The synthesis and mesomorphic properties of 2,2′,3-tri- and 2,2′,3,3′-tetra-fluoro-1,1′:4′,1″-terphenyls for high dielectric biaxiality ferroelectric liquid crystal mixtures

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Liquid crystalline 1,1′:4′,1″-terphenyls with three and four lateral fluoro substituents and alkyl or alkoxy substituents in the 4- and 4′-positions have been synthesised. Synthetic strategies employed were convergent and involved the use of arylboronic acids and aryl halides in palladium-catalysed cross-coupling reactions. These syntheses are of particular interest because issues of selective metallation (at positions *ortho* to a fluoro substituent) and selective coupling reactions (bromo *versus* iodo sites) are involved, not all of which proceed as expected. All the trifluoroterphenyls and most of the tetrafluoroterphenyls generate the smectic C phase, the phase stability and temperature range of which were found to be highly dependent upon the relative lengths of the two terminal chains. The 2,2′,3- and 2,2′,3,3′-patterns of lateral fluoro substitution in 1,1′:4′,1″-terphenyls generate materials of high lateral dipole and enable the formulation of ferroelectric mixtures with a high dielectric biaxiality which is very important in τV minimum driving schemes.

Introduction

When ferroelectricity in tilted smectic liquid crystals was first discovered by Meyer[1] nearly 25 years ago smectic liquid crystals were just a curiosity and undesirable in the context of nematic materials for displays. Accordingly, very few compounds exhibiting the smectic C phase (chiral or achiral) were known. The invention of the surface-stabilised ferroelectric display device by Clark and Lagerwall in 1980[2] demonstrated the potential for extremely short switching times and high multiplexability. The massive commercial potential of this device resulted in intense research into new materials that exhibit the chiral smectic C phase. The primary aims were to produce good mesomorphic behaviour (low melting point and a wide chiral smectic C temperature range) and to generate as high a spontaneous polarisation as possible (to ensure very short switching times). Many chiral materials were produced, but a variety of problems such as chemical and photochemical instability, poor mesomorphic behaviour and a high viscosity proved them to be unsuitable for commercial realisation of a ferroelectric display. It emerged that a high spontaneous polarisation was not as beneficial to molecular switching as at first thought. It also became well recognised that the best way of achieving ferroelectricity in liquid crystals is to use a base mixture of achiral compounds which enables the fine-tuning of the mesomorphic behaviour, and allows the tailoring of many important physical properties, such as birefringence and particularly the requirement for a low viscosity. Such achiral host mixtures need to be doped with a chiral material which then confers chirality to the whole mixture; removal of the macroscopic helical structure then generates the required ferroelectric properties. Ideally, the quantity of the required chiral material should be as low as possible so as to minimise the viscosity, but must be sufficiently high to provide the necessary spontaneous polarisation.[3–6]

The very nature of the smectic C phase means that there is a requirement for the molecules to be polar and non-symmetrical so as to generate molecular tilting. Generally, it was thought that the tilting was generated by the presence of terminal outboard dipoles that work in opposition of each other, and this theory was supported by all the smectic C materials known at the time.[7] Such materials contain polar ester groups and polar ether oxygens in terminal alkoxy chains, and these are very good structural units for the generation of the tilted smectic C phase, and, despite high polarity, some materials with very low melting points were produced.[8–10] The main disadvantage of such polar materials when considering their use in display applications is their very high viscosity. Phenylpyrimidines are somewhat unusual materials in that they generate the smectic C phase without the need for an ester moiety. The necessary polarity for molecular tilting is provided by an ether oxygen and by the heterocyclic nitrogens. The lack of interannular twisting due to the removal of steric crowding in the bay region ensures high longitudinal polarisability which confers reasonably high liquid crystal phase stability, in fact very high stability for two-ring compounds. The two-ring architecture of phenylpyrimidines also ensures a low viscosity and makes them well-suited for ferroelectric mixtures for displays.[4,11,12]

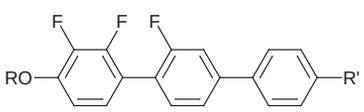
More recently, the smectic C phase has been generated in materials without any oxygen function. These materials use lateral fluoro substituents to provide the sole source of polarity for molecular tilting.[13,14] Even with the fluoro substituents in the centre of the molecule, the smectic C phase is exhibited, provided that the terminal chains are of unequal length. Such materials do however, require three rings, but a reasonably low viscosity is achieved by the use of two short alkyl chains. The use of two lateral fluoro substituents *ortho* to each other gives better mesomorphic properties and a better overall combination of other physical properties.[13,15] A most important advantage of the *ortho* difluoroterphenyls is their high degree of dielectric biaxiality which is very important in τV minimum ferroelectric devices.[16,17] Ferroelectric mixtures based on the *ortho* difluoroterphenyls show a minimum in their response time–voltage relationship. The minimum is a result of the high degree of dielectric biaxiality shown by the difluoroterphenyls, and it offers many advantages for ferroelectric devices such as high levels of multiplexability, high contrast ratios, wide viewing angles and short switching times. In order to achieve the optimum combination of a short switching time and low operating voltage it is important that dielectric biaxiality is high; of course, this requirement is in addition to the usual requirements of ferroelectric mixtures such as appropriate mesomorphic behaviour and low viscosity. A high spontaneous polarisation is

undesirable because it increases the voltage at which the above mentioned minimum occurs, but a high dielectric biaxiality moves the minimum towards lower voltage which is beneficial.

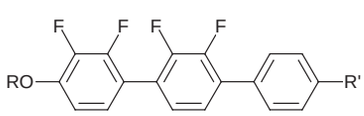
The whole advantage of the τV minimum operating system depends critically on the properties of the ferroelectric mixture.[5,16,17] The dielectric biaxiality is proportional to smectic C phase stability and perpendicular dielectric permittivity, and hence materials with a high smectic C phase stability and a lateral dipole confer high values of dielectric biaxiality; a relationship confirmed by the high dielectric biaxiality values of the difluoroterphenyls which have high smectic C phase stability and high negative values of dielectric anisotropy.[16] In the design of new, improved host materials for ferroelectric mixtures for τV minimum operation it is important to generate a very high lateral dipole whilst minimising any increase in viscosity, and of course maintaining good mesomorphic behaviour. The two fluoro substituents of the *ortho* difluoroterphenyls are inherently fixed on the same side of the molecule and so reinforce each other to generate a high lateral dipole.[13,15,16] It is also known from many different sources that the 2,2′-difluoro substituents in a biphenyl moiety tend to attract each other to their van der Waals minimum so providing a high lateral dipole.[18–20] Another important molecular structural feature that considerably increases the lateral dipole is the special relationship between an ether oxygen of the terminal alkoxy chain and the adjacent fluoro substituent in a phenyl ring; it is thought that in this case there is a mesomeric effect from the oxygen which enhances the polarity of the fluoro substituent.[13,15]

The aim of this work was to synthesise a series of terphenyl compounds with three fluoro substituents that are located so as to combine attributes of the *ortho* difluoroterphenyls, the adjacent ether oxygen, and the 2,2′ relationship. As far as possible this molecular architecture would have all three, or all four, fluoro substituents on one side of the molecule and hence generate a particularly high lateral dipole and a high dielectric biaxiality. Additionally, this arrangement of fluoro substituents should minimise any increase in molecular breadth and so minimise the reduction in liquid crystal phase stability expected from the introduction of a third lateral fluoro substituent, and hopefully ensure the generation of the tilted smectic C phase due to the expected increased lateral dipole. Minimised molecular breadth should also help to keep the viscosity reasonably low.

A wide range of homologues of the trifluoroterphenyls (**I**) and tetrafluoroterphenyls (**II**) have been synthesised in order to



I



II

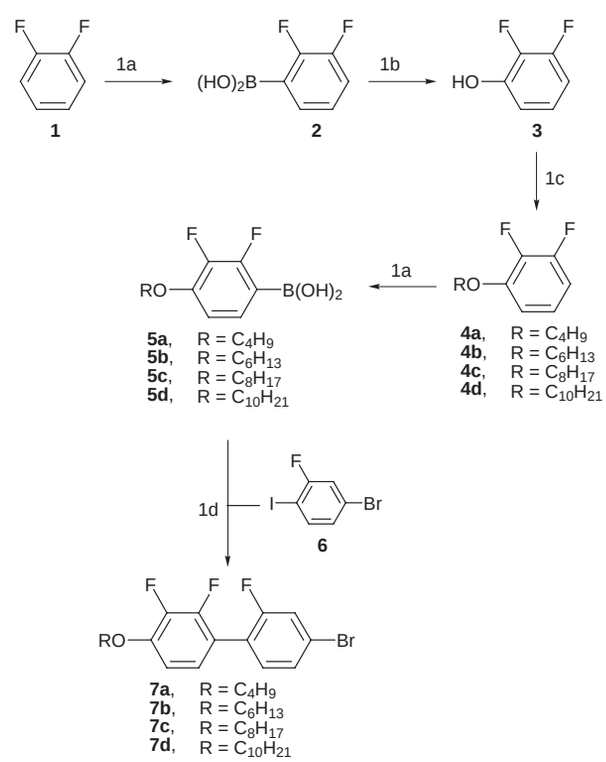
(a) fully evaluate the effect of a third, and a fourth, lateral fluoro substituent on melting points, transition temperatures and mesophase morphology, and (b) to find the optimum combination of terminal chain lengths that generates a material with as low a melting point as possible and that exhibits a smectic C phase over as wide a temperature range as possible.

Synthesis of materials

To be commercially-viable, ferroelectric displays will need to outperform existing nematic displays, and in order to achieve this the physical properties of the materials must be finely tuned. Of course, as the required physical properties of liquid crystals become increasingly exacting, then the molecular structures become more complex in order to provide those properties; hence, far more consideration in terms of synthetic strategy and methodology is required than for more simple systems.

It is difficult, if not impossible, to use conventional electrophilic substitution when the substituents are required in the inner core positions of a multiaryl system because of steric hindrance and probable incompatible directing and activating effects from existing substituents. Accordingly, the only viable synthetic strategy is a convergent one that involves the synthesis of the subunits with the desired substitution pattern. The joining together of the appropriate subunits would then generate the desired multiaryl materials. Such carbon–carbon bond-forming metal-catalysed cross-coupling reactions have been well developed over many years,[13,21–24] and the preferred method involves an arylboronic acid (or the ester derivative) with an aryl iodide, bromide, chloride or trifluoromethanesulfonate. The coupling reactions involving boronic acids were established in the synthesis of liquid crystals through the synthesis of the *ortho* difluoroterphenyls as mentioned above.[13]

In view of the fact that these tri- and tetra-fluoroterphenyls contain fluoro substituents in more than one ring, two coupling reactions per system were essential for efficient synthesis. Several synthetic routes were used in the synthesis of the tri- and tetra-fluoro substituted terphenyls, initially because of availability of intermediates from other syntheses and also in an attempt to find the most efficient routes and methodologies. The principal synthetic approach involved the use of 4-bromo-2-fluoro-1-iodobenzene (**6**) as a vital, commercially-available material (Scheme 1). The synthesis of the essential alkoxy-

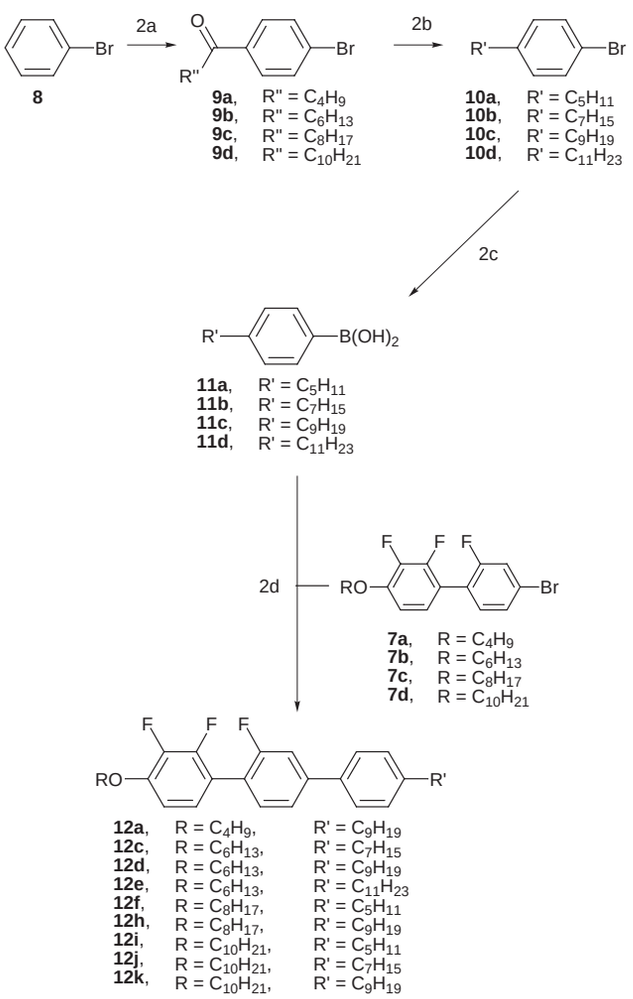


Scheme 1 1a, (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl. 1b, H_2O_2, THF. 1c, RBr, K_2CO_3, butanone. 1d, $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME.

difluorophenylboronic acids (**5a**–**d**) was elegantly accomplished from 1,2-difluorobenzene through the sequential exploitation of the acidic protons.[13] Although four steps were required to generate each boronic acid (**5**) the methods were all operationally simple and the overall yields were high. The coupling reactions of these highly substituted arylboronic acids with the

bromofluoroiodobenzene (**6**) were required to be selective in order to provide the intermediates **7a**–**d**.

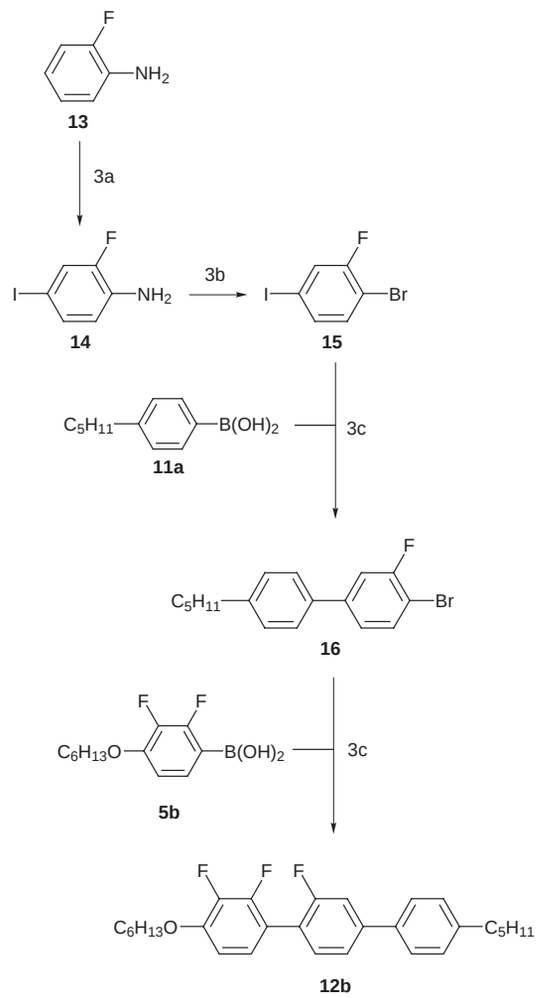
Initial results were not encouraging as extensive double coupling was found to occur. This result was somewhat unexpected because normally the iodo unit would be the much preferred site of coupling, and in this case, the fluoro substituent *ortho* to the iodo unit should provide activation. However, in this coupling the boronic acid unit also has an *ortho* fluoro substituent thus producing increased steric hindrance, this combined with less steric hindrance at the bromo site seems to ruin the expected good selectivity. On further investigation it was found that a reduced reaction temperature (65 °C) provided much enhanced selectivity and virtually eliminated the coupling at the bromo site. The intermediates were purified by column chromatography and Kugelrohr distillation and reasonably good yields were isolated. Greater efficiency may have been possible by not purifying intermediates **7a**–**d** and performing the second coupling reaction either *in situ* or on the crude product. However, it was felt that problems may have been eventually encountered in the purification of the final terphenyl materials. As shown in Scheme 2, the second coupling reaction required



Scheme 2 2a, R″COCl, $AlCl_3$. 2b, $NH_2NH_2{\cdot}H_2O$, KOH, diethylene glycol. 2c, (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl. 2d, $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME.

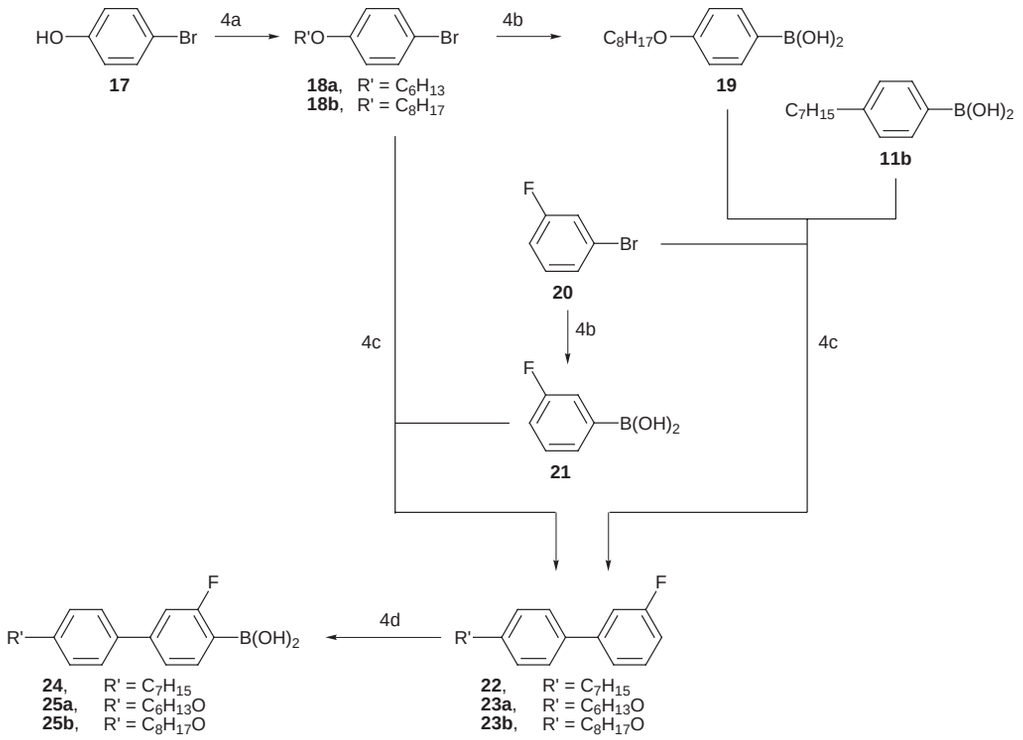
the appropriate alkylphenylboronic acids (**11a**–**d**), which were prepared from bromobenzene (**8**) through a three-step synthesis. In each case, a Friedel–Crafts acylation followed by reduction facilitated the introduction of the alkyl chain,[13] and the subsequent exploitation of the bromo substituent furnished the desired boronic acids (**11a**–**d**).[14] The coupling of these alkylphenylboronic acids to the purified bromotrifluorobiphenyl intermediates (**7a**–**d**) was carried out under reflux conditions (80 °C) to give excellent yields of the desired liquid crystalline terphenyls (**12**, Scheme 2). Any low yields recorded were caused by poor returns on recrystallisation due to a large volume of solvent being required to circumvent the formation of gels.

During the optimisation of the synthetic routes, an alternative coupling strategy (Scheme 3) was investigated which



Scheme 3 3a, I_2, $NaHCO_3$, H_2O. 3b, (i) $NaNO_2$, HBr, H_2O; (ii) CuBr, HBr, H_2O. 3c, $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME.

involved the initial selective coupling at an iodo site that is not sterically hindered. It was expected that coupling of boronic acid **11a** to 1-bromo-2-fluoro-4-iodobenzene (**15**) would give excellent selectivity because in this case the better leaving group is not sterically hindered, but the bromo leaving group is. However, in this case the initial coupling reaction involves a boronic acid (**11a**) without a 2-substituent and so steric hindrance is not influential; more importantly here, the bromo substituent of compound **15** is *ortho* to the electron-withdrawing fluoro substituent and so is activated towards coupling. Hence, unfortunately, the selectivity of compound **15** (Scheme 3) was found to be worse than that of compound **6** (Scheme 1), in fact the bromofluorobiphenyl intermediate (**16**) was isolated in just 35% yield. Additionally, unlike compound **6**, the isomeric compound **15** is not commercially available and must be synthesised. However, iodination of 2-fluoroaniline (**13**) occurs at the desired 4-position and the product (**14**) is easily purified to give a good isolated yield.[25] The diazotisation of compound **14** to generate the necessary bromo-substituted compound (**15**) is straightforward and reasonably high yielding. An alternative synthesis of compound **15** has already been developed by Hird



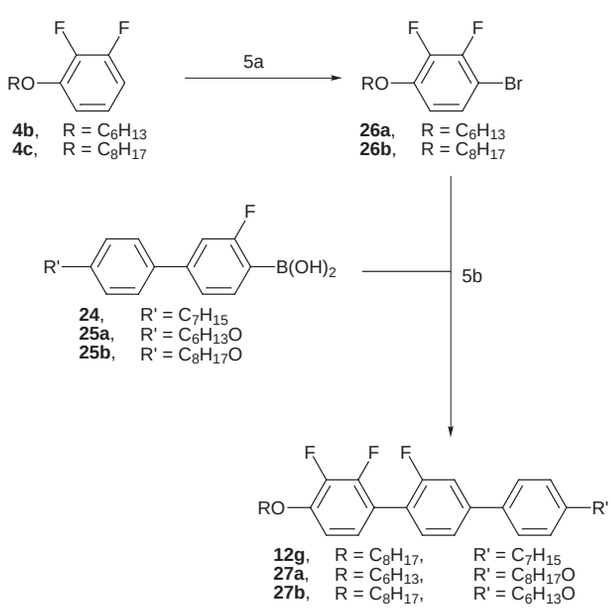
Scheme 4 4a, R′Br, K_2CO_3, butanone. 4b, (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl. 4c, $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME. 4d, (i) sec-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.

and co-workers,[26] but the route is longer and less efficient than that reported here. Overall, the first strategy (Schemes 1 and 2), described above is preferable to that outlined in Scheme 3, and so was employed to prepare the majority of compounds of type **12**.

The two analogous strategies described above (Schemes 1–3) both involved ambiguity in the form of a selective coupling reaction. In each case, selectivity was acceptable and provided a good route to the desired liquid crystals. However, another strategy was investigated that does not involve a selective coupling, but does involve a possible issue of selective lithiation after the first coupling reaction (Scheme 4). Compounds **22**, **23a** and **23b** were prepared by a palladium-catalysed cross-coupling reaction, either involving the fluoro-substituted phenyl bromide (**20**) and the phenylboronic acid (*e.g.*, compound **19**) or involving the fluoro-substituted boronic acid (**21**) and phenyl bromide (*e.g.*, **18**); clearly for the preparation of a wide range of homologues the latter approach is more efficient. Compounds **22**, **23a** and **23b** have two acidic protons.

It was found that only secondary butyllithium effected the removal of an acidic proton, and the proton in the 4-position was selectively abstracted to generate the lithium salt. This result can be explained in terms of the steric hindrance to proton-removal from the bay region (2-position). The result is useful when considering the synthesis of liquid crystals which have a linear construction of the multiaryl core because a boronic acid can be selectively generated at the 4-position (compounds **24**, **25a** and **25b**), and the subsequent coupling reactions will then produce the desired liquid crystalline materials (**12g**, **27a** and **27b**). This strategy involving the boronic acid of the biphenyl unit necessitates the preparation of the bromo-substituted alkoxydifluorophenyl unit (**26a** and **26b**) which was easily accomplished (Scheme 5) by electrophilic bromination in the expected position *para* to the alkoxy substituent (the *ortho* position is sterically hindered by the long chain).

The introduction of a bromo substituent at the desired position of compounds **4a** and **4b** can be accomplished by exploiting the acidic proton, but was found to be less efficient than the

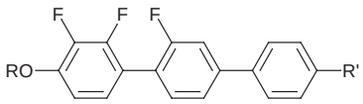


Scheme 5 5a, Br_2, $CHCl_3$. 5b, $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME.

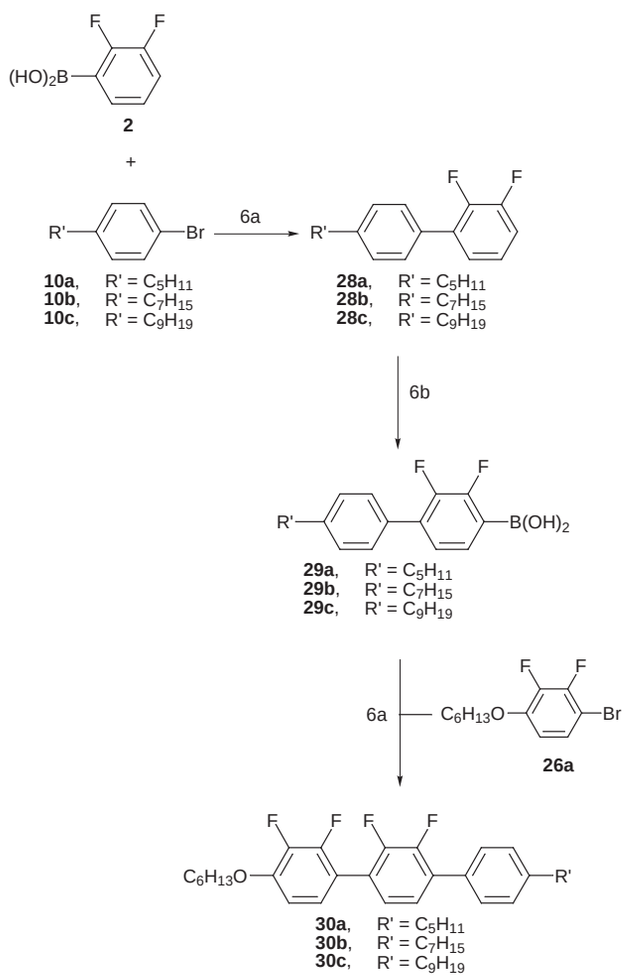
method used. The coupling reactions involving the fluoro-substituted biphenylboronic acids (**24**, **25a** and **25b**) were not very high-yielding due to considerable hydrodeboronation of the boronic acids which is due in part to the steric hindrance at the site of coupling. Nevertheless, this synthetic strategy may prove useful in some circumstances.

The choice of strategy involved in the synthesis of the tetrafluoroterphenyls (Scheme 6) is more clear cut because two of the rings both have *ortho* difluoro substituents. A coupling of the difluorophenylboronic acid (**2**) to aryl bromides (**10a**–**c**) provides the appropriate difluorobiphenyl unit which has an acidic proton. Exploitation of the acidic proton in compounds **28a**–**c** with *n*-butyllithium provided boronic acids **29a**–**c** which were then coupled to the difluorophenyl bromide **26a** to generate final liquid crystalline compounds (**30a**–**c**).

Table 1 Transition temperatures for 4-alkoxy-4″-alkyl-2,2′,3-trifluoroterphenyls (**12a**–**k**)



Compound			Transition Temperatures/°C								
No.	R	R′	Cryst		S_C		S_A		N		Iso
12a	C_4H_9	C_9H_{19}	·	57.7	·	87.0	·	89.1	·	112.9	·
12b	C_6H_{13}	C_5H_{11}	·	43.8	·	(38.1)			·	112.3	·
12c	C_6H_{13}	C_7H_{15}	·	40.1	·	75.7			·	111.8	·
12d	C_6H_{13}	C_9H_{19}	·	47.9	·	91.5			·	109.6	·
12e	C_6H_{13}	$C_{11}H_{23}$	·	51.2	·	95.2	·	98.6	·	106.2	·
12f	C_8H_{17}	C_5H_{11}	·	47.3	·	50.2			·	110.3	·
12g	C_8H_{17}	C_7H_{15}	·	48.0	·	81.0			·	108.8	·
12h	C_8H_{17}	C_9H_{19}	·	55.4	·	95.0			·	107.3	·
12i	$C_{10}H_{21}$	C_5H_{11}	·	56.1	·	(52.1)			·	102.1	·
12j	$C_{10}H_{21}$	C_7H_{15}	·	56.0	·	83.2			·	104.5	·
12k	$C_{10}H_{21}$	C_9H_{19}	·	59.6	·	95.9			·	104.4	·



Scheme 6 6a, $Pd(PPh_3)_4$, 2 M Na_2CO_3, DME. 6b, (i) n-BuLi, THF; (ii) $(MeO)_3B$, THF; (iii) 10% HCl.

Discussion of mesophase morphology and transition temperatures

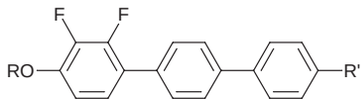
Table 1 shows the transition temperatures of a series of eleven alkylalkoxytrifluoroterphenyls with a 2,2′,3-trifluoro substitution pattern. The most striking feature of these novel materials is their relatively low melting points (between 40 and 60 °C), far lower than expected when considering their high polarity due to the presence of three fluoro substituents and an alkoxy chain. Reasonably high smectic C phase stability is seen for some homologues, notably those with longer terminal chains. The tendency of the molecules towards tilting is strong relative to the overall smectic phase stability, a fact emphasised by the lack of orthogonal smectic phases.

To gain some appreciation of the significance of the melting points, transition temperatures and mesophase morphology of the novel trifluoroterphenyls (**12a**–**k**, Table 1) it is essential to compare them with some analogous difluoroterphenyls (Table 2).[13,19] As would be expected based on the increased interannular twisting and the extra breadth over a greater portion of the molecule, the third fluoro substituent at the 2′-position has reduced transition temperatures considerably. Comparisons for all homologues are not possible, and in any case would be tedious and unnecessary, but comparisons of **12b** with **31a**, **12f** with **31b**, **12i** with **31c**, **12g** with **31d** and **12j** with **31e** (Tables 1 and 2) are useful. In general, the nematic phase stability has been reduced by around 45 °C, but the smectic phase stability has been much more affected (a common result of lateral fluoro substitution within the core due to a disruption in lamellar packing of the constituent molecules) and is down by between 65 and 107 °C.

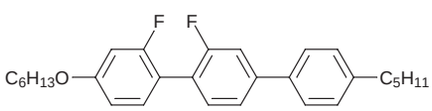
The influence of the terminal chain lengths between the analogous trifluoro- and difluoro-terphenyls is most interesting, and explains the large variation in the effect of the additional fluoro substituent in the 2′-position on the smectic phase stability. For the difluoroterphenyls (**31a**–**e**)[13] there is very little variation in smectic phase stability with varying terminal chain length. However, for the trifluoroterphenyls (**12a**–**k**, Table 1) the smectic phase stability is very low at short chain lengths, yet reasonably high for long terminal chains; the length of the alkyl chain in the unfluorinated ring is most critical (see later for more detailed discussion). The difluoroterphenyls (**31a**–**e**) tend to exhibit the smectic A phase above the smectic C phase, basically showing that the smectic tendency is very strong relative to the tendency of the molecules to tilt, although not significantly so because the smectic A range is very short in most cases; in fact compound **31a** does not exhibit a smectic A phase, most certainly due to the shorter terminal chains keeping the smectic tendency below that of the tendency of the molecules to tilt. The reduction in smectic A phase stability due to the third (2′-) fluoro substituent is greater than the reduction in the smectic C phase stability, and for the trifluoroterphenyls the tilting power of the molecules is maintained throughout the full extent of the smectic tendency (see later for a more detailed discussion).

Comparison of the trifluoroterphenyls with the 2,2′-difluoroterphenyls[19] (Table 2) is only possible for one homologue (compounds **12b** and **32**). However, it is an interesting comparison because it shows clearly the influence of the outer-edge fluoro substituent in enhancing the smectic phase stability, in this case

Table 2 Transition temperature for selected difluoroterphenyls (**31a**–**e** and **32**)[13,19]



Compound			Transition Temperatures/°C								
No.	R	R′	Cryst		S_C		S_A		N		Iso
31a	C_6H_{13}	C_5H_{11}	·	97.5	·	145.5			·	166.0	·
31b	C_8H_{17}	C_5H_{11}	·	93.5	·	144.0	·	148.0	·	159.0	·
31c	$C_{10}H_{21}$	C_5H_{11}	·	88.0	·	143.5	·	154.5	·	161.5	·
31d	C_8H_{17}	C_7H_{15}	·	89.5	·	148.0	·	151.5	·	154.0	·
31e	$C_{10}H_{21}$	C_7H_{15}	·	85.5	·	147.0	·	149.0	·	150.0	·



32

Cryst 31.5 N 114.0 Iso

by at least 50 °C since compound **32** supercools in the nematic phase down to −18 °C (this contrasts with the effect of an inner-core lateral fluoro substituent). In this comparison where the third fluoro substituent is occupying an outer-edge position, no inter-annular twisting occurs and so longitudinal polarisability is maintained, yet space is now filled by a polar substituent with no increase in molecular breath which allows better lamellar packing of the constituent molecules, hence the substantial increase in smectic phase stability. The nematic phase does not involve a lamellar packing of the molecules, so the phase stability is less dependent on polarity and hence the $T_{N–I}$ values of compounds **12b** and **32** are very similar. This comparison of compound **12b** with compound **32** contrasts markedly with the situation discussed above where the third fluoro substituent is at the inner-core 2′-position (comparison of compound **12b** with compound **31a**).

A comparative discussion of the various homologues of the novel trifluoroterphenyls (**12a**–**k**, Table 1) is interesting because the transition temperatures are quite varied and depend, critically in some cases, upon the length of the terminal chains. Such a situation provides excellent evidence of the need to synthesise a wide range of homologues when seeking specific mesomorphic behaviour. Here the effect of increasing the alkyl and/or alkoxy terminal chain lengths on melting points, transition temperatures and mesophase morphology will be discussed. Melting points are notoriously difficult to predict, but as already stated in earlier comparisons, compounds **12a**–**k** do have surprisingly low melting points (40 to 60 °C). The melting points of liquid crystals are often relatively high for short terminal chains (C_1 to C_4), fall for medium chain lengths (C_5 to C_8) and then rise again at longer chain lengths, the exact boundaries between short, medium and long depend on the rest of the molecular structure. The alkylalkoxytrifluoroterphenyls certainly follow this trend for the changing alkoxy chain length (compounds **12a**, **12d**, **12h** and **12k**) where the short butoxy chain provides a high melting point (57.7 °C), the longer hexyloxy chain confers a lower melting point of 47.9 °C, but further increases in the length of the alkoxy chain causes a high melting point for compound **12k**. However, compounds **12a** and **12c** have the same total length of terminal chains, but the former compound shows the higher melting point because of the short alkoxy terminal chain.

At the other end of the temperature range of mesomorphism, the nematic phase stabilities (clearing temperatures) are all fairly similar (102 to 113 °C). In most liquid crystalline molecular architectures, as the total length of terminal chains increases the nematic phase stability decreases, and generally this situation is seen for compounds **12a**–**k** (Table 1). The highest nematic phase stabilities are seen for those compounds with short alkoxy terminal chains (*e.g.*, compounds **12a** and **12b**) and the lowest are seen for compounds **12i**–**k** with long alkoxy terminal chains (see also Figs. 1 and 2).

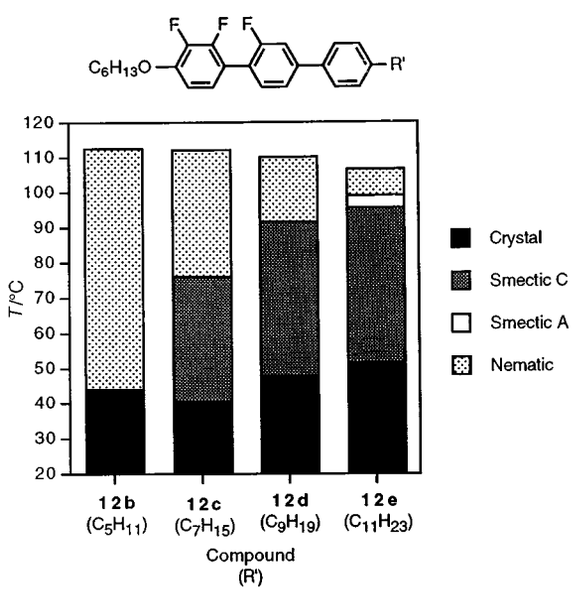
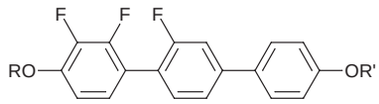


Fig. 1 Effect on transition temperatures of increasing the terminal alkyl chain length.

The alkoxyalkyltrifluoroterphenyls shown in Table 1 (**12a**–**k**) were designed as possible host materials for ferroelectric mixtures and hence the smectic C phase stability is of great importance (although these materials were also targeted due to their expected high dielectric biaxiality). The smectic C phase stabilities for the compounds **12a**–**k** show enormous variation with the length of the terminal chains and range from 38.1 °C (compound **12b**) for the shortest terminal chain length combination right up to 95.9 °C (compound **12k**) for the longest combination. This interesting dependency of smectic C phase stability on the terminal chain lengths is well illustrated by Figs. 1 and 2. It is understandable that the smectic phase stability of compounds **12** should generally be fairly low given the high degree of lateral fluoro substitution (see earlier comparison with the difluoroterphenyls), therefore it should perhaps follow that long terminal chains would be vital to uphold smectic phases, hence the strong dependency. On the other hand, when smectic phase

Table 3 Transition temperatures for 4,4″-dialkoxy-2,2′,3-trifluoroterphenyls (**27a,b**)



Compound			Transition Temperatures/°C							
No.	R	R′	Cryst		S_C		S_A	N		Iso
27a	C_6H_{13}	C_8H_{17}	·	52.1	·	124.6		·	141.6	·
27b	C_8H_{17}	C_6H_{13}	·	55.5	·	112.6		·	138.4	·

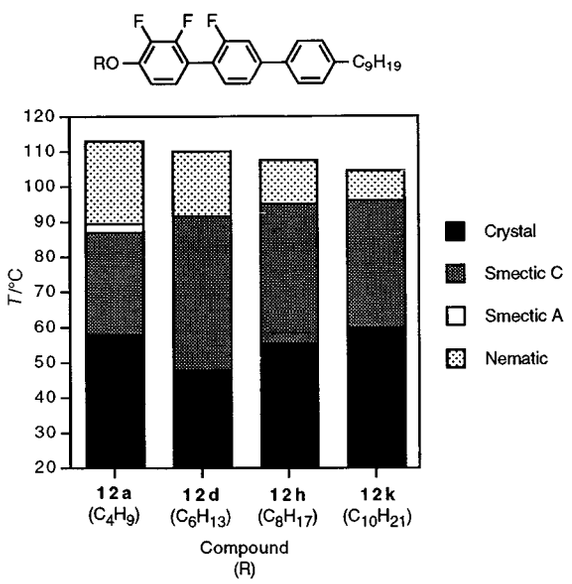
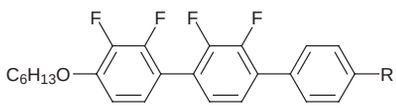


Fig. 2 Effect on transition temperatures of increasing the terminal alkoxy chain length.

stability is inherently much higher, as in the *ortho* difluoroterphenyls (**31a**–**e**), then the length of the terminal chains will be less important.

Most significantly, the smectic C phase stability is very dependent on the length of the terminal alkyl chain in the unfluorinated ring (Fig. 1) which is exemplified by the value of 91.5 °C for compound **12d** (C_9H_{19}), yet the value for the C_5H_{11} homologue (compound **12b**) is only 38.1 °C. However, the increasing trend levels off and the smectic C phase stability for the $C_{11}H_{23}$ homologue (compound **12e**) at 95.2 °C is little higher than that of compound **12d**, and by this chain length the maximum limit of the smectic C phase stability for this class of compound has been reached because compound **12e** exhibits a smectic A phase. The smectic C phase stability does not vary much with the length of the terminal alkoxy chain (Fig. 2), but there are slight increases to be seen with increasing length. It is probable that the greater dependency of smectic C phase stability on the length of the terminal alkyl chain is because this chain is further away from the molecular broadening of the lateral fluoro substituents which makes for more effective lamellar attractions between the molecules. It is interesting that the smectic A phase only appears in two compounds where relatively the alkyl chain is long and the alkoxy chain is short, but the absence of a smectic A phase in other compounds (Table 1) illustrates the strong tendency of the molecules towards tilting, no doubt as a result of the very high lateral dipole. It is usually the case that a useful liquid crystal is one with the combination of a low melting point and a wide temperature range of the desired mesophase, hence compounds **12c**, **12d** and **12g** with melting points below 50 °C look the most promising, however, when included in multi-component mixtures compounds **12e**, **12h** and **12k** may prove particularly valuable because of their relatively high smectic C phase stabilities (all above 95 °C).

Table 4 Transition temperatures for 4-alkoxy-4″-alkyl-2,2′,3,3′-tetrafluoroterphenyls (**30a–c**)



Compound		Transition Temperatures/°C						
No.	R	Cryst		S_C		N		Iso
30a	C_5H_{11}	·	61.1	·		·	107.5	·
30b	C_7H_{15}	·	55.1	·	(50.7)	·	103.1	·
30c	C_9H_{19}		60.7	·	64.5	·	100.7	·

Dialkoxy compounds often have much higher melting points than their alkoxyalkyl analogues. However, the melting points of compounds **27a** and **27b** (Table 3) are only slightly higher than compounds **12d** and **12g** (Table 1). The additional alkoxy chain has enhanced the smectic C phase stability by around 32 °C resulting in the generation of materials with high smectic C phase stabilities and wide S_C phase ranges (72.5 and 57.1 °C, compounds **27a** and **27b** respectively). The nematic phase stability has been increased to a similar extent as the smectic C phase stability which is surprising given the polar nature of the ether oxygen. Compound **27a** with the longer terminal chain in the unfluorinated ring has a significantly higher smectic C phase stability than the isomeric compound (**27b**), this trend is discussed above for the alkoxy-alkyl analogues (Table 1).

The inclusion of a fourth fluoro substituent at the 3′-position of the terphenyl core was expected to increase the lateral dipole because this fluoro substituent is inherently fixed next to the one in the 2′-position, which as discussed above is closely directional with the other two fluoro substituents in the 2- and 3-positions. Such materials would be expected to generate increased dielectric biaxiality in ferroelectric mixtures. However, the structural architecture would also be expected to increase melting points due to the higher polarity and to reduce liquid crystal phase stability, especially the smectic phase stability, due to the additional interannular twist and from the increased breadth over a greater area of the molecule. Hence these materials would not be suitable as major host components of ferroelectric mixtures, but they may well prove useful in small quantities for enhancing the dielectric biaxiality. In fact the melting points are quite low considering the polarity of the system, but as expected the liquid crystal phase stability, especially that of the smectic C phase, has been reduced significantly (Table 4). In the case of the short chain homologue (**30a**) the smectic C phase has been eliminated to leave a nematogen. For the longer chain homologues (**30b**,**c**) the smectic C phase stability is reduced by around 30 °C when compared to the analogous trifluoroterphenyls described above (compounds **12c** and **12d**, Table 1). This reduction in smectic C phase stability is much less than that seen for the introduction of the third fluoro substitu-

ent at the 2′-position because the fourth fluoro substituent is in the 3′-position which is shielded by that substituent. Overall, the smectic phase stability of the tetrafluoroterphenyls is reduced by around 100 °C in comparison with the *ortho* difluoroterphenyls (Table 2), but no directly comparable homologue is available. The tetrafluoroterphenyls do have a reasonable smectic C phase stability and hence should be promising materials for the evaluation of the importance of dielectric biaxiality in ferroelectric mixtures.

Conclusions

A wide range of materials have been synthesised with multiple fluoro substituents in strategic lateral positions in order to generate a large lateral dipole to provide a high dielectric biaxiality. Some interesting synthetic methods have been used including the development of selective palladium-catalysed cross-coupling reactions and selective low temperature lithiations to generate vital fluoro-substituted intermediates. It has been shown that highly polar materials with multiple lateral fluoro substituents can have low melting points and generate a reasonably high smectic C phase stability, which makes them suitable components in ferroelectric mixtures. These fluoro-substituted materials confer a high dielectric biaxiality on ferroelectric mixtures and a forthcoming paper by our collaborators at DERA (Malvern) will discuss the whole range of physical properties of the materials and their effect in ferroelectric mixtures (*e.g.*, dielectric biaxiality, viscosity and switching times).

Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H and ^{13}C NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). Elemental analysis (Fisons EA1108 CHN) data were obtained for each final compound prepared (**12a**–**k**, **27a**,**b** and **30a**–**c**). The progress of reactions was frequently monitored using a Chrompack 9001 capillary gas chromatograph fitted with a CP-SIL 5 CB 10 m × 0.25 mm, 0.12 μm column (Cat. No. 7700). Transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH2 polarising microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station). The purities of intermediates were checked by GLC analysis (see above) and the purity of each final compound (**12a**–**k**, **27a**,**b** and **30a**–**c**) was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and were found to be >99.9% pure in each case. Purification of compounds by column chromatography employed silica gel (Prolabo) of 35–75 μm particle size.

The preparation of intermediates (**2**, **3**, **4a**–**d**, **5a**–**d**, **9a**–**d**, **10a**–**d**, **18a**,**b**, **28a**–**c**, **29a**–**c**)[13] and (**11a**–**d**, **19**)[14] and **21**[19] have been reported previously. Tetrakis(triphenylphosphine)-palladium(0) was prepared according to the literature procedure.[27] Compounds **1**, **6**, **8**, **13**, **17** and **20** were purchased from Aldrich.

4′-Bromo-4-butoxy-2,2′,3-trifluorobiphenyl 7a

Tetrakis(triphenylphosphine)palladium(0) (1.62 g, 1.40 mmol) and compound **5a** (7.13 g, 0.031 mol) were added sequentially to a stirred mixture of compound **6** (8.43 g, 0.028 mol), sodium carbonate (40.0 ml, 2 mol dm^{-3}) and 1,2-dimethoxyethane (40 ml) under a nitrogen atmosphere. The stirred mixture was heated at 75 °C (just below reflux) until GLC analysis revealed a complete reaction (2 h). The cooled mixture was poured into water and the product was extracted into ether (×2). The combined ethereal extracts were washed with brine, dried ($MgSO_4$) and the solvent was removed *in vacuo*. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless oil which was further purified by Kugelrohr distillation (175 °C at 0.25 mmHg) to yield a colourless crystalline solid. Yield 4.64 g (46%); mp 54–55 °C; δ_H (270 MHz; $CDCl_3$) 0.99 (3H, t), 1.52 (2H, sext), 1.83 (2H, quint), 4.09 (2H, t), 6.80 (1H, ddd), 7.00 (1H, ddd), 7.22 (1H, dd), 7.30–7.39 (2H, m); IR ν_{max}(KBr)/cm^{-1} 1310; MS (*m*/*z*) 360 (M$^+$), 358 (M$^+$).

4′-Bromo-2,2′,3-trifluoro-4-hexyloxybiphenyl 7b

Quantities: compound **5b** (4.85 g, 0.019 mol); compound **6** (5.12 g, 0.017 mol). The experimental procedure was as described for the preparation of compound **7a** to give a colourless oil. Yield 3.20 g (49%); δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.20–1.55 (6H, m), 1.85 (2H, quint), 4.05 (2H, t), 6.79 (1H, ddd), 7.00 (1H, ddd), 7.22 (1H, dd), 7.29–7.39 (2H, m); IR ν_{max}(KBr)/cm^{-1} 1310; MS *m*/*z* 388 (M$^+$), 386 (M$^+$).

4′-Bromo-2,2′,3-trifluoro-4-octyloxybiphenyl 7c

Quantities: compound **5c** (3.03 g, 0.011 mol); compound **6** (2.90 g, 9.64 mmol). The experimental procedure was as described for the preparation of compound **7a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 9 : 1] to give a colourless liquid which was further purified by Kugelrohr distillation (150 °C at 0.2 mmHg) to yield a colourless solid. Yield 2.42 g (60%); mp 43–44 °C; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 1.20–1.55 (10H, m), 1.85 (2H, quint), 4.07 (2H, t), 6.79 (1H, ddd), 7.01 (1H, ddd), 7.23 (1H, dd), 7.31–7.39 (2H, m); IR ν_{max}(KBr)/cm^{-1} 1315; MS *m*/*z* 416 (M$^+$), 414 (M$^+$).

4′-Bromo-4-decyloxy-2,2′,3-trifluorobiphenyl 7d

Quantities: compound **5d** (6.91 g, 0.022 mol); compound **6** (6.00 g, 0.020 mol). The experimental procedure was as described for the preparation of compound **7a** to give a colourless crystalline solid (95% pure by GLC). Yield 5.67 g (64%); mp 36–38 °C; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 1.20–1.55 (14H, m), 1.84 (2H, quint), 4.07 (2H, t), 6.79 (1H, ddd), 7.00 (1H, ddd), 7.22 (1H, dd), 7.30–7.39 (2H, m); IR ν_{max}(KBr)/cm^{-1} 1315; MS *m*/*z* 444 (M$^+$), 442 (M$^+$).

4-Butoxy-2,2′,3-trifluoro-4″-nonylterphenyl 12a

Quantities: compound **11c** (1.85 g, 7.46 mmol); compound **7a** (2.23 g, 6.22 mmol). The experimental procedure was as described for the preparation of compound **7a**, except that the stirred reaction mixture was heated under reflux until GLC analysis revealed a complete reaction (overnight for convenience). The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (9 : 1) to yield colourless crystals. Yield 2.33 g (78%); transitions (°C) Cryst 57.7 S_C 87.0 S_A 89.1 N 112.9 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 1.00 (3H, t), 1.20–1.44 (12H, m), 1.45–1.72 (4H, m), 1.84 (2H, quint), 2.65 (2H, t), 4.10 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.46 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 482 (M$^+$); Found: C, 77.09%; H, 7.68%; $C_{25}H_{37}F_3O$ requires: C, 77.15%; H, 7.73%.

2,2′,3-Trifluoro-4″-heptyl-4-hexyloxyterphenyl 12c

Quantities: compound **11b** (1.09 g, 4.96 mmol); compound **7b** (1.60 g, 4.13 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (3 : 1) to yield colourless crystals. Yield 1.19 g (60%); transitions (°C)

Cryst 40.1 S_C 75.7 N 111.8 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.20–1.56 (14H, m), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.08 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.46 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 482 (M^+); Found: C, 77.12%; H, 7.70%; $C_{23}H_{33}F_3O$ requires C, 77.15%; H, 7.73%.

2,2′,3-Trifluoro-4-hexyloxy-4″-nonylterphenyl 12d

Quantities: compound **11c** (1.16 g, 4.66 mmol); compound **7b** (1.50 g, 3.88 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 9:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals. Yield 1.38 g (70%); transitions (°C) Cryst 47.9 S_C 91.5 N 109.6 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.92 (3H, t), 1.20–1.56 (18H, m), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.46 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1295; MS *m*/*z* 510 (M^+); Found: C, 77.51%; H, 7.98%; $C_{27}H_{41}F_3O$ requires: C, 77.61%; H, 8.09%.

2,2′,3-Trifluoro-4-hexyloxy-4″-undecylterphenyl 12e

Quantities: compound **11d** (1.37 g, 4.96 mmol); compound **7b** (1.60 g, 4.13 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography (silica gel; hexane–ethyl acetate, 9:1) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (3:1) to yield colourless crystals. Yield 0.87 g (39%); transitions (°C) Cryst 51.2 S_C 95.2 S_A 98.6 N 106.2 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.92 (3H, t), 1.19–1.43 (20H, m), 1.49 (2H, quint), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.46 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 538 (M^+); Found: C, 77.92%; H, 8.40%; $C_{29}H_{45}F_3O$ requires: C, 78.03%; H, 8.42%.

2,2′,3-Trifluoro-4-octyloxy-4″-pentylterphenyl 12f

Quantities: compound **11a** (0.69 g, 4.85 mmol); compound **7c** (1.25 g, 3.01 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 4:1] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (2:1) to yield colourless crystals. Yield 0.74 g (51%); transitions (°C) Cryst 47.3 S_C 50.2 N 110.3 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.20–1.56 (14H, m), 1.66 (2H, quint), 1.85 (2H, quint), 2.66 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); IR (KBr) ν_{max}(KBr)/cm^{-1} 1295; MS *m*/*z* 482 (M^+); Found: C, 77.06%; H, 7.65%; $C_{25}H_{37}F_3O$ requires: C, 77.15%; H, 7.73%.

2,2′,3-Trifluoro-4″-nonyl-4-octyloxyterphenyl 12h

Quantities: compound **11c** (1.66 g, 6.70 mmol); compound **7c** (2.31 g, 5.58 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (2:1) to yield colourless crystals. Yield 2.18 g (73%); transitions (°C) Cryst 55.4 S_C 95.0 N 107.3 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.90 (3H, t), 1.20–1.55 (22H, m), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 538 (M^+); Found: C, 78.01%; H, 8.40%; $C_{29}H_{45}F_3O$ requires: C, 78.03%; H, 8.42%.

4-Decyloxy-2,2′,3-trifluoro-4″-pentylterphenyl 12i

Quantities: compound **11a** (0.77 g, 4.00 mmol); compound **7d** (1.48 g, 3.01 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (19:1) to yield colourless crystals. Yield 1.28 g (83%); transitions (°C) Cryst 56.1 (S_C 52.1) N 102.1 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.91 (3H, t), 1.19–1.55 (18H, m), 1.66 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1295; MS *m*/*z* 510 (M^+); Found: C, 77.60%; H, 8.06%; $C_{27}H_{41}F_3O$ requires: C, 77.61%; H, 8.09%.

4-Decyloxy-2,2′,3-trifluoro-4″-heptylterphenyl 12j

Quantities: compound **11b** (0.85 g, 4.02 mmol); compound **7d** (1.48 g, 3.01 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (19:1) to yield colourless crystals. Yield 0.74 g (46%); transitions (°C) Cryst 56.0 S_C 83.2 N 104.5 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.20–1.56 (22H, m), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.33–7.47 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1295; MS *m*/*z* 538 (M^+); Found: C, 77.96%; H, 8.39%; $C_{29}H_{45}F_3O$ requires: C, 78.03%; H, 8.42%.

4-Decyloxy-2,2′,3-trifluoro-4″-nonylterphenyl 12k

Quantities: compound **11c** (0.95 g, 3.82 mmol); compound **7d** (1.41 g, 2.86 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol–ethyl acetate (2:1) to yield colourless crystals. Yield 1.47 g (91%); transitions (°C) Cryst 59.6 S_C 95.9 N 104.4 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (6H, 2 × t), 1.20–1.56 (26H, m), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.82 (1H, ddd), 7.09 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 566 (M^+); Found: C, 78.39%; H, 8.66%; $C_{31}H_{49}F_3O$ requires: C, 78.41%; H, 8.71%.

2-Fluoro-4-iodoaniline 14

Coarse powdered iodine (500 g, 1.97 mol) was added, in portions, to a stirred mixture of compound **13** (353 g, 3.18 mol) and sodium hydrogen carbonate (260 g, 3.10 mol) in water (800 ml) at 60–80 °C. The mixture was maintained at this temperature for a further 2 h, poured onto ice and left overnight. The water and the residual oil were decanted from the solid product and steam distilled to recover compound **13**. The solid product was dissolved in ether, washed with water, dried ($MgSO_4$) and the solvent was removed *in vacuo*. The residue was recrystallised from cyclohexane to yield purple-tinted crystals. Yield 360 g (77%); mp 52–54 °C (lit. 52–54 °C);[25] δ_H (270 MHz; $CDCl_3$) 3.55 (2H, broad s), 6.52 (1H, dd), 7.20 (1H, ddd), 7.27 (1H, dd); IR ν_{max}(KBr)/cm^{-1} 3500–2200, 3400, 3320; MS *m*/*z* 237 (M^+).

1-Bromo-2-fluoro-4-iodobenzene 15

A solution of sodium nitrite (22.8 g, 0.33 mol) in water (40 ml) was added dropwise to a stirred, cooled (0 °C) suspension of compound **14** (70.0 g, 0.30 mol) in hydrobromic acid (48% w/v, 200 ml). The solution was stirred at 0 °C for 30 min and then added in portions to a stirred, boiling solution of copper(I) bromide (50.0 g, 0.35 mol) in hydrobromic acid (48% w/v, 100

ml). The stirred mixture was boiled for a further 15 min and left to cool overnight. Water was added and the product was extracted into ether (×2), the combined ethereal extracts were washed with water, 10% w/v sodium hydroxide solution and water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was distilled to give a pale pink, crystalline solid. The product was further purified by column chromatography (silica gel; hexane) to yield a colourless crystalline solid. Yield 58.6 g (65%); mp 37–38 °C; (lit. 36–37 °C);[26] bp 108–112 °C at 15 mmHg (lit. 118–120 °C at 15 mmHg);[26] δ_H (270 MHz; $CDCl_3$) 7.26 (1H, dd), 7.35 (1H, ddd), 7.46 (1H, dd); MS *m*/*z* 302 (M^+), 300 (M^+).

4-Bromo-3-fluoro-4′-pentylbiphenyl 16

Quantities: compound **11a** (6.59 g, 0.034 mol); compound **15** (9.39 g, 0.031 mol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless liquid which was further purified by Kugelrohr distillation (150 °C at 0.2 mmHg) to yield a colourless oil. Yield 3.48 g (35%); δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.25–1.44 (4H, m), 1.64 (2H, quint), 2.64 (2H, t), 7.19–7.29 (3H, m), 7.33 (1H, dd), 7.45 (2H, d), 7.56 (1H, dd); MS *m*/*z* 322 (M^+), 320 (M^+).

2,2′,3-Trifluoro-4-hexyloxy-4″-pentylterphenyl 12b

Quantities: compound **5b** (1.17 g, 4.55 mmol); compound **16** (1.17 g, 3.64 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.22 g (74%); transitions (°C) Cryst 43.8 (S_C 38.1) N 112.3 Iso; δ_H (270 MHz; $CDCl_3$) 0.91 (3H, t), 0.92 (3H, t), 1.27–1.56 (10H, m), 1.66 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.33–7.48 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1295; MS *m*/*z* 454 (M^+); Found: C, 76.56%; H, 7.26%; $C_{23}H_{33}F_3O$ requires: C, 76.63%; H, 7.32%.

3-Fluoro-4′-heptylbiphenyl 22

Quantities: compound **11b** (10.00 g, 0.046 mol); compound **20** (8.00 g, 0.046 mol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless liquid which was further purified by Kugelrohr distillation (160 °C at 0.2 mmHg) to yield a colourless oil. Yield 5.56 g (45%); δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 1.21–1.40 (8H, m), 1.64 (2H, quint), 2.64 (2H, t), 6.95–7.04 (1H, m), 7.20–7.31 (3H, m), 7.32–7.40 (2H, m), 7.48 (2H, d); MS *m*/*z* 270 (M^+).

3-Fluoro-4′-hexyloxybiphenyl 23a

Quantities: compound **21** (3.92 g, 0.028 mol); compound **18a** (2.33 g, 6.44 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 4:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 4.99 g (83%); mp 33-34 °C; δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.25–1.54 (6H, m), 1.80 (2H, quint), 4.00 (2H, t), 6.92–7.02 (3H, m), 7.23 (1H, ddd), 7.29–7.40 (2H, m), 7.49 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1245; MS *m*/*z* 272 (M^+).

3-Fluoro-4′-octyloxybiphenyl 23b

Quantities: compound **19** (6.25 g, 0.025 mol); compound **20** (3.50 g, 0.020 mol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 7:3] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 4.52 g (75%); mp 42–43.5 °C; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 1.20–1.55 (10H, m), 1.80 (2H, quint), 4.00 (2H, t), 6.90–7.02 (3H, m), 7.24 (1H, ddd), 7.29–7.40 (2H, m), 7.49 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1260; MS *m*/*z* 300 (M^+).

3-Fluoro-4′-heptylbiphenyl-4-ylboronic acid 24

sec-Butyllithium (17.69 ml; 1.3 mol dm^{-3} in cyclohexane, 0.023 mol) was added dropwise to a stirred, cooled (−78 °C) solution of compound **22** (5.40 g, 0.020 mol) in dry THF (150 ml) under dry nitrogen. The mixture was stirred at −78 °C for 2 h and a solution of trimethyl borate (4.78 g, 0.046 mol) in dry THF (30 ml) was added dropwise at −78 °C. The stirred mixture was allowed to warm to room temperature overnight and 10% hydrochloric acid (100 ml) was added. The mixture was stirred for 1 h and the product was extracted into ether (×2) and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a cream-coloured, waxy solid. Yield 6.22 g (99%).

3-Fluoro-4′-hexyloxybiphenyl-4-ylboronic acid 25a

Quantities: compound **23a** (4.97 g, 0.018 mol); *sec*-butyllithium (15.92 ml; 1.3 mol dm^{-3} in cyclohexane, 0.021 mol); trimethyl borate (3.75 g, 4.12 ml, 0.036 mol). The experimental procedure was as described for the preparation of compound **24**. Yield 5.56 g (98%).

3-Fluoro-4′-octyloxybiphenyl-4-ylboronic acid 25b

Quantities: compound **23b** (4.50 g, 0.015 mol); *sec*-butyllithium (13.10 ml; 1.3 mol dm^{-3} in cyclohexane, 0.017 mol); trimethyl borate (3.12 g, 3.43 ml, 0.030 mol). The experimental procedure was as described for the preparation of compound **24**. Yield 5.16 g (100%).

1-Bromo-2,3-difluoro-4-hexyloxybenzene 26a

A solution of bromine (7.9 ml, 24.5 g, 0.155 mol) in chloroform (30 ml) was added dropwise to a heated (65 °C), stirred solution of compound **4b** (13.23 g, 0.062 mol) in chloroform (120 ml). The mixture was maintained at 65 °C for 2 h, allowed to cool to room temperature, quenched with water and washed with 10% *w*/*v* sodium metabisulfite solution. The chloroform extract was washed with brine, dried ($MgSO_4$), and the solvent removed *in vacuo*. The crude product was distilled to give a colourless oil. Yield 15.9 g (87%); bp 94–98 °C at 0.15 mmHg; δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.20–1.55 (6H, m), 1.80 (2H, quint), 4.00 (2H, t), 6.64 (1H, ddd), 7.18 (1H, ddd); IR ν_{max}(KBr)/cm^{-1} 1300, 1080; MS *m*/*z* 294 (M^+), 292 (M^+).

1-Bromo-2,3-difluoro-4-octyloxybenzene 26b

Quantities: compound **4c** (7.25 g, 0.030 mol); bromine (4.0 ml, 12.0 g, 0.076 mol). The experimental procedure was as described for the preparation of compound **26a** to give a colourless oil. Yield 7.50 g (78%); bp 114–118 °C at 0.2 mmHg; δ_H (270 MHz; $CDCl_3$) 0.90 (3H, t), 1.20–1.54 (10H, m), 1.80 (2H, quint), 4.00 (2H, t), 6.65 (1H, ddd), 7.18 (1H, ddd); IR ν_{max} (KBr)/cm^{-1} 1300, 1080; MS *m*/*z* 322 (M^+), 320 (M^+).

2,2′,3-Trifluoro-4″-heptyl-4-octyloxyterphenyl 12g

Quantities: compound **24** (2.75 g, 8.76 mmol); compound **26b** (2.25 g, 7.01 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)] to give a colourless solid

which was recrystallised from ethanol–ethyl acetate (2:1) to yield colourless crystals. Yield 0.76 g (21%); transitions (°C) Cryst 48.0 S_C 81.0 N 108.8 Iso; δ_H (270 MHz; $CDCl_3$) 0.90 (6H, 2 × t), 1.20–1.57 (18H, m), 1.65 (2H, quint), 1.85 (2H, quint), 2.65 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 7.08 (1H, ddd), 7.27 (2H, d), 7.34–7.47 (3H, m), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1295; MS *m*/*z* 510 (M^+); Found: C, 77.59%; H, 8.02%; $C_{27}H_{41}F_3O$ requires: C, 77.61%; H, 8.09%.

2,2′,3-Trifluoro-4-hexyloxy-4″-octyloxyterphenyl 27a

Quantities: compound **25b** (2.52 g, 7.32 mmol); compound **26a** (1.72 g, 5.86 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 17:3] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.51 g (50%); transitions (°C) Cryst 52.1 S_C 124.6 N 141.6 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.22–1.56 (16H, m), 1.83 (4H, 2 × quint), 4.01 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 6.98 (2H, d), 7.08 (1H, ddd), 7.32–7.43 (3H, m), 7.54 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 512 (M^+); Found: C, 74.89%; H, 7.61%; $C_{26}H_{39}F_3O_2$ requires: C, 74.97%; H, 7.67%.

2,2′,3-Trifluoro-4″-hexyloxy-4-octyloxyterphenyl 27b

Quantities: compound **25a** (2.32 g, 7.33 mmol); compound **26b** (1.88 g, 5.86 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography [silica gel; petroleum fraction (bp 40–60 °C)–dichloromethane, 19:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 0.54 g (18%); transitions (°C) Cryst 55.5 S_C 112.6 N 138.4 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.20–1.60 (16H, m), 1.83 (4H, 2 × quint), 4.01 (2H, t), 4.09 (2H, t), 6.81 (1H, ddd), 6.98 (2H, d), 7.08 (1H, ddd), 7.31–7.43 (3H, m), 7.54 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1285; MS *m*/*z* 512 (M^+); Found: C, 74.87%; H, 7.59%; $C_{26}H_{39}F_3O_2$ requires: C, 74.97%; H, 7.67%.

2,2′,3,3′-Tetrafluoro-4-hexyloxy-4″-pentylterphenyl 30a

Quantities: compound **29a** (1.99 g, 6.55 mmol); compound **26a** (1.86 g, 5.46 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography (silica gel; hexane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (3:1) to yield colourless crystals. Yield 1.09 g (42%); transitions (°C) Cryst 61.1 N 107.5 Iso; δ_H (270 MHz; $CDCl_3$) 0.91 (3H, t), 0.92 (3H, t), 1.29–1.56 (10H, m), 1.67 (2H, quint), 1.84 (2H, quint), 2.66 (2H, t), 4.09 (2H, t), 6.83 (1H, ddd), 7.09 (1H, ddd), 7.16 (1H, ddd), 7.25 (1H, ddd), 7.29 (2H, d), 7.53 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 472 (M^+); Found: C, 73.63%; H, 6.79%; $C_{23}H_{32}F_4O$ requires: C, 73.71%; H, 6.83%.

2,2′,3,3′-Tetrafluoro-4″-heptyl-4-hexyloxyterphenyl 30b

Quantities: compound **29b** (2.39 g, 7.20 mmol); compound **26a** (2.04 g, 6.00 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography (silica gel; hexane–dichloromethane, 9:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.69 g (56%); transitions (°C) Cryst 55.1 (S_C 50.7) N 103.1 Iso; δ_H (270 MHz; $CDCl_3$) 0.89 (3H, t), 0.92 (3H, t), 1.21–1.56 (14H, m), 1.66 (2H, quint), 1.86 (2H, quint), 2.66 (2H, t), 4.09 (2H, t), 6.83 (1H, ddd), 7.08 (1H, ddd), 7.16 (1H, ddd), 7.25 (1H, ddd), 7.29 (2H, d), 7.50 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 500 (M^+); Found: C, 74.29%; H, 7.18%; $C_{25}H_{36}F_4O$ requires: C, 74.38%; H, 7.25%.

2,2′,3,3′-Tetrafluoro-4-hexyloxy-4″-nonylterphenyl 30c

Quantities: compound **29c** (2.45 g, 6.82 mmol); compound **26a** (1.94 g, 5.68 mmol). The experimental procedure was as described for the preparation of compound **12a**. The crude product was purified by column chromatography (silica gel; hexane–dichloromethane, 9:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals. Yield 1.69 g (56%); transitions (°C) Cryst 60.7 S_C 64.5 N 100.7 Iso; δ_H (270 MHz; $CDCl_3$) 0.88 (3H, t), 0.92 (3H, t), 1.20–1.56 (18H, m), 1.66 (2H, quint), 1.85 (2H, quint), 2.66 (2H, t), 4.09 (2H, t), 6.82 (1H, ddd), 7.08 (1H, ddd), 7.15 (1H, ddd), 7.25 (1H, ddd), 7.29 (2H, d), 7.50 (2H, d); IR ν_{max}(KBr)/cm^{-1} 1300; MS *m*/*z* 528 (M^+); Found: C, 74.88%; H, 7.57%; $C_{27}H_{40}F_4O$ requires: C, 74.97%; H, 7.63%.

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