–}I}$ of around 25 °C, and a more marked reduction in the smectic phase stability, as seen here, is typical of the many later examples, however, the significant increase in melting point is rather unusual, with a marked reduction in melting point being by far the most common effect of a lateral fluoro substituent.

An important property of liquid crystals for displays is a high positive dielectric anisotropy, and the ubiquitous cyanobiphenyls (CBs),[67] and the later *trans*-alkylcyclohexylcyanophenyls (PCHs)[68] and *trans-trans*-alkylcyanobicyclohexylnitriles (CCHs)[69] serve this purpose very well. However, the advent of more complex devices based on high levels of multiplex-addressing necessitated materials that showed a very steep electrooptic characteristic. It was found the optimum solution was to use relatively non-polar nematic liquid crystals, such as those shown in Table 5,[66] as the basis of a nematic mixture of low viscosity, and to use the terminal cyano materials (CBs, PCHs, and CCHs) as components to provide the necessary positive dielectric anisotropy ($\Delta\varepsilon$). The additional molecular breadth conferred by a lateral fluoro substituent generates a low k_{33}/k_{11} (k_{11} and k_{33} are respectively the splay and bend elastic constants), and the polarity of the fluoro substituent enhances the perpendicular permittivity ($\varepsilon_\perp$) and hence tends to give a low $\Delta\varepsilon/\varepsilon_\perp$; the low value of both these parameters ensures the necessary steep electrooptic characteristic. As can be seen from Table 5, the parent system (compound

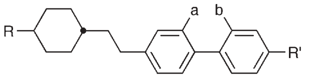


39
C 101.0 SmC 108.0 N 147.0 I (°C)



40
C 117.0 N 120.5 I (°C)

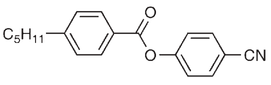
Table 5 Transition temperatures (°C) of fluorinated cyclohexylethylbiphenyls[66]



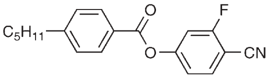
Compound					Transition Temperatures/°C								
No.	R	R′	a	b	C		SmB		SmA		N		I
41	C_3H_7	C_3H_7	H	H	•	67.0	—	—	•	119.0	•	144.0	•
42	C_3H_7	C_3H_7	F	H	•	59.0	—	—	•	(34.0)	•	109.0	•
43	C_3H_7	C_3H_7	H	F	•	40.0	—	—	—	—	•	108.0	•
44	C_3H_7	C_2H_5	F	H	•	34.0	—	—	•	(15.0)	•	97.0	•
45	C_3H_7	C_2H_5	H	F	•	27.5	—	—	—	—	•	97.0	•
46	C_2H_5	C_3H_7	F	H	•	34.0	—	—	—	—	•	80.0	•
47	C_2H_5	C_3H_7	H	F	•	21.3	—	—	—	—	•	78.0	•
48	C_5H_{11}	C_2H_5	F	H	•	23.0	•	27.0	•	55.0	•	104.5	•
49	C_5H_{11}	C_2H_5	H	F	•	23.5	—	—	•	(14.0)	•	103.0	•

41) is not suitable as a nematic material because of a high melting point, and a strong smectic tendency. However, lateral fluoro substitution serves to reduce the melting point, and to reduce or eliminate the smectic tendency, to leave useful nematic materials of low viscosity for display applications. Those compounds where a = F (**42**, **44**, **46** and **48**) show a reduced melting point, but do tend to retain a slight smectic tendency, and these are referred to as the I′ compounds. Those compounds (**43**, **45**, **47** and **49**) with the fluoro substituent in the other benzene ring of the biphenyl core (b = F), often referred to as the I compounds, generally show much lower melting points, and no smectic tendency at all, except for the case where R is relatively long (compound **49**). In general, the I and I′ compounds show the typical behaviour of lateral fluoro-substituted compounds of much reduced melting point, and lower phase transition temperatures, with the smectic phase thermal stability particularly affected, hence the ability of lateral fluoro substituents to turn completely useless parent systems of high liquid crystallinity into ideal candidates for application in nematic mixtures for liquid crystal displays.

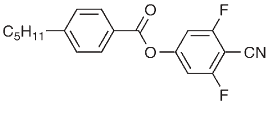
The use of lateral fluoro substituents in a location next to the terminal fluoro substituent has already been discussed above, with the result of generating a higher positive dielectric anisotropy. However, such a location and aims have origins in terminal cyano-substituted materials, with the main focus of research on fluoro-substituted esters such as compound **51** and other homologues.[70–73] In comparison to the parent system (compound **50**), a fluoro substituent (compound **51**) reduces the $T_{N–I}$ value by around 30 °C, and a second lateral fluoro substituent inherently fixed on the other side of the molecule, has a similar further influence on the $T_{N–I}$ value.[71]



50
C 64.5 (N 55.5) I (°C)
Δε = 40.1



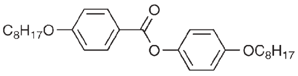
51
C 30.5 (N 24.5) I (°C)
Δε = 41.0



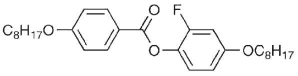
52
C 29.5 (N -8.0) I (°C)
Δε = 61.0

The first fluoro substituent (compound **51**) confers only a slight enhancement to the positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp}$) because of the near-equal contribution to both the parallel ($\varepsilon_{//}$) and perpendicular ($\varepsilon_{\perp}$) permittivities. However, the second fluoro substituent (compound **52**) counters the first in terms of $\varepsilon_{\perp}$ and adds greatly to $\varepsilon_{//}$, hence providing a very high positive dielectric anisotropy. The fluoro-substituted compounds such as **51** and **52** do not have the appropriate $T_{N–I}$ values to be major components of nematic mixtures for displays, but only small quantities are required to significantly enhance the positive dielectric anisotropy.[71,74]

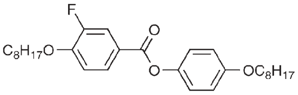
Esters are commonly used as linking groups in liquid crystals because they extend the molecular length, and enhance the polarizability anisotropy (*e.g.*, compound **53**), and importantly, they are relatively simple to synthesize.[1,27,28] Lateral fluoro substitution has been studied extensively in liquid crystalline esters with exciting results of both academic and commercial significance.[70–78] The influence of a lateral fluoro substituent on melting point, mesophase morphology, and transition temperatures can depend greatly on the location within the core. Two terminal alkoxy chains in esters tend to generate the smectic C phase due to the substantial lateral polarity which aids molecular tilting (compound **53**). One fluoro substituent at an 'inner-core' position (compound **54**) dramatically reduces the smectic phase stability (55 °C), lowers the $T_{N–I}$ value by just 26 °C, and causes a reduction in melting point (12 °C). One fluoro substituent at the 'outer-edge' position (compound **55**) of the benzoate ring tends to fill free space where the terminal chain meets the core, which serves to extend the effectiveness of the lateral intermolecular forces of attraction, which uphold liquid crystal transition temperatures, and is particularly effective for smectic phases. Hence, compound **55** has a similar melting point to the parent system (compound **53**), the smectic phase stability has been reduced by just 4 °C, yet the $T_{N–I}$ value is 15.5 °C lower. The other outer-core location of the fluoro substituent (compound **56**) has a more dramatic influence in changing the mesophase morphology. The smectic phase stability is now higher than that of the parent system (compound **53**), but in the form of the smectic A phase, and the nematic phase has been eliminated. The polar nature of the fluoro substituent means that the location is significant for generation of tilted phases, such as the smectic C phase, that depend strongly on molecular polarity. Where only one terminal alkoxy chain is present, the parent ester (compound **57**) exhibits the orthogonal smectic A phase rather than the tilted smectic C phase. However, the use of two lateral fluoro substituents (compound **58**) serves to alter the mesophase morphology to generate the smectic C phase in place of the smectic A phase because of the enhanced molecular tilting from the increased lateral polarity of the two lateral fluoro substituents.[79] In some locations a lateral fluoro substituent can be shielded by the breath of the molecular core, and so it tends not to reduce the liquid crystal phase stability so markedly as other locations, and can, because of space-filling, actually confer a higher value of liquid crystal phase stability than that of the parent system. For example, the bicyclooctane core is large and barrel-shaped, and tends to shield a lateral fluoro substituent that is nearby, hence compound **60** has a slightly higher T_{N-I} value than that of the parent system (compound **59**). However, in the bicyclooctanecarboxylate systems, when the fluoro substituent is at an 'outer-edge' position (compound **61**) the T_{N-I} is reduced by a typical 26 °C, which contrasts with the comparison of the benzoate systems shown above.[77]



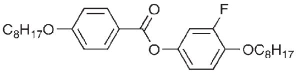
53
C 63.0 SmC 74.0 N 91.0 I (°C)



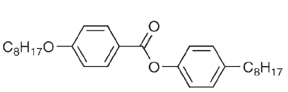
54
C 48.0 (SmC 19.0) N 65.0 I (°C)



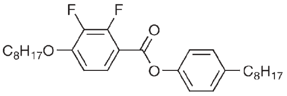
55
C 63.5 SmC 70.0 N 75.5 I (°C)



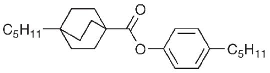
56
C 56.5 (SmC 55.0) SmA 78.0 I (°C)



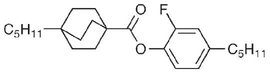
57
C 54.0 SmA 64.0 N 66.0 I (°C)



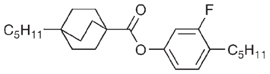
58
C 37.0 SmC 49.0 N 57.0 I (°C)



59
C 31.0 N 64.5 I (°C)

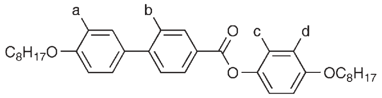


60
C 26.0 N 65.0 I (°C)



61
C 44.5 (N 38.5) I (°C)

Table 6 Transition temperatures (°C) of some fluoro-substituted phenyl biphenylcarboxylates[78]



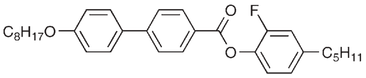
No.	a	b	c	d	C		SmB		SmC		SmA		N		I
62	H	H	H	H	•	110.0	•	116.0	•	165.0	•	200.0	—	—	•
63	F	H	H	H	•	93.0	—	—	•	167.5	•	182.5	—	—	•
64	H	H	H	F	•	85.0	—	—	•	149.5	•	192.5	—	—	•
65	H	H	F	H	•	68.0	—	—	•	137.0	—	—	•	172.0	•
66	H	F	H	H	•	87.0	—	—	•	140.5	—	—	•	164.0	•

As mentioned above, a lateral fluoro substituent is most useful in generating a tilted smectic C phase. The tilted smectic C phase is used as the basis of ferroelectric mixtures which are used in commercial microdisplays for a wide variety of applications.[6,9,80–85] Parent system, compound **62** (Table 6), exhibits a smectic C phase due to the polarity of the two terminal alkoxy chains and the ester linking group. However, the melting point is high, and an underlying smectic B phase is exhibited, both undesirable features for ferroelectric display applications. Compounds **63** and **64** both have fluoro substituents at 'outer-edge' locations, and both show a reduced melting point, and in a similar trend to that seen in the two-ring esters above, compound **63** has a higher smectic C phase stability than isomer **64**, indeed actually higher than the parent system, but the smectic A phase stability is lower. The 'inner-core' positions of the fluoro substituent (compounds **65** and **66**) show much lower smectic phase stability, but it is all exhibited as the tilted smectic C phase, and this much lower smectic phase stability allows the nematic phase to be generated.[78] Melting points can be further reduced by using one alkoxy chain and one alkyl chain (compound **67**),[86] and in comparison with compound **65** a smectic A phase is also seen because of the reduced lateral dipole arising from the use of only one alkoxy terminal chain. The reduced viscosity of compounds such as **67** is also beneficial for the intended application, but the reduced melting point reveals the underlying ordered smectic B phase which is disadvantageous.

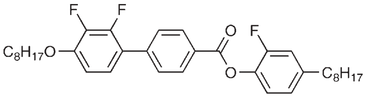
In such three-ring systems there is plenty of scope for using three fluoro substituents, and provided that they are in appropriate locations, a low melting point can be obtained, and underlying ordered smectic phases can be eliminated, but clearly, the overall liquid crystal phase transition temperatures will become much lower. For example, compound **68** shows a very low melting point for a three-ring structure, and yet despite three fluoro substituents, a smectic C phase is exhibited to 84.5 °C.[78]

In these ester systems it is clear to see that fluoro substituents in lateral positions offer much scope for various different locations, and multiple fluoro-substitution. The melting points can be much reduced, and the materials can be tailored to generate a specific mesomorphism depending on the location of the fluoro substituent(s), and importantly, the physical properties, and ultimate suitability for applications can be optimized.

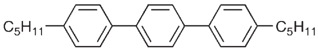
As can be seen from the transition temperatures of compounds **69–71**,[87,88] the terphenyl core offers good prospects for the generation of liquid crystal phases because it has a very high length to breath ratio and a very high polarizability anisotropy. Hence, such a core unit would be expected to support a lateral fluoro substituent or two, and still be capable



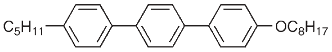
67
C 49.0 (SmB 30.0) SmC 121.0 SmA 128.0 N 164.5 I (°C)



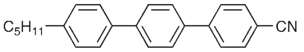
68
C 45.0 SmC 84.5 N 120.5 I (°C)



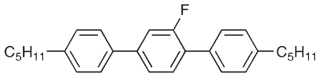
69
C 192.0 SmA 213.0 I (°C)



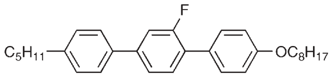
70
C 194.5 B 211.0 SmA 221.5 I (°C)



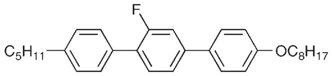
71
C 130.0 N 239.0 I (°C)



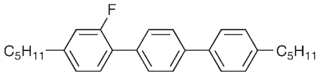
72
C 51.5 B 62.0 SmA 109.5 N 136.5 I (°C)



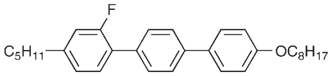
73
C 47.0 (J 40.0) SmI 53.5 SmC 116.5 SmA 130.0 N 155.0 I (°C)



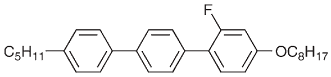
74
C 69.0 G 83.0 B 100.5 SmC 124.5 SmA 158.0 N 161.0 I (°C)



75
C 72.5 SmC 80.0 N 136.0 I (°C)



76
C 102.0 (SmI 99.5) SmC 137.5 N 160.0 I (°C)



77
C 69.0 (K 25.0 J 43.5) SmC 119.0 N 158.0 I (°C)

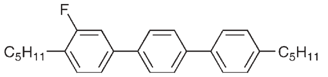
of generating high liquid crystal transition temperatures. In a typical unsymmetrical 4,4″-disubstituted terphenyl (*e.g.*, compound **70**), there are 6 different positions in a total of 12 that a fluoro substituent can be located, thus 6 monofluoro-substituted compounds are possible. As will be illustrated, widely different mesomorphic behaviour, physical properties, and suitability for applications can be generated by fluoro-substitution in these various different positions. Thus, terphenyls offer much scope for a systematic study of lateral fluoro substitution in liquid crystals. In general there can be considered two types of location for a lateral fluoro substituent in such terphenyls, 'inner-core' and 'outer-edge'. At an 'inner-core' location (*e.g.*, compounds **72–77**),[87,89–91] a lateral fluoro substituent causes much disruption in the side-to-side intermolecular packing, and hence smectic phase stability is severely depressed, which allows the generation of a nematic phase. Also, at such an 'inner-core' location, the fluoro substituent causes an inter-annular twisting, which is greater than that caused by the hydrogen, at the appropriate join of the two benzene rings, which reduces the polarizability anisotropy, and hence further reduces the liquid crystal phase thermal stability.

Additionally, in the appropriate structural situation, the lateral dipole generated by the fluoro substituent causes a molecular tilting and hence the generation of tilted smectic phases, such as the smectic C phase. For example, the lateral fluoro substituent in compound **72** has caused a massive reduction in melting point of 140.5 °C, and a very significant reduction in the smectic phase stability of 103.5 °C, which has enabled the generation of a nematic phase to 136.5 °C. In the case of compound **72** the molecular structure is quite symmetrical, with identical terminal chains, and so molecular tilting is not facilitated. Compounds **73** and **74** have very similar structures which differ only in the direction of the fluoro substituent, however, as can be seen, they exhibit significantly different mesomorphic behaviour. Compound **73** has the lower transition temperatures because the inter-annular twisting is at a point which leaves a relatively untwisted biphenyl section that has a simple alkyl chain, whereas compound **74** has the situation that has a relatively untwisted biphenyl section with an alkoxy chain, which confers a higher polarizability anisotropy, hence the higher transition temperatures. Interestingly, both compounds **73** and **74** generate a tilted smectic C phase, and indeed more ordered tilted smectic phases, this is because of the combination of the polarity of the lateral fluoro substituent and the ether oxygen in the terminal chain. As expected, both compounds **73** and **74** exhibit higher transition temperatures than the dialkyl analogue **72** because of the enhanced polarizability anisotropy. Compounds **75–77** also have an 'inner-core' lateral fluoro substituent,[87] however, there is now a clear imbalance in the symmetry, and this facilitates the generation of a tilted smectic C phase in preference to the orthogonal smectic A phase seen in compound **72**. Interestingly, the different location of the fluoro substituent in compound **75** has had no effect on the nematic clearing point ($T_{\mathrm{N-I}}$ value), but the smectic phase stability is around 30 °C lower than for compound **72**.

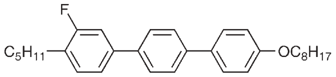
The alkyl-alkoxy analogues (**76** and **77**) both show the tilted smectic C phase, as expected, because of the combination of lateral dipoles from the fluoro substituent and the ether oxygen. However, compound **76** has a relatively untwisted alkoxy-substituted biphenyl section that does not contain a fluoro substituent, and hence the smectic C phase stability is much higher than that for compound **77** which only contains and alkyl chain in the relatively untwisted biphenyl section. Compounds **75–77** do not exhibit a smectic A phase and show the smectic C phase until the smectic phase stability collapses to a nematic phase, which is in contrast to the respective set of compounds **72–74**, whereas the respective nematic clearing points are very similar.[87]

Those terphenyls with the lateral fluoro substituent at an 'outer-edge' position (compounds **78–80**),[87] have a completely different mesomorphism and transition temperatures to the comparable terphenyls with the lateral fluoro substituent at an 'inner-core' location (compounds **72–77**). The fluoro substituent at the 'outer-edge' position tends to fill space with a polar unit, facilitating the side-to-side intermolecular forces of attraction, and hence upholding the smectic phase stability, despite the steric effect, and the nematic phase is not exhibited. Additionally, there is no additional interannular twisting from a fluoro substituent, which means that the polarizability anisotropy will be relatively high, thus supporting high transition temperatures. Compound **79** exhibits the tilted smectic C phase, as expected, because of the separation of the lateral dipoles from the fluoro substituent and the ether oxygen, however, where the fluoro substituent and the ether oxygen are close together at the same end of the core, then molecular tilting is not so facilitated.

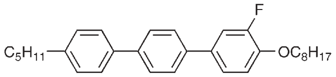
The influence of a lateral fluoro substituent in terminal nitrile materials is rather dominated by the strongly polar cyano group, and so smectic phases are not seen. Like the parent system (compound **71**), the two fluoro-substituted materials are both nematogens regardless of the location of the lateral fluoro substituent. However, as can be seen, the clearing point is much lower for the 'inner-core' location (compound **81**) than for the 'outer-edge' location (compound **82**), melting points are similar and lower than the parent system in both cases.[92]



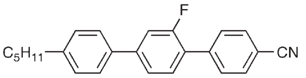
78
G 156.5 SmA 185.5 I (°C)



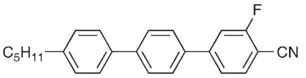
79
G 170.5 SmC 176.5 SmA 202.5 I (°C)



80
G 146.0 B 158.0 SmA 195.0 I (°C)



81
C 82.0 N 143.0 I (°C)

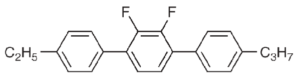


82
C 85.0 N 182.0 I (°C)

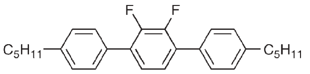
The very high liquid crystal phase stability of the terphenyl core means that compounds with two and three lateral fluoro substituents can provide interesting properties which make them suitable for device applications.[7,93–95] Even more lateral fluoro substituents can be tolerated, but these compounds have a higher polarity, and tend to have high melting points, combined with low liquid crystal phase stability.[7,93] As mentioned earlier, for terphenyls with different terminal chains there are 6 different locations for a lateral fluoro substituent. However, with two fluoro substituents the number of possible different compounds increases to 24, and all compounds have liquid crystalline, and other physical properties, that depend strongly on the locations of the two fluoro substituents.

The most promising location for two fluoro substituents is next to each other, *i.e.*, *ortho*-difluoroterphenyls. Such a combination has both fluoro substituents inherently fixed on one side of the molecule which minimizes the molecular breath, and as a result liquid crystal phase transition temperatures are upheld. In terms of physical properties, the viscosity tends to be relatively low because of the minimized molecular breadth, and the lateral dipole generated by the additive combination of the two fluoro substituents confers a strong negative dielectric anisotropy, which proved crucial in the development of liquid crystal mixtures for vertically-aligned nematic (VAN) displays.[7] However, *ortho*-difluoroterphenyls have origins in the search for smectic C host materials for ferroelectric mixtures.[79,93]

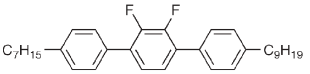
There are two possible types of *ortho*-difluoroterphenyls, one where the two fluoro substituents are at an 'inner-core' position in the centre ring (*e.g.*, compounds **83–86**),[7,93] one where the two fluoro substituents occupy an outer ring (*e.g.*, compounds **87–90**),[93] and as might be expected from the discussion of the monofluoroterphenyls, the liquid crystal properties and other physical properties are markedly different.



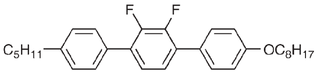
83
C 73.0 N 115.2 I (°C)



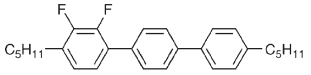
84
C 60.0 N 120.0 I (°C)



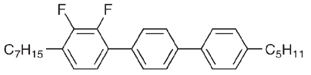
85
C 49.0 SmC 77.0 SmA 93.0 N 108.5 I (°C)



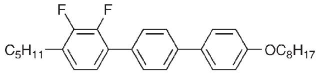
86
C 48.5 SmC 95.0 N 141.5 I (°C)



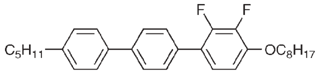
87
C 81.0 SmC 115.5 SmA 131.5 N 142.0 I (°C)



88
C 56.0 SmC 105.5 SmA 131.0 N 136.0 I (°C)



89
C 89.0 SmC 155.5 SmA 165.0 N 166.0 I (°C)

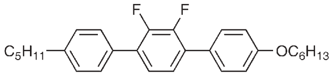


90
C 93.5 SmC 144.0 SmA 148.0 N 159.0 I (°C)

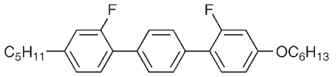
Where the terminal chains are relatively short, and both alkyl (*e.g.*, compounds **83** and **84**), then the materials are nematogens to a high temperature, although melting points are higher than ideal. Nevertheless, these materials find use in VAN mixtures because they confer a relatively low viscosity (around 90 mPa s), and a reasonably high negative dielectric anisotropy (−2.5).[7] Longer chain homologues (*e.g.*, compound **85**) generate smectic phases, which is a common trend of liquid crystal compounds, and because of the strong lateral dipole, the tilted smectic C phase is a strong feature. When one of the terminal chains is alkoxy (*e.g.*, compound **86**), the lateral dipole of the ether oxygen combines with that from the two lateral fluoro substituents, and the full extent of the smectic phase stability is exhibited as the tilted smectic C phase. The latter two compounds (**85** and **86**) find use as ferroelectric host materials for ferroelectric devices.[82,83,93]

When the two fluoro substituents are in an outer ring (*e.g.*, compounds **87–90**), smectic phases are prevalent because of the 'outer-edge' fluoro substituent (see discussion on monofluoroterphenyls), however, the 'inner-core' fluoro substituent moderates the influence, and a nematic phase tends to be also exhibited, but only over a relatively short temperature range. The dialkyl compounds (*e.g.*, **87** and **88**) have a much lower viscosity, and lower melting points than the alkyl-alkoxy analogues (*e.g.*, compounds **89** and **90**), and hence these compounds are suitable for use in ferroelectric host mixtures for ferroelectric devices.[82,83,93] Note the much higher transition temperatures for compound **89** compared with those for compound **90**, which is due to the respective alkoxy and alkyl substituted relatively untwisted biphenyl sections (see discussion of the monofluorosubstituted terphenyls).

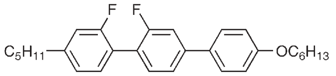
Where the two fluoro substituents are not inherently fixed on one side of the molecule then the overall molecular breadth is increased, and so liquid crystal phase stability will be reduced, with the smectic phase stability most affected.[96,97] This situation is exemplified by comparing compound **91** with compound **92**. Despite a lower melting point, compound **92** does not exhibit a smectic phase, and the nematic clearing point is reduced by 18 °C. Moving the two fluoro substituents into the same bay region (compound **93**) leaves only one inter-annular twist, and their close proximity enhances polarity, which facilitates the generation of a smectic C phase, albeit at low temperature. However, the nematic phase stability of compound **93** is rather lower than might be expected, perhaps as a result of a significant inter-annular twisting caused by two fluoro substituents. Compound **94** has the two fluoro substituents inherently fixed either side of the molecule, which confers a significant increase in molecular breath, and as expected, smectic phases are not exhibited, and the nematic clearing point is 32 °C lower than for compound **91**.[93,96,97]



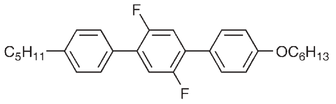
91
C 54.0 SmC 67.0 N 149.0 I (°C)



92
C 45.0 N 131.0 I (°C)



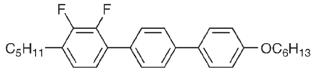
93
C 52.0 (SmC 41.5) N 122.0 I (°C)



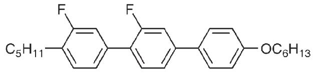
94
C 51.0 N 117.0 I (°C)

As already seen for the *ortho*-difluoroterphenyls, a fluoro substituent in an ‘outer-edge’ location tends to support the generation of smectic phases because of the space-filling influence of the polar substituent (*e.g.*, the high smectic phase stability of compound **95**).[93]

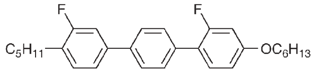
However, even when both fluoro substituents are not inherently fixed on the same side of the molecule, provided an ‘outer-edge’ fluoro substituent is present then smectic phase stability is still high. Indeed, compound **96** is smectogenic with very high liquid crystal phase stability, largely due to the relatively untwisted alkoxy-substituted biphenyl section. In contrast, compound **97** has a relatively untwisted alkyl-substituted biphenyl section, and this causes much reduced liquid crystal phase stability, and allows a nematic phase to be exhibited, however, the separation of the polarity due to the fluoro substituents more favours molecular tilting and the smectic C phase stability is actually higher by more than 28 °C, despite a reduction of more than 31 °C in the overall smectic phase stability. When both lateral fluoro substituents are inherently fixed either side of the molecule it might be expected that the increased molecular breath would eliminate smectic phases to generate a nematogen. However, as can be seen from compound **98**, the smectic phase stability is still very high because of the fluoro substituent in the ‘outer-edge’ position. Indeed the liquid crystal phase stability of compound **96** is higher than that of compound **97**, which is due to the relatively untwisted alkoxy-substituted biphenyl section, which does not feature in compound **97**.[96,97]



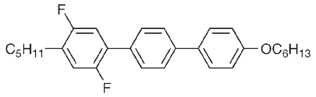
95
C 101.5 SmC 156.5 SmA 167.0 N 171.5 I (°C)



96
C 45.0 SmC 64.0 SmA 156.0 I (°C)

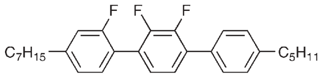


97
C 75.5 SmC 92.5 SmA 124.5 N 139.0 I (°C)

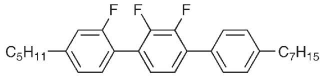


98
C 77.0 SmC 87.5 SmA 136.0 N 142.0 I (°C)

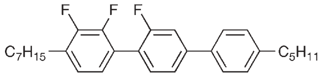
Given the transition temperatures of the difluoroterphenyls, further fluoro-substitution of terphenyls is obviously viable, and in addition to some interesting trends in liquid crystal properties and other physical properties, such materials can still be useful compounds for inclusion in mixtures for commercial devices. However, around 20 years ago it was thought that multiple fluoro substituents would be expected to confer a high polarity with the expectation of high melting points, but as can be seen from compounds **99**–**102**, melting points are very low, and nematic phase stability is reasonably high.[94,95] The location of the lateral fluoro substituents relative to the two terminal chains makes virtually no difference to the liquid crystal properties of compounds **99** and **100**. Here the fluoro substituents are all at ‘inner-core’ positions and so smectic phases are not seen, and the nematic clearing points are quite low, however, viscosity of these compounds is actually lower than the *ortho*-difluoro analogues (*e.g.*, compounds **83**–**85**) presumably because of the smoothing effect on the core created by the additional fluoro substituent. The relative locations of the terminal chains for isomers **101** and **102** makes no difference to the nematic phase stability, but the smectic phase stability of compound **102** is much greater. One particular point of interest with these trifluoroterphenyls is that the melting points are much lower where the fluoro substituents are located at an outer-core position, which is in stark contrast to the situation with the difluoro terphenyls, but melting points of liquid crystals are notoriously difficult to predict and explain. The negative dielectric anisotropy of these trifluoroterphenyls is higher than for the *ortho*-difluoroterphenyls because of the tendency of the fluoro substituents to co-align, this feature is useful in materials for VAN devices.[7]



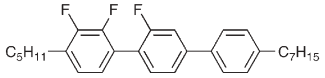
99
C 41.2 N 69.9 I (°C)



100
C 44.2 N 68.9 I (°C)

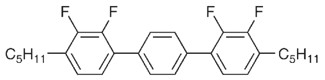


101
C 22.7 (SmC 8.2) N 75.5 I (°C)

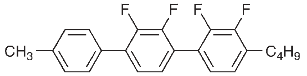


102
C ? SmC 37.2 SmA 51.7 N 75.0 I (°C)

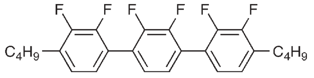
Compounds with four and six lateral fluoro substituents (*e.g.*, compounds **103**–**105**)[7] have been developed to provide even higher values of negative dielectric anisotropy. However, inevitably liquid crystal phase stability is much reduced, and because of the increased polarity, melting points are high. Also, because 'outer-edge' fluoro substituents now feature, viscosity is rather high. In comparison with the *ortho*-difluoroterphenyls (**83–85**), which are discussed above, the viscosity of compounds **103–105** is extremely high, however, the desired effect of higher negative dielectric anisotropy has been achieved by the use of additional lateral fluoro substituents. The first intended reason for the development of compounds based on the *ortho*-difluorophenyl moiety was to generate the smectic C phase for host materials for ferroelectric applications, and as can be seen from many of the examples above, the *ortho*-difluoroterphenyls were very successful. However, in order to provide materials with a lower birefringence, biphenyl analogues were developed, some of which include a *trans*-1,4-disubstituted cyclohexane ring for enhanced liquid crystal phase stability.[98–101] The success of the dimethylene-linked cyclohexylbiphenyls developed for nematic applications (see compounds **41–49**) in terms of low melting points and low viscosity proved a good place to begin, except that longer terminal chains were employed, as was an alkoxy chain, for optimum chances of generating a smectic C phase. Compound **106** shows the potential for the generation of smectic phases from the general structure, and the polarity generated from an *ortho*-difluorophenyl moiety might be expected to confer molecular tilting and generate the desired smectic C phase. As an outer ring, the *ortho*-difluorophenyl unit in compound **107** causes the elimination of the smectic B phase, and allows for a nematic phase, but no molecular tilting is seen. However, with the *ortho*-difluorophenyl unit as the central ring, molecular tilting does occur, and the smectic C phase is generated to moderately high temperature (*e.g.*, compounds **108** and **109**), and very low melting points arise.[98]



103
C 88.0 N 89.2 I (°C)
$\Delta\varepsilon = -4.3$, $\gamma_1 = 210$ mPa s



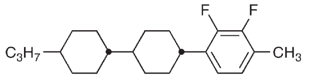
104
C 85.0 (N 50.5) I (°C)
$\Delta\varepsilon = -5.5$, $\gamma_1 = 277$ mPa s



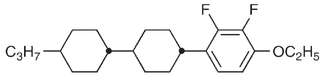
105
C 97.0 I (°C)
$\Delta\varepsilon = -7.2$, $\gamma_1 = 345$ mPa s

Directly-linked *trans*-1,4-disubstituited cyclohexylbiphenyls (*e.g.*, compounds **110** and **111**) also show a strong tendency for molecular tilting, but melting points are much higher.[101]

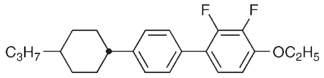
The negative dielectric anisotropy conferred by the *ortho*-difluorophenyl unit provides an ideal basis for the development of materials for VAN applications. Indeed, from such compounds, the required nematic phase is much more easily obtained than the smectic C phase, required for ferroelectric applications. In order to ensure desirable attributes of a low viscosity, a low birefringence and a high nematic phase stability, most materials designed for VAN applications are three-ring structures based on *ortho*-difluorophenyls with a *trans*-1,4-disubstituted cyclohexane ring (*e.g.*, compounds **112–115**).[7,10,16,102,103] Compound **112** has a very high nematic phase stability and a reasonably low viscosity, but the negative dielectric anisotropy is lower than desired. However, although compound **113** has a much higher negative dielectric anisotropy, due to the combination of the two lateral fluoro substituents and the adjacent ether oxygen, that very structural combination is also responsible for the very much higher viscosity. Hence, as always with liquid crystal mixtures for display applications a compromise situation is required.



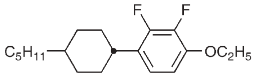
112
C 67.0 N 145.3 I (°C)
$\Delta\varepsilon = -2.7$, $\gamma_1 = 218$ mPa s



113
C 79.0 (SmB 78.0) N 184.5 I (°C)
$\Delta\varepsilon = -5.9$, $\gamma_1 = 413$ mPa s

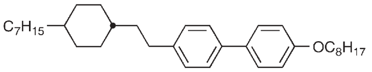


114
C 80.0 N 173.3 I (°C)
$\Delta\varepsilon = -5.9$, $\gamma_1 = 233$ mPa s

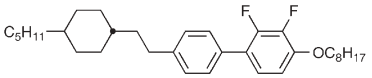


115
C 49.0 (N 12.9) I (°C)
$\Delta\varepsilon = -6.2$, $\gamma_1 = 110$ mPa s

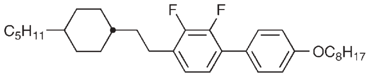
The biphenyl system (compound **114**) is a significant overall improvement because the high negative dielectric anisotropy, and the high nematic phase stability of compound **113** are retained, but the viscosity is markedly reduced. The two-ring compound (**115**) is an important component because the negative dielectric anisotropy is even higher than is generated by the same moiety in compounds **113** and **114**, and the



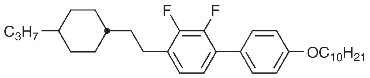
106
C 55.0 SmB 157.0 SmA 163.0 I (°C)



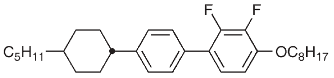
107
C 59.0 SmA 113.5 N 124.0 I (°C)



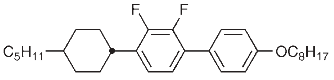
108
C 32.5 SmC 55.0 SmA 83.0 N 122.0 I (°C)



109
C 38.5 SmC 68.5 SmA 88.0 N 119.0 I (°C)



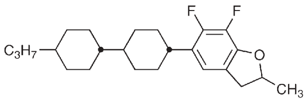
110
C 53.5 SmC 57.0 SmA 125.5 N 142.0 I (°C)



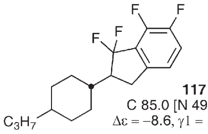
111
C 74.5 SmC 75.0 SmA 94.0 N 142.0 I (°C)

viscosity is significantly lower, both because of the smaller structure. The only disadvantage of compound **115** is the very low nematic phase stability, but this is off-set in the overall mixtures by the very high clearing points of other components such as compounds **112–114**.

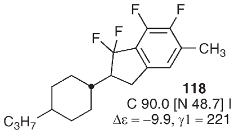
The difluorophenyl unit has two fluoro substituents that reinforce to confer a high lateral dipole, and hence this unit has been incorporated into many other molecular architectures, largely in attempts to provide an enhanced negative dielectric anisotropy for VAN applications, but also as an anticipated means of generating the tilted smectic C phase for ferroelectric applications. Compounds with an ether oxygen such as **113–115** show enhanced negative dielectric anisotropy, but the enhancement is limited by the free-rotation of the carbon–oxygen bond. Compound **116** serves to restrict the rotation by employing a fused ring dihydrobenzofuran system, and hence the negative dielectric anisotropy is higher, but the clearing point is markedly reduced by the angular core, however, the greatest disadvantage is the massive viscosity.[8] A similar approach is taken in the 1,1,6,7-tetrafluoroindanes (*e.g.*, compounds **117** and **118**),[8] except here a difluoromethylene unit is used to combine with the *ortho*-difluorophenyl unit to enhance the negative dielectric anisotropy, and a massive enhancement is achieved in both cases. Viscosity of compounds **117** and **118** is reasonably low, however, the nematic phase stability is low in both cases, but this would not cause problems when incorporated in appropriate nematic mixtures.[8]



116
C 112.0 (N 105.1) I (°C)
$\Delta\varepsilon = -6.7$, $\gamma_1 = 1254$ mPa s

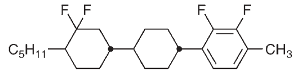


117
C 85.0 [N 49.4] I (°C)
$\Delta\varepsilon = -8.6$, $\gamma_1 = 142$ mPa s

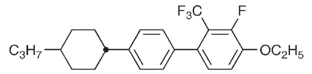


118
C 90.0 [N 48.7] I (°C)
$\Delta\varepsilon = -9.9$, $\gamma_1 = 221$ mPa s

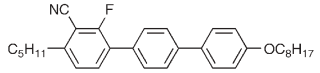
A difluoromethylene unit in cyclohexane ring (compound **119**, see also compounds **123** and **124**) provides an interesting alternative location for lateral fluoro substituents, and in compound **119** the unit enhances negative dielectric anisotropy compared with compound **112**, however, viscosity is increased markedly.[7] The replacement of a fluoro substituent for a trifluoromethyl group (compound **120**)[7] has had the desired effect of enhancing the negative dielectric anisotropy, but the viscosity has increased significantly, and the clearing point has been decreased considerably compared with compound **114**. In a similar way, a lateral fluoro substituent has been combined with a lateral nitrile group (compounds **121** and **122**).[104] When the bulky nitrile group is at the 'outer-edge' (compound **121**) the smectic C and smectic A phases are exhibited, but when the lateral units are reversed (compound **122**) a nematogen results. Such results are consistent with those discussed above for 'inner-core' and 'outer-edge' locations for monofluoroterphenyls (compounds **74–80**).[87]



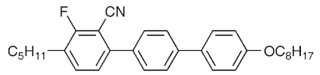
119
C 61.0 N 128.9 I (°C)
$\Delta\varepsilon = -4.6$, $\gamma_1 = 549$ mPa s



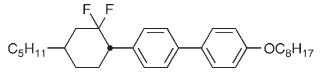
120
C 80.0 [N 44.0] I (°C)
$\Delta\varepsilon = -7.3$, $\gamma_1 = 637$ mPa s



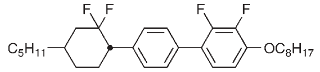
121
C 61.5 SmC 84.5 SmA 160.5 I (°C)



122
C 89.0 N 100.0 I (°C)



123
C 95.0 B 99.0 N 147.0 I (°C)



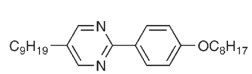
124
C 43.5 N 107.5 I (°C)

As has been seen previously, two *ortho* fluoro substituents has proved an excellent unit for generating the tilted smectic C phase. Consequently, the influence of two lateral fluoro substituents as part of a cyclohexane ring, similar to that seen in compound **119**, was investigated (compounds **123** and **124**).[99,101] However, the influence of the fluoro substituents in the cyclohexane ring is markedly different to that seen for lateral fluoro substituents in an aromatic ring (see compounds **110** and **111**). Compound **123** is most certainly not conducive to the generation of the smectic C phase, with a high melting point, a crystal B phase, and a nematic phase. The additional use of an *ortho*-difluorophenyl unit in compound **124** produces a nematogen with a low melting point, despite the presence of a fluoro substituent in an 'outer-edge' position.

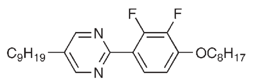
Lateral fluoro substituents have been employed in heterocyclic systems in order to generate the smectic C phase for ferroelectric applications. Phenylpyrimidines (*e.g.*, compound **125**) with reasonably long chains exhibit the smectic C phase because of the lateral dipole from the heterocyclic nitrogens and the ether oxygen,[105–107] however, an *ortho*-difluorophenyl unit was additionally investigated to assess the scope for enhanced smectic C phase stability, and more importantly for high dielectric biaxiality, which crucially requires a large lateral dipole.[105,108] As can be seen from the comparison of compounds **125** and **126**, the two lateral fluoro substituents have served to ensure that all the smectic phase stability is exhibited as the tilted smectic C phase, an indication of the enhanced lateral dipole, however, lower phase stability results from the increased molecular breadth.

Phenylpyridines (*e.g.*, compounds **127** and **128**) also show a strong tendency for the tilted smectic C phase, but only when the heterocyclic nitrogen is at an 'inner-core' location (compound **127**). The fluorinated pyridines follow the same trend as the parent pyridines, with compound **129** showing a smectic C phase and compound **130** showing a smectic A phase, with the clearing point of compound **130** being much reduced by the relatively large inter-annular twisting of the 'inner-core' lateral fluoro substituent.[102]

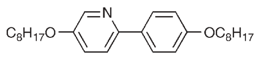
Other heterocyclic systems to additionally employ lateral fluoro substituents are the extensive range of 1,3-dioxinanes and 1,3,2-dioxaborinanes (*e.g.*, compounds **131–133**),[109–111] which were primarily designed to generate a smectic C phase in materials of low birefringence. In the case of compounds **131** and **132**, the polarity from the heterocyclic oxygens combines with that from the lateral fluoro substituents to generate a strong smectic C phase which exists for the whole smectic



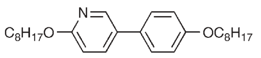
125
C 35.0 SmC 60.0 SmA 75.0 I (°C)



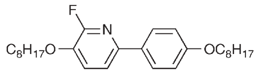
126
C 43.0 SmC 54.0 I (°C)



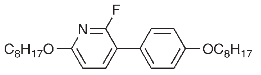
127
C 76.0 (SmX 75.0) SmC 110.0 I (°C)



128
C 50.0 SmB 69.0 SmA 80.0 I (°C)

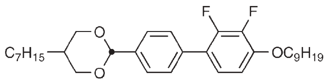


129
C 81.0 SmC 89.0 I (°C)

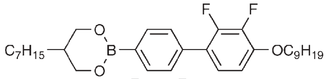


130
C 48.0 (SmA 40.0) I (°C)

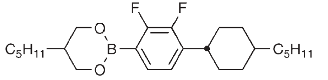
temperature range to a much higher level than the analogous cyclohexane system (compound **110**).[109,111] Combining a 1,3,2-dioxaborinane with a cyclohexane ring (*e.g.*, compound **133**) generates a compound that is nematogenic, as expected considering the use of two terminal alkyl chains, however, the nematic phase stability is quite high.[110]



131
C 57.0 SmC 110.7 N 130.5 I (°C)



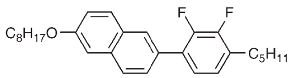
132
C 73.0 SmC 81.5 N 109.5 I (°C)



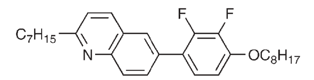
133
C 58.3 N 106.0 I (°C)

The difluorophenylnaphthalene (compound **134**) shows the same mesomorphic behaviour as the analogous terphenyl (compound **89**), however, the shorter, broader core depresses the smectic liquid crystal phase stabilities by around 100 °C, and the nematic clearing point by around 80 °C, to leave a monotropic smectic C phase of low phase stability.[93,112]

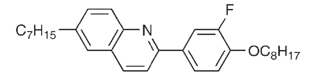
Lateral fluoro substituents have been incorporated in quinoline liquid crystals (*e.g.*, compounds **135–137**)[113] to generate a large lateral dipole, and hence a high dielectric biaxiality. When the heterocyclic nitrogen is at the 'outer-edge' position (compound **135**) only a smectic A phase is seen, however, when it is located at the 'inner-core' position (compound **136**), the smectic C, smectic A and nematic phases all feature, and the smectic C phase has a reasonably wide temperature range. A lateral fluoro substituent next to the heterocyclic nitrogen (compound **137**) generates a strong lateral dipole, but only a smectic A phase is exhibited, which is consistent with the 'outer-edge' location of the heterocyclic nitrogen.



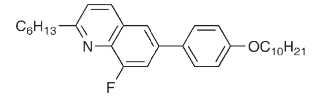
134
C 58.5 (SmC 44.5) SmA 75.0 N 83.5 I (°C)



135
C 42.4 SmA 73.7 I (°C)



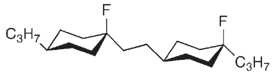
136
C 46.5 SmC 82.5 SmA 95.6 N 97.4 I (°C)



137
C 49.2 SmA 92.4 I (°C)

A useful alternative lateral location of a fluoro substituent is at an axial position of a cyclohexane ring (*e.g.*, compounds **138–142**).[16,103,114] Such materials can exhibit a strong negative dielectric anisotropy, and have been targeted for use in VAN applications. Compound **138** shows a moderate negative dielectric anisotropy and a very low viscosity, unfortunately there is a strong tendency towards the smectic B phase, however, in mixtures the nematic phase stability is fairly high. Two axial fluoro substituents (compound **139**) enhance significantly the negative dielectric anisotropy, illustrating the tendency of the two lateral fluoro substituents to be located in the same direction, however, the viscosity is also increased markedly.[16,103,114]

138
C 30.0 SmB 112.0 [N 66.5] I (°C)
$\Delta\varepsilon = -1.7$, $\gamma_1 = 62$ mPa s



139
C 78.0 SmB 105.0 [N 76.5] I (°C)
$\Delta\varepsilon = -4.6$, $\gamma_1 = 198$ mPa s

140
C 48.0 SmB 95.0 N 102.3 I (°C)
$\Delta\varepsilon = -1.7$, $\gamma_1 = 47$ mPa s

141
C 13.0 SmB 37.0 N 79.8 I (°C)
$\Delta\varepsilon = -1.9$, $\gamma_1 = 41$ mPa s

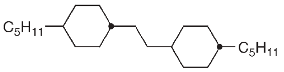
142
C 74.0 (SmB 70.0) N 83.0 I (°C)
$\Delta\varepsilon = -3.8$, $\gamma_1 = 156$ mPa s

Comparing compound **140** with compound **138**, the use of the alkenic terminal chain has reduced the smectic B phase stability and enhanced the nematic phase stability, yet the negative dielectric anisotropy is retained, and the viscosity is even lower. The use of two alkenic terminal chains (compound **141**) takes these issues further, but the nematic phase stability is not as high as seen in compound **140**. Similarly, the relatively high viscosity of the difluoro-substituted compound (**139**) has been reduced markedly by the use of two terminal alkenic chains (compound **142**).[16,103,114]

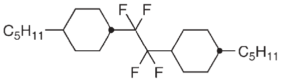
Fluoro substituents in a linking group

Fluoro substituents on a linking group are a relatively recent development in the design of liquid crystal materials, largely because of relatively difficult syntheses, and also because they have no immediately obvious overall benefit to physical properties, perhaps quite the contrary in terms the expected higher viscosity. However, recent research has shown that fluoro substituents on linking groups, particularly when combined with fluoro substituents in lateral and terminal locations, can be used to tailor mesomorphic behaviour, enhance dielectric anisotropy, and in some cases actually reduce viscosity, all to the benefit of nematic mixtures for display applications.

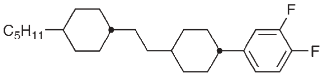
Compound **143** shows a low melting point and a very high smectic B phase stability, with a relatively low nematic phase stability of 78.8 °C as measured by extrapolation (denoted by the square brackets). On totally fluorinating the linking group (compound **144**), an overall stiffer core is generated, which as expected increases liquid crystal phase stability quite significantly, in particular the nematic phase stability is now very high, which is of course useful for display applications, however, the smectic B phase stability is also markedly higher. Compound **145** has a very high nematic phase stability, but the analogous material with the perfluorinated linking group (compound **146**) shows a much higher nematic phase stability, but a smectic B phase has been induced to high phase stability. In both comparisons, the dielectric anisotropy and viscosity are both virtually unchanged on fluorination of the linking group.[16,115]



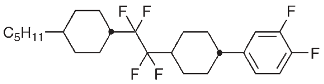
143
C 44.0 SmB 108.0 [N 78.8] I (°C)
$\Delta\varepsilon = 0.5$, $\gamma_1 = 134$ mPa s



144
C 33.0 SmB 138.0 N 139.8 I (°C)
$\Delta\varepsilon = 0.1$, $\gamma_1 = 138$ mPa s

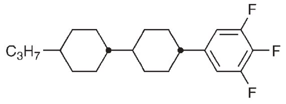


145
C 39.0 N 104.3 I (°C)
$\Delta\varepsilon = 5.5$, $\gamma_1 = 247$ mPa s

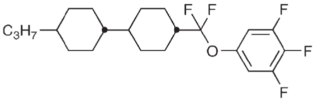


146
C 95.0 SmB 121.0 N 178.1 I (°C)
$\Delta\varepsilon = 5.4$, $\gamma_1 = 267$ mPa s

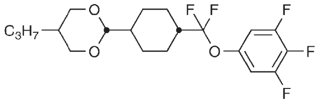
The main aim of fluorination at a linking group is to enhance the positive dielectric anisotropy for active matrix display applications. The use of the –CF_2O– linking group delivers remarkable results in the design of materials of positive dielectric anisotropy.[7,11,16,116] Compound **26** has good attributes for use in displays with a fairly high positive dielectric anisotropy, acceptable viscosity, and a reasonably high nematic phase stability. A linking group that includes polar units such as fluorine and oxygen would perhaps be expected to enhance the nematic phase stability, and deliver a higher positive dielectric anisotropy, but a lower viscosity would be most unexpected, however, as can be seen from compound **147** all these advantageous parameters have been realized. The positive dielectric anisotropy is doubled by using the dioxinane ring (compound **148**), but the viscosity has increased markedly, and the nematic phase stability is much reduced.[7]



26
C 66.0 N 94.1 I (°C)
$\Delta\varepsilon = 9.7$, $\gamma_1 = 171$ mPa s



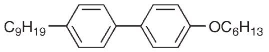
147
C 44.0 N 105.3 I (°C)
$\Delta\varepsilon = 10.5$, $\gamma_1 = 145$ mPa s



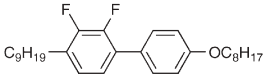
148
C 64.0 (SmB 48.0) N 68.5 I (°C)
$\Delta\varepsilon = 20.6$, $\gamma_1 = 207$ mPa s

The simple alkyl-alkoxybiphenyl (compound **149**) shows solely a smectic B phase with no tendency for molecular tilting.[27] The use of two lateral fluoro substituents (compound **150**) does confer a tendency towards molecular tilting, but the liquid crystal phase stability is very low because of the poor length to breadth ratio.[93]

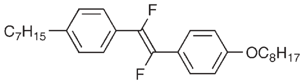
Linking groups extend the molecular length, and can enhance the liquid crystal phase stability quite significantly, and depending on the nature of that linking group, the nature of the mesophase morphology can also be altered. The difluoroethene linking group in difluorostilbenes (*e.g.*, compounds **151** and **152**)[117] extends the molecular length, and is conjugated with both rings which increases the polarizability anisotropy. Hence, the liquid crystal phase stability of compound **151** is very high for a two-ring mesogen, and more importantly the polarity of the fluoro substituents in combination with the ether oxygen exerts a molecular tilting effect and provides a smectic C phase. An additional two lateral fluoro substituents in compound **152** reduces the nematic phase stability far more than that of the smectic C phase stability, and a lower melting point results. In comparison with the analogous difluorobiphenyl (compound **150**), the liquid crystalline properties of the difluorostilbene (compound **152**) are significantly better for ferroelectric applications. The ester linking group is considered to be very good for generating the tilted smectic C phase, but a comparison of compound **151** with the analogous ester (compound **57**) shows the superiority of the difluoroethene unit.[117]



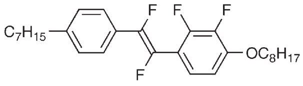
149
C 34.0 SmB 82.0 I (°C)



150
C 25.0 (SmC 11.5) SmA 33.0 N 34.0 I (°C)



151
C 38.0 SmC 83.5 SmA 89.0 N 110.5 I (°C)



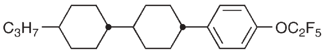
152
C 22.0 SmC 56.0 N 60.5 I (°C)

Fluoro substituents in the terminal chains

There are many different ways of classifying fluoro substituents that are incorporated into terminal chains. One such classification has already been discussed (compounds **18–21**), where the fluoro substituents are part of a small terminal unit designed to generate positive dielectric anisotropy. Since the terminal unit is small, the nematic phase, as determined by the overall core structure, dominates.

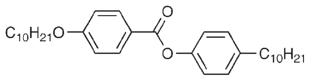
Alternatively, fluoro substituents can constitute a whole terminal chain in the form of a perfluorocarbon chain or a semifluorocarbon chain located within a hydrocarbon chain. In both these cases the fluorocarbon moiety is rather conformationally rigid, which tends to markedly enhance the smectic character of mesogens (see earlier discussion centred around Table 2). There is only one carbon difference between compounds **19** and **153**, yet the smectic B phase stability is enhanced by over 80 °C as a result of the greater stiffness of the terminal perfluoro chain.[11]

19
C 39.0 SmB 70.0 N 154.7 I (°C)

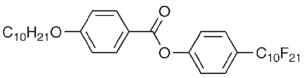


153
C 119.0 SmB 152.0 N 168.6 I (°C)

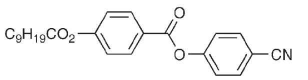
An interesting comparison results from a series of esters (compounds **154–157**) where the influence of a perfluorinated chain, which is conformationally much stiffer than an alkyl chain, is well illustrated.[118] The conventional ester (compound **154**) shows a smectic A phase, as would be expected from this core unit with such long terminal chains. Replacement of the decyl chain with a perfluorodecyl chain (compound **155**) causes an increase in the smectic A phase stability of 50 °C, and despite a vast increase in the melting point, a monotropic smectic C phase is now revealed. Terminal cyano-substituted liquid crystals usually exhibit the nematic phase for short terminal chains, with the introduction of the a smectic A phase with longer chain lengths, hence ester **156** shows the expected smectic A and nematic phases. The change to a perfluorinated terminal chain (compound **157**) has vastly increased the smectic A phase stability, eliminated the nematic phase, and unusually for a terminal nitrile compound, a smectic C phase is exhibited to high temperature.



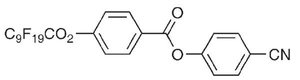
154
C 66.6 SmA 75.1 I (°C)



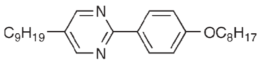
155
C 113.4 (SmC 110.9) SmA 125.5 I (°C)



156
C 67.1 SmA 73.8 N 87.0 I (°C)



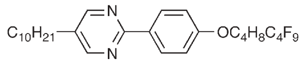
157
C 128.8 SmC 129.8 SmA 184.6 I (°C)



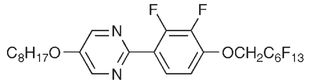
125
C 35.0 SmC 60.0 SmA 75.0 I (°C)

As discussed above (compounds **125** and **126**), phenylpyrimidines have been targeted as host materials for ferroelectric mixtures, however, the smectic C phase stability is a little low. Accordingly, analogous materials with semi-fluorinated chains have been developed to enhance the smectic C phase stability.[105,119]

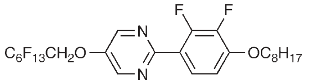
Compound **158** is a typical example, and compared with compound **125** the smectic C phase stability is 20 °C higher, and the smectic A phase stability is 31 °C higher.[119] Compounds **159** and **160** are interesting variations, with a short hydrocarbon unit and a long fluorocarbon chain. Compound **159** has a very high overall smectic phase stability, but it is exhibited principally as the smectic A phase. However, when the chains are reversed, and the lateral fluoro substituents are separated from the fluorinated chain, then molecular tilting is most dominant, and all the smectic phase stability is seen as the smectic C phase.[105]



158
C 58.0 SmC 80.0 SmA 106.0 I (°C)



159
C 65.0 (SmC 64.0) SmA 138.0 I (°C)



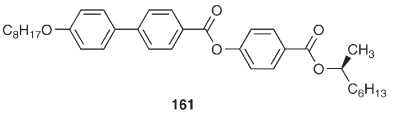
160
C 77.0 SmC 127.0 I (°C)

The nature of smectic phases are dominated by the interaction of the terminal chains, and in addition to using fluorocarbon chains to enhance smectic phase stability, they have been evaluated for the influence on physical properties. Clearly, hydrocarbon chains are compatible, and so if both chains are hydrocarbon then considerable interaction results, the very criterion that drives the generation of smectic phases. However, employing one hydrocarbon chain and one fluorocarbon chain will cause an incompatibility of the layers and influence physical properties. One of the first reported examples of the influence of fluoro substituents in a terminal chain on physical properties (*e.g.*, compound **163**) is in the design of antiferroelectric (SmC*anti) liquid crystals of very high tilt angle for a specific device application which requires a tilt angle of 45°.[120,121] The overall core structure of compound **162**[120] is identical to that commonly used to generate the SmC*anti phase (*e.g.*, compound **161**),[122] except that one terminal chain contains an ester unit with a perfluoroalkyl chain attached. In comparison with the analogous hydrocarbon system (compound **162**), the perfluoro chain has enhanced the smectic A phase stability by just 11 °C, but the antiferroelectric phase stability has increased by 28 °C, more significantly, the tilt angle of the fluorinated material (compound **163**) is 40°.[120] As can be seen, in comparison with compound **161**, which contains just a simple alkoxy terminal chain, the fluorinated terminal chain in combination with the ester unit (compound **163**) serves to decrease markedly the smectic A phase stability, but the SmC*ferro and the SmC*anti phase stabilities are virtually unchanged. A series of analogous materials with lateral fluoro substituents followed, which in some cases (*e.g.*, compound **164**) serve to reduce the melting point and enhance the tilt angle (45°), however, some locations of fluoro substituent cause a reduction in tilt angle.[123]

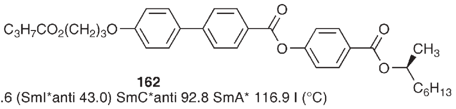
More recent work on a wider range of terminal groups has also investigated their influence on tilt angle, and the work also serves to provide an understanding of the phase segregation properties of materials with fluorinated terminal chains (*e.g.*, compounds **165** and **166**),[124] also based on the common core structure seen in compound **161**. The presence of the lone proton at the end of the fluorocarbon chain (compound **165**) drastically reduces the liquid crystal phase stability in comparison with the perfluorinated analogue (compound **163**), and indeed the liquid crystal phase stability is even lower than for the hydrocarbon analogue (compound **162**). Such a result is most unusual because the terminal chain of compound **165** would still be expected to be rather stiff, and therefore expected to have higher liquid crystal phase stability than the hydrocarbon analogue (compound **162**). However, this result shows the influence of microphase segregation, where the lone proton in the chain of compound **165** causes an incompatibility with the fluorinated section, and lower liquid crystal phase stability results. The usual effect of a branched terminal chain is to reduce liquid crystal phase stability, however, compound **166** with a branched perfluorinated terminal chain has an identical smectic A phase stability to the straight chain system (compound **163**), although the ferroelectric, and especially the antiferroelectric phase stabilities are much reduced, in keeping with the usual effect of such a bulky group.[124]

A short fluorocarbon section to the chiral terminal chain has been employed in compound **167**, and this unit has caused a significant enhancement of liquid crystal phase stability in the SmA*, SmC*ferro, and SmC*anti mesophases, each by around 30 °C, when compared with compound **161**.[125]

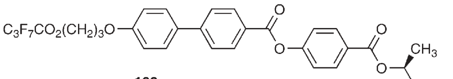
Compound **168** also has a fluoro carbon unit in the chiral terminal chain, however, in this case it is located at the chiral



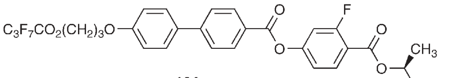
161
C 73.5 SmC*anti 118.8 SmC*ferri 119.8 SmC*ferro 121.6 SmC*alpha 122.6 SmA* 147.7 I (°C)



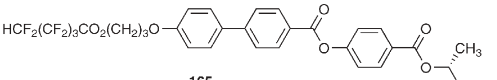
162
C 66.6 (SmI*anti 43.0) SmC*anti 92.8 SmA* 116.9 I (°C)



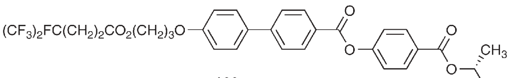
163
C 83.6 (SmI*anti 54.0) SmC*anti 119.7 SmC*ferro 123.5 SmA* 128.8 I (°C)



164
C 61.5 SmC*anti 103.0 SmC*ferro 109.0 SmA* 120.0 I (°C)

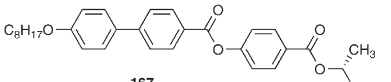


165
C 63.6 SmC*anti 80.3 SmC*ferro 83.0 SmA* 85.1 I (°C)

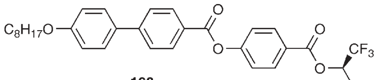


166
C 51.9 SmC*anti 98.8 SmC*ferro 116.5 SmA* 128.8 I (°C)

centre as a branched unit. Hence, for steric reasons, the liquid crystal phase stability is reduced when compared with compound **161**, however, the tilted phases (SmC*anti and SmC*ferro) are much less affected than the smectic A phase. The particular purpose of the CF$_3$ group in compound **168** is to use the polarity, and the restricted rotation at the chiral centre to ensure a high spontaneous polarization for antiferroelectric mixtures for display applications.[126]



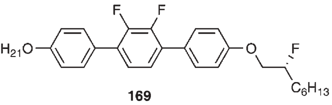
167
C 120.9 SmC*anti 154.4 SmC*ferro 158.3 SmA* 173.0 I (°C)



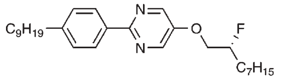
168
C 84.5 SmC*anti 108.0 SmC*ferro 109.0 SmA* 121.0 I (°C)

A single fluoro substituent at a chiral centre has also been widely utilized in materials to confer a spontaneous polarization for application in ferroelectric mixtures for displays, however, such materials tend to have a rather tight pitch which is disadvantageous because the pitch must be unwound to confer ferroelectricity.[119,127–129] The fluoro substituent is small and highly polar, and hence when located at branched chiral centre, materials with liquid crystal phases, particularly the desired smectic C phase, and a reasonably low viscosity, can be designed that exhibit a reasonably high spontaneous polarization. However, such chiral materials need not necessarily be liquid crystalline, provided that they do not depress the liquid crystal phase stability of the overall mixture unduly, but clearly the more liquid crystalline the nature, the more chiral material can be added, within reason, to the benefit of the spontaneous polarization. Compound **169** has a difluoroterphenyl core for compatibility in mixtures with the difluoroterphenyl host materials (*e.g.*, compounds **83–90**) discussed previously.[129]

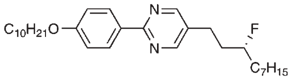
Compound **169** shows a high smectic C phase stability, which is useful for ferroelectric applications, however, the presence of a blue phase (BP1*) is indicative of the tight pitch, as mentioned above.[129] The pyrimidine-based compounds **170** and **171** find use in ferroelectric mixtures based on phenylpyrimidine host materials (*e.g.*, compounds **125** and **126**), usually high percentages (20%) are used in order to confer a reasonably high spontaneous polarization, but the overall smectic C phase stability does not suffer because they both exhibit the chiral smectic C phase to high temperature.[130] Compound **172** has a fluoro substituent at the chiral centre as for compounds **169–171**, however, the presence of a semi-fluorinated terminal chain confers a very high smectic C phase stability, which is useful for the ultimate application in ferroelectric mixtures.[128]



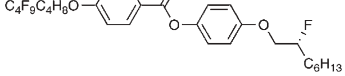
169
C 88.6 SmC*ferro 144.1 SmA* 154.9 N* 157.3 BP1* 157.8 I (°C)



170
C 53.0 SmC*ferro 67.0 SmA* 82.0 I (°C)

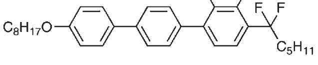


171
C 85.0 (SmC*ferro 84.0) SmA* 86.0 I (°C)

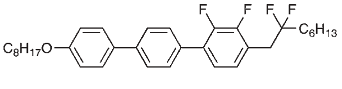


172
C 93.8 SmC*ferro 107.0 SmA* 119.4 I (°C)

Liquid crystals with a high lateral dipole are necessary for ferroelectric mixtures of high dielectric biaxiality.[82,83] Compounds **173** and **174** both have a difluoromethylene unit as part of a terminal chain, which was designed to enhance the lateral dipole from the two lateral fluoro substituents.[131] Since the dipole moment of the parent system (*e.g.*, compound **89**) is 3.29, a much higher dipole moment is conferred on the alpha difluoro system (compound **173**) and the beta difluoro compound (**174**) has a slightly higher value. Interestingly, the research also revealed that whereas the mesophase morphology of the alpha difluoro system (compound **173**) is similar to that of the parent system (compound **89**), when the difluoromethylene unit is in the beta position of the chain (compound **174**), all of the smectic phase stability is exhibited as the tilted smectic C phase, which is of the alternating tilt variety, analogous to the SmC*anti phase seen in chiral materials.[131]



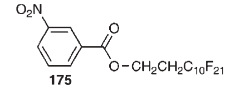
173
C 120.9 SmC 127.1 SmA 153.8 I (°C)



174
C 93.0 SmCalt 135.6 N 136.1 I (°C)

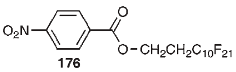
The use of relatively rigid perfluoro chains can confer liquid crystallinity on compounds with only one ring, or even no rings at all. The fact that compound **175** exhibits a smectic liquid crystal phase, albeit of an unidentified nature,[132] is surprising because the length to breadth ratio is not of the order normally expected for the generation of liquid crystal phases.

However, the rigidity of the perfluorinated section of the chain in compound **175** serves to provide an extended core, and thus the structure supports liquid crystallinity.[132] It is unusual that the 1,3-disubstituted structure (compound **175**) has the same clearing point as the 1,4-disubstituted analogue (compound **176**),[133] which emphasizes that the dominant reason for the liquid crystallinity is the fluorinated chain combined with the polarity of the nitro group rather than the molecular shape. Further evidence that liquid crystal phases can be generated to reasonably high temperatures by the use of a relatively rigid perfluorinated terminal chain is provided by compounds **177** and **178** with a terminal ester group and a terminal nitrile group respectively.[134] The polarizability of the tropone ring system is sufficient to facilitate the generation of a smectic A liquid crystal phase in 2,5-disubstituted structures (*e.g.*, compound **179**) albeit monotropic and of low phase stability.[135] However, when a perfluorinated chain section is included (compound **180**), the smectic A phase stability is enhanced significantly.[135] Compound **181** has a ten carbon hydrocarbon unit (relatively flexible) joined to a ten carbon fluorocarbon unit which is relatively rigid, and hence provides the necessary dichotomous structure to facilitate a self-assembled lamellar phase structure, in this case in the form of a tilted disordered crystalline smectic mesophase (G or J). Structures such as compound **181** are amphiphilic, non-ionic surfactants, and facilitate the generation of lyotropic liquid crystal phases in water solvent.[136,137]



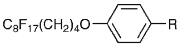
175

C 62.0 SmX 92.0 I (°C)



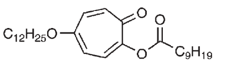
176

C 105.0 (SmX 85.0 SmA 92.0) I (°C)



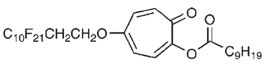
177, R = CO_2CH_3 C 69 SmA 81 I (°C)

178, R = CN C 72 SmA 73 I (°C)



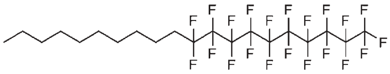
179

C 48.0 (SmA 46.0) I (°C)



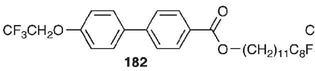
180

C 109.0 SmA 134.0 I (°C)

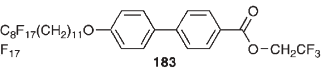


181

C 46.9 G or J 63.3 I (°C)



182



183

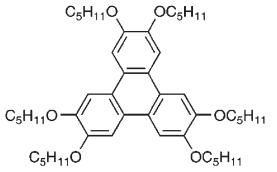
Compounds **182** and **183** are highly significant in the generation of reduced symmetry mesophases from achiral molecules. The alternating segments of hydrocarbon and fluorocarbon facilitate the molecular self-assembly in a polar, asymmetric manner, and the mesophases generated are termed polyphilic. The bulk polarization of these compounds is parallel to the direction of the molecules and orthogonal to the layer planes, and hence they are often termed longitudinal ferroelectrics, and are particularly suitable for non-linear optical applications.[138,139]

Fluoro substituents in discotic liquid crystals

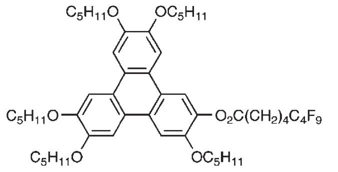
Compounds consisting of a central disc-shaped core surrounded by several peripheral moieties can generate liquid crystal phases because of the resulting structural anisotropy.[1,140] Such compounds were discovered in 1977,[141] and hence much fewer examples exist than for calamitic systems that have also been advantaged in numbers by the vast research for suitable materials for the various commercially-lucrative display applications. Additionally, discotic liquid crystals are generally more restricted by the very nature of the available units, and also by the much greater difficulty of synthesis. Hence most examples of discotic liquid crystals are relatively simple, and are based on substituted aromatic cores, such as 1,2,3,4,5,6-hexasubstituted benzene, and more commonly 2,3,6,7,10,11-hexasubstituted triphenylenes, with identical peripheral units.[1,140] The triphenylene types are now well established in the research arena as they are promising targets for the wide variety of organic semi-conductor and photovoltaic solar cell type applications.[142–145] More recently, the large discotic core systems based on hexa-*peri*-hexabenzocoronenes have been investigated for enhanced charge carrier mobility.[31,146–148]

Fluoro substitution has proved enormously beneficial for the properties in calamitic liquid crystals, hence such substitution has been targeted in the discotic systems. Important requirements are for the columns to be well-ordered, yet the materials have to be processible into thin films of ordered columnar mesophases. The use of a single fluorinated peripheral chain in compound **185** has markedly reduced the columnar phase stability when compared with the parent hydrocarbon system (compound **184**), which is to be expected because of the incompatibility of the fluorinated chain with the five hydrocarbon chains.[30] However, the materials with all six fluorinated chains (compound **186**) shows an extremely high columnar phase stability, which exemplifies the similar enhancing power on liquid crystal phase stability as seen in calamitic systems.[30] Just a single trifluoromethyl group at the end of each chain in compound **187** confers a remarkably high columnar phase stability in comparison with analogous parent systems (*e.g.*, compounds **184** and **188**), however, the melting point is also very high.[149]

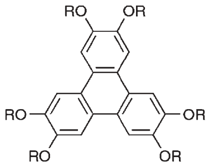
The influence on mesophase stability of a fluoro substituent within the triphenylene core of a discotic liquid crystal is interesting. Fluoro-substitution in the core of calamitic systems almost always caused a significant reduction in liquid crystal phase stability because of the increase in molecular breadth. However, with discotic systems, the core fluoro substituent (compound **189**) is in the plane of the core, and hence will only increase the molecular breadth very slightly, nevertheless, melting point is reduced significantly when compared with the parent system (compound **188**).[29] On the other hand, the fluoro substituent will fill space, and tend to enhance the intermolecular forces of attraction within the columns, and hence the columnar phase stability is much higher than the parent system (compound **188**).



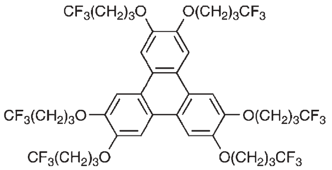
184
C 69.0 Col$_h$ 122.0 I (°C)



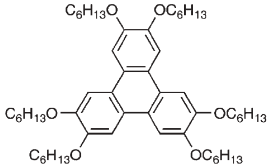
185
C 38.0 Col$_h$ 98.0 I (°C)



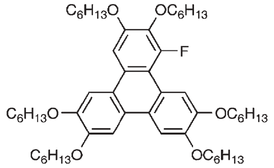
186, R = $C_6F_{13}(CH_2)_3O_2CCH_2O$
C 30.0 Col$_h$ 210.0 decomp (°C)



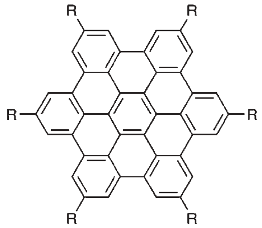
187
C 132.0 Col$_h$ 171.0 I (°C)



188
C 67.0 Col$_h$ 100.0 I (°C)



189
C 39.0 Col$_h$ 116.0 I (°C)



190, R = $C_{12}H_{25}$
C 105.0 Col$_h$ ~250 decomp (°C)

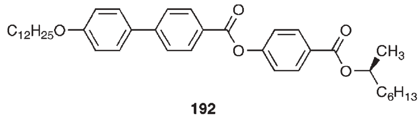
191, R = $C_6F_{13}(CH_2)_6$
C120.0 Col$_h$ ~300 decomp (°C)

The hexa-*peri*-hexabenzocoronenes (*e.g.*, compound **190**) show very high melting points and extremely high columnar phase stability, importantly they also show the highest charge carrier mobilities of all organic molecules.[146,147] However, they also show significant lateral conduction between the columns, which drastically reduces the potential one-dimensional charge carrier mobility. Hence, the analogous materials (*e.g.*, compound **191**)[31] were prepared with fluorinated chains at the periphery to act as a shield around the columns, reduce lateral conduction, and hence improve one-dimensional charge carrier mobilities. In terms of transition temperatures there is no benefit to the use of fluorinated chains, since the columnar phase stability is extremely high in both cases, and the melting point is higher for the fluorinated analogue.

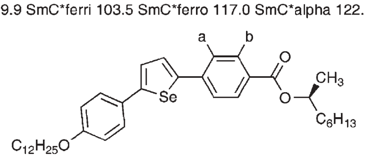
Fluoro substituents in banana-shaped and bent-core liquid crystals

Liquid crystal phases can be generated by compounds with bent-core molecular architectures, however, the phase stability is usually reduced significantly when compared with the analogous linear systems, but the mesophase morphology is usually similar (*e.g.*, compare compounds **192** and **193**).[150,151]

Fluoro-substituted analogues of the selenophene bent-core systems were synthesised (compounds **194–196**)[151] in order to assess the scope for reduced melting points, and because these selenophene materials were designed to facilitate the elucidation of the structure of the various types of chiral smectic C phase, the fluoro substituents were expected to reduce melting point, and enhance the temperature ranges of the various phases. Where the fluoro substituent is at the 'outer-edge' position (compound **194**), the melting point has increased, but the liquid crystal phase stability has been reduced by around 6 °C throughout. A fluoro substituent at the 'inner-core' position (compound **195**) has a dramatically different influence, with melting point much reduced, and all the chiral smectic C phases eliminated to leave a smectic A phase with a vastly reduced phase stability. Use of fluoro substituents in both positions (compound **196**) provides a lower melting point, and the temperature range of the antiferroelectric phase is wider, but the temperature range of the ferrielectric phase has been reduced to just 1 °C.[151]

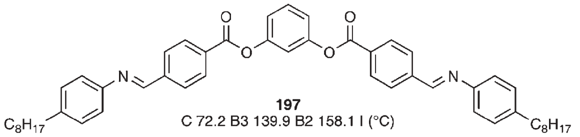


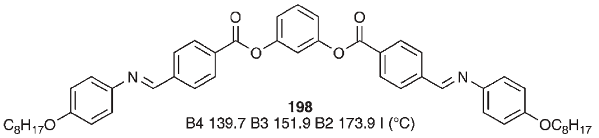
192
C 72.9 SmC*anti 99.9 SmC*ferri 103.5 SmC*ferro 117.0 SmC*alpha 122.2 SmA* 132.7 I (°C)

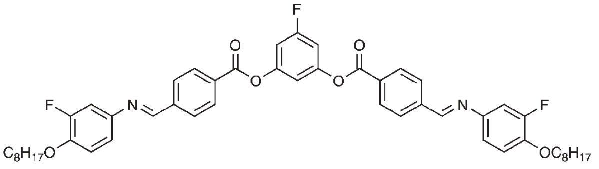


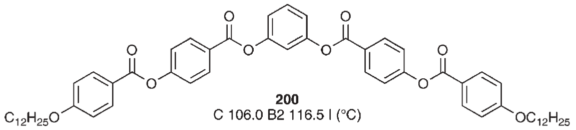
193, a = H, b = H
C 67.7 SmC*anti 97.8 SmC*ferri 99.0 SmC*ferro 109.4 SmA* 116.6 I (°C)
194, a = H, b = F
C 75.5 SmC*anti 91.8 SmC*ferri 92.1 SmC*ferro 98.9 SmA* 109.1 I (°C)
195, a = F, b = H
C 48.0 SmA* 79.3 I (°C)
196, a = F, b = F
C 46.3 SmC*anti 79.9 SmC*ferri 83.3 SmC*ferro 84.3 SmA* 93.7 I (°C)

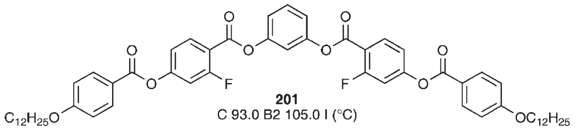
Bent-core molecular architectures did not receive much attention in respect of liquid crystal phases until about 10 years ago, when bent-core materials of a symmetrical style (*e.g.*, compounds **197** and **198**)[152] were evaluated as potential polar materials for ferroelectric applications. It was found that such symmetrical, bent-core materials (commonly referred to as banana-shaped) exhibited a whole new type of liquid crystal phase that was not in the same miscibility classification as conventional calamitic liquid crystal phases, but nevertheless possessed similar attributes of ordered fluids comparable with smectic phases. Further, some of these so-called banana liquid crystal phases were found to exhibit reduced symmetry properties in the form of an equal proportion of oppositely handed domains that can show helical ordering, and ferroelectric or antiferroelectric switching properties, despite the achiral structure of the constituent molecules. With tremendous fundamental academic interest, and possible commercial riches to be discovered, much research in this fascinating area followed, and the topic is the subject of several informative reviews.[38,153–157] Naturally, given the dramatic influence of fluoro substituents on calamitic and discotic types of liquid crystals, much attention has been given to fluoro substitution in the banana liquid crystals. Compound **199** was synthesised to enable the orientational order parameter to be determined, and to carry out conformational studies using ^{19}F NMR.[36] The mesophase morphology has changed in comparison with compound **198**, with the generation of different variations of the B5 phase, but the B2 phase is still present, albeit of reduced thermal stability.

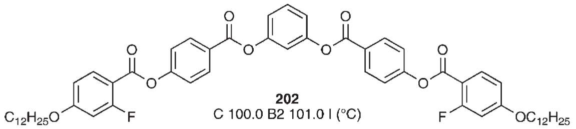

197
C 72.2 B3 139.9 B2 158.1 I (°C)

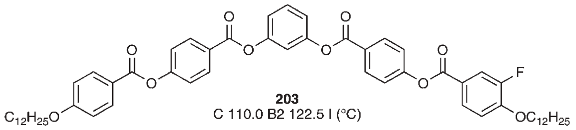

198
B4 139.7 B3 151.9 B2 173.9 I (°C)


199
C 113.0 B5F 131.0 B5A'''' 135.5 B5A''' 137.0 B5A'' 138.9 B5A' 139.8 B2 163.5 I (°C)


200
C 106.0 B2 116.5 I (°C)

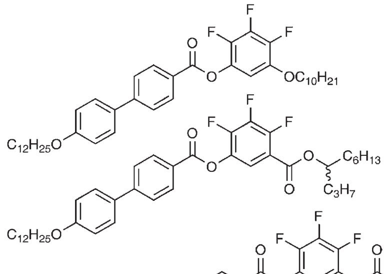

201
C 93.0 B2 105.0 I (°C)


202
C 100.0 B2 101.0 I (°C)

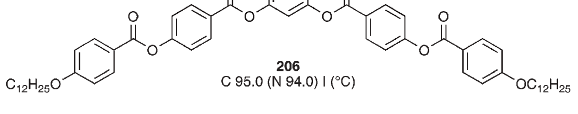

203
C 110.0 B2 122.5 I (°C)

Fluoro substituents appear in many other banana liquid crystals (*e.g.*, compounds **201–203**), and in most cases the aims and objectives were to provide a greater understanding of the structure–property relationships of such systems, in particular to assess the influence of the fluoro substituents on melting point, transition temperatures, mesophase morphology and physical properties.[37,39] Fluoro substituents in the 'arms' of the banana-shaped structure have been most extensively investigated, largely because of the greater number of possibilities for comparison, and relative ease of synthesis. In general, such lateral fluoro substitution tends to reduce melting points and liquid crystal phase stability, although the former influence is more marked. Banana liquid crystals where the imine linking group is replaced by an ester moiety have much lower clearing points (compare compounds **198** and **200**), and in the case of compound **200**, a relatively high melting point reduces the temperature range of the mesophase to just 10 °C. The melting points of compounds **201** and **202** are reduced by the use of two lateral fluoro substituents. Where the two fluoro substituents are closer to the molecular centre (compound **201**) the melting point is more markedly reduced than analogous substitution further from the centre (compound **202**). However, the B2 phase stability is depressed to a greater extent in compound **202** when compared with compound **201** which unfortunately leaves just a 1 °C temperature range of the B2 phase.[37] More recently, unsymmetrical banana liquid crystals have been reported with a fluoro substituent in only one of the 'arms' (*e.g.*, compound **203**).[39] It is perhaps surprising that the clearing point of compound **203** is higher than that of the parent system (compound **200**), however, the fluoro substituent is at an 'outer-edge' location, which fills free space and tends to support smectic-like phases, this feature is discussed earlier for lateral fluoro-substituted calamitic liquid crystals. Further examples of fluoro-substituted banana liquid crystals can be found in a recent review.[38]

A range of 1,2,3-trifluoro-substituted materials (*e.g.*, compound **204**) were designed such that a very high lateral dipole would be generated, thus conferring a high dielectric biaxiality for potential use in ferroelectric applications.[139] Such a pattern of fluoro substitution dictated a bent-core molecular architecture, however, despite the bent-core, these materials generate 'conventional' calamitic mesomorphism, and are not banana liquid crystals, hence the term hockey-stick molecules is often used. Interestingly, the calamitic mesomorphism is not actually conventional because the smectic C phase exhibited by these achiral molecules (*e.g.*, compound **204**) consists of equal proportions of oppositely handed domains that show ferroelectric switching, rather like the situation seen in certain liquid crystal phases exhibited by banana materials. A similar material (compound **205**) shows a smectic C phase with solely a right handed helical structure, much the same as an enantiopure compound does, despite the racemic nature of the compound, perhaps indicating that the bent-core nature of compound **205** is revealing a very slight enantiomeric excess.[139]


204
C 68.5 SmC 76.0 SmA 82.5 I (°C)

205
C 38.0 SmC* 50.0 SmA* 76.5 I (°C)


206
C 95.0 (N 94.0) I (°C)

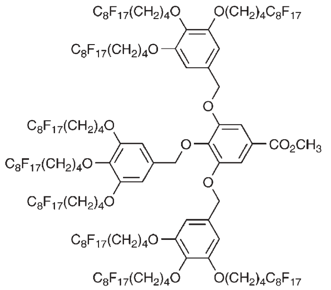
Compound **206** has a molecular construction similar to a banana liquid crystal such as compound **200**, however, the fluoro substituents next to the ester linkages cause a straightening of the constituent molecules, and hence compound **206** exhibits calamitic mesomorphism in the form of the nematic phase. However, the nematic phase exhibited by compound **206** is not a conventional nematic phase because it consists of an equal proportion of oppositely handed domains in much the same manner as the smectic C phase exhibited by compound **204**, and no homeotropic texture could be found.[158] Similar results have been found in a lateral chloro-substituted compound of otherwise identical structure.[159]

Fluoro substituents in supramolecular liquid crystals

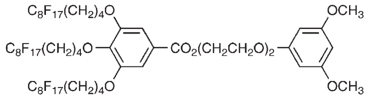
Initially, it may seem surprising that many compounds that do not correspond to the usual molecular architectures of rods, discs or bananas discussed above also exhibit liquid crystal phases. However, such molecular architectures have structural moieties that confer a particular shape and specific intermolecular forces of attraction, thus facilitating the generation of molecular aggregates, or supramolecular entities. Such supramolecular entities are often rod-shaped or disc-shaped, and can also be cone-shaped or spherical-shaped, and hence can then self-organize to generate calamitic, columnar, or sometimes cubic liquid crystal phases.[160,161]

Fluoro substituents can confer the necessary molecular shape and intermolecular forces of attraction to confer such self-assembly, and hence facilitate self-organization into various types of liquid crystal phases depending on the structural nature of the materials. Compound **207** possesses perfluorinated terminal chains in the periphery of the wedge-shaped, second-generation dendron, and the conformational rigidity of these chains facilitates the self-assembly into cone-shaped supramolecular aggregates, which then self-organize into a hexagonal columnar liquid crystal phase.[162]

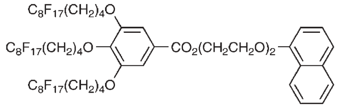
Compounds **208** and **209** are examples of first-generation dendrons that have perfluorinated terminal chains in the periphery of a benzene ring, attached to an aromatic electron-donor moiety by an ethyleneoxy chain. These dendrons self-assemble through π-stacking, and the resultant supramolecular aggregates self-organize into columnar liquid crystal phases. Several examples of different electron-donor aromatic units have been reported, and these have been designed to facilitate charge transport through the resultant columns for potential use in semi-conductor applications.[163]



207
C 84.5 Col_h 92.0 I (°C)



208
C ? Col_r 77.9 I (°C)

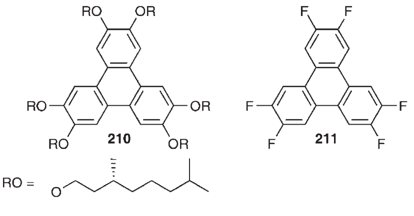


209
C ? Col_r 48 col_h 75 I (°C)

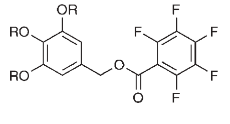
Triphenylene and perfluorotriphenylene melt at 199 °C and 109 °C respectively, yet an equimolar mixture forms a supramolecular complex that melts at a much higher temperature (252 °C). Such arene–perfluoroarene interactions are well-established, and are discussed above with the example of benzene (**8**) and hexafluorobenzene (**9**). Compound **210** exhibits a hexagonal columnar liquid crystal phase to very low temperature. However, an equimolar mixture of compound **210** with perfluorotriphenylene (**211**) benefits from arene–perfluoroarene interactions which confer a supramolecular complex that shows a hexagonal columnar liquid crystal phase to 104 °C.[164]

Such arene–perfluoroarene interactions have more recently been exploited with the arene and the perfluoroarene moieties in the same molecule (*e.g.*, compounds **212** and **213**). The molecules aggregate such that the alkoxy chains are at the periphery, and the disc-shaped supramolecular aggregates then self-organize into a columnar mesophase. The shorter chain homologue (compound **212**) has a low melting points and exhibits a columnar mesophase at room temperature, whereas the longer chain homologue (compound **213**) has a rather higher melting point, and a slightly lower, monotropic columnar mesophase stability.[165]

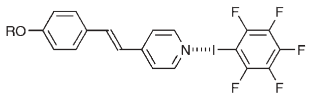
It is well-established that calamitic liquid crystal phases can be generated by carboxylic acids of relatively short molecular length because dimerization by intermolecular hydrogen bonding creates a supramolecular system of greater molecular length, thus facilitating the generation of liquid crystal phases (see compounds **39** and **40**). Complexes **214** and **215** exhibit liquid crystal phases because of so-called halogen bonding, despite the non-mesogenic nature of the stilbazoles and pentafluoro-iodobenzene.[166] Halogen bonding is a similar interaction to hydrogen bonding, and requires an iodide because of the high polarizability, and the iodide must be adjacent to electron-withdrawing fluoro substituents to make it a sufficiently strong Lewis acid to attract the lone pair on the heterocyclic nitrogen of the pyridine moiety. The shorter chain homologues of **214** and **215** are monotropic nematogens, whereas the longer chain homologues exhibit solely the smectic A phase.[166] Similarly, complexes between stilbazoles and diiodoperfluoroalkanes (*e.g.*, **216** and **217**) generate liquid crystal phases, however, these are all monotropic nematogens regardless of the length of the alkoxy terminal chain.[167] It is perhaps surprising that the clearing point of these long complexes (**216** and **217**) are only around 20 °C higher than for the much shorter complexes (**214** and **215**).[167]



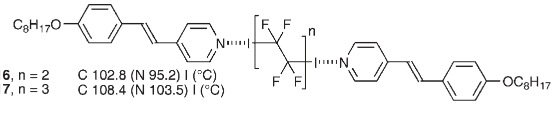
210 **211**
compounds **210** and **211** (1:1)
C ? Col_{hd1} 21 Col_{hd2} 104 I (°C)



212, R = $C_{12}H_{25}$ C < RT Col_{ho} 40 I (°C)
213, R = $C_{14}H_{29}$ C 62 (Col_{ho} 37) I (°C)



214, R = C_6H_{13} C 78 (SmA 70 N 76) I (°C)
215, R = $C_{10}H_{21}$ C 70 SmA 81.5 I (°C)

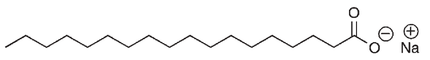


216, n = 2 C 102.8 (N 95.2) I (°C)
217, n = 3 C 108.4 (N 103.5) I (°C)

Fluoro substituents in lyotropic liquid crystals and biological significance

Lyotropic liquid crystals are materials that generate liquid crystal phases as a consequence of association with a solvent system (usually water, but can be a hydrocarbon or a fluorocarbon solvent), and the concentration of liquid crystal in that solvent determines the phase transitions and the mesophase morphology. However, lyotropic liquid crystals can also be temperature-dependent, and hence temperature at every given concentration of a compound in a solvent will also dictate the phase transitions and mesophase morphology. Accordingly, the characterization of lyotropic liquid crystals is far more complex than for thermotropic liquid crystals, and is usually presented in the form of graphical phase diagrams rather than the simple temperature listings as seen in the many and varied examples of thermotropic liquid crystals detailed above.[1,168–171] Thermotropic liquid crystals are much more widely known largely because of their much easier characterization, and their great technological importance in display, thermochromic and electron transport applications. However, lyotropic liquid crystals pre-date their thermotropic cousins, and indeed the annual production of lyotropic liquid crystals in household cleaning and cosmetic products far exceeds that of thermotropic liquid crystals. Perhaps of greater importance, and certainly of more recent and increasing investigations, is the fact that biological systems, notably cell membranes and DNA, are lyotropic liquid crystals. Accordingly, biological processes and life itself depend critically upon lyotropic liquid crystals.[172,173] Lyotropic liquid crystals consist of amphiphilic molecules where one part of the molecule is hydrophilic, and another part is hydrophobic. These amphiphilic molecules interact with appropriate solvent molecules to organize into various liquid crystalline mesophases at various concentrations and temperature.

Usually, these amphiphilic molecules are based on anionic long chain carboxylate salts (*e.g.*, compound **218**), cationic long chain quaternary ammonium salts (*e.g.*, compound **219**), or a non-ionic long chain hydrocarbon attached to a multiethyleneoxy chain (*e.g.*, compound **220**).[1,168–171] However, such lyotropic liquid crystal systems can also include a perfluorinated chain, which is bulkier, stiffer, and considerably more hydrophobic than an alkyl chain. The most simple molecular architecture is seen in compounds such as **181**, where the hydrocarbon chains serves as the hydrophilic section (unlike in compounds **220** where the hydrocarbon chain is hydrophobic), and the hydrophobic section is provided by the perfluorinated chain to generate a non-ionic lyotropic liquid crystalline system.[136,137]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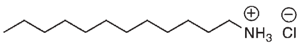
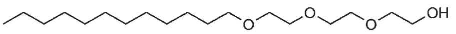
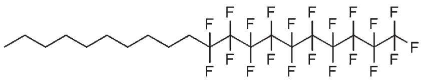
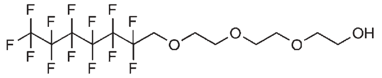
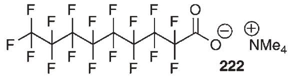
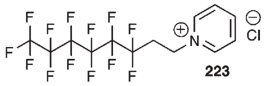

219


220


181
C 46.9 G or J 63.3 I (°C)

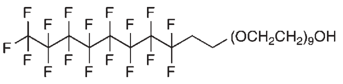

221

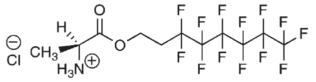

222


223

Naturally, given the remarkable properties of the fluoro substituent as detailed above, many more examples of fluoro-substituted lyotropic liquid crystals have been investigated. In general, fluorinated surfactants are very effective in decreasing the surface tension, down to values of 15 mN m^{-1}; they also tend to be more hydrophobic, and their weaker affinity for water confers lower critical micellar concentration (cmc) values.[174] Compound **221** is similar to compound **220** in that both are non-ionic lyotropic liquid crystals, and both possess a multi-ethyleneoxy chain as the hydrophilic section. However, the perfluorinated chain of compound **221** is much more hydrophobic than the hydrocarbon chain of compound **220**. Compound **221** exhibits the sponge phase, the reverse bicontinuous cubic phase, the lamellar phase, and the reverse micellar phase, at various concentrations in water.[174] Compounds **222**[175] and **223**[176] are examples of anionic and cationic fluorinated lyotropic liquid crystals respectively. Compound **222** in water exhibits a lamellar phase, which exits at high surfactant concentrations and low temperature, additionally, an unusual discoidal nematic phase is generated.[175]

Silica support structures have been targeted for catalyst, drug delivery and sensor applications because of their high specific surface area and uniform pore size. Lyotropic liquid crystal structures can provide templates for the synthesis of such mesoporous silica by room temperature precipitation and subsequent extraction of the liquid crystal. Naturally, fluorinated lyotropic liquid crystals have different properties to hydrocarbon analogues, they form aggregates more easily, with lower curvature, and in particular have a higher thermal stability. These attributes allow for very small pore sizes in the case of compound **223**,[176] and in the case of compound **224** allow an enhanced level of silica condensation which generates a more stable silica structure.[177]


224


225

On a different theme, compound **225** represents an interesting combination of an amino acid (L-alanine) and a fluorocarbon chain. As discussed above, the fluorocarbon chain is stiffer and more hydrophobic than a hydrocarbon chain, and so serves to enhance the helical twisting in the chiral nematic phase conferred by the enantiopure amino acid moiety to generate outstanding values of helical twisting power (htp).[49]

Concluding remarks

We have been introduced to liquid crystals; these fascinating fluids possess molecular ordering, which confers anisotropic properties that have been exploited in liquid crystal displays for a massive range of essential products. We have seen that fluorine is a remarkable substituent in a wide variety of organic compounds, largely due to a fascinating combination of properties and attributes, including small size, monoatomic nature, high electronegativity, low polarizability, very strong C–F bond conferring very high stability, low surface tension of liquids, and low surface energy of solids. Not surprisingly, such amazing properties enable fluoro-substituted materials to serve in a great many applications, including refrigeration, foam-blowing, structural and functional polymers, lubricants, gases for the etching process in microchips for electronics, anaesthetics, pharmaceuticals, and of course liquid crystals for displays (LCDs) which constitute a significant part of this review.

We have seen in great detail the immense scope for combining these two exciting topics of liquid crystals and fluorine into fluorinated liquid crystals. We have seen that by necessity, the molecular structures that generate liquid crystalline phases are rather stylized, and the most common is rod-like or calamitic, but others include discotic and banana, and also amphiphilic systems that show lyotropic liquid crystalline phases. The small size of the fluoro substituent enables it to be incorporated into such stylized structures without undue disruption, and hence liquid crystalline phases can still be exhibited. However, it is the combination of the small size and high polarity which serves to modify melting point, mesophase morphology, transition temperatures, and the range of physical properties including optical anisotropy, dielectric anisotropy, and visco-elastic properties.

However, we have also seen that there are many different positions within a liquid crystal structure that a fluoro substituent can be located, including (i) a terminal position (ii) within a terminal chain, as a semi-fluorinated or perfluorinated chain, or simply one fluoro substituent at a chiral centre, (iii) as part of a linking group, and (iv) a lateral position. We have seen that such a variety of locations for fluoro substituents in liquid crystal structures has enabled the interesting and advantageous tailoring of properties, both for the fundamental, academic purposes of establishing structure–property relationships, and for materials targeted towards commercially successful liquid crystal display applications.

Research into novel liquid crystal materials continues at a strong pace, in many areas, for example, banana liquid crystals, chirality issues in liquid crystals, biaxial nematic liquid crystals, semi-conductor liquid crystals, and there is considerable targeted research to improve materials for existing display applications. One particularly exciting area of major research for the future is likely to be in the area of lyotropic liquid crystals, and their impact on biological processes and systems, upon which, life so critically depends. Fluorinated liquid crystals will no doubt feature most strongly in all of these future developments. One thing is certain, the combination of the unique properties of liquid crystals that serve as liquids, yet have molecular ordering, and the remarkable and fascinating influence of fluoro substituents on their properties, will ensure an exciting and prosperous future for fluorinated liquid crystals.

References

1 P. J. Collings and M. Hird, 'Introduction to Liquid Crystals Chemistry and Physics', Taylor and Francis, London, 1997.
2 P. J. Collings and J. S. Patel, in 'Handbook of Liquid Crystal Research', Oxford University Press, Oxford, 1997.
3 D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, in 'Handbook of Liquid Crystals', Wiley-VCH, Chichester, 1998.
4 G. W. Gray, in 'Thermotropic Liquid Crystals', Wiley, Chichester, 1987.
5 S. M. Kelly, 'Flat Panel Displays Advanced Organic Materials', ed. J. A. Connor, Royal Society of Chemistry, Cambridge, 2000.
6 S. T. Lagerwall, 'Ferroelectric and Antiferroelectric Liquid Crystals', Wiley-VCH, Weinheim, 1999.
7 D. Pauluth and K. Tarumi, *J. Mater. Chem.*, 2004, **14**, 1219.
8 M. Bremer and L. Lietzau, *New J. Chem.*, 2005, **29**, 72.
9 S. T. Lagerwall, *Ferroelectrics*, 2004, **301**, 15.
10 M. Klasen, M. Bremer and K. Tarumi, *Jpn. J. Appl. Phys.*, 2000, **39**, L1180.
11 P. Kirsch and M. Bremer, *Angew. Chem., Int. Ed.*, 2000, **39**, 4216.
12 R. E. Banks, in 'Fluorine Chemistry at the Millennium', Elsevier, Oxford, 2000.
13 R. E. Banks, B. E. Smart and J. C. Tatlow, in 'Organofluorine Chemistry: Principles and Commercial Applications', Plenum Press, New York, 1994.
14 R. D. Chambers, 'Fluorine in Organic Chemistry', Blackwell, Oxford, 2004.
15 K. Johns and G. Stead, *J. Fluorine Chem.*, 2000, **104**, 5.
16 P. Kirsch, 'Modern Fluoroorganic Chemistry', Wiley-VCH, Weinheim, 2004.
17 K. Uneyama, 'Organofluorine Chemistry', Blackwell, Oxford, 2006.
18 D. O'Hagan and H. S. Rzepa, *Chem. Commun.*, 1997, 645.
19 M. Hird and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1998, **323**, 1.
20 M. Hird, J. W. Goodby, R. A. Lewis and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 2003, **401**, 1.
21 J. K. Nagel, *J. Am. Chem. Soc.*, 1990, **112**, 4740.
22 K. D. Sen and C. K. Jorgensen, 'Electronegativity', Springer, New York, 1987.
23 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
24 W. Caminati, S. Melandri, P. Moreschini and P. G. Favero, *Angew. Chem., Int. Ed.*, 1999, **38**, 2924.
25 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 1210.
26 C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021.
27 D. Demus, H. Demus and H. Zaschke, 'Flussige Kristalle in Tabellen', Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1974.
28 D. Demus and H. Zaschke, 'Flussige Kristalle in Tabellen Volume II', Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1984.
29 N. Boden, R. J. Bushby, A. N. Cammidge, S. Duckworth and G. Headdock, *J. Mater. Chem.*, 1997, **7**, 601.
30 U. Dahn, C. Erdelen, H. Ringsdorf, R. Festag, J. H. Wendorff, P. A. Heiney and N. C. Maliszewskyj, *Liq. Cryst.*, 1995, **19**, 759.
31 B. Alameddine, O. F. Aebischer, W. Amrein, B. Donnio, R. Deschenaux, D. Guillon, C. Savary, D. Scanu, O. Scheidegger and T. A. Jenny, *Chem. Mater.*, 2005, **17**, 4798.
32 D. W. Bruce, S. C. Davis, D. A. Dunmur, S. A. Hudson, P. M. Maitlis and P. Styring, *Mol. Cryst. Liq. Cryst.*, 1992, **215**, 1.
33 D. W. Bruce and S. A. Hudson, *J. Mater. Chem.*, 1994, **4**, 479.
34 J. L. Serrano, in 'Metallomesogens – Synthesis, Properties, and Applications', VCH, Weinheim, 1996.
35 N. J. Thompson, J. W. Goodby and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1992, **214**, 81.
36 H. Nadasi, W. Weissflog, A. Eremin, G. Pelzl, S. Diele, B. Das and S. Grande, *J. Mater. Chem.*, 2002, **12**, 1316.
37 R. Amaranatha Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2003, **30**, 1031.
38 M. Hird, *Liq. Cryst. Today*, 2005, **14**, 9.
39 H. N. Shreenivasa Murthy and B. K. Sadashiva, *J. Mater. Chem.*, 2004, **14**, 2813.
40 T. Kitazume and T. Ohnogi, *J. Fluorine Chem.*, 1990, **47**, 459.
41 T. Kitazume, T. Ohnogi and K. Ito, *J. Am. Chem. Soc.*, 1990, **112**, 6608.

42 N. F. Cooray, M. Kakimoto, Y. Imai and Y. Suzuki, *Macromolecules*, 1994, **27**, 1592.
43 R. 1609 Karapinar, M. O'Neill, C. J. Newsome, N. Gough and M. Hird, *Ferroelectrics*, 1998, **213**, 171.
44 R. Karapinar, M. O'Neill and M. Hird, *J. Phys. D: Appl. Phys.*, 2002, **35**, 900.
45 S. Puntambekar, M. C. Holmes and M. S. Leaver, *Liq. Cryst.*, 2000, **27**, 743.
46 M. H. Ropers and M. J. Stebe, *Langmuir*, 2003, **19**, 3137.
47 J. Esquena, C. Rodriguez, C. Solans and H. Kunieda, *Microporous Mesoporous Mater.*, 2006, **92**, 212.
48 S. C. Sharma, H. Kunieda, J. Esquena and C. R. Abreu, *J. Colloid Interface Sci.*, 2006, **299**, 297.
49 M. Acimis and E. B. Karaman, *J. Colloid Interface Sci.*, 2006, **300**, 1.
50 K. Bergt, PhD Thesis, University of Halle, Halle, 1925.
51 Y. Goto, T. Ogawa, S. Sawada and S. Sugimori, *Mol. Cryst. Liq. Cryst.*, 1991, **209**, 1.
52 V. F. Petrov, *Liq. Cryst.*, 1995, **19**, 729.
53 K. Tarumi, M. Bremer and B. Schuler, *IEICE Trans. Electron.*, 1996, **E79–C**, 1035.
54 P. Kirsch, M. Bremer, M. Heckmeier and K. Tarumi, *Angew. Chem., Int. Ed.*, 1999, **38**, 1989.
55 K. Tarumi, M. Bremer and T. Geelhaar, *Annu. Rev. Mater. Sci.*, 1997, **27**, 423.
56 D. Demus, Y. Goto, S. Sawada, E. Nakagawa, H. Saito and R. Tarao, *Mol. Cryst. Liq. Cryst.*, 1995, **260**, 1.
57 H. Takatsu, H. Ohnishi, K. Kobayashi, W. Becker, M. Seki, M. Tazume, T. Nakajima, H. Saito, B. Simon-Hittich and S. Naemura, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 171.
58 A. I. Pavluchenko, N. I. Smirnova, V. F. Petrov, Y. A. Fialkov, A. Shelyazhenko and S. V. Yagupolsky, *Mol. Cryst. Liq. Cryst.*, 1991, **209**, 225.
59 K. Kanie, S. Takehara and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1875.
60 E. Bartman, *Ber. Bunsen-Ges. Phys. Chem.*, 1993, **97**, 1349.
61 H. J. Mueller and W. Haase, *Mol. Cryst. Liq. Cryst.*, 1983, **92**, 63.
62 K. S. Shibata, K. Miyazawa and Y. Goto, *Chem. Commun.*, 1997, 1309.
63 A. Raviol, W. Stille and G. Strobl, *J. Chem. Phys.*, 1995, **103**, 3788.
64 M. A. Osman, *Mol. Cryst. Liq. Cryst.*, 1985, **128**, 45.
65 G. W. Gray and B. Jones, *J. Chem. Soc.*, 1954, 2556.
66 P. Balkwill, D. Bishop, A. Pearson and I. Sage, *Mol. Cryst. Liq. Cryst.*, 1985, **123**, 1.
67 G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, 1973, **9**, 130.
68 R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 100.
69 R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 133.
70 S. M. Kelly, *Helv. Chim. Acta*, 1984, **67**, 1572.
71 G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1989, **172**, 165.
72 S. M. Kelly and H. Schad, *Helv. Chim. Acta*, 1984, **67**, 1580.
73 H. Schad and S. M. Kelly, *J. Chem. Phys.*, 1984, **81**, 1514.
74 D. G. McDonnell, E. P. Raynes and R. A. Smith, *Liq. Cryst.*, 1989, **6**, 515.
75 R. Dabrowski, J. Dziaduszek, W. Drzewinski, K. Czuprynski and Z. Stolarz, *Mol. Cryst. Liq. Cryst.*, 1990, **191**, 171.
76 G. W. Gray, C. Hogg and D. Lacey, *Mol. Cryst. Liq. Cryst.*, 1981, **67**, 1.
77 G. W. Gray and S. M. Kelly, *Mol. Cryst. Liq. Cryst.*, 1981, **75**, 109.
78 M. Chambers, R. Clemitson, D. Coates, S. Greenfield, J. A. Jenner and I. C. Sage, *Liq. Cryst.*, 1989, **5**, 153.
79 V. Reiffenrath, J. Krause, H. J. Plach and G. Weber, *Liq. Cryst.*, 1989, **5**, 159.
80 K. Iio and S. Kondoh, *Ferroelectrics*, 2006, **344**, 441.
81 T. D. Wilkinson, W. A. Crossland and A. B. Davey, *Ferroelectrics*, 2002, **278**, 799.
82 J. C. Jones, M. J. Towler and J. R. Hughes, *Displays*, 1993, **14**, 86.
83 A. J. Slaney, V. Minter and J. C. Jones, *Ferroelectrics*, 1996, **178**, 65.
84 M. D. Wand, R. T. Vohra, W. N. Thurmes and K. M. More, *Ferroelectrics*, 1998, **213**, 187.
85 M. Hird, J. W. Goodby and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 2001, **360**, 1.
86 V. Brimmell, J. Constant, H. A. Pedlingham, E. P. Raynes and A. K. Samra, *Liq. Cryst.*, 1989, **6**, 545.
87 G. W. Gray, M. Hird and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1991, **195**, 221.
88 G. W. Gray, K. J. Harrison and J. A. Nash, *J. Chem. Soc., Chem. Commun.*, 1974, 431.
89 L. K. M. Chan, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1988, **158B**, 209.
90 L. K. M. Chan, G. W. Gray, D. Lacey, T. Srithanratana and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1987, **150B**, 335.
91 L. K. M. Chan, G. W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, 1985, **123**, 185.
92 D. Coates, I. Sage, S. Greenfield, G. W. Gray, D. Lacey, K. J. Toyne, L. K. M. Chan and M. Hird, in 'Fluorinated 4″-cyano substituted tephenyls', US Patent, 5312563, 1994.
93 G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1989, 2041.
94 M. E. Glendenning, J. W. Goodby, M. Hird and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1999, 481.
95 M. E. Glendenning, J. W. Goodby, M. Hird and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 2000, 27.
96 G. W. Gray, M. Hird and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1991, **204**, 43.
97 M. Hird, K. J. Toyne, G. W. Gray, D. G. McDonnell and I. C. Sage, *Liq. Cryst.*, 1995, **18**, 1.
98 M. Hird, G. W. Gray and K. J. Toyne, *Liq. Cryst.*, 1992, **11**, 531.
99 M. Hird, K. J. Toyne, A. J. Slaney, J. W. Goodby and G. W. Gray, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2337.
100 M. Hird, K. J. Toyne and G. W. Gray, *Liq. Cryst.*, 1994, **16**, 625.
101 M. Hird, K. J. Toyne, A. J. Slaney and J. W. Goodby, *J. Mater. Chem.*, 1995, **5**, 423.
102 V. Reiffenrath and M. Bremer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1386.
103 P. Kirsch and K. Tarumi, *Angew. Chem., Int. Ed.*, 1998, **37**, 484.
104 M. Hird, R. A. Lewis, K. J. Toyne, J. J. West and M. K. Wilson, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3479.
105 A. E. Pausch, T. Geelhaar, E. Poetsch and U. Finkenzeller, *Proc. SPIE–Int. Soc. Opt. Eng.*, 1992, **1665**, 128.
106 T. Geelhaar, *Ferroelectrics*, 1988, **85**, 329.
107 H. Zaschke, *J. Prakt. Chem.*, 1975, **317**, 617.
108 J. W. Goodby, M. Hird, R. A. Lewis and K. J. Toyne, *Chem. Commun.*, 1996, 2719.
109 C. C. Dong, P. Styring, L. K. M. Chan and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1997, **302**, 289.
110 G. Sun, B. Chen, H. Tang, G. Shi and S. Xu, *Liq. Cryst.*, 2004, **31**, 1151.
111 C. C. Dong, P. Styring, J. W. Goodby and L. K. M. Chan, *J. Mater. Chem.*, 1999, **9**, 1669.
112 L. Taylor, R. M. Richardson, J. Ebbutt and J. C. Jones, *Mol. Cryst. Liq. Cryst.*, 1995, **263**, 255.
113 R. A. Lewis, J. W. Goodby, M. Hird and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1999, **332**, 339.
114 P. Kirsch, M. Heckmeier and K. Tarumi, *Liq. Cryst.*, 1999, **26**, 449.
115 P. Kirsch, M. Bremer, F. Huber, H. Lannert, A. Ruhl, M. Lieb and T. Wallmichrath, *J. Am. Chem. Soc.*, 2001, **123**, 5414.
116 P. Kirsch, M. Bremer, A. Taugerbeck and T. Wallmichrath, *Angew. Chem., Int. Ed.*, 2001, **40**, 1480.
117 J. W. Goodby, P. Hindmarsh, M. Hird, R. A. Lewis and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 2001, **364**, 889.
118 M. E. Neubert, S. S. Keast, C. C. Law, M. C. Lohman and J. C. Bhatt, *Liq. Cryst.*, 2005, **32**, 781.
119 A. Sakaigawa and H. Nohira, *Ferroelectrics*, 1993, **148**, 71.
120 W. Drzewinski, K. Czuprymski, R. Dabrowski and M. Neubert, *Mol. Cryst. Liq. Cryst.*, 1999, **328**, 401.
121 K. D'have, P. Rudquist, M. Matuszczyk, S. T. Lagerwall, H. Pauwels and R. Dabrowski, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2000, **3955**, 33.
122 A. D. L. Chandani, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, 1989, **28**, L1261.

123 A. I. Stipetic, J. W. Goodby, M. Hird, Y. M. Raoul and H. F. Gleeson, *Liq. Cryst.*, 2006, **33**, 819.

124 S. J. Cowling, A. W. Hall, J. W. Goodby, Y. Wang and H. F. Gleeson, *J. Mater. Chem.*, 2006, **16**, 2181.

125 S. Wu and C. Lin, *Liq. Cryst.*, 2005, **32**, 1053.

126 A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa and H. Takezoe, *J. Mater. Chem.*, 1994, **4**, 997.

127 S. Nakamura and H. Nohira, *Mol. Cryst. Liq. Cryst.*, 1990, **185**, 199.

128 H. Liu and H. Nohira, *Liq. Cryst.*, 1996, **20**, 581.

129 N. Gough, D. D. Parghi, R. A. Lewis and M. Hird, *Mol. Cryst. Liq. Cryst.*, 1999, **332**, 347.

130 T. Kusumoto, K. Ogino, K. Sato, T. Hiyama, S. Takehara and K. Nakamura, *Chem. Lett.*, 1993, 1243.

131 J. W. Goodby, M. Hird, J. C. Jones, R. A. Lewis, I. C. Sage and K. J. Toyne, *Ferroelectrics*, 2000, **243**, 19.

132 S. Takenaka, *J. Chem. Soc., Chem. Commun.*, 1992, 1748.

133 X. Bao and L. R. Dix, *Mol. Cryst. Liq. Cryst.*, 1996, **281**, 291.

134 G. Johansson, V. Percec, G. Ungar and K. Smith, *Chem. Mater.*, 1997, **9**, 164.

135 A. Mori, K. Uno, H. Takeshita and S. Takematsu, *Liq. Cryst.*, 2005, **32**, 107.

136 J. F. Rabolt, T. P. Russell and R. J. Twieg, *Macromolecules*, 1984, **17**, 2786.

137 C. Viney, T. P. Russell, L. E. Depero and R. J. Twieg, *Mol. Cryst. Liq. Cryst.*, 1989, **168**, 63.

138 F. Tournilhac, L. M. Blinov, J. Simon and S. V. Yablonsky, *Nature*, 1992, **359**, 621.

139 M. Hird, J. W. Goodby, N. Gough and K. J. Toyne, *J. Mater. Chem.*, 2001, **11**, 2732.

140 S. Chandrasekhar, *Liq. Cryst.*, 1993, **14**, 3.

141 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 1977, **9**, 471.

142 N. Boden, R. J. Bushby and A. N. Cammidge, *J. Chem. Soc., Chem. Commun.*, 1994, 465.

143 J. W. Goodby, M. Hird, K. J. Toyne and T. Watson, *J. Chem. Soc., Chem. Commun.*, 1994, 1701.

144 H. Bengs, F. Closs, T. Frey, D. Funhoff, H. Ringsdorf and K. Siemensmeyer, *Liq. Cryst.*, 1993, **15**, 565.

145 J. A. Rego, S. Kumar and H. Ringsdorf, *Chem. Mater.*, 1996, **8**, 1402.

146 A. Fechtenkotter, K. Saalwachter, M. A. Harbison, K. Mullen and H. W. Spiess, *Angew. Chem., Int. Ed.*, 1999, **38**, 3039.

147 A. M. van der Craats, J. M. Warman, A. Fechtenkotter, J. D. Brand, M. A. Harbison and K. Mullen, *Adv. Mater.*, 1999, **11**, 1469.

148 J. Wu, M. D. Watson, N. Tchebotareva, Z. Wang and K. Mullen, *J. Org. Chem.*, 2004, **69**, 8194.

149 N. Terasawa, H. Monobe, K. Kiyohara and Y. Shimizu, *Chem. Commun.*, 2003, 1678.

150 A. J. Seed, M. Hird, P. Styring, H. F. Gleeson and J. T. Mills, *Mol. Cryst. Liq. Cryst.*, 1997, **299**, 19.

151 M. Hird, J. W. Goodby, K. J. Toyne, H. F. Gleeson, I. P. Buxton, A. J. Seed and M. R. Herbert, *Mol. Cryst. Liq. Cryst.*, 2001, **365**, 213.

152 T. Niori, T. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.

153 G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, 1999, **11**, 707.

154 G. Pelzl, I. Wirth and W. Weissflog, *Liq. Cryst.*, 2001, **28**, 969.

155 C. Tschierske and G. Dantlgraber, *Pramana*, 2003, **61**, 455.

156 A. R. Reddy and C. Tschierke, *J. Mater. Chem.*, 2006, **16**, 907.

157 H. Takezoe and Y. Takanishi, *Jpn. J. Appl. Phys.*, 2006, **45**, 507.

158 M. Hird, Y. M. Raoul, J. W. Goodby and H. F. Gleeson, *Ferroelectrics*, 2005, **309**, 95.

159 G. Pelzl, A. Eremin, S. Diele, H. Kresse and W. Weissflog, *J. Mater. Chem.*, 2002, **12**, 2591.

160 J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89.

161 J. M. Lehn, ‘Supramolecular Chemistry’, VCH, Weinheim, 1995.

162 V. Percec, M. Glodde, G. Johansson, S. K. Balagurusamy and P. A. Heiney, *Angew. Chem., Int. Ed.*, 2003, **42**, 4338.

163 V. Percec, M. Glodde, M. Peterca, A. Rapp, I. Schnell, H. W. Spiess, T. K. Bera, Y. Miura, S. K. Balagurusamy, E. Aqad and P. A. Heiney, *Chem.–Eur. J.*, 2006, **12**, 6298.

164 M. Weck, A. R. Dunn, K. Matsumoto, G. W. Coates, E. B. Lobkovsky and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 1999, **38**, 2741.

165 K. Kishikawa, K. Oda, S. Aiyo and S. Kohmoto, *Angew. Chem., Int. Ed.*, 2007, **46**, 764.

166 H. L. Nguyen, P. N. Horton, M. B. Hursthouse, A. C. Legon and D. W. Bruce, *J. Am. Chem. Soc.*, 2004, **126**, 16.

167 P. Metrangolo, C. Prasang, G. Resnati, R. Liantonio, A. C. Whitwood and D. W. Bruce, *Chem. Commun.*, 2006, 3290.

168 J. Lydon, *Curr. Opin. Colloid Interface Sci.*, 2004, **8**, 480.

169 G. J. T. Tiddy, *Phys. Rep.*, 1980, **57**, 1.

170 D. J. Mitchell, G. J. T. Tiddy, L. Waring, T. Bostock and M. P. McDonald, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 975.

171 C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.

172 J. Seddon and R. Templer, *New Sci.*, 1991, **1769**, 45.

173 J. W. Goodby, *Liq. Cryst.*, 1998, **24**, 25.

174 M. H. Ropers and M. J. Stebe, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4029.

175 O. Regev, M. S. Leaver, R. Zhou and S. Puntambekar, *Langmuir*, 2001, **17**, 5141.

176 S. E. Rankin, B. Tan, H. Lehmler, K. P. Hindman and B. L. Knutson, *Microporous Mesoporous Mater.*, 2004, **73**, 197.

177 J. L. Blin and M. J. Stebe, *Microporous Mesoporous Mater.*, 2005, **87**, 67.