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Laterally fluorinated liquid crystals containing the 2,2′-bithiophene moiety

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The synthesis and systematic evaluation of the influence of lateral mono-, di- and tetra-fluorination of the terminal phenyl ring on mesomorphic properties in seven novel series of suitably fluoro-substituted 5-*n*-alkyl-5′-(4-*n*-decyloxyphenyl)-2,2′-bithienyls is reported. Compared with their non-fluorinated parent counterparts, lateral fluorination eliminates high order smectic phases and reduces thermal stability, to reveal compounds exhibiting a selection of nematic, smectic A and smectic C phase types. As the number of fluoro-substituents increases from one to two, mesophase thermal stability drops drastically; the disposition of the second fluoro-substituent is important. Across-axis disposition is more detrimental than along-axis. However, complete fluorination does not destroy mesophase formation. Indeed, tetrafluorophenyl compounds are more stable than certain 3,5- and 2,6-difluoro compunds. The extrapolated birefringence for members of a series of 5-*n*-alkyl-5′-(2,3-difluoro-4-*n*-decyloxyphenyl)-2,2′-bithienyls is approximately 0.21.

1. Introduction

The influence of lateral fluorination has been widely researched following the realization that lateral fluorination can advantageously modify mesomorphic properties, such that the material in question may be useful in electro-optic applications [1–16]. A lateral fluorine atom is a particularly apt substituent because of its relatively small size (the van der Waals radii of fluorine and hydrogen are 1.47 and 1.2 Å, respectively), which can be accommodated by the molecular core without excessive molecular broadening. Furthermore, knowledge of the influence of lateral fluorination allows synthetic chemists to engineer: (i) mesogens with either positive or negative dielectric anisotropy ($\Delta\varepsilon$) as a result of the moderately polar C–F bond; (ii) low melting mesogens, (iii) nematic and smectic C phase forming materials from initial materials that are dominant in high order smectic liquid crystal phases and/or smectic crystal phases.

Similarly bent core structures have gained significant exposure over the last decade primarily due to the occurrence of polar switching in banana-like mesogens as first reported by Niori *et al.* in 1996 [17, 18]. Bent-core structures are also being investigated, for example, in the quest for the elusive biaxial nematic phase [19], flexoelectric switching [20] and high birefringence materials [21]. However, prior to this recent upsurge in interest, kinked or bent-core structures for many years had been neglected because they contradicted the readily held notion that mesomorphic materials comprise elongated lath-like structures, i.e. calamitic molecular architecture. Thus, the vast majority of liquid crystals reported employ one or more rigid, linear 1,4-disubstituted phenylene rings as part of their molecular core to generate a calamitic molecular architecture. The replacement of such linear units where the exocyclic bond angle is 180° by the relatively non-linear 2,5-disubstituted thiophene moiety (exocyclic bond angle, 148°) disrupts linearity and consequently disrupts the lamellar-like packing arrangement of the molecules. The reduced, or lack of, linearity of the molecule is also attributed to the position of the 2,5-disubstituted thiophene moiety within the molecule, which ultimately affects liquid crystallinity. For example, Schubert *et al.* [22] first reported that liquid crystallinity is lost when a thiophene ring is placed in a central position, whereas when placed in a terminal position it is retained. However, researchers have shown that by suitably increasing the molecular

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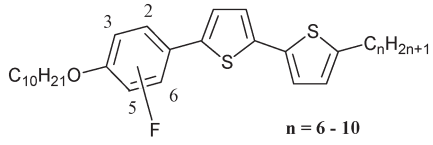
length-to-breadth ratio, centrally disposed 2,5-disubstituted thiophene rings may be tolerated such that they exhibit mesogenic properties [23–26].

Heterocyclic rings are further beneficial because their heteroatom may cause changes in a variety of parameters such as molecular shape, polarity, polarizability and dielectric anisotropy [27]. In particular we have explored the chemistry and mesomorphic properties derived from thiophene in some detail [23]. Thiophene is a π-excessive sulfur-containing aromatic heterocycle. Its chemistry is dominated by a willingness to participate in electrophilic aromatic substitution at the C2- (α) and C5- (α) positions of the ring, which affords a natural bend or kink in the structure (exocyclic bond angle, 148°). Such an arrangement is intermediate between classical bent core systems, which have a much narrower angle, and classical calamitic structures. There should be a greater tendency to exhibit classical calamitic phases, albeit with modified properties.

Herein, in our quest to explore further the availability of thiophene-based liquid crystals, preferably those that are nematogenic with moderately high birefringence for potential use in photonic applications, we report the combination of two topical areas of liquid crystal science to achieve our goal. To this effect, the combined influence of lateral fluorination and kinked geometry is envisaged to generate low melting, nematogenic liquid crystals with a moderately high birefringence. Thus, we report the synthesis and liquid crystal characteristics of seven novel fluorinated, heterocyclic systems, viz. series 1–7.



Series 1 -7

2. Results and discussion

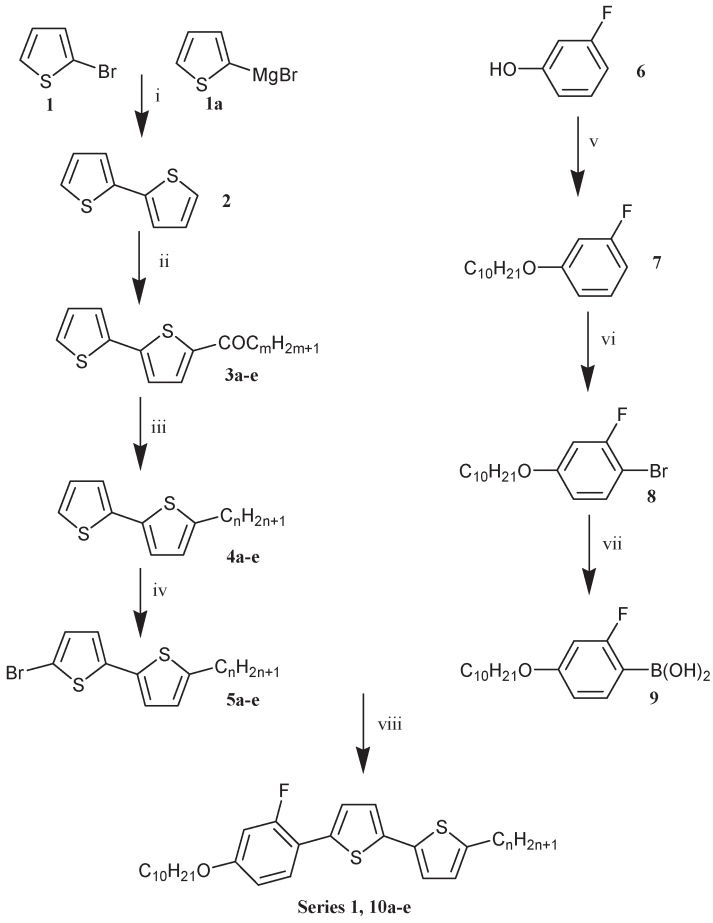
2.1. *Synthesis*

The synthetic pathways leading to the novel series of fluoro-substituted 5-*n*-alkyl-5′-(4-*n*-decyloxyphenyl)-2,2′-bithienyls are depicted in schemes 1–7. The 5-*n*-alkyl-5′-bromo-2,2′-bithienyls **5a**–**e** are common to schemes 1–6 because they are key intermediates leading to the preparation of mono- (series 1 and 2) and di-fluoro-substituted 5-*n*-alkyl-5′-(4-*n*-decyloxyphenyl)-2,2′-bithienyls (series 3–6). Compounds **5a**–**e** were prepared by Kumada-type homo-coupling [28] of commercial 2-bromothiophene **1** with the Grignard reagent of 2-bromothiophene **1a** to afford 2,2′-bithiophene **2** in high yield (94%). Titanium tetrachloride mediated Friedel–Crafts [29] acylation with an appropriate range of alkanoyl chlorides followed by Huang–Minlon [30] modification of the Wolff–Kishner reduction of the intermediate ketones **3a**–**e** yielded a variety of 5-*n*-alkyl-2,2′-bithienyls **4a**–**e**. Subsequent bromination of **4a**–**e** furnished the desired 5-*n*-alkyl-2,2′-bithienyls **5a**–**e** as key intermediates, which on Suzuki–Miyaura crosscoupling [31] with appropriate mono- or di-fluoro-substituted phenylboronic acids **9**, **13**, **18**, **23**, **29** and **35**, produced the desired novel series of mono- (series 1 and 2) and di-fluoro-substituted 5-*n*-alkyl-5′-(4-*n*-decyloxyphenyl)-2,2′-bithienyls (series 3–6). The fluoro-substituted phenyl boronic acids were prepared by standard methods either via *ortho*-directed low temperature lithiation [32] or low temperature halogen-lithiation exchange of a suitable precursor followed by trimethyl borate quench and acidic work-up.

The tetrafluoro-substituted 5-*n*-alkyl-5′-(4-*n*-decyloxyphenyl)-2,2′-bithienyls **41a**–**e** (series 7) were prepared using the Stille crosscoupling methodology [33]. The tributyltin derivative of 2,2′-bithiophene **37**, prepared via α-lithiation of 2,2′-bithiophene **2** and stannyl chloride quench, was crosscoupled with commercial 1-bromo-2,3,4,5,6-pentafluorobenzene to give 5-pentafluorophenyl-2,2′-bithienyl **38** in moderate yield (57%). Nucleophilic substitution of the *para*-disposed fluoro-substituent by sodium decoxide produced the decyloxy-substituted compound **39**. Friedel–Crafts acylation of **39**, followed by reduction of the intermediate ketone **40**, generated the desired members of a series of 5-*n*-alkyl-5′-(4-*n*-decyloxy-2,3,5,6-tetrafluorophenyl)-2,2-bithienyls **41a**–**e** (series 7). The synthesis of the parent, non-fluorinated compounds, series 8, has been reported previously in [34].

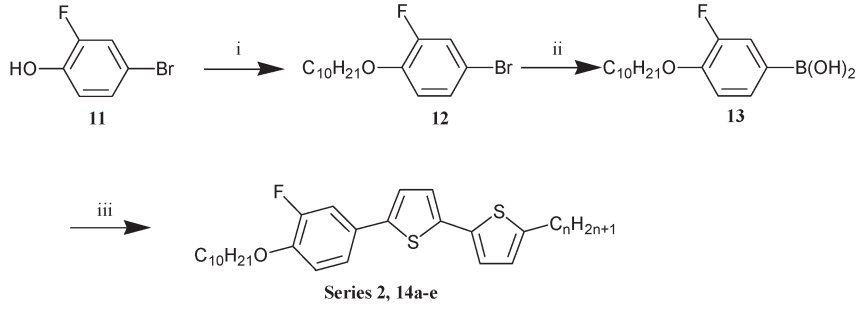
2.2. *Mesomorphic properties*

Measurements of transition temperature and microscopic observations of mesophase textures were made using an Olympus BH-2 polarizing microscope in conjunction with a Mettler FP52 hot stage and FP5 control unit. The transition temperatures were confirmed by thermal analysis undertaken using a Perkin-Elmer DSC7 differential scanning calorimeter at heating and cooling rates of $10^{\circ}C\,min^{-1}$, and are listed in tables 1–7. Typical textures were observed for the nematic, SmA and SmC phase types. For example, the onset of the nematic phase was best observed on cooling from the isotropic liquid, whereby formation of highly coloured droplets (nematic droplets) emanating from a dark isotropic background was detected. Similarly, the Sm A phase showed both hometropic and focal-conic



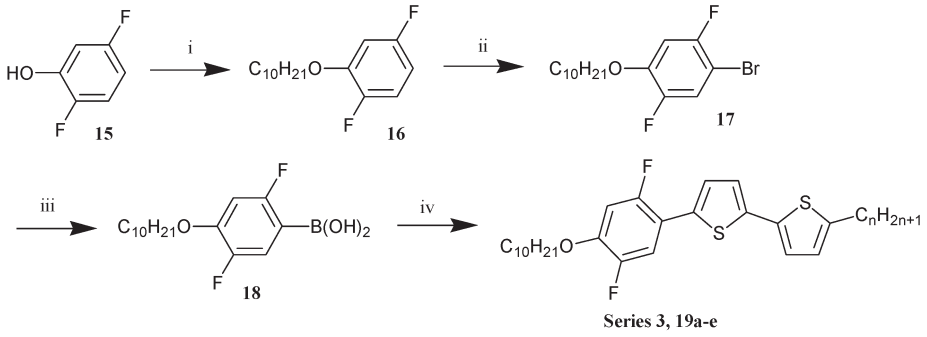
Reagents and conditions: i. $[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]NiCl_2$, diethyl ether, reflux; ii. $C_mH_{2m+1}COCl$, $TiCl_4$, CH_2Cl_2; iii. $NH_2NH_2.H_2O$, KOH, diethylene glycol, reflux; iv. a. 1.6M n-BuLi,-10°C, THF, b. Br_2, -78°C; v. $C_{10}H_{21}Br$, K_2CO_3, acetone, reflux; vi. Br_2, $CHCl_3$; vii. a. 1.6M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; viii. $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux.

Scheme 1



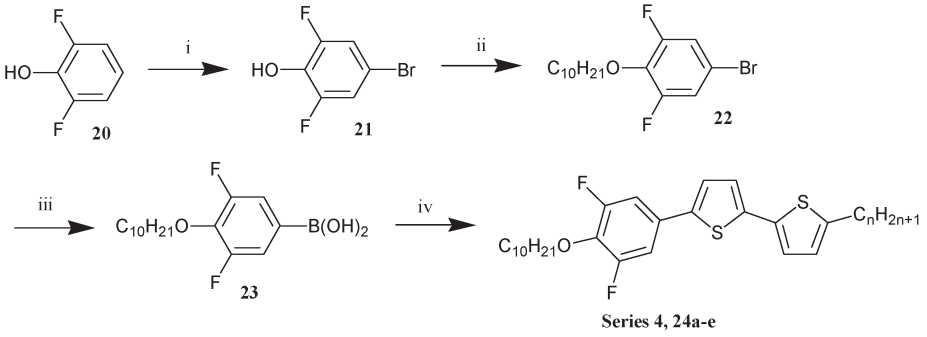
Reagents and conditions: i. $C_{10}H_{21}Br$, K_2CO_3, acetone, reflux; ii. a. 1.6M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; iii. (**5a-e**), $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux.

Scheme 2



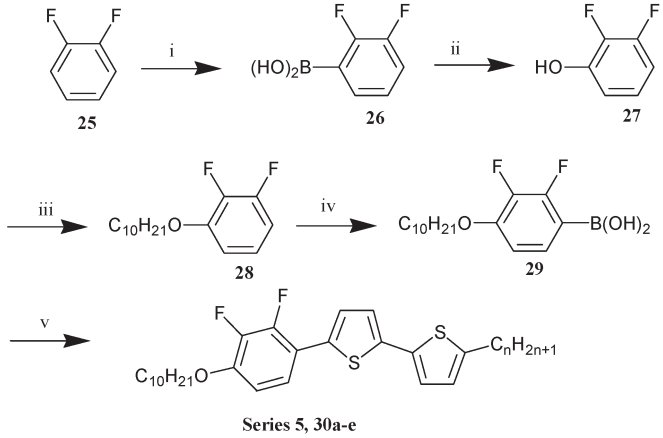
Reagents and conditions: i. $C_{10}H_{21}Br$, K_2CO_3, acetone, reflux; ii. Br_2, $CHCl_3$; iii. a. 1.6M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; iv. (**5a-e**), $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux.

Scheme 3



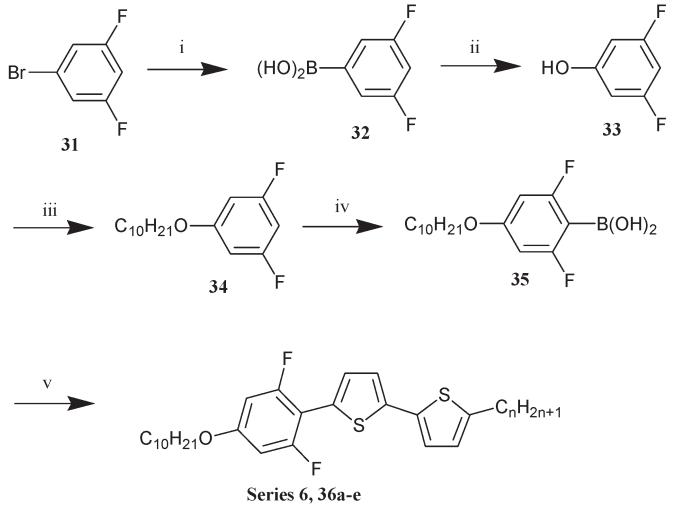
Reagents and conditions: i. *N*-Bromosuccinimide, DMF; ii. $C_{10}H_{21}Br$, K_2CO_3, acetone, reflux; iii. a. 2.5M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; iv. (**5a-e**), $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux.

Scheme 4



Reagents and conditions: i. 2.5M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; ii. H_2O_2; iii. $C_{10}H_{21}Br$, K_2CO_3, acetone, reflux iv. a. 2.5M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; v. (**5a-e**), $Pd(PPh_3)_4$, 2M Na_2CO_3, 1,2-dimethoxyethane, reflux.

Scheme 5

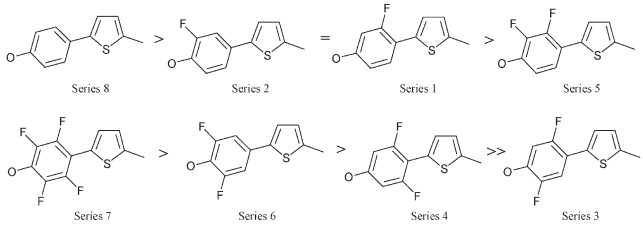


Reagents and conditions: i. 2.5M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; ii. H_2O_2; iii. $C_{10}H_{21}Br$, K_2CO_3, acetone, reflux; iv. a. 2.5M BuLi, -78°C, THF, b. $B(OCH_3)_3$, c. H^+; v. (**5a-e**), $Pd(PPh_3)_4$, 2M Na_2CO_3, THF, DMF, reflux.

Scheme 6

fan textures and the SmC phase produced a schlieren and broken fan texture.

The effect of mono-, di- and tetra-fluoro-substitution of the phenyl ring on mesomorphic properties of several series of suitably fluoro-substituted 5-*n*-alkyl-5′-(4-*n*-decyloxyphenyl)-2,2′-bithienyls (series 1–7) compared with the parent non-fluorinated counterparts (series 8) is best evaluated by comparing data for the same homologue for each series. To this effect, table 8 summarizes mesomorphic data for the $n=6$ homologue for series 1–8, from which the following thermal stability order may be deduced.

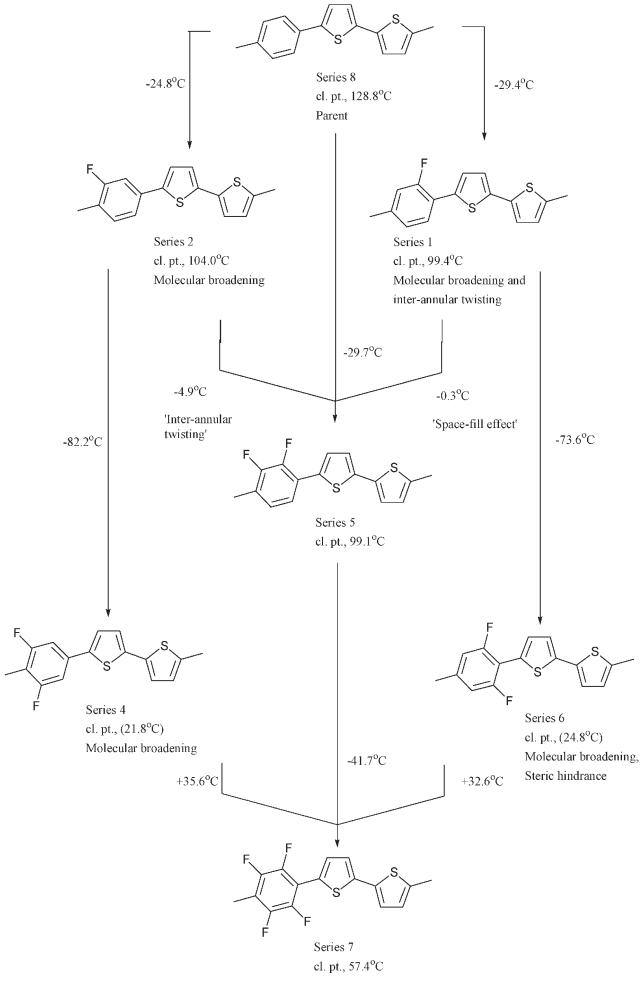


Surprisingly, complete lateral fluorination (series 7) is not detrimental to mesophase thermal stability. The $n=6$ homologue of series 7 (**41a**) is a low melting, enantiotropic nematogen and thermally more stable than its difluoro-counterparts where the fluoro-substituents are disposed across the molecular long axis, i.e. series 4 (**24a**), series 6 (**36a**) and series 3 (**19a**). In fact, across-axis disposition of two fluoro-substituents is highly detrimental to mesophase formation, as exemplified by **19a** which is not liquid crystalline whilst **24a** and **36a** at best, are monotropic liquid crystals.

Compared with the non-fluorinated parent compound (series 8) [34], lateral fluorination clearly promotes the occurrence of the nematic phase (series 1, **10a**; series 2, **14a**; series 5, **30a**; series 7, **41a**), which is absent in the parent compound. Except for series 3 (**19a**), which is not liquid crystalline and higher melting than the parent compound, lateral fluorination lowers the melting point and eliminates high order smectic phases (SmF and CrG). The occurrence of the SmC is noted for the 2-fluoro- (**10a**), 3-fluoro- (**14a**) and 2,3-dfluoro-compounds (**30a**) alone. An enantiotropic SmA phase is induced in the 3-fluoro-compound (**14a**), whereas a monotropic SmA phase is observed for the 3,5- (**24a**) and 2,6-difluoro-compounds (**36a**).

The influence of lateral fluorination and disposition of fluoro-substitution on mesomorphic properties is best summarized in the flow-chart below, which may be tentatively discussed in terms of molecular broadening, inter-annular twisting, reduced molecular length-to-breadth ratio and reduced anisotropy of molecular polarizability. Starting with the non-fluorinated parent analogue (series 8), introduction of a single fluoro-substituent in either the 2- or 3-position lowers m.p., mesophase thermal stability and, overall phase range. The fluoro-substituent located *ortho*- to the interannular phenyl–thiophene ring junction (series 1, −29.4°C) is

more detrimental to thermal stability than is its isomeric counterpart where the substituent is located *meta*- to the ring junction (series 2, −24.8°C). The latter is situated in a less sterically hindered position than the former, which increases inter-annular twist, increases molecular breadth, reduces effective pi-overlap and mesomeric relay of electrons, thus lowering the overall magnitude of the anisotropy of molecular polarizability.



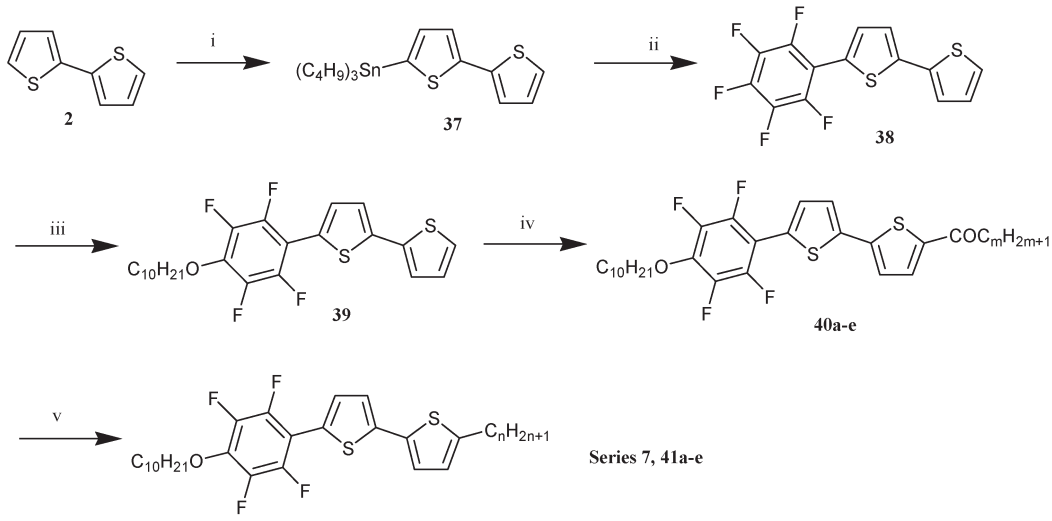
The introduction of a second fluoro-substituent and its disposition is extremely interesting, since it may have either a minimal or a drastic effect on mesophase thermal stability. A second fluoro-substituent introduced on the same side of the molecular long axis (series 5) lowers the thermal stability nominally by a few degrees centigrade, whereas a second fluoro-substituent disposed across-axis lowers stability by over 70°C and, in the case of series 3, liquid crystallinity is completely destroyed (see table 8).

When the second fluoro-substituent is introduced on an 'outer edge' (*meta*- to the interannular phenyl–thiophene ring junction and *ortho*- to the decyloxy terminal chain) in series 1 to give series 5, it serves simply to fill space, i.e. a space-filling effect, and the thermal stability decreases by a nominal 0.3°C. Disposition of a second fluoro-substituent on an 'inner edge' (*ortho*- to the interannular phenyl–thiophene ring junction and *meta*- to the decyloxy terminal chain) lowers the thermal stability by 4.9°C, which is not as drastic as expected. It appears that there is minimal increase in interannular twisting and only very slight molecular broadening.

Across-axis substitution of a second fluoro-substituent, as stated above, is much more detrimental to mesophase thermal stability. Comparison of series 2 with series 4 reveals a decrease in thermal stability of 82.2°C, which may be attributed tentatively to an increase in molecular broadening and effective reduction of the length to breadth ratio. Once again, we are surprised to find that across-axis substitution of a second fluoro-substituent on an 'inner edge', i.e. comparison of series 1 with series 6, although leading to reduction in thermal stability by 73.6°C, is less detrimental than the case for 'outer edge' substitution. It was envisaged that 'inner edge' substitution would increase the inter-annular twist angle due to steric strain. It appears that the second fluoro-substituent may be residing in a 'protective pocket' and is partially shielded. The first 'inner edge' fluoro-substituent 'absorbs' most of the steric strain and locks the structure. The second fluoro-substituent is then 'fixed' since if it attempts further rotation it will experience both steric and electrostatic repulsion from the sulphur atom of the thiophene ring.

In the case where one fluoro substituent is located on an 'inner edge' and the second is on an 'outer edge' but disposed across the molecular axis, i.e. series 3, then mesomorphic properties are completely eliminated. In this situation it is very difficult to rationalize such behaviour based on molecular broadening, interannular twisting and steric strain, since the isomeric compounds (series 4–6) experience similar forces but are liquid crystalline. It appears that dipolar effects must also play a considerable part in either stabilization or destabilization of thermal stability.

Two fluoro-substituents (*ortho*- to one another) located on the same side of the molecular axis will significantly increase the transverse dipole moment and appear to exert a stabilizing effect; whereas, an across-axis fluoro-substituent will either contribute to the dipole moment of the molecular long axis (series 4 and 6) with partial stabilization, or cause cancellation of



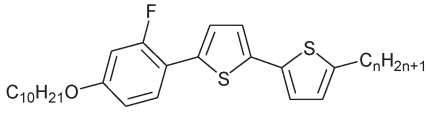
Reagents and conditions: i. 2.5M BuLi, 0 °C, THF, b. $(C_4H_9)_3SnCl$, -78°C, H^+; ii. C_6F_5Br, $[(C_6H_5)_3P]_2PdCl_2$, THF, reflux; iii. $C_{10}H_{21}OH$, NaH, pyridine; iv. $C_mH_{2m+1}COCl$, $SnCl_4$, CH_2Cl_2; v. $AlCl_3$, $LiAlH_4$, diethyl ether, $CHCl_3$, reflux.

Scheme 7

dipoles due to their across-axis diagonal disposition (series 3), resulting in severe destabilization. However, as will be alluded later, dipolar contributions alone are not the reasons for destabilization since the tetra-fluoro compounds (series 7) are liquid crystalline despite cancellation of dipoles.

Lateral fluoro-substitution in the remaining two positions in either series 4 or 6, to give the fully fluorinated system (series 7), surprisingly increases thermal stability. Inclusion of either two fluoro-substituents *ortho*- to the terminal decyloxy chain or two fluoro-substituents *ortho*- to the interannular phenyl–thiophene ring junction increases thermal stability by 35.6 and 32.6°C, respectively. However, inclusion of an additional two fluoro-substituents across the molecular long axis in series 5 destabilizes thermal stability by 41.7°C.

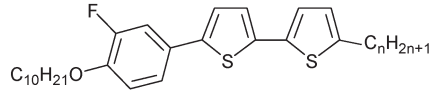
Table 1. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 1, **10a**–**e**.



Series 1, 10a-e

n-Alkyl	Compound	Cr–SmC	SmC–N	N–I
6	**10a**	82.0	87.5	99.4
		41.72	*0.14*	*1.28*
7	**10b**	77.4	91.7	102.4
		43.67	*0.22*	*1.72*
8	**10c**	78.6	94.2	101.1
		49.91	*0.21*	*1.76*
9	**10d**	76.0	96.9	102.4
		48.65	*0.24*	*2.53*
10	**10e**	79.3	98.2	101.2
		53.47	*0.36*	*2.66*

Table 2. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 2, **14a**–**e**.

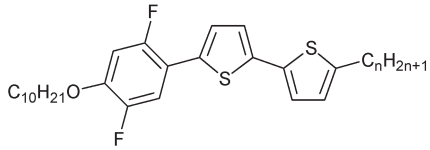


Series 2, 14a-e

n-Alkyl	Compound	Cr–SmC	SmC–SmA	SmA–N	SmC/SmA/N–I
6	**14a**	72.5	102.3	103.6	104.0
		38.13	*0.19*	—[a]	*5.21*[b]
7	**14b**	69.5	106.7	—	107.7
		26.60	—[a]		*6.77*[b]
8	**14c**	69.6	—	—	107.4
		32.16			*7.09*
9	**14d**	69.1	—	—	109.3
		38.15			*8.75*
10	**14e**	75.1	—	—	109.7
		29.53			*8.45*

[a]Enthalpy of transition is concealed by an adjacent transition.
[b]Enthalpy of transition on cooling.

Table 3. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 3, **19a**–**e**.



Series 3, 19a-e

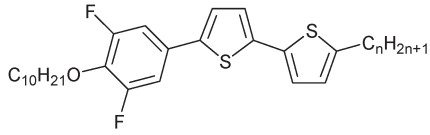
n-Alkyl	Compound	Cr–I	Cr–N	SmC–N	N–I	I–Cr
6	**19a**	93.5	—	—	—	86.1
		45.12				*44.26*
7	**19b**	91.0	—	—	—	88.6
		33.35				*31.17*
8	**19c**	88.2	—	—	—	84.8
		35.97				*30.21*
9	**19d**	85.0	—	—	[84.4][a]	—
		33.38			*2.39*	
10	**19e**	—	81.1	[80.6][a]	83.7	—
			26.59	*0.76*[b]	*1.95*	

[a]Square brackets signify monotropic transition. [b]Enthalpy of transition on cooling.

2.3. *Molecular modelling*

Minimized energy space-filling models of each of the $n=6$ homologues for series 1–8 were produced using Chem Draw 3D™ as part of the Chem Draw Ultra 8.0 program. The structures were minimized using MM2 computations assuming that the molecule was in the gas phase at absolute zero. The minimum energy calculations ($kcal\,mol^{-1}$) showed that there was a large freedom of rotation of the phenyl ring (up to 25° rotation permitted) with respect to the adjoining thiophene ring, either when there was no fluoro substitution (parent) or when the substitution was in the 3- (series 2) or 3,5-positions (series 5). There was an increased restriction to the rotation with fluoro substitution in the 2-position (series 1) but when the substitution was in the 2,6-positions (series 6) there was

Table 4. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 4, **24a**–**e**.

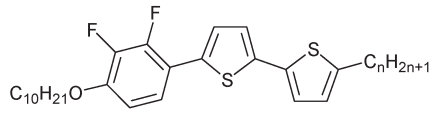


Series 4, 24a-e

n-Alkyl	Compound	Cr–I	SmA/I
6	**24a**	29.8	[21.8][a]
		38.65	*5.21*[b]
7	**24b**	35.5	[28.1][a]
		28.19	*6.77*[b]
8	**24c**	41.3	[36.1][a]
		44.51	*7.41*[b]
9	**24d**	46.0	[42.0]
		44.95	*8.82*[b]
10	**24e**	50.3	[47.0]
		38.06	*6.89*[b]

[a]Square brackets signifies monotropic transition. [b]Enthalpy of transition on cooling.

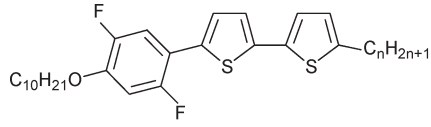
Table 5. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 5, **30a**–**e**.



Series 5, 30a-e

n-Alkyl	Compound	Cr–SmC	SmC–N	SmC/N–I
6	**30a**	61.1	88.5	99.1
		25.10	*1.01*	*1.56*
7	**30b**	72.0	94.9	101.6
		24.41	*1.09*	*2.72*
8	**30c**	74.0	98.4	101.6
		32.54	*1.62*	*2.47*
9	**30d**	78.4	102.0	103.6
		34.79	*1.63*	*3.57*
10	**30e**	79.3	—	103.8
		36.55		*7.53*

Table 6. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 6, **36a**–**e**.



Series 6, 36a-e

n-Alkyl	Compound	Cr–I	SmA–I	I–Cr
6	**36a**	30.1	[24.8][a]	—
		38.82	*5.20*[b]	
7	**36b**	36.1	[33.0][a]	—
		40.89	*6.19*[b]	
8	**36c**	43.1	[34.2][a]	—
		45.13	*7.32*	
9	**36d**	46.6	[41.3][a]	—
		41.06	*7.81*[b]	
10	**36e**	49.2	—	28.0
		24.23		*16.82*

[a]Square brackets signify monotropic transition. [b]Enthalpy of transition on cooling.

total restriction to the rotation, even a rotation of 1°–2° from the minimum energy conformation led to a large increase to the steric energy of the conformers. The tetra-fluoro compound (series 7) gives an almost 'fixed' conformer, which must have the ability to pack in a favourable manner to induce a stabilized liquid crystal state.

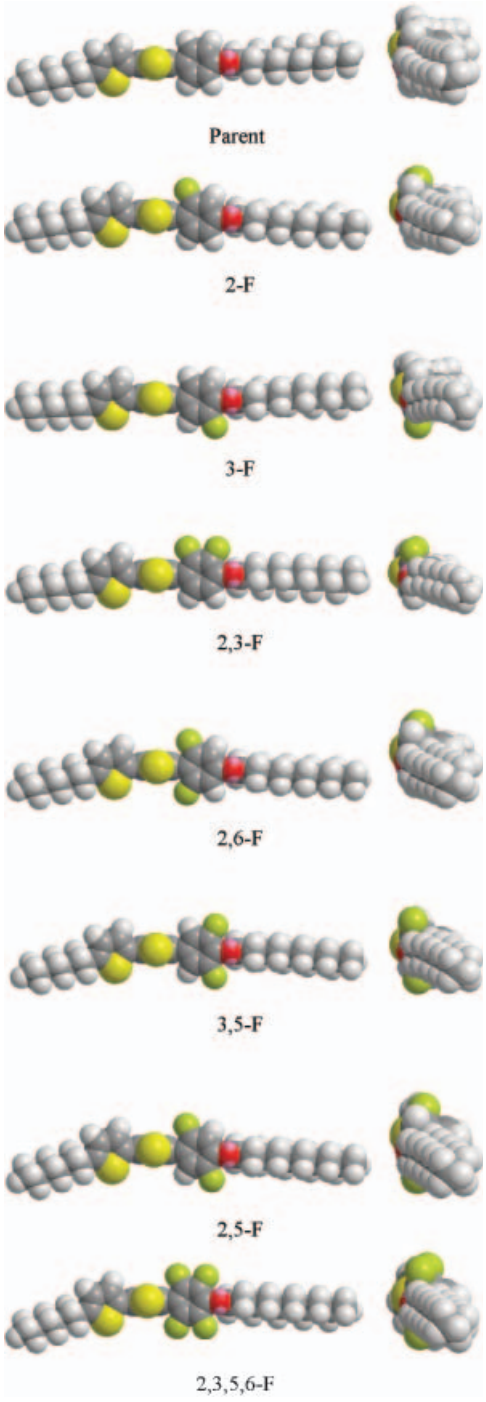
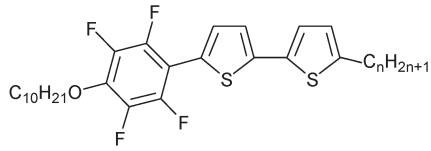


Table 7. Transition temperatures (°C) and enthalpies (in italics, $\Delta H/kJ\,mol^{-1}$) for members of series 7, **41a**–**e**.



Series 7, 41a-e

n-Alkyl	Compound	Cr–SmA/N	SmC–SmA	SmA–N	N–I
6	**41a**	41.5	—	—	57.4
		33.46			*0.80*
7	**41b**	39.3	[31.8][a]	[33.3][a]	62.4
		35.62	—[b]	—[b]	*1.01*
8	**41c**	49.1	[41.4]	[48.9][a]	62.3
		42.83	—[b]	*0.37*[c]	*1.26*
9	**41d**	45.6	—	60.5	66.3
		31.84		*0.94*	*1.79*
10	**41e**	53.2	[51.4]	65.0	66.6
		51.42	—[b]	*2.14*	*2.00*

[a]Square brackets signify monotropic transition. [b]Enthalpy of transition too small to be evaluated. [c]Enthalpy of transition on cooling.

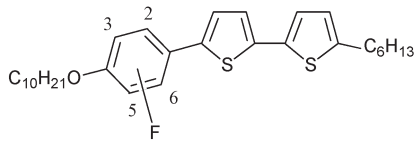
2.4. *Preliminary birefringence study*

Measurement of the birefringence of compounds (n=6–10) in series 5 was carried out using an Atago DR-M4 Abbé refractometer fitted with a 589 nm filter. Each compound from the series was dissolved in a nematic host (ZLI3086, Merck) up to 20% by weight and then the 20% mixtures were diluted to give 10% and 5% mixtures. Values of n_e and n_o were determined at four temperature intervals, 49, 40, 30 and 25°C. The calculated value of Δn was plotted against temperature and the line of best fit was used to extrapolate the birefringence of each compound. The extrapolated values are given in table 9. Solubility of the long chain analogues (n=9 and 10) became increasingly poor in the host mixture and these compounds crystallized out at low temperatures over relatively short timescales, as a result no measurements were taken at 25°C for the higher concentrations, leading to an increase in the error on extrapolation. The error on the extrapolated birefringence is ±20%.

3. Experimental

The structural integrity of the intermediates and final products was evidenced by ^{1}H NMR spectroscopy (JEOL FX60Q 270 MHz spectrometer) with tetramethylsilane as the internal standard, and infrared

Table 8. Mesomorphic properties of the $n=6$ homologue for series 1–8



Series (compound number)	Position of fluoro-substituent	m.p./°C	cl. pt/°C	Phase range/°C	Phase types
1 (**10a**)	2	82.0	99.4	17.4	SmC, N
2 (**14a**)	3	72.5	104.0	31.5	SmC, SmA, N
3 (**19a**)	2,5	93.5	—	—	—
4 (**24a**)	3,5	29.8	(21.8)	—	Monotropic SmA
5 (**30a**)	2,3	61.1	99.1	38.0	SmC, N
6 (**36a**)	2,6	30.1	(24.8)		Monotropic SmA
7 (**41a**)	2,3,5,6	41.5	57.4	16.1	N
8[a]	—	83.8	128.8	45.0	CrG, SmF, SmC

[a]See [34].

spectroscopy (Perkin-Elmer FT1605 spectrophotometer). Mass spectra were determined with a Finnigan MAT ITMS spectrometer.

3.1. *2,2′-Bithienyl 2 (scheme 1)*

In an inert atmosphere of nitrogen, a solution of commercial 2-bromothiophene **1** (40.0 g, 245 mmol) in dry diethyl ether (200 ml) was added dropwise to a suspension of magnesium turnings (7.1 g, 294 mmol) in dry diethyl ether (50 ml) at such a rate that the solvent boiled gently. On complete addition, the reaction mixture was maintained at gentle reflux for a further 1 h and cooled to 0°C. The resultant intermediate Grignard reagent **1a** was added dropwise to a mixture of 2-bromothiophene **1** (33.0 g, 202 mmol), [1,3-*bis* (diphenylphosphino)propane]nickel(II) chloride (1.1 g, 2 mmol) and dry diethyl ether (100 ml) maintained at 0°C. After stirring for 3 h at room temperature the reaction mixture was cooled (−10°C), quenched with saturated ammonium chloride solution (300 ml) and transferred to a separating funnel. The organic layer was isolated whilst the aqueous layer was extracted with diethyl ether (2×200 ml). The combined organic fractions were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The resultant crude product was purified by Claisen distillation to afford 2,2′-bithiophene **2** (31.6 g, 94%), as a colourless liquid, b.p. 98–103°C/0.2 mm Hg, which crystallized on standing as pale green plates, m.p. 31–32°C (lit. [28] 33°C). IR ν_{max} (KBr)/cm^{-1} 3104m, 3063m (arom. C–H str.), 1416 (C=C str.), 828s, 698s (C–H o.o.p.d). δ_H (270 MHz; $CDCl_3$; Me_4Si) 6.9–7.2 (6 H, m, ThH).

Table 9. Extrapolated birefringence values for compounds of series 5.

	Temperature interval			
Chain length, n	49	40	30	25
6	0.2024	0.2232	0.2396	0.2392
7	0.1796	0.1912	0.2106	0.2111
8	0.1756	0.1875	0.2111	0.2140
9	0.1730	0.1875	0.2004	0.2105
10	0.1729	0.1774	0.2041	0.2201

3.2. *5-n-Alkanoyl-2,2′-bithienyls 3a–e (scheme 1)*

Titanium(IV) chloride (2.6 ml, 24 mmol) was added, portionwise, to a cooled (−10°C), stirred solution of the appropriate acid chloride (24 mmol) and 2,2′-bithienyl **2** (3.3 g, 20.0 mmol) in dry CH_2Cl_2. The reaction mixture was stirred for 4 h at room temperature, poured on to a mixture of ice (50 g) and concentrated HCl (50 ml) and allowed to stir for 1 h. The crude product was extracted with CH_2Cl_2 (3×50 ml) and the combined organic extracts were washed with saturated sodium hydrogen carbonate solution (3×100 ml), water (2×100 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude residue recrystallised from ethanol to yield the pure 5-*n*-alkanoyl-2,2′-bithienyls **3a**–**e** (70–85%), as a

pale yellow solid: **3a**, COC_5H_{11}, m.p. 75–76°C; **3b**, COC_6H_{13}, m.p. 83–84°C; **3c**, COC_7H_{15}, m.p. 75–77°C ; **3d**, COC_8H_{17}, m.p. 76–77°C; **3e**, COC_9H_{19}, m.p. 78–80°C.

The following spectroscopic data refer to 5-*n*-decanoyl-2,2′-bithienyl **3e** and are typical of the series: ν_{max} (KBr)/cm^{-1} 3104m, 3063m (C–H str.), 2921s, 2852s (aliph. C–H str), 1651 (C=O str.), 801s, 696s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.8 (14 H, m, $7 \times CH_2$), 2.9 (2 H, t, $COCH_2CH_2$–), 7.0–7.5 (5 H, m, ThH).

3.3. *5-n-Alkyl-2,2′-bithienyls 4a–e (scheme 1)*

A mixture of the appropriate ketone **3a**–**e** (10.0 mmol), hydrazine hydrate (5 ml, 100 mmol) and ethylene glycol (100 ml) was heated gradually to reflux condition over a 2 h period. The excess of hydrazine hydrate was then removed by atmospheric distillation. The reaction temperature was raised 210°C for 1 h, cooled to room temperature and potassium hydroxide pellets (11.2 g, 200 mmol) were added. The reaction mixture was re-heated to reflux for 3 h and then poured onto a mixture of ice (50 g) and concentrated HCl (50 ml). The crude product was extracted in to $CHCl_3$ (3×100 ml), which was washed with water (2×100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by vacuum distillation (Kugelrohr) to afford the 5-*n*-alkyl-2,2′-bithienyl **4a**–**e** (70–80%), as a pale yellow oil: **4a**, C_6H_{13}, b.p. 155/0.2; **4b**, C_7H_{15}, b.p. 170/0.3; **4c**, C_8H_{17}, b.p.195/0.1; **4d**, C_9H_{19}, b.p. 205/0.1; **4e**, $C_{10}H_{21}$, b.p. 210°C/0.1 mm Hg.

The following spectroscopic data refer to 5-*n*-octyl-2,2′-bithienyl **4c** and are typical of the series: ν_{max} (KBr)/cm^{-1} 2974s, 2925s (C–H str), 1452w (aliph. C–H def.), 880m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.7 (12 H, m, $6 \times CH_2$), 2.7 (2 H, t, ThCH_2CH_2–), 6.6–7.1 (5 H, m, ThH).

3.4. *5-n-Alkyl-5′-bromo-2,2′-bithienyls 5a–e (scheme 1)*

In an inert atmosphere of nitrogen, 1.6M butyl lithium (8 ml, 12 mmol) was injected into a cooled (−10°C) solution of the appropriate 5-*n*-alkyl-2,2′-bithienyl **4a**–**e** (10 mmol) in dry THF (60 ml). The reaction mixture was allowed to warm to room temperature and maintained thus for 1 h. The reaction mixture was then cooled (−78°C) and bromine (0.5 ml, 10 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight and quenched with water (100 ml). The crude product was extracted with $CHCl_3$ (2×50 ml) and the combined organic extract was washed with 2M aqueous sodium hydroxide (100 ml), water (100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude residue was vacuum distilled (Kugelrohr) to furnish pure **5a**–**e** (66–81%), as a pale yellow oil which solidified on standing: **5a**, C_6H_{13}, b.p. 190/0.4; **5b**, C_7H_{15}, b.p. 200/0.3; **5c**, C_8H_{17}, b.p. 240/0.1; **5d**, C_9H_{19}, b.p. 245°C/0.1 mm Hg; **5e**, $C_{10}H_{21}$, m.p. 43–44°C.

The following spectroscopic data refer to 5-bromo-5′-decyl-2,2′-bithienyl **5e** and are typical of the series: ν_{max} (KBr)/cm^{-1} 3061w, 2952s, 2920s (C–H str), 1428w (aliph. C–H def.), 802m, 786s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si): 0.9 (3 H, t, CH_3), 1.2–1.8 (16 H, m, $8 \times CH_2$), 2.8 (2 H, t, ThCH_2CH_2–), 6.6–7.2 (4 H, m, ThH).

3.5. *1-n-Decyloxy-3-fluorobenzene 7 (scheme 1)*

A vigorously stirred mixture of commercial 3-fluorophenol **6** (20.0 g, 178 mmol), 1-bromodecane (43.0 g, 196 mmol), dry acetone (200 ml) and anhydrous potassium carbonate (54.0 g, 392 mmol) was heated under continuous reflux for 24 h. Thereafter, the cooled reaction mixture was filtered to remove inorganic salts (discarded) and filtrate was evaporated to dryness *in vacuo* to remove the acetone. The resultant crude residue was taken up in diethyl ether (100 ml), washed with water (100 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Vacuum distillation (Claisen) of the residue furnished the pure compound **7** (24.3 g, 90%), b.p. 162°C/0.1 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 2927s, 2855s (C–H str), 1590 (C=C str.), 1489s, 1468s (aliph. C–H def.), 1244 (C–O str.), 822m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.5 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 3.9 (2 H, t, ArOCH_2CH_2–), 6.8–7.3 (4 H, dd, ArH).

3.6. *4-Bromo-3-decyloxy-1-fluorobenzene 8 (scheme 1)*

A solution of bromine (4.1 ml, 80 mmol) in dry $CHCl_3$ (50 ml) was added dropwise to a stirred solution of 1-*n*-decyloxy-3-fluorobenzene **7** (20.0 g, 80 mmol) in dry $CHCl_3$ (50 ml) maintained at 20°C. After addition, the reaction temperature was raised to 35°C and maintained for 3 h. It was then cooled to room temperature, washed with brine (2×100 ml), 10% aqueous sodium hydroxide solution (2×100 ml), water (2×100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. Vacuum distillation (Kugelrohr) of the crude residue furnished compound **8** (23.6 g, 89%), b.p. 175°C/0.1 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 2922s, 2853s (C–H str), 1604s, 1583s (C=C str.), 1489s, 1468s (aliph. C–H def.), 1291s (C–O str.), 832s, 794s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, $7 \times CH_2$), 1.8

(2 H, quint., CH_2), 3.9 (2 H, t, ArOCH_2CH_2–), 6.6 (2 H, m, ArH), 7.3 (1 H, t, ArH).

3.7. *4-n-Decyloxy-2-fluorophenylboronic acid 9 (scheme 1)*

In an inert atmosphere of nitrogen, 1.6M butyl lithium (41.8 ml, 67 mmol) was injected into a cooled (−78°C), stirred solution of 4-bromo-3-*n*-decyloxy-1-benzene **8** (20.0 g, 60 mmol) in dry THF (100 ml). After addition, the reaction temperature was maintained at −78°C for 1 h, followed by the addition of trimethyl borate (20.8 ml, 180 mmol) and allowed to warm to room temperature overnight. The reaction was cooled (0°C), acid quenched (4M HCl, 100 ml) and extracted into diethyl ether (3 × 100 ml). The combined organic extract was washed with water (100 ml), dried ($MgSO_4$) and solvent removed under reduced pressure. The crude residue was recrystallized from light petroleum ether (b.p. 40–60°C) to yield compound **9** (16.4 g, 93%), m.p. 87–89°C, as a white solid. ν_{max} (KBr)/cm^{-1} 3700–3200s (br O–H str.), 2924s, 2853s (C–H str), 1622s, 1567s (C=C str.), 1432m (aliph. C–H def.), 1350s (O–H def.), 1291s (O–H str.), 842m, 649m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, 7 × CH_2), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.4–6.8 (2 H, m, ArH), 7.7 (1 H, t, ArH). No OH signal observed.

3.8. *5-n-alkyl-5′-(4-n-decyloxy-2-fluorophenyl)-2,2′-bithienyls 10a–e (scheme 1, series 1)*

In an atmosphere of nitrogen, a solution of 4-*n*-decyloxy-2-fluorophenylboronic acid **9** (0.63 g, 2.14 mmol) in ethanol (10 ml) was added in one portion to a vigorously stirred mixture of the appropriate 5-*n*-alkyl-5′bromo-2,2′-bithienyl **5a**–**e** (1.2 mmol), *tetrakis*(triphenylphosphine)palladium(0) (0.3 mol%), 2M aqueous sodium carbonate (30 ml) and 1,2-dimethoxyethane (15 ml). The resultant reaction mixture was heated under reflux for several hours whilst its progress was monitored by thin layer chromatography. Once deemed complete, the reaction mixture was cooled and the product extracted into diethyl ether (3 × 50 ml). The combined organic extract was washed with water (50 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The resulting crude residue was purified by column chromatography on silica gel eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from 9/1 ethanol/ethyl acetate to afford compound **10a**–**e** (series 1) (30–40%), as pale yellow solids. The melting points and mesomorphic transition temperatures of members of series 1 are listed in table 1.

The following spectroscopic data refer to 5-*n*-nonyl-5′-(4-*n*-decyloxy-2-fluorophenyl)-2,2′-bithienyl **10d** and are typical of the series. Found: C, 73.00; H, 8.69. $C_{33}H_{47}FOS_2$ requires C, 73.02; H, 8.73%. ν_{max} (KBr)/cm^{-1} 2915s (C–H str.), 1622m, 1575m, 1240s (C–O str.), 840s, 797s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, 2 × CH_3), 1.2–1.7 (30 H, m, 15 × CH_2), 2.8 (2 H, t, ThCH_2CH_2–), 4.0 (2 H, t, ArOCH_2CH_2), 6.65 (3 H, m, ArH), 7.0 (1 H, d, ArH), 7.10 (1 H, d, ArH), 7.25 (1 H, m, ArH), 7.5 (1 H, t, ArH).

3.9. *4-Bromo-1-n-decyloxy-2-fluorobenzene 12 (scheme 2)*

Alkylation of commercial 4-bromo-2-fluorophenol **11** (15.0 g, 78 mmol) with 1-bromodecane (24.3 g, 110 mmol), in dry acetone (200 ml) and anhydrous potassium carbonate (32.2 g, 234 mmol) was achieved using a similar procedure to that described for compound **7**. After work-up, vacuum distillation of the crude product afforded the pure compound **12** (25.8 g, 95%), b.p. 155–160°C/0.1 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 2924s, 2853s (C–H str), 1606s, 1576s (C=C str.), 1484s, 1404s (aliph. C–H def.), 1262s (C–O str.), 880s, 860m, 814s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, 7 × CH_2), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.8 (1 H, t, ArH), 7.2 (2 H, t, ArH).

3.10. *4-n-Decyloxy-3-fluorophenylboronic acid 13 (scheme 2)*

This preparation was effected using the procedure described for 4-n-decyloxy-2-fluorophenylboronic acid **9**. Quantities: compound **12** (15.0 g, 45 mmol); 1.6M *n*-BuLi (30.9 ml, 50 mmol); trimethyl borate (15.6 ml, 135 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 60–80°C) to furnish compound **13** (12.3 g, 93%), m.p. 79–81°C, as a white solid. ν_{max} (KBr)/cm^{-1} 3600–3000s (br O–H str.), 2924s, 2851s (C–H str), 1612s (C=C str.), 1423m (aliph. C–H def.), 1376s (O–H def.), 1273s (O–H str.), 820m, 739m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, 7 × CH_2), 1.9 (2 H, quint., CH_2), 4.1 (2 H, t, ArOCH_2CH_2–), 7.1 (1 H, t, ArH), 7.9 (2 H, m, ArH). No OH signal observed.

3.11. *5-n-Alkyl-5′-(4-n-decyloxy-3-fluorophenyl)-2,2′-bithienyls 14a–e (scheme 2, series 2)*

Compounds **14a**–**e** were prepared using analogous methodology to the synthesis of compounds **10a**–**e** (series 1). Quantities: compound **13** (2.14 mmol);

5-*n*-alkyl-5′-bromo-2,2′-bithienyl **5a**–**e** (1.2 mmol); *tetrakis*(triphenylphosphine)palladium(0) (0.3 mol%), 2M aqueous sodium carbonate (30 ml); 1,2-dimethoxyethane (15 ml). The resulting crude residue was purified by column chromatography on silica gel, eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from a mixture of 9/1 ethanol/ethyl acetate to afford the pure compounds **14a**–**e** (35–50%), as pale yellow solids. The melting points and mesomorphic transition temperatures of members of series 2 are listed in table 2.

The following spectroscopic data refer to 5-*n*-hexyl-5′-(4-*n*-decyloxy-3-fluorophenyl)-2,2′-bithienyl **14a** and are typical of the series. Found: C, 71.53; H, 8.59. $C_{30}H_{41}FOS_2$ requires C, 71.94; H, 8.27%; ν_{max} (KBr)/cm^{-1} 2955m, 2919s, 2850s (C–H str.), 1538m, 1516m, 1283s (C–O str.), 868m, 850m, 793s (C–H o.o.p.d). δ_H (270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, $2 \times CH_3$), 1.2–1.7 (24 H, m, $12 \times CH_2$), 2.8 (2 H, t, ThCH_2CH_2–), 4.0 (2 H, t, ArOCH_2CH_2–), 6.65 (1 H, d, ArH), 7.0 (3 H, m, ArH), 7.3 (3 H, m, ArH).

3.12. *1-n-Decyloxy-2,5-difluorobenzene 16 (scheme 3)*

Alkylation of commercial 2,5-difluorophenol **15** (10.0 g, 77 mmol) with 1-bromodecane (18.7 g, 85 mmol), in dry acetone (200 ml) and anhydrous potassium carbonate (31.8 g, 231 mmol) was achieved using a similar procedure to that described for the preparation of 1-decyloxy-3-fluorobenzene **7**. After work-up, the crude product was purified by vacuum distillation to furnish compound **16** (18.5 g, 89%), b.p. 120–121°C/0.1 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 2926s, 2854s (C–H str), 1616s, 1506s (C=C str.), 1468s, 1407s (aliph. C–H def.), 1388, 1272s (C–O str.), 865s, 824m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.5 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.5 (1 H, m, ArH), 6.7 (1 H, m, ArH), 6.9 (1 H, m, ArH).

3.13. *4-Bromo-1-n-decyloxy-2,5-difluorobenzene 17 (scheme 3)*

Bromination was effected using a similar method to that described for the preparation of 4-bromo-3-decyloxy-1-fluorobenzene **8**. Quantities: bromine (2.8 ml, 55 mmol) in dry $CHCl_3$ (50 ml); compound **16** (15.0 g, 55 mmol) in dry $CHCl_3$ (50 ml) maintained at 20°C. After work-up, the crude product was vacuum distilled to afford compound **17** (13.1 g, 68%), b.p. 160–162°C/2 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 2926s, 2854s (C–H str), 1616s, 1506s (C=C str.), 1468s (aliph. C–H def.), 1272s (C–O str.), 865s, 824s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.5 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.7 (1 H, dd, ArH), 7.2 (1 H, dd, ArH).

3.14. *4-n-Decyloxy-2,5-difluorophenylboronic acid 18 (scheme 3)*

This preparation was effected using the procedure described for 4-*n*-decyloxy-2-fluorophenylboronic acid **9**. Quantities: compound **17** (12.0 g, 34 mmol); 1.6M *n*-BuLi (23.4 ml, 37 mmol); trimethyl borate (11.8 ml, 102 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 40–60°C) to furnish compound **18** (9.9 g, 93%), m.p. 112–113°C, as a white solid. ν_{max} (KBr)/cm^{-1} 3700–3000s (br O–H str.), 2953s, 2922s, 2850m (C–H str), 1628s, 1518s (C=C str.), 1432s, 1397s, 1272s (O–H str.), 832m, 776m, 717m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.2 (2 H, s, OH; disappears on D_2O), 6.6 (1 H, dd, ArH), 7.4 (1 H, dd, ArH).

3.15. *5-n-Alkyl-5′-(4-n-decyloxy-2,5-difluorophenyl)-2,2′-bithienyls 19a–e (scheme 3, series 3)*

Compounds **19a**–**e** were prepared using analogous methodology to the synthesis of compounds **10a**–**e** (series 1). Quantities: compound **18** (0.63 g, 2.01 mmol); compounds **5a**–**e** (1.2 mmol); *tetrakis*(triphenylphosphine)palladium(0) (0.3 mol%), 2M aqueous sodium carbonate (25 ml); 1,2-dimethoxyethane (25 ml). The resulting crude residue was purified by column chromatography on silica gel, eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from a mixture of 9/1 ethanol/ethyl acetate to afford the pure compounds **19a**–**e** (35–55%), as pale yellow solids. The melting point and mesomorphic transition temperatures of members of series 3 are listed in table 3.

The following spectroscopic data refer to 5-*n*-heptyl-5′-(4-*n*-decyloxy-2,5-difluorophenyl)-2,2′-bithienyl **19b** and are typical of the series. Found: C, 69.98; H, 8.04. $C_{31}H_{42}F_2OS_2$ requires C, 69.87; H, 7.96%. ν_{max} (KBr)/cm^{-1} 2955m, 2932s, 2852s (C–H str.), 1632m, 1534m, 1514m, 1467m, 1277s (C–O str.), 866m, 792s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si): 0.9 (6 H, t, $2 \times CH_3$), 1.2–1.7 (26 H, m, $13 \times CH_2$), 2.8 (2 H, t, ThCH_2CH_2–), 4.0 (2 H, t, ArOCH_2CH_2–), 6.75 (2 H, m, ArH), 7.0 (2 H, m, ArH), 7.25 (2 H, m, ArH).

3.16. *4-Bromo-2,6-difluorophenol 21 (scheme 4)*

A solution of *N*-bromosuccinimide (34.0 g, 192 mmol) in dry DMF (150 ml) was added dropwise to a solution of commercial 2,6-difluorophenol **20** (25.0 g, 192 mmol) in dry DMF and stirred for 24 h at room temperature.

Thereafter, the reaction was poured into water (500 ml) and the crude product extracted with $CHCl_3$ (3 × 150 ml). The combined organic extract was washed with water (2 × 100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo* to yield compound **21** (38.2 g, 95%), which was used without further purification. ν_{max} (film)/cm^{-1} 3650–3100 (br OH str.), 2926w (C–H str), 1601s, 1495s (C=C str.), 1348s (aliph. C–H def.), 1283s, 1218s (C–O str. or O–H def.), 881s, 857s, 576 (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.3 (1 H, s, OH), 7.2 (2 H, m, ArH).

3.17. *1-Bromo-4-n-decyloxy-3,5-difluorobenzene 22 (scheme 4)*

Alkylation of compound **21** (35.0 g, 167 mmol) with 1-bromodecane (51.7 g, 234 mmol), in dry acetone (400 ml) and anhydrous potassium carbonate (69.1 g, 501 mmol) was achieved using a similar procedure to that described for the preparation of compound **7**. After work-up, vacuum distillation of the crude product afforded the pure compound **22** (53.6 g, 92%), b.p. 162–166°C/0.8 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 3098w, 2928s, 2856s (C–H str), 1582, 1500s (C=C str.), 1468s, 1424s (aliph. C–H def.), 1237s (C–O str.), 880s, 864m, 841s, 778m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.5 (14 H, m, 7 × CH_2), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 7.0 (2 H, m, ArH).

3.18. *4-n-Decyloxy-3,5-difluorophenylboronic acid 23 (scheme 4)*

This preparation was effected using the procedure described for 4-n-decyloxy-2-fluorophenylboronic acid **9**. Quantities: compound **22** (10.0 g, 29 mmol); 2.5M *n*-BuLi (12.8 ml, 32 mmol); trimethyl borate (10.1 ml, 87 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 60–80°C) to furnish compound **23** (8.5 g, 94%), m.p. 56°C, as a white solid. ν_{max} (KBr)/cm^{-1}: 3600–3000s (br O–H str.), 2923s, 2853m (C–H str), 1583s (C=C str.), 1451s, 1421s, 1360s (O–H def.), 1230m, 814m, 772m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.5 (14 H, m, 7 × CH_2), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 5.5 (2 H, s, OH; disappears on D_2O), 7.0 (2 H, m, ArH).

3.19. *5-n-Alkyl-5′-(4-n-decyloxy-3,5-difluorophenyl)-2,2′-bithienyls 24a–e (scheme 4, series 4)*

Compounds **24a**–**e** were prepared using analogous methodology to that for the synthesis of compounds **10a**–**e** (series 1). Quantities: compound **23** (0.63 g, 2.01 mmol); 5-n-alkyl-5′-bromo-2,2′-bithienyl **5a**–**e** (1.2 mmol); *tetrakis*(triphenylphosphine)palladium(0) (0.3 mol%); 2M aqueous sodium carbonate (30 ml); 1,2-dimethoxyethane (15 ml). The resulting crude residue was purified by column chromatography on silica gel, eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from a mixture of 9/1 ethanol/ethyl acetate to afford the pure compounds **24a**–**e** (30–45%), as pale yellow solids. The melting points and mesomorphic transition temperatures of members of series 4 are listed in table 4.

The following spectroscopic data refer to compound **24b** and are typical of the series. Found: C, 69.98; H, 8.15. $C_{31}H_{42}F_2OS_2$ requires C, 69.87; H, 7.96%. ν_{max} (KBr)/cm^{-1} 2954m, 2923s, 2852s (C–H str.), 1590w, 1501m, 1456s, 1230s (C–O str.), 877w, 792m, 721w (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, 2 × CH_3), 1.2–1.7 (26 H, m, 13 × CH_2), 2.8 (2 H, t, ThCH_2CH_2–), 4.1 (2 H, t, ArOCH_2CH_2–), 6.70 (1 H, d, ArH), 6.9 (1 H, t, ArH), 7.0 (1 H, d, ArH), 7.10 (1 H, d, ArH), 7.25 (2 H, m, ArH).

3.20. *2,3-Difluorophenylboronic acid 26 (scheme 5)*

This preparation was effected using the procedure described for compound **9**. Quantities: commercial 1,2-difluorobenzene **25** (20.0 g, 175 mmol); 2.5M *n*-BuLi (77.0 ml, 193 mmol); trimethyl borate (60.7 ml, 525 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 40–60°C) to yield compound **26** (26.1 g, 95%), m.p. 230°C dec, as a white solid. ν_{max} (KBr)/cm^{-1} 3600–3000s (br O–H str.), 1625s, 1472s (C=C str.), 1374s (O–H def.), 826s, 744s, 678s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.1 (2 H, s, OH; disappears on D_2O), 7.1 (2 H, m, ArH), 7.6 (1 H, t, ArH).

3.21. *2,3-Difluorophenol 27 (scheme 5)*

Hydrogen peroxide (30%, 50 ml) was added dropwise to a stirred solution of compound **26** (26.0 g, 164 mmol) in diethyl ether (200 ml) at such a rate that gentle reflux was maintained. Thereafter, the reaction was heated at reflux for 1 h and cooled. The crude product was extracted into diethyl ether (2 × 100 ml), washed with 10% aqueous ammonium ferrous sulphate solution (4 × 50 ml), water (100 ml), dried ($MgSO_4$) and the solvent was removed under pressure. The resultant crude residue was vacuum distilled to furnish 2,3-difluorophenol **27** (17.1 g, 79%), b.p. 60°C/15 mm Hg (Lit., m.p. 34–36°C), as a colourless liquid. ν_{max} (film)/cm^{-1} 3600–3200s (br O–H str.), 1628s, 1510s, 1479s (C=C str.), 1377s, 1306s, 1252s (O–H def.), 820s, 771s, 705s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.4 (1 H, s, OH; disappears on D_2O), 6.6–6.8 (2 H, m, ArH), 7.0 (1 H, m, ArH).

3.22. *1-Decyloxy-2,3-difluorobenzene 28 (scheme 5)*

Alkylation of 2,3-difluorophenol **27** (17.0 g, 131 mmol) with 1-bromodecane (40.5 g, 183 mmol), in dry acetone (250 ml) and anhydrous potassium carbonate (54.0 g, 392 mmol) was achieved using a similar procedure to that described for the preparation of compound **7**. After work-up, the crude product was purified by vacuum distillation to furnish compound **28** (26.5 g, 76%), b.p. 126–128°C/1.0 mm Hg, as a colourless oil. ν_{max} (film) 2924s, 2854s (C–H str), 1620s, 1514s (C=C str.), 1482s, 1391m (aliph. C–H def.), 1254s (C–O str.), 820s, 765s, 723s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.7 (2 H, m, ArH), 6.9 (1 H, m, ArH).

3.23. *4-n-Decyloxy-2,3-difluorophenylboronic acid 29 (scheme 5)*

This preparation was effected using the procedure described for compound **9**. Quantities: compound **28** (20.0 g, 74 mmol); 2.5M *n*-BuLi (32.4 ml, 81 mmol); trimethyl borate (25.7 ml, 222 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 40–60°C) to afford compound **29** (19.1 g, 83%), m.p. 99–103°C, as a white solid. ν_{max} (KBr)/cm^{-1} 3600–3000s (br O–H str.), 2954s, 2923, 2850m (C–H str), 1625s, 1519s (C=C str.), 1468s, 1362s (O–H def.), 1305m, 817m, 778s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 5.5–5.9 (2 H, br. s, OH; disappears on D_2O), 6.7 (1 H, t, ArH), 7.4 (1 H, t, ArH).

3.24. *5-n-Alkyl-5′-(4-n-decyloxy-2,3-difluorophenyl)-2,2′-bithienyls 30a–e (scheme 5, series 5)*

Compounds **30a–e** were prepared using analogous methodology to that for the synthesis of compounds **10a–e** (series 1). Quantities: compound **29** (0.63 g, 2.01 mmol); 5-*n*-alkyl-5′-bromo-2,2′-bithienyl **5a–e** (1.2 mmol); *tetrakis*(triphenylphosphine)palladium(0) (0.3 mol%), 2M aqueous sodium carbonate (30 ml); 1,2-dimethoxyethane (25 ml). The resulting crude residue was purified by column chromatography on silica gel, eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from a mixture of 9/1 ethanol/ethyl acetate to afford the pure compounds **30a–e** (30–45%), as pale yellow solids. The melting point and mesomorphic transition temperatures of members of series 5 are listed in table 5.

The following spectroscopic data refer to compound **30d** and are typical of the series. Found: C, 70.52; H, 8.32. $C_{33}H_{46}F_2OS_2$ requires C, 70.68; H, 8.27%. ν_{max} (KBr)/cm^{-1} 2918s, 2850s (C–H str.), 1513m, 1493m, 1290s (C–O str.), 797s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, $2 \times CH_3$), 1.2–1.7 (30 H, m, $15 \times CH_2$), 2.8 (2 H, t, ThCH_2CH_2–), 4.0 (2 H, t, ArOCH_2CH_2–), 6.70 (2 H, m, ArH), 7.0 (1 H, d, ArH), 7.1 (1 H, d, ArH), 7.25 (2 H, m, ArH).

3.25. *3,5-Difluorophenylboronic acid 32 (scheme 6)*

This preparation was effected using the procedure described for compound **9**. Quantities: commercial 1-bromo-3,5-difluorobenzene **31** (30.0 g, 155 mmol); 2.5M *n*-BuLi (68.4 ml, 171 mmol); trimethyl borate (53.7 ml, 465 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 40–60°C) to yield compound **32** (23.1 g , 95%), m.p. 106–108°C, as a white solid. ν_{max} (KBr)/cm^{-1} 3600–3200s (br O–H str.), 1625s, 1565m, 1460s (C=C str.), 1349s (O–H def.), 792s, 631w (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 4.8–5.3 (2 H, br s, OH; disappears on D_2O), 6.9 (2 H, t, ArH), 7.4 (1 H, m, ArH).

3.26. *3,5-Difluorophenol 33 (scheme 6)*

3,5-Difluorophenol **33** was prepared using methods analogous to those for the synthesis of 2,3-difluorophenol **27**. Quantities: compound **32** (23.0 g, 146 mmol); hydrogen peroxide (30%, 50 ml); diethyl ether (150 ml). Vacuum distillation of the crude residue afforded 3,5-difluorophenol **33** (15.4 g, 81%), b.p. 80°C/15 mm Hg, as a colourless liquid. ν_{max} (film)/cm^{-1} 3650–3200s (br O–H str.), 3082m, 1600s, 1506s, 1480s (C=C str.), 1292s, 1244s (O–H def.), 841s, 770s, 705s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 5.6–6.0 (1 H, s, OH; disappears on D_2O), 6.8 (2 H, m, ArH), 7.0 (1 H, m, ArH).

3.27. *1-Decyloxy-3,5-difluorobenzene 34 (scheme 6)*

Alkylation of 3,5-difluorophenol **33** (15.0 g, 115 mmol) with 1-bromodecane (35.6 g, 161 mmol), in dry acetone (250 ml) and anhydrous potassium carbonate (47.6 g, 392 mmol) was achieved using a similar procedure to that described for the preparation of compound **7**. After work-up, the crude product was purified by vacuum distillation to furnish compound **34** (24.5 g 79%), b.p. 130°C/0.2 mm Hg, as a colourless oil. ν_{max} (film)/cm^{-1} 2925s, 2855s (C–H str), 1595s, 1498s (C=C str.), 1475s, 1425m (aliph. C–H def.), 1292s (C–O str.), 841s, 778s, 707s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.0 (2 H, t, ArOCH_2CH_2–), 6.8 (3 H, m, ArH).

3.28. *4-n-Decyloxy-2,6-difluorophenylboronic acid 35 (scheme 6)*

This preparation was effected using the procedure described for compound **9**. Quantities: compound **34** (20.0 g, 74 mmol); 2.5M *n*-BuLi (32.4 ml, 81 mmol); trimethyl borate (25.7 ml, 222 mmol). After work-up, the crude product was recrystallized from light petroleum ether (b.p. 40–60°C) to afford compound **35** (22.1 g, 95%), m.p. 67–69°C, as a white solid. ν_{max} (KBr)/cm^{-1} 3600–3150s (br O–H str.), 2955s, 2919, 2850m (C–H str), 1612s, 1590s, 1506s (C=C str.), 1452s, 1364s (O–H def.), 1284m, 824m, 795s, 661 (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.6 (14 H, m, $7 \times CH_2$), 1.8 (2 H, quint., CH_2), 4.1 (2 H, t, ArOCH_2CH_2-), 6.9 (1 H, t, ArH), 7.5 (1 H, m, ArH) ppm. No OH signal observed.

3.29. *5-n-Alkyl-5′-(4-n-decyloxy-2,6-difluorophenyl)-2,2′-bithienyls 36a–e (scheme 6, series 6)*

In an inert atmosphere (nitrogen), a solution of the appropriate 5-*n*-alkyl-5′-bromo-2,2′-bithienyl **5a–e** (2.95 mmol) and *tetrakis*(triphenylphosphine)palladium(0) (0.3 mol%) dissolved in a mixture of dry DMF (25 ml) and dry THF (25 ml) was stirred at room temperature for 0.5 h. Anhydrous sodium carbonate (0.7 g, 6.50 mmol), compound **35** (1.0 g, 3.25 mmol) and dry ethanol (5 ml) were added to the vigorously stirred mixture, which was then heated under continuous reflux for 12 h. The crude product was extracted with diethyl ether (3×50 ml) and the combined extract washed with water (100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The resulting crude residue was purified by column chromatography on silica gel, eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from a mixture of 1/4 ethyl acetate/ethanol to yield the pure compounds **36a–e** (35–50%), as pale yellow solids. The melting points and mesomorphic transition temperatures of members of series 6 are listed in table 6.

The following spectroscopic data refer to compound **36a** and are typical of the series. Found: C, 69.48; H, 7.88. $C_{30}H_{40}F_2OS_2$ requires C, 69.45; H, 7.79%. ν_{max} (KBr)/cm^{-1} 2954m, 2918s, 2850s (C–H str.), 1591w, 1504m, 1457s, 1295s (C–O str.), 794s, 726w (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, $2 \times CH_3$), 1.2–1.7 (24 H, m, $12 \times CH_2$), 2.8 (2 H, t, ThCH_2CH_2–), 4.1 (2 H, t, ArOCH_2CH_2–), 6.70 (1 H, d, ArH), 6.90 (1 H, t, ArH), 7.0 (1 H, d, ArH), 7.10 (1 H, d, ArH), 7.25 (2 H, m, ArH).

3.30. *5-(Tri-n-butyltin)-2,2′-bithienyl 37 (scheme 7)*

In an inert atmosphere (nitrogen), 2.5M butyllithium (53.0 ml, 132 mmol) was added to a cooled (0°C), stirred, solution of 2,2′-bithienyl **2** (20.0 g, 120 mmol) in dry THF (150 ml). The reaction temperature was raised and held at room temperature for 4 h, and subsequently cooled to −78°C. Tri-*n*-butyltin chloride (39.1 ml, 144 mmol) was added dropwise and on complete addition the reaction mixture was allowed to warm to room temperature. The reaction mixture was reduced to one half of its total volume *in vacuo* and light petroleum ether (b.p. 40–60°C) (100 ml) was added to effect precipitation of lithium chloride, which was removed by filtration. The filtrate was dried ($MgSO_4$) and the solvent removed *in vacuo*. Vacuum distillation of the crude residue yielded pure compound **37** (34.6 g, 63%), b.p. 210°C/0.1 mm Hg, as a pale yellow liquid. ν_{max} (film)/cm^{-1} 3074w, 2955s, 2929, 2870m (C–H str), 1464s, 1413m, 1376m, 837s, 795s, 688s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (9 H, t, $3 \times CH_3$), 1.1 (6 H, m, $3 \times CH_2$), 1.3 (6 H, m, $3 \times CH_2$), 1.6 (6 H, m, $3 \times CH_2$), 6.9–7.3 (5 H, m, ThH).

3.31. *5-Pentafluorophenyl-2,2′-bithienyl 38 (scheme 7)*

In an inert atmosphere (nitrogen), a mixture of commercial pentafluorobromobenzene (20.7 g, 84 mmol), compound **37** (34.0 g, 75 mmol), *bis*(triphenylphosphine)palladium(II) chloride (2.6 g, 3.7 mmol) and dry THF (500 ml) was heated at reflux temperature for 20 h. The reaction mixture was cooled to room temperature, poured into water (300 ml) and the crude product extracted with diethyl ether (4×100 ml). The combined organic extract was washed with water (2×100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. Vacuum sublimation (130°C/0.4 mm Hg) of the crude residue furnished the pure compound **38** (14.3 g, 57%), m.p. 140–142°C, as a yellow solid. ν_{max} (KBr)/cm^{-1} 2955s, 2870m (C–H str), 1526s, 1490m, 842m, 797s, 696s (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 7.05 (1 H, m, ThH), 7.2–7.3 (3 H, m, ThH), 7.45 (1H, m, ThH).

3.32. *5-(4-n-Decyloxy-2,3,5,6-tetrafluorophenyl)2,2-bithienyl 39 (scheme 7)*

In an inert atmosphere (nitrogen), a solution of compound **38** (10.0 g, 30 mmol) in dry pyridine (100 ml) was added dropwise to a cooled (0°C) solution of sodium decoxide (36 mmol) [prepared from sodium hydride (0.86 g, 36 mmol) and an excess of dry decanol (50 ml)]. The reaction mixture was allowed to warm to room temperature overnight and then poured into 2M aqueous hydrochloric acid (200 ml). The crude product was extracted with diethyl ether (3×100 ml), washed with water (2×100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The crude residue was purified by column chromatography on silica gel, eluting with light

petroleum ether (b.p. 40–60°C), to afford pure compound **39** (10.8 g, 76%), m.p. 39–41°C, as a pale yellow solid. ν_{max}(KBr)/cm^{-1} 2920s, 1499s, 1484s, 1390s, 1178s, 798s; δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (3 H, t, CH_3), 1.2–1.7 (14 H, m, $7\times CH_2$), 1.8 (2 H, quint., CH_2), 4.2 (2 H, t, ArOCH_2CH_2–), 7.0 (1 H, d, ThH), 7.2 (3 H, m, ThH), 7.4 (1 H, m, ThH).

3.33. *5-n-Alkanoyl-5′-(4-n-decyloxy-2,3,5,6-tetrafluorphenyl)-2,2′bithienyls 40a–e (scheme 7)*

Friedel–Crafts acylation of compound **39** was effected using a similar procedure to that described for the preparation of 5-*n*-alkanoyl-2,2′-bithienyls **3**. Quantities: compound **39** (1.0 g, 2.10 mmol), appropriate acid chloride (2.30 mmol), tin(IV) chloride (2.3 ml, 2.3 mmol). After work-up, the crude residue was purified by column chromatography on silica gel, eluting with a mixture of 7/3 light petroleum ether (b.p. 40–60°C)/CH_2Cl_2 followed by recrystallization from a mixture of 1/1 ethanol/ethyl acetate to afford the pure compounds **40a**–**e**. Transition temperatures: **40a**, C_6H_{13}, Cr 98.7 SmA 138.9 I; **40b**, C_7H_{15}, Cr 100.2 SmA 140.6 I; **40c**, C_8H_{17}, Cr 105.1 SmA 139.9 I; **40d**, C_9H_{19}, Cr 107.5 SmA 140.3 I with monotropic SmA (100.9) SmC; **40e**, $C_{10}H_{21}$, Cr 111.3 SmC 122.1 SmA 139.3°C I. The following spectroscopic data refer to 5-*n*-decanoyl-5′-(4-*n*-decyloxy-2,3,5,6-tetrafluorophenyl)-2,2′-bithienyl and are typical of the series. ν_{max} (KBr)/cm^{-1} 2094m, 2918s, 2850s (aliph. C–H str), 1664 (C=O str.), 1520m, 1483s, 1390w, 799s, 696m (C–H o.o.p.d); δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, $2\times CH_3$), 1.2–1.5 (26 H, m, $13\times CH_2$), 1.8 (4 H, m, $2\times CH_2$), 2.9 (2 H, t, COCH_2CH_2–), 4.3 (2 H, t, ArOCH_2CH_2–), 7.23 (1 H, d, ThH), 7.3 (1 H, d, ThH), 7.47 (1 H, d, ThH), 7.62 (1 H, d, ThH).

3.34. *5-n-Alkyl-5′-(4-n-decyloxy-2,3,5,6-tetrafluorophenyl)-2,2-bithienyls 41a–e (series 7, scheme 7)*

In an inert atmosphere (nitrogen), a suspension of powdered anhydrous aluminium chloride (0.37 g, 2.78 mmol) in dry diethyl ether (30 ml) was added to a stirred solution of $LiAlH_4$ (1.40 ml, 1.40 mmol) in dry diethyl ether (10 ml). On complete addition, a solution of the appropriate compound **40a**–**e** (0.55 mmol) in dry $CHCl_3$ (30 ml) was added dropwise to the reaction mixture, which was then heated under reflux for 6 h. The cooled reaction mixture was poured onto ice-cold 4M aqueous hydrochloric acid (100 ml) and extracted with diethyl ether (3×100 ml). The combined organic extract was washed with water (100 ml), dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was purified by column chromatography on silica gel, eluting with light petroleum ether (b.p. 40–60°C), followed by recrystallization from a mixture of 9/1 ethanol/ethyl acetate to yield the desired compound **41a**–**e** (series 7) (60–80%), as pale yellow crystals. The melting points and mesomorphic transition temperatures of members of series 7 are listed in table 7.

The following spectroscopic data refer to 5-*n*-nonyl-5′-(4-*n*-decyloxy-2,3,5,6-tetrafluorophenyl)-2,2′-bithienyl and are typical of the series. Found: C, 66.45; H, 7.49. $C_{33}H_{44}F_4OS_2$ requires C, 66.40; H, 7.45%. ν_{max} (KBr)/cm^{-1} 2924m, 2852s (aliph. C–H str), 1468s, 880w, 795m (C–H o.o.p.d). δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.9 (6 H, t, $2\times CH_3$), 1.2–1.5 (26 H, m, $13\times CH_2$), 1.7–1.8 (4 H, m, $2\times CH_2$), 2.8 (2 H, t, ThCH_2CH_2–), 4.2 (2 H, t, ArOCH_2CH_2–), 6.7 (1 H, d, ThH), 7.0 (1 H, d, ThH), 7.1 (1 H, d, ThH), 7.4 (1 H, d, ThH).

4. Summary

Laterally fluorinated non-linear structures comprising suitably substituted 2,2′-bithiophene can be tailored to produce mesormorphic compounds. The mesomorphic properties are dependent upon the number and disposition of lateral fluoro-substituents. Compared with their non-fluorinated parent counterparts, lateral fluorination eliminates high order smectic phases and reduces thermal stability to reveal compounds exhibiting a selection of nematic, smectic A and smectic C phase types. The disposition of two fluoro-substituents is important because across-axis disposition is evidently more detrimental to mesophase thermal stability than along-axis substitution. Complete fluorination, to our surprise, does not destroy mesomorphic properties; indeed, tetrafluorophenyl-compounds are more stable than certain 3,5- and 2,6-difluoro-compounds. Molecular modelling, albeit at a very simplistic level, reveals that the tetrafluoro-compounds have less rotational freedom and thus may be locked in a structure conducive to mesophase formation. The extrapolated birefringence for members of a series of 5-*n*-alkyl-5′-(2,3-difluoro-4-*n*-decyloxyphenyl)-2,2′-bithienyls is approximately 0.21.

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