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## Liquid Crystals

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Andrew I. Stipetic<sup>a</sup>; John W. Goodby<sup>a</sup>; Michael Hird<sup>a</sup>; Yann M. Raoul<sup>a</sup>; Helen F. Gleeson<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Hull, Hull HU6 7RX, UK <sup>b</sup> Department of Physics, University of Manchester, Manchester M13 9PL, UK

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# High tilt antiferroelectric esters bearing a perfluorobutanoyloxy terminal chain: the influence of lateral fluoro substituents on mesomorphic behaviour, tilt angle, and spontaneous polarization

ANDREW I. STIPETIC†, JOHN W. GOODBY†, MICHAEL HIRD\*†, YANN M. RAOUL† and HELEN F. GLEESON‡

†Department of Chemistry, University of Hull, Hull HU6 7RX, UK

‡Department of Physics, University of Manchester, Manchester M13 9PL, UK

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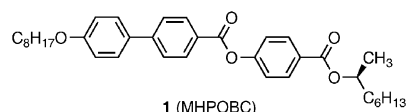
Novel liquid crystalline esters have been synthesized with a perfluorocarbonyloxy terminal chain and lateral fluoro substituents in order to determine their influence on mesomorphic behaviour, tilt angle and spontaneous polarization. Certain locations of lateral fluoro substituents provide for very low melting points and reasonably wide temperature ranges of the antiferroelectric phase, and can generate enhanced tilt angles of up to 45°, although spontaneous polarization is always lower than for the parent system without lateral fluoro substituents. Thus, these novel materials, particularly as components in mixtures, should be useful in high tilt antiferroelectric (orthoconic) applications.

## 1. Introduction

Antiferroelectric liquid crystals have been the subject of much research attention since their discovery in 1989 [1], and were quickly targeted as the basis for liquid crystal displays with various attractive advantages over existing nematic and ferroelectric technologies [2, 3]. Such advantages include fast, tri-state switching, wide angles of view due to in-plane molecular switching, good grey-scale capability and shock resistance. However, significant competition from much improved nematic displays [4], and problems in obtaining suitable materials quelled the interest somewhat.

The antiferroelectric liquid crystal phase is now fairly common, but those materials that do exhibit this interesting phase are of a very similar molecular architecture, for example, to the well known material MHPOBC (compound **1**) [1–3]. Such a restriction is a major problem because useful liquid crystals are required to have a low melting point and a wide temperature range of the desirable liquid crystal phase, and of course to exhibit a whole host of other desirable physical properties. The use of lateral fluoro substituents in liquid crystal compounds has long been used to beneficially modify the material properties, particularly in terms of lower melting points and wider liquid crystal temperature ranges [5–11]; indeed fluoro-substituted

liquid crystals constitute by far the bulk of commercial nematic mixtures for liquid crystal displays [4, 12].



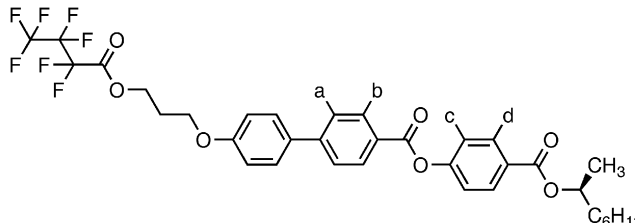
C 73.5 SmC\*anti 118.8 SmC\*ferri 119.8 SmC\*ferro 121.6 SmC\*alpha 122.6 SmA\* 147.7 I

Recently, the discovery that antiferroelectric liquid crystals with a 45° tilt angle can provide a device format with two bright scattered states and one completely black state between crossed polarizers, and requires no molecular alignment, has renewed research interest into suitable materials [13]. Now, in addition to the need for lower melting points and a wider temperature range of the antiferroelectric phase, a much higher tilt angle of around 45° is targeted. A tilt angle of 40° has been generated in compound **2** (see table 1) reported by Dabrowski and co-workers [14, 15], which has a similar structure to MHPOBC, but incorporates a perfluorocarbonyloxy terminal chain which causes the higher tilt angle.

The aims of this work were to use the same perfluorocarbonyloxy terminal chain as employed by Dabrowski (compound **2**), which provides an excellent basis for antiferroelectric materials of high tilt angle, and investigate the influence of lateral fluoro substituents within the core structure, in terms of melting

\*Corresponding author. Email: m.hird@hull.ac.uk

Table 1. The mesomorphic properties for a range of esters bearing a perfluorobutanoyloxy terminal chain with lateral fluoro substituents.



Compound No.	Substituents				Transition temperatures (°C)				Properties						
	a	b	c	d	C	SmC* anti	SmC* ferro	SmA*	I	P <sub>s</sub> /nC cm <sup>-2</sup>	Tilt angle				
2 <sup>a</sup>	H	H	H	H	•	83.6	•	119.7	•	123.5	•	128.8	•	500	40°
3	H	H	F	H	•	57.0	•	104.0	•	105.0	—	—	•	340	38°
4	H	H	H	F	•	61.5	•	103.0	•	109.0	•	120.0	•	400	45°
5	H	H	F	F	•	66.0	•	95.0	•	99.0	•	104.0	•	380	38°
6	H	F	H	H	•	63.0	•	104.5	•	108.5	•	115.5	•	400	45°
7	F	F	H	H	•	43.0	•	90.0	•	99.0	•	111.0	•	350	41°
8	H	F	F	H	•	22.5	—	—	•	83.0	—	—	•	320	38°
9	H	F	H	F	•	64.5	•	90.5	•	96.5	•	107.5	•	400	45°
10	F	F	F	H	•	67.5	•	(65.5)	•	69.0	•	78.5	•	360	35°

<sup>a</sup>Compound **2** also exhibits a monotropic SmI\*anti phase at 54°C.

points, transition temperatures, mesophase morphologies, tilt angle and spontaneous polarization. The fluoro substituent is of very small size and high electronegativity, and hence dramatically influences the above mentioned parameters in liquid crystals [5–11], and in most cases provides materials with desirable properties for applications in liquid crystal displays [4, 12]. Hence such an investigation as reported here seemed a useful way forward, and compound **2** was re-synthesized in order to evaluate the material in the same consistent manner as the novel materials with lateral fluoro substituents.

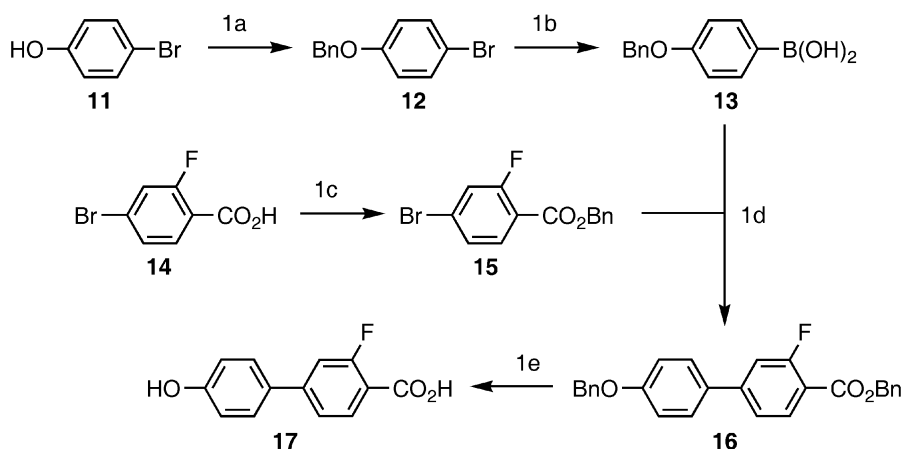
In order to maintain liquid crystal phase stability, particularly of smectic phases, the best location for a fluoro substituent is at an outer-core position [5–11]. In such a location, particularly next to a conformationally flexible ester linking group, the polarity of the fluoro substituent would be expected to be of greatest influence, be it additive or subtractive, on tilt angle and spontaneous polarization. Hence, materials were evaluated with lateral fluoro substituents in positions (b), (c) and (d) of the structure shown in table 1 because most influence would be expected at such positions of conformational flexibility and polarity. The inner-core position (a) has also been investigated because of an expected significant reduction in melting point due to the enhanced inter-annular twisting caused—a well known influence of such a location of a lateral fluoro substituent [5–11].

## 2. Synthesis of materials

The commercial availability of biphenyl unit **22** facilitated the synthesis of the parent system, whereas the required lateral fluoro-substituted analogues (**17** and **21**) had to be synthesized. A Suzuki coupling of a benzyl-protected boronic acid (**13**) and a benzyl-protected bromide (**15**) generated the doubly protected biphenyl (**16**), which was deprotected through hydrogenolysis to give an overall efficient synthesis of the required lateral fluoro-substituted biphenyl hydroxyacid unit **17** (scheme 1).

A Suzuki coupling [6, 16–19] between boronic acid **18** and the benzyl-protected bromide **12** generated the difluorobiphenyl unit **19**. Compound **19** has an acidic proton next to the fluoro substituents which was exploited with butyllithium at low temperature [5, 6] to generate an aryllithium salt which was quenched with solid carbon dioxide; subsequent acidification gave an efficient introduction of the required carboxylic acid group (compound **19**). Removal of the benzyl protecting group of compound **20** by hydrogenolysis gave the required biphenyl hydroxy acid (compound **21**) with two lateral fluoro substituents (scheme 2).

Next to the difficult aspect of the synthesis (scheme 3). As with all multiple esters there are several ways to effect the synthesis, and liquid crystalline phenyl biphenylcarboxylates, such as MHPOBC (compound **1**) are usually synthesized by the esterification of the appropriate biphenylcarboxylic acid and phenol



Scheme 1

- 1a ... BnCl, K<sub>2</sub>CO<sub>3</sub>, butanone.  
 1b ... (i) n-BuLi, THF; (ii) (MeO)<sub>3</sub>B; (iii) 10% HCl.  
 1c ... BnOH, DIAD, TPP, THF.  
 1d ... Pd(PPh<sub>3</sub>)<sub>4</sub>, DME, Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O.  
 1e ... H<sub>2</sub>, Pd/C, EtOAc.

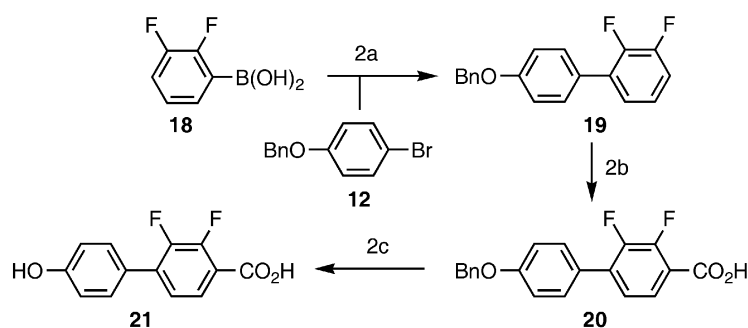
units [1, 20–24]. This route is the most convergent approach, and offers the most scope if the aim is to synthesize a range of analogues with lateral fluoro substituents, which is the case here.

Accordingly, we required a range of biphenylcarboxylic acids containing the perfluoro chain (compounds **26** to **28**). The propoxy linking unit was introduced first, through a simple alkylation, which yielded compounds **23** to **25** as grey intractable solids, which could not be characterized, but isolation was facilitated by the very poor solubility. The perfluoro moiety was introduced through the condensation of the perfluorobutanoic acid with

alcohols **23** to **25** to give excellent overall yields of the desired biphenylcarboxylic acids **26** to **28**. The desired liquid crystal esters (**2** to **10**) were then generated using the various combinations of acids **26** to **28** and phenols **29** to **32** [22] in the common, efficient DCC, DMAP esterification [25].

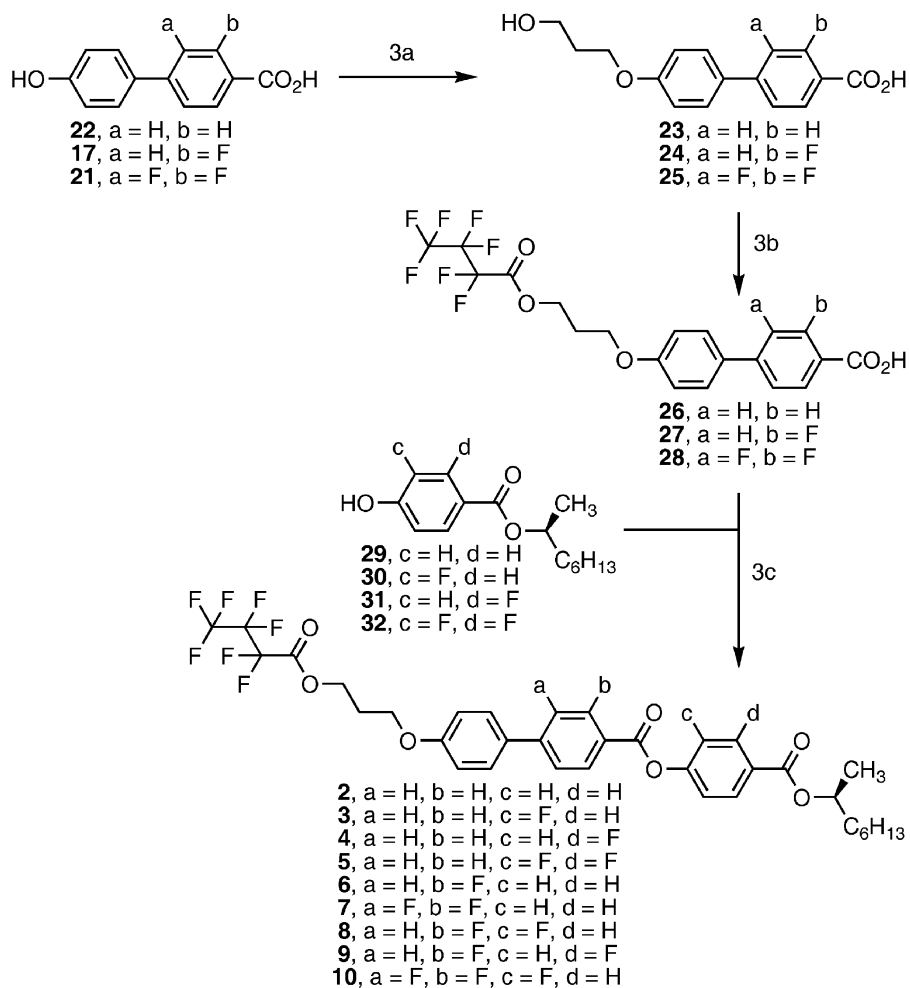
### 3. Melting points, transition temperatures and mesophase morphology

It is useful first to consider the difference between the parent system, compound **2** [14, 15] and compound **1** (MHPOBC) [1] with the conventional alkoxy terminal



Scheme 2

- 2a ... Pd(PPh<sub>3</sub>)<sub>4</sub>, DME, Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O.  
 2b ... (i) n-BuLi, THF; (ii) CO<sub>2</sub>(solid); (iii) 36% HCl.  
 2c ... H<sub>2</sub>, Pd/C, EtOAc.



Scheme 3

3a ... 3-bromopropanol, NaOH, KI, MeOH.

3b ... heptafluorobutanoic acid, PTSA, toluene.

3c ... DCC, DMAP, DCM.

chain. A perfluoro chain is much stiffer than a hydrocarbon chain, and so usually the smectic A and smectic C transition temperatures are much higher [26, 27], yet here the perfluoro chain has caused a 40°C reduction in the smectic A phase stability (clearing point), and left the smectic C phase stability little changed. The likely reason for this anomaly is the flexible ester linkage in the perfluoro chain, which separates the perfluoro chain from the core; this flexibility would tend to uphold the tilted smectic phases, and that is seen here with very little difference in the antiferroelectric and ferroelectric phase stabilities.

As the results in table 1 show, the melting points for all the compounds with lateral fluoro substituents are much lower than for the known parent system (**2**); however, there is enormous variation depending on the

location of the substitution. Mesophase morphologies for the novel materials with lateral fluoro substituents are rather similar to that of the parent system. However, the transition temperatures are, as expected, somewhat lower, but in most cases the antiferroelectric phase stability is reduced by less than the melting point, which provides wider temperature ranges for the desired antiferroelectric phase. The highest melting point for the novel materials is seen for the trifluoro compound (**10**) which is explained by the increased polarity outweighing the steric disruption to the molecular packing. As expected in the trifluoro system (**10**) where one of the fluoro substituents is at an inner-core position, the transition temperatures are significantly reduced, which, when combined with the relatively high melting point, has resulted in a monotropic

antiferroelectric phase and a clearing point reduced by 50°C when compared with the known parent system (**2**). The next highest melting point (66°C) is seen for the *ortho*-difluoro system (**5**), which is accounted for by both fluoro substituents being at outer-core positions, and the high polarity of both fluoro substituents being inherently fixed on one side of the molecule. However, since both lateral fluoro substituents are at an outer-core position in compound **5**, the transition temperatures are reasonably well upheld to generate similar mesophase temperature ranges to those seen in the parent system (**2**). As expected, the *ortho*-difluoro compound (**7**) has a particularly low melting point (43°C) because of the influence of the inner-core fluoro substituent at position (a) in enhancing the inter-annular twisting of the biphenyl section of the core [6–11].

Despite compound **7** possessing a lateral fluoro substituent at an inner-core position, the transition temperatures are very similar to the isomeric difluoro compound (**5**) except for the smectic A\* phase stability, thus generating a wider temperature range of the antiferroelectric phase (47°C) when compared with that of the parent system (36°C). Unexpectedly, compound **8** with two fluoro substituents both at outer-core positions (b and c) has a very low melting point (22°C); a possible explanation is that the molecular breadth is particularly large because the two fluoro substituents are in separate sections of the core, and so have a tendency to locate on either side of the molecule, hence disrupting molecular packing. Such a situation would also explain the lack of a smectic A\* phase and a much lower than expected clearing point. The isomeric difluoro compound (**9**) is in sharp contrast to compound **8** in generating a relatively high melting point, which can be explained in part by the location of a fluoro substituent at position (d) which is a genuine outer-edge position, well known for space-filling effects which uphold melting points and liquid crystal phase stability [6, 8–11]. However, these rather marked differences in mesomorphic behaviour of compound **9** when compared with compound **8** suggest that the two fluoro substituents tend to be aligned on one side of the molecules; this situation has been seen before where both fluoro substituents are pointing in the same direction, whereas those of compound **8** point towards each other [6, 8–11].

The compounds with a single lateral fluoro substituent (**3**, **4** and **6**) benefit from reasonably reduced melting points and upheld transition temperatures to generate enhanced temperature ranges of the desired antiferroelectric phase by between 5 and 11°C when compared with the parent system (compound **2**). The

reduction in melting point is due to the steric influence of the single fluoro substituent, and the transition temperatures of the smectic phases are reasonably well upheld because of the outer-edge location. Compound **3** stands out because of the combination of a reasonably low melting point and a high antiferroelectric phase stability, which gives the widest temperature range of the antiferroelectric phase (47°C). Unusually, for a compound (**3**) with an outer-core lateral fluoro substituent (albeit pointing towards the centre of the molecule), no smectic A\* phase is exhibited, showing the likely preference for the lateral fluoro substituent at position (c) to increase the molecular breath rather than in the conformation as shown in the general structure within table 1.

#### 4. Physical properties (spontaneous polarization and tilt angle)

The spontaneous polarizations and tilt angles of compounds **1** to **10** have all been evaluated in the same manner (see Experimental section) for consistency of comparison. Compound **1** (MHPOBC) was found to have a spontaneous polarization of 130 nC cm<sup>-2</sup> and a tilt angle of 23°; such values are consistent with those reported previously [1, 3, 23]. Similarly, the values for the parent perfluoro system (compound **2**) are consistent with those reported previously.

It is clear that the location of a lateral fluoro substituent causes a subtle variation in the values of spontaneous polarization and tilt angle and, as expected, the spontaneous polarization values are intrinsically linked to the tilt angle. For compound **3**, where the lateral fluoro substituent points towards the molecular centre, a reduced tilt angle (38°) is recorded, and a markedly lower spontaneous polarization was found in comparison with the parent system. However, when the lateral fluoro substituent points towards the molecular periphery (compound **4**) a particularly high tilt angle of 45° is seen, and although the spontaneous polarization is higher than for compound **3** it is still much lower than for the parent system (compound **2**). So although spontaneous polarization is linked to tilt angle, as expected, the spontaneous polarization values for the lateral fluoro compounds are always lower than for the parent system, whereas the tilt angle can be higher or lower depending on the particular location. The lateral fluoro substituents cause a steric effect and also influence polarity. The tilt angle is likely to depend on both the steric effects and polarity of the lateral fluoro substituent, whereas the spontaneous polarization will largely depend on the polarity.

Compound **5** has a fluoro substituent in each of the positions of compounds **3** and **4**, and the spontaneous

polarization is intermediate between the values for the two monofluoro systems, yet the tilt angle is limited to that of compound **3** ( $38^\circ$ ). Compound **6** has a lateral fluoro substituent in the biphenyl section of the core in the location next to an ester group, rather similar to compound **4**, but of course not at the molecular periphery. Compound **6** exhibits identical maximum values for spontaneous polarization and tilt angle to the isomeric system (**3**), indicating that the location of the fluoro substituent next to the carbonyl group is influential. The most likely explanation is the occurrence of preferred conformers due to the interaction of the lateral fluoro substituent and the adjacent ester linking groups. Compound **9** has a lateral fluoro substituent adjacent to both core ester linking groups, which might be expected to lead to a higher spontaneous polarization and a higher tilt angle; however, the values are identical, in each case, to those for compounds **4** and **6**. Where the lateral fluoro substituents are not adjacent to the carbonyl group of the core ester linking groups (compounds **3**, **5**, **8** and **10**), the tilt angles are always lower than for the parent system, and where an additional fluoro substituent is not adjacent to the core ester linking groups (compounds **5**, **7**, **8** and **10**) the tilt angle is further 'diluted'.

## 5. Summary

In comparison with the parent system (compound **2**), lateral fluoro-substitution has been successful in reducing melting points in all cases, mostly by around  $20^\circ\text{C}$ , but in one example (compound **8**) the melting point was  $60^\circ\text{C}$  lower at  $22^\circ\text{C}$ . In general, the fluoro-substituted esters have identical mesophase morphology to the parent system; however, as expected, the transition temperatures are lower. Nevertheless, all monofluoro examples (compounds **3**, **4** and **6**), and one difluoro example (compound **7**) exhibit the antiferroelectric phase over a wider temperature range.

Spontaneous polarization values for the fluoro-substituted materials ( $300\text{--}400\text{ nC cm}^{-2}$ ) are always lower than for the parent system ( $500\text{ nC cm}^{-2}$ ), but nevertheless still much higher than for analogous compounds (e.g. **1**) without the perfluoro terminal chain ( $130\text{ nC cm}^{-2}$ ). More significantly, the tilt angle values are enhanced to the desired  $45^\circ$  for compounds **4**, **6** and **9**, where the lateral fluoro substituents are adjacent to the carbonyl groups of the ester linkages.

Overall, two compounds (**4** and **6**) are outstanding for the combination of melting point and antiferroelectric phase stability to leave a wide temperature range for the antiferroelectric phase. Moreover, these compounds also show a higher tilt angle ( $45^\circ$  in each case) than

the parent system, although the spontaneous polarization values are lower in each case ( $400\text{ nC cm}^{-2}$ ). Such materials should be useful components in antiferroelectric mixtures for high tilt (orthoconic) applications.

## 6. Experimental

### 6.1. Characterization

Structural information on materials was obtained, where appropriate, by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (JEOL Eclipse 400 MHz spectrometer), and by mass spectrometry (Finnigan-MAT 1020 spectrometer). Specific optical rotations,  $[\alpha]_{\text{D}}$ , for the final compounds (**2** to **10**) were determined at  $22^\circ\text{C}$  in chloroform using a Bendix-NPL Automatic Polarimeter Type 143A. The progress of some reactions, and the purity of certain materials, was analysed by gas liquid chromatography (GLC) using a Varian CP3380 gas chromatograph with a 10 m, 0.25 mm internal diameter, 0.12 mm fused silica capillary column. Melting points and transition temperatures were determined using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 temperature controller; these values were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and Mettler Toledo DSC822e). Elemental analysis (Fisons EA1108 CHN) data were obtained for the final compounds (**2** to **10**); the purity of each was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16051) and found to be  $>99.5\%$  in each case.

The spontaneous polarization and tilt angles were evaluated in electro-optic cells (5 micron thickness with antiparallel rubbed polyimide alignment layers) purchased from Instec Inc. (USA). The spontaneous polarizations were measured as a function of temperature, using equipment purchased from Instec Inc. (USA), employing a triangular wave, and the values quoted in table 1 are the maximum values. Similarly, the tilt angles were measured as a function of temperature, and the values quoted in table 1 are the maximum values.

### 6.2. Materials synthesis

Compounds **11**, **14** and **22** were purchased from Aldrich Chemicals Limited, compound **18** was purchased from Kingston Chemicals Limited, and compounds **29** to **32** were prepared according to the literature procedure [22].

**6.2.1. 1-Benzyloxy-4-bromobenzene (12).** A stirred mixture of compound **11** (60.0 g, 0.347 mol), benzyl

chloride (44.75 g, 0.354 mol), potassium carbonate (96.0 g, 0.696 mol) and butanone (900 ml) was heated under reflux for 24 h (GLC analysis revealed a complete reaction). The cooled mixture was filtered, the filtrate was evaporated, and the residue recrystallized from ethanol to yield colourless crystals. Yield 69.4 g (76%), m.p. 59–60°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.05(2H, s), 6.89(2H, d,  $J=8$  Hz), 7.32–7.47(7H, m). MS  $m/z$  264( $\text{M}^+$ ), 262( $\text{M}^+$ ).

**6.2.2. 4-Benzyloxyphenylboronic acid (13).** *n*-Butyllithium (25 ml, 2.5M in hexane, 0.063 mol) was added dropwise to a stirred, cooled ( $-78^\circ\text{C}$ ) solution of compound **12** (30.00 g, 0.114 mol) in dry THF (600 ml). The mixture was stirred at  $-78^\circ\text{C}$  for 30 min, trimethyl borate (24.00 g, 0.230 mol) was added dropwise whilst maintaining the temperature below  $-65^\circ\text{C}$ , and the mixture was allowed to warm to room temperature overnight. 10% Hydrochloric acid (200 ml) was added and the mixture was stirred for 1 h at room temperature. The product was extracted into ether ( $\times 2$ ) and the combined ethereal extracts were washed with water, and dried ( $\text{MgSO}_4$ ). The solvent was removed *in vacuo* and the residue was stirred in hexane for 1 h and filtered off as a colourless powder. Yield 21.5 g (83%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.12(2H, d), 6.96(2H, d,  $J=8$  Hz), 1.85(2H, quint), 7.32–7.42(5H, m), 7.72(2H, d,  $J=8$  Hz), 7.78(2H, s). MS  $m/z$  228( $\text{M}^+$ ).

**6.2.3. Benzyl 4-bromo-2-fluorobenzoate (15).** Triphenylphosphine (16.77 g, 0.064 mol) was added quickly to a stirred solution of compound **14** (14.00 g, 0.064 mol), benzyl alcohol (6.91 g, 0.064 mol) and DIAD (12.93 g, 0.064 mol) in THF (500 ml) at room temperature. The solution was stirred at room temperature overnight (TLC analysis revealed a complete reaction). The solvent was removed *in vacuo* and the crude product purified by column chromatography (silica gel/hexane-ethyl acetate, 9:1) to yield a colourless solid. Yield 18.82 g (95%), m.p. 44–45°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.37(2H, s), 7.32–7.42(5H, m), 7.43–7.47(2H, m), 7.84(1H, dd,  $J=8$  Hz,  $J=8$  Hz). MS  $m/z$  310( $\text{M}^+$ ), 308( $\text{M}^+$ ).

**6.2.4. Benzyl 4'-benzyloxy-3-fluorobiphenyl-4-carboxylate (16).** Compound **13** (15.05 g, 0.066 mol) was added quickly to a stirred mixture of compound **5** (17.00 g, 0.055 mol), tetrakis(triphenylphosphine)palladium(0) (2.00 g, 1.73 mmol) and sodium carbonate (11.66 g, 0.110 mol) in DME (150 ml) and water (110 ml) under nitrogen. The stirred mixture was heated under reflux for 14 h (GLC and TLC analyses revealed a complete

reaction) and poured into water. The product was extracted into ether ( $\times 2$ ) and the combined ethereal extracts were washed with brine, and dried ( $\text{MgSO}_4$ ). The solvent was removed *in vacuo* and the crude product purified by column chromatography (silica gel/hexane-DCM, 2:1) to give a colourless solid which was recrystallized from ethanol-ethyl acetate (10:1) to yield colourless crystals. Yield 14.83 g (65%), m.p. 111–112°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.12(2H, s), 5.41(2H, s), 7.07(2H, d,  $J=8$  Hz), 7.30–7.50(12H, m), 7.57(2H, d,  $J=8$  Hz), 8.02(1H, dd,  $J=8$  Hz,  $J=8$  Hz). MS  $m/z$  412( $\text{M}^+$ ).

**6.2.5. 3-Fluoro-4'-hydroxybiphenyl-4-carboxylic acid (17).** A shaken mixture of compound **16** (14.00 g, 0.034 mol) and 10% palladium/carbon (1 g) in ethyl acetate (300 ml) was hydrogenated at 30 psi for 16 h. The catalyst was filtered off through hyflo, and the filtrate was evaporated to yield a colourless solid which was recrystallized from ethyl acetate to yield colourless crystals. Yield 6.77 g (86%), m.p.  $>300^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  6.54(1H, s), 6.86(2H, d,  $J=8$  Hz), 7.50–7.56(2H, m), 7.61(2H, d,  $J=8$  Hz), 7.87(1H, dd,  $J=8$  Hz,  $J=8$  Hz), 9.82(1H, s). MS  $m/z$  232( $\text{M}^+$ ).

**6.2.6. 4'-Benzyloxy-2,3-difluorobiphenyl (19).** Quantities: Compound **12** (30.00 g, 0.114 mol), compound **18** (21.60 g, 0.137 mol). The experimental procedure was as described for the preparation of compound **16**. The crude product was purified by column chromatography (silica gel/hexane with the gradual introduction of DCM) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals. Yield 19.46 g (58%), m.p. 89–90°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.14(2H, s), 7.07(2H, d,  $J=8$  Hz), 7.10–7.20(3H, m), 7.35–7.52(7H, m). MS  $m/z$  296( $\text{M}^+$ ).

**6.2.7. 4-Benzyloxy-2,3-difluorobiphenyl-4-carboxylic acid (20).** *n*-Butyllithium (25.3 ml, 2.5M in hexane, 0.063 mol), was added dropwise to a stirred, cooled ( $-78^\circ\text{C}$ ) solution of compound **19** (17.00 g, 0.057 mol) in dry THF (600 ml). The mixture was stirred at  $-78^\circ\text{C}$  for 1 h, poured onto crushed solid carbon dioxide and allowed to warm to room temperature. The solvent was removed *in vacuo* and the residue was dissolved in hot acetic acid. After cooling, the product was filtered off and washed with much hot water, and recrystallized from acetic acid to yield colourless crystals. Yield 16.5 g (85%), m.p. 174–175°C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  5.15(2H, s), 7.12(2H, d,  $J=8$  Hz), 7.20–7.60(9H, m), carboxylic acid proton not observed. MS  $m/z$  340( $\text{M}^+$ ).

**6.2.8. 2,3-Difluoro-4'-hydroxybiphenyl-4-carboxylic acid (21).** Quantities: compound **20** (16.00 g, 0.047 mol),



10% palladium/carbon (1 g). The experimental procedure was as described for the preparation of compound **16** to yield colourless crystals. Yield 10.9 g (93%), m.p. >300°C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 6.52(1H, s), 6.82(2H, d, *J*=8 Hz), 6.28(2H, dd, *J*=8 Hz, *J*=1 Hz), 7.40(1H, ddd, *J*=8 Hz, *J*=8 Hz, *J*=1 Hz), 7.90(1H, ddd, *J*=8 Hz, *J*=8 Hz, *J*=1 Hz), 10.10(1H, s). MS *m/z* 250(M<sup>+</sup>).

**6.2.9. 4'-(3-Hydroxypropoxy)biphenyl-4-carboxylic acid (23).** A solution of sodium hydroxide (2.80 g, 0.070 mol) in water (20 ml), and a solution of 3-bromopropan-1-ol (6.50 g, 0.047 mol) in methanol (40 ml) were added sequentially to a stirred solution of compound **22** (5.00 g, 0.023 mol) in methanol (150 ml) at 60°C. Potassium iodide (0.25 g, 1.5 mmol) was added in one portion, and the stirred mixture was heated under reflux for 72 h (TLC analysis revealed a complete reaction). The mixture was cooled and poured into 10% hydrochloric acid (100 ml) and the resulting precipitate was filtered off, washed with much water, followed by much methanol, and dried *in vacuo* (P<sub>2</sub>O<sub>5</sub>) to give a grey solid. The crude material was used directly in the next step because of its intractable nature due to extremely poor solubility at room temperature; hence it was not characterized. Yield 4.20 g (67%).

**6.2.10. 3-Fluoro-4'-(3-hydroxypropoxy)biphenyl-4-carboxylic acid (24).** Quantities: compound **17** (5.00 g, 0.022 mol), 3-bromopropan-1-ol (6.15 g, 0.044). The experimental procedure was as described for the preparation of compound **23** to yield a grey intractable solid. Yield 4.67 g (73%).

**6.2.11. 2,3-Difluoro-4'-(3-hydroxypropoxy)biphenyl-4-carboxylic acid (25).** Quantities: compound **21** (5.00 g, 0.020 mol), 3-bromopropan-1-ol (5.60 g, 0.040 mol). The experimental procedure was as described for the preparation of compound **23**, yielding a grey intractable solid. Yield 4.17 g (68%).

**6.2.12. 4'-(3-Perfluorobutanoyloxypropoxy)biphenyl-4-carboxylic acid (26).** A stirred solution of compound **23** (4.20 g, 0.015 mol), perfluorobutanoic acid (12.90 g, 0.060 mol) and PTSA (0.40 g, 2.1 mmol) in toluene (120 ml) was heated under reflux (Dean–Stark) for 16 h. The mixture was cooled and the resulting precipitate filtered off and washed with toluene. The crude product was purified by column chromatography (silica gel/DCM with the gradual introduction of methanol) to yield a colourless solid which was recrystallized from toluene to yield colourless crystals. Yield 5.35 g (76%), transitions (°C) Cr 189 SmC 255 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ

2.25(2H, quint), 4.10(2H, t), 4.61(2H, t), 6.99(2H, d, *J*=8 Hz), 7.56(2H, d, *J*=8 Hz), 7.62(2H, d, *J*=8 Hz), 8.07(2H, d, *J*=8 Hz), carboxylic acid proton not observed. MS *m/z* 468(M<sup>+</sup>).

**6.2.13. 3-Fluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-carboxylic acid (27).** Quantities: compound **24** (5.00 g, 0.017 mol) and perfluorobutanoic acid (14.60 g, 0.068 mol). The experimental procedure was as described for the preparation of compound **26** to yield colourless crystals. Yield 5.03 g (61%), transitions (°C) Cr 181 SmC 229 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.25(2H, quint), 4.10(2H, t), 4.61(2H, t), 6.97(2H, d, *J*=8 Hz), 7.54(2H, m), 7.65(2H, d, *J*=8 Hz), 8.14(1H, dd, *J*=8 Hz, *J*=8 Hz), carboxylic acid proton not observed. MS *m/z* 486(M<sup>+</sup>).

**6.2.14. 2,3-Difluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-carboxylic acid (28).** Quantities: compound **25** (5.00 g, 0.016 mol), perfluorobutanoic acid (13.75 g, 0.064 mol). The experimental procedure was as described for the preparation of compound **26** to yield colourless crystals. Yield 4.68 g (58%), transitions (°C) Cr 148 SmC 198 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.25(2H, quint), 4.10(2H, t), 4.61(2H, t), 6.88(2H, d, *J*=8 Hz), 7.37(2H, dd, *J*=8 Hz, *J*=8 Hz), 7.42(1H, ddd, *J*=8 Hz, *J*=8 Hz, *J*=1 Hz), 7.94(1H, ddd, *J*=8 Hz, *J*=8 Hz, *J*=1 Hz), carboxylic acid proton not observed. MS *m/z* 504(M<sup>+</sup>).

**6.2.15. (S)-(+)-1-Methylheptyl 4-[4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy]benzoate (2).** DCC (0.5832 g, 2.83 mmol) was added in one portion a stirred mixture of compound **26** (1.2012 g, 2.57 mmol), compound **29** (0.6423 g, 2.57 mmol) and DMAP (0.1174 g, 0.96 mmol) in dry DCM (200 ml) at room temperature. The mixture was stirred at room temperature overnight (TLC analysis revealed a complete reaction), the DCU was filtered off and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel/hexane-DCM, 2/1 with the gradual introduction of further DCM) to give a colourless solid which was recrystallized from ethanol/ethyl acetate (5/1) to yield colourless crystals. Yield 1.05 g (58%), transitions (°C) Cr 83.6 (SmI\*anti 54.0) SmC\*anti 119.7 SmC\*ferro 123.5 SmA\* 128.8 I (in agreement with the literature values [14, 15]). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88(3H, t), 1.25–1.42(11H, m, including 3H, d), 1.62(1H, m), 1.75 (1H, m), 2.27(2H, quint), 4.14(2H, t), 4.65(2H, t), 5.18(1H, sext), 7.01(2H, d, *J*=8 Hz), 7.32(2H, d, *J*=8 Hz), 7.61(2H, d, *J*=8 Hz), 7.69(2H, d, *J*=8 Hz), 8.14(2H, d, *J*=8 Hz), 8.24(2H, d, *J*=8 Hz). MS *m/z* 700(M<sup>+</sup>).

Elemental analysis: calc. for  $C_{35}H_{35}F_7O_7$ , C 60.00, H 5.04; found, C 59.88, H 5.02%.  $[\alpha]_D^{25} = +19.54^\circ$ .

**6.2.16. (S)-(+)-1-Methylheptyl 3-fluoro-4-[4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy] benzoate (3).** Quantities: compound **26** (1.2068 g, 2.58 mmol) and compound **30** (0.6962 g, 2.60 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 1.17 g (63%), transitions ( $^\circ C$ ) Cr 57.0 SmC\*anti 104.0 SmC\*ferro 105.0 I.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88(3H, t), 1.22–1.42(11H, m, including 3H, d), 1.62(1H, m), 1.78 (1H, m), 2.30(2H, quint), 4.14(2H, t), 4.65(2H, t), 5.18(1H, sext), 7.02(2H, d,  $J=8$  Hz), 7.38(1H, dd,  $J=8$  Hz,  $J=8$  Hz), 7.63(2H, d,  $J=8$  Hz), 7.73(2H, d,  $J=8$  Hz), 7.89–7.93(2H, m), 8.28(2H, d,  $J=8$  Hz). MS  $m/z$  718( $M^+$ ). Elemental analysis: calc. for  $C_{35}H_{34}F_8O_7$ , C 58.50, H 4.77; found, C 58.41, H 4.70%.  $[\alpha]_D^{25} = +17.47^\circ$ .

**6.2.17. (S)-(+)-1-Methylheptyl 2-fluoro-4-[4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy] benzoate (4).** Quantities: compound **26** (1.2127 g, 2.59 mmol) and compound **31** (0.6981 g, 2.60 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 1.24 g (67%), transitions ( $^\circ C$ ) Cr 61.5 SmC\*anti 103.0 SmC\*ferro 109.0 SmA\* 120.0 I.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88(3H, t), 1.22–1.42(11H, m, including 3H, d), 1.61(1H, m), 1.73 (1H, m), 2.27(2H, quint), 4.12(2H, t), 4.63(2H, t), 5.16(1H, sext), 6.99(2H, d,  $J=8$  Hz), 7.07–7.12(2H, m), 7.60(2H, d,  $J=8$  Hz), 7.69(2H, d,  $J=8$  Hz), 8.01(1H, dd,  $J=8$  Hz,  $J=8$  Hz), 8.22(2H, d,  $J=8$  Hz). MS  $m/z$  718( $M^+$ ). Elemental analysis: calc. for  $C_{35}H_{35}F_7O_7$ , C 60.00, H 5.04; found, C 59.88, H 5.02%.  $[\alpha]_D^{25} = +17.38^\circ$ .

**6.2.18. (S)-(+)-1-Methylheptyl 2,3-difluoro-4-[4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy] benzoate (5).** Quantities: compound **26** (1.2018 g, 2.57 mmol) and compound **32** (0.7357 g, 2.57 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 1.12 g (59%), transitions ( $^\circ C$ ) Cr 66.0 SmC\*anti 95.0 SmC\*ferro 99.0 SmA\* 104.0 I.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88(3H, t), 1.24–1.45(11H, m, including 3H, d), 1.63(1H, m), 1.74(1H, m), 2.27(2H, quint), 4.13(2H, t), 4.64(2H, t), 5.18(1H, sext), 7.00(2H, d,  $J=8$  Hz), 7.15(1H, ddd,  $J=8$  Hz,  $J=8$  Hz,  $J=2$  Hz), 7.62(2H, d,  $J=8$  Hz), 7.71(2H, d,  $J=8$  Hz), 7.77(1H, ddd,  $J=8$  Hz,  $J=8$  Hz,  $J=2$  Hz), 8.25(2H, d,  $J=8$  Hz). MS  $m/z$  736( $M^+$ ). Elemental analysis: calc. for  $C_{35}H_{33}F_9O_7$ , C 57.07, H 4.52; found, C 56.93, H 4.47%.  $[\alpha]_D^{25} = +17.53^\circ$ .

**6.2.19. (S)-(+)-1-Methylheptyl 4-[3-fluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy] benzoate (6).** Quantities: compound **27** (1.0211 g, 2.10 mmol) and compound **29** (0.5488 g, 2.19 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 0.76 g (50%), transitions ( $^\circ C$ ) Cr 63.0 SmC\*anti 104.5 SmC\*ferro 108.5 SmA\* 115.5 I.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88(3H, t), 1.19–1.39(11H, m, including 3H, d), 1.62(1H, m), 1.72 (1H, m), 2.26(2H, quint), 4.12(2H, t), 4.62(2H, t), 5.14(1H, sext), 7.00(2H, d,  $J=8$  Hz), 7.32(2H, d,  $J=8$  Hz), 7.40(1H, dd,  $J=10$  Hz,  $J=2$  Hz), 7.47(1H, dd,  $J=8$  Hz,  $J=2$  Hz), 7.60(2H, d,  $J=8$  Hz), 8.12(2H, d,  $J=8$  Hz), 8.15(1H, dd,  $J=8$  Hz,  $J=8$  Hz). MS  $m/z$  718( $M^+$ ). Elemental analysis: calc. for  $C_{35}H_{34}F_8O_7$ , C 58.50, H 4.77; found, C 58.39, H 4.71%.  $[\alpha]_D^{25} = +15.11^\circ$ .

**6.2.20. (S)-(+)-1-Methylheptyl 4-[2,3-difluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy] benzoate (7).** Quantities: compound **28** (1.0621 g, 2.11 mmol), compound **29** (0.5504 g, 2.20 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 0.85 g (55%), transitions ( $^\circ C$ ) Cr 43.0 SmC\*anti 90.0 SmC\*ferro 99.0 SmA\* 111.0 I.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88(3H, t), 1.19–1.39(11H, m, including 3H, d), 1.62(1H, m), 1.72 (1H, m), 2.26(2H, quint), 4.12(2H, t), 4.62(2H, t), 5.14(1H, sext), 7.00(2H, d,  $J=8$  Hz), 7.30–7.35(3H, m), 7.56(2H, dd,  $J=8$  Hz,  $J=1$  Hz), 7.89(1H, ddd,  $J=8$  Hz,  $J=8$  Hz,  $J=1$  Hz), 8.13(2H, d,  $J=8$  Hz). MS  $m/z$  736( $M^+$ ). Elemental analysis: calc. for  $C_{35}H_{33}F_9O_7$ , C 57.07, H 4.52; found: C 56.98, H 4.51%.  $[\alpha]_D^{25} = +12.32^\circ$ .

**6.2.21. (S)-(+)-1-Methylheptyl 3-fluoro-4-[3-fluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy] benzoate (8).** Quantities: compound **27** (1.0435 g, 2.15 mmol), compound **30** (0.6018 g, 2.25 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 0.65 g (41%), transitions ( $^\circ C$ ) Cr 22.5 SmC\*ferro 83.0 I.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.88(3H, t), 1.19–1.39(11H, m, including 3H, d), 1.62(1H, m), 1.72 (1H, m), 2.26(2H, quint), 4.12(2H, t), 4.62(2H, t), 5.14(1H, sext), 7.00(2H, d,  $J=8$  Hz), 7.36(1H, dd,  $J=8$  Hz,  $J=8$  Hz), 7.40(1H, dd,  $J=10$  Hz,  $J=2$  Hz), 7.47(1H, dd,  $J=8$  Hz,  $J=2$  Hz), 7.60(2H, d,  $J=8$  Hz), 7.87–7.93(3H, m). MS  $m/z$  736( $M^+$ ). Elemental analysis: calc. for  $C_{35}H_{33}F_9O_7$ , C 57.07, H 4.52; found, C 57.02, H 4.52%.  $[\alpha]_D^{25} = +16.55^\circ$ .

**6.2.22. (S)-(+)-1-Methylheptyl 2-fluoro-4-[3-fluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy]benzoate (9).** Quantities: compound **27** (1.0521 g, 2.16 mmol), compound **31** (0.6006 g, 2.24 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 0.91 g (57%), transitions (°C) Cr 64.5 SmC\*anti 90.5 SmC\*ferro 96.5 SmA\* 107.5 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88(3H, t), 1.19–1.39(11H, m, including 3H, d), 1.62(1H, m), 1.72 (1H, m), 2.26(2H, quint), 4.12(2H, t), 4.62(2H, t), 5.14(1H, sext), 7.00(2H, d, *J*=8 Hz), 7.10–7.15(2H, m), 7.41(1H, dd, *J*=10 Hz, *J*=2 Hz), 7.49(1H, dd, *J*=8 Hz, *J*=2 Hz), 7.60(2H, d, *J*=8 Hz), 8.05(1H, dd, *J*=8 Hz, *J*=8 Hz), 8.15(1H, dd, *J*=8 Hz, *J*=8 Hz). MS *m/z* 736(M<sup>+</sup>). Elemental analysis: calc. for C<sub>35</sub>H<sub>33</sub>F<sub>9</sub>O<sub>7</sub>, C 57.07, H 4.52; found, C 56.99, H 4.48%. [ $\alpha$ ]<sub>D</sub>=+16.18°.

**6.2.23. (S)-(+)-1-Methylheptyl 3-fluoro-4-[2,3-difluoro-4'-(3-perfluorobutanoyloxypropoxy)biphenyl-4-ylcarbonyloxy]benzoate (10).** Quantities: compound **28** (1.0577 g, 2.10 mmol), compound **30** (0.6120 g, 2.28 mmol). The experimental procedure was as described for the preparation of compound **2**, to yield colourless crystals. Yield 0.89 g (56%), transitions (°C) Cr 67.5 (SmC\*anti 65.5) SmC\*ferro 69.0 SmA\* 78.5 I. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.88(3H, t), 1.19–1.39(11H, m, including 3H, d), 1.62(1H, m), 1.72 (1H, m), 2.26(2H, quint), 4.12(2H, t), 4.62(2H, t), 5.14(1H, sext), 6.99(2H, d, *J*=8 Hz), 7.32(1H, ddd, *J*=8 Hz, *J*=8 Hz, *J*=1 Hz), 7.36(1H, dd, *J*=8 Hz, *J*=8 Hz), 7.55(2H, dd, *J*=8 Hz, *J*=1 Hz), 7.87–7.93(3H, m). MS *m/z* 754 (M<sup>+</sup>). Elemental analysis: calc. for C<sub>35</sub>H<sub>32</sub>F<sub>10</sub>O<sub>7</sub>, C 55.71, H 4.27; found, C 55.62, H 4.22%. [ $\alpha$ ]<sub>D</sub>=+12.57°.

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