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Synthesis and mesomorphic properties of 1,1-difluoroalkyl-substituted biphenylthienyl and terphenyl liquid crystals. A comparative study of mesomorphic behavior relative to alkyl, alkoxy and alkanoyl analogs†

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A variety of biphenylthienyl and terphenyl-based liquid crystalline materials were prepared that incorporate a 1,1-difluoropentyl terminal group. The mesogenic properties of these compounds were compared and contrasted with analogs where the CF_2 moiety was replaced by a $-CH_2-$, -O- or -CO- group. The 1,1-difluoroalkyl group is unique in its behavior and tends to promote orthogonal smectic phase behavior.

Introduction

The materials requirements for ferroelectric liquid crystal displays are stringent, and fine-tuning of the physical properties of mesogenic materials combined with careful formulation of mixtures is required for optimal results. Low viscosity, high photochemical and thermal stability, high dielectric biaxiality and a wide range of the smectic C (S_C) phase are just a few of the required characteristics for useful materials.[1–4]

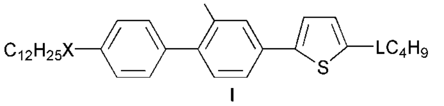
To further augment the physical properties of mesogens required for ferroelectric applications we are targeting heterocycle-based materials such as thiophenes, which possess low viscosities and large lateral dipoles that aid in increasing dielectric biaxiality. Such a property is extremely important for use in surface-stabilized liquid crystal displays that are based on either a C_1 or C_2 chevron geometry.[1,5–7] Liquid crystals containing thiophene in the rigid core are known to have lower viscosities than the corresponding phenyl derivatives and possess fast response times in the presence of an electric field.[8,9] Ideally, the thiophene ring should be substituted in the 2- and 5-positions to give the most linear architecture and therefore the highest clearing points.[10,11] A number of ferroelectric materials containing this heterocycle are known, although no sustained efforts have been reported toward improving the dielectric biaxiality of such units, possibly due to difficulties in synthesis. This paper represents our initial progress toward this goal.

In an effort to further enhance the dielectric biaxiality it was decided to incorporate a polar 1,1-difluoroalkyl unit adjacent to the thiophene core (**Ia**). This was expected to substantially improve the dielectric biaxiality of the resulting mesogens and support tilted phase behavior according to the Wulf,[12] McMillan[13] and Goodby[14] models. In addition, this group was expected to have only a small detrimental effect on the mesophase stability [relative to the pentyl analogs (**Ib**: L = CH_2)] due to the somewhat larger size of the CF_2 group *vis-à-vis* the CH_2 group.[15]

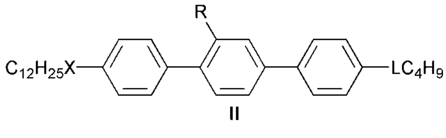
The materials targeted in this initial study are achiral and were designed to provide some insight into the types and breadth of mesophase transitions supported by the CF_2 linking unit. Other linking unit-containing thienyl materials **Ib–Id** (L = $-CH_2-$, -O-, -CO-) were also synthesized in order to allow us to better understand the influence of the $-CF_2-$ moiety. In order to assess the impact of incorporating a thiophene ring into these systems, we also targeted the analogous phenyl-containing mesogens (**II**). The corresponding laterally fluorinated analogs were also prepared and characterized in order to elucidate the influence of lateral core fluorination in such materials. An evaluation of the hydrolytic and thermal stability, and mesomorphic behavior, of all materials is presented.

Until our preliminary communication[16] there had been no reports of liquid crystals containing a 1,1-difluoroalkylthienyl moiety. In fact, there was only one article describing the incorporation of a 1,1-difluoroalkyl chain into any liquid crystalline material. Bartmann prepared one $-C_6H_4-CF_2CH_3$ and two $-C_6H_4-CF_2H$ containing mesogens.[17] Subsequent to the completion of our work, a publication by Goodby *et al.*[18] described the mesomorphic behavior of a variety of α,α-difluoro and β,β-difluoroalkylterphenyls. Unfortunately, except for general schemes, no synthetic details were presented. Even in non-liquid crystal chemistry there are remarkably few examples of the synthesis of (1,1-difluoroalkyl)arenes and, even then, compounds of general structure $ArCF_2(CH_2)_nCH_3$ when $n > 1$ are not known as far as we have been able to ascertain.[19–23]

Lateral core substituents have been used extensively to alter the mesomorphic behavior of liquid crystalline compounds. Lateral core fluorine substitution has proven to be especially useful in this area due to the relatively small size and high electronegativity of the fluorine atom.[24,25] Introduction of



I



II

a...L = CF_2
b...L = CH_2
c...L = O
d...L = C(O)

R = H,F
X = O,CH_2

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†Electronic supplementary information (ESI) available: experimental details for compounds **4**, **9**, **10**, **12**, **15–19**, **25–39**, **45** and **49**. See http://www.rsc.org/suppdata/jm/b1/b102059p/

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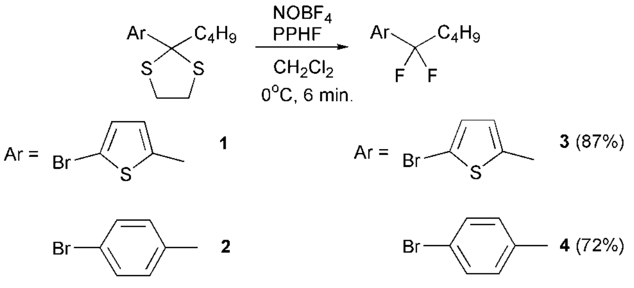
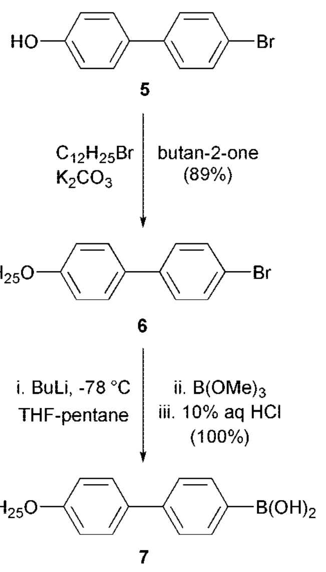
lateral fluorine substituents in terphenyl compounds *ortho* to a ring junction within the molecular core causes an inter-annular twist and disrupts conjugation. In addition, the effective molecular breadth is increased and intermolecular packing is somewhat compromised. The replacement of hydrogen with fluorine in the mesogenic core generally results in a minimal depression in the mesophase thermal stability, while often (although not always) giving rise to a drastic reduction in melting point. Additionally, higher ordered smectic phases present in many non-fluorinated materials may be suppressed or completely eliminated in laterally core fluorinated analogs, thus aiding in mixture formulation. Laterally core fluorinated terphenyls provide a particularly effective example of these effects.[26] Given the above factors we felt it prudent to additionally synthesize the laterally core-fluorinated analogs **Ia–Id** (R = F) and **IIa–IId** (R = F) and to therefore explore the impact of lateral fluorination in the (1,1-difluoropentyl)thienyl systems. Comparisons with the analogous phenyl systems and with the alkyl, alkoxy and alkanoyl analogs of both of the above cores would provide a broad survey of the impact of lateral fluorination. In line with trends observed previously with lateral fluorine substitution, we expected to see a decrease in melting points and to enhance the possibility of obtaining disordered tilted mesophases such as the smectic C phase.

Synthesis

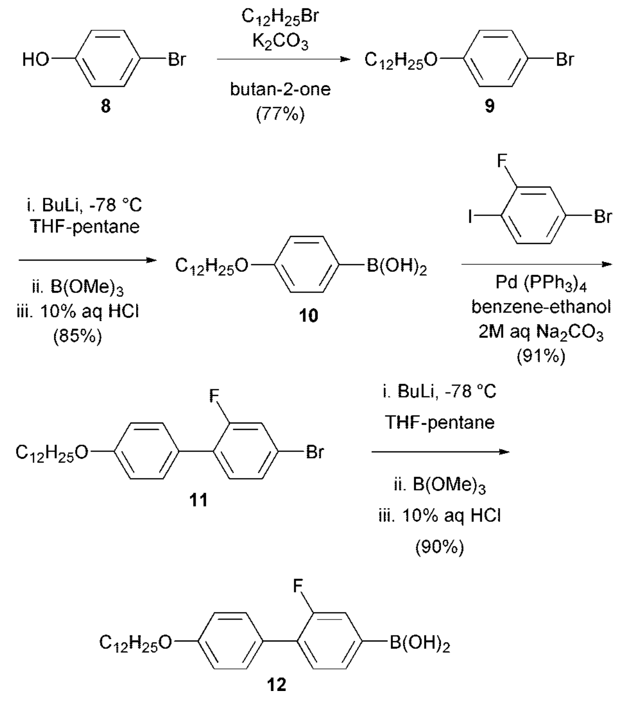
The synthesis of each target mesogen exploited a palladium-catalyzed Suzuki coupling[27,28] of suitably functionalized aryl bromide and arylboronic acid building blocks (Schemes 1–8). The key intermediates in the synthesis of the majority of our mesogenic targets were 1,1-difluoropentyl bromoaromatic building blocks **3** and **4** (Scheme 1) and biphenylboronic acids **7**, **12**, **18** and **19** (Schemes 2–4).



Scheme 1

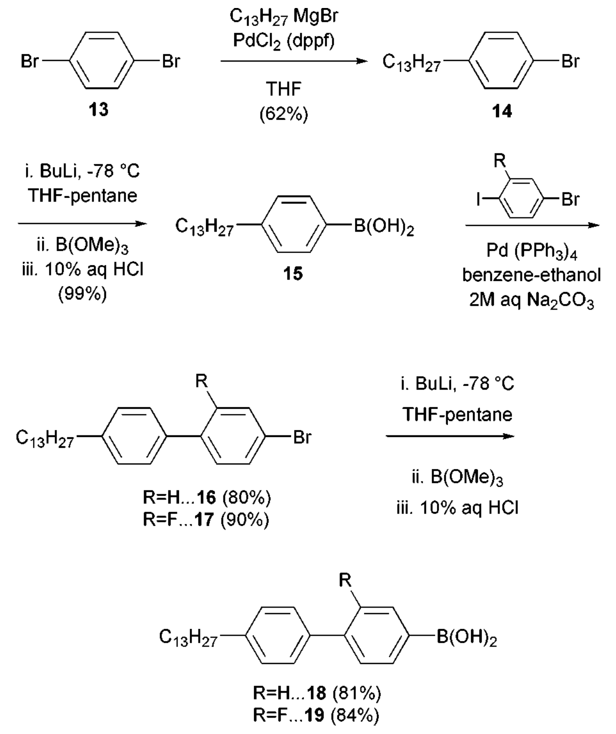


Scheme 2

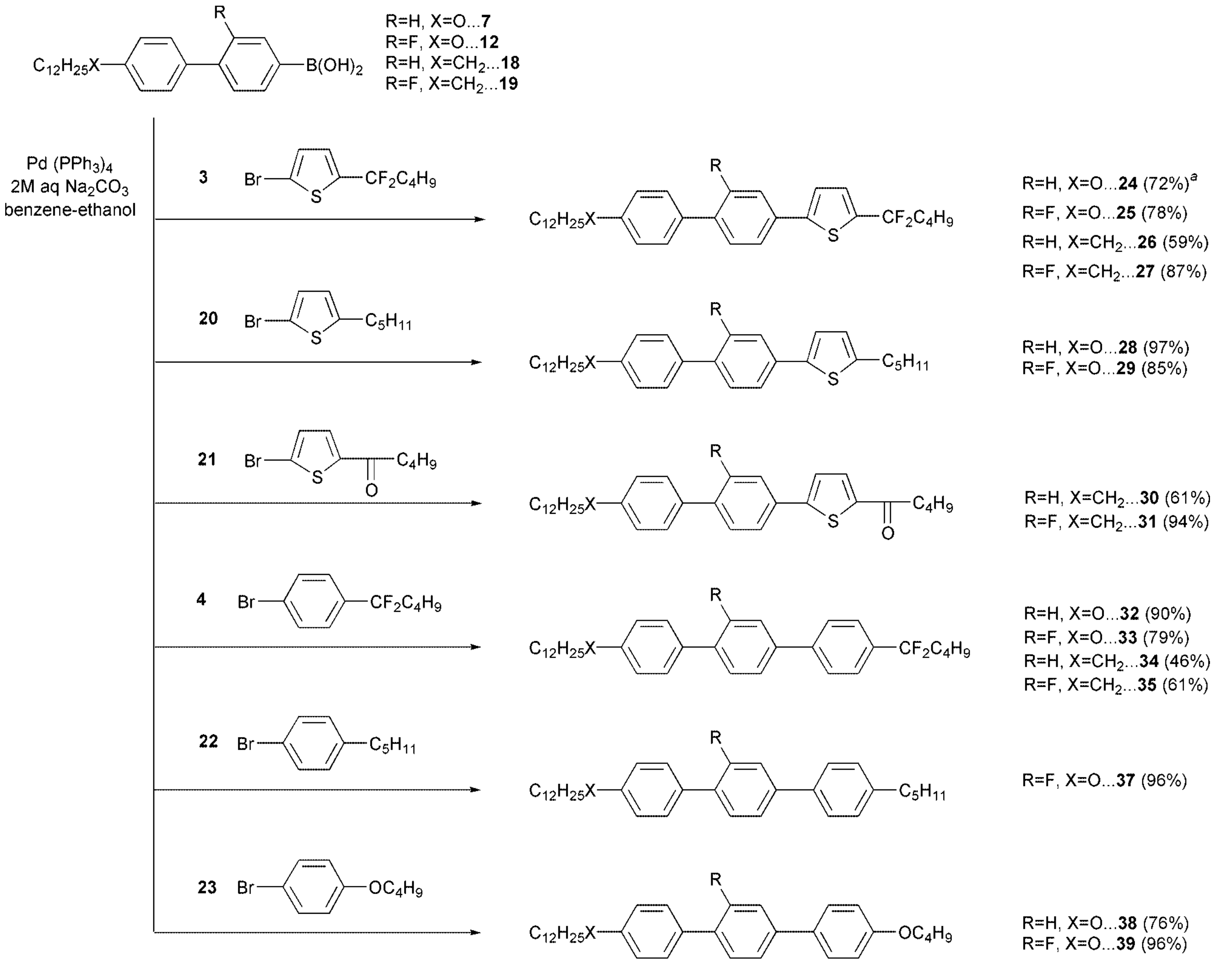


Scheme 3

Boronic acid **7** was prepared from the corresponding bromide **6**, which was obtained from the commercial 4-bromo-4′-hydroxybiphenyl using Williamson's ether synthesis (Scheme 2).[29] The intermediate aryl bromide **16** required for the synthesis of boronic acid **18** was obtained using selective[30] Suzuki coupling of 4-tridecylphenylboronic acid (**15**) with 1-bromo-4-iodobenzene (Scheme 4). The bromobenzene derivative **14** required for the synthesis of **15** was made by PdCl$_2$(dppf)-catalyzed reaction of tridecylmagnesium bromide with 1,4-dibromobenzene.[31] This procedure allowed for a one-step synthesis of the required aryl bromide **14** as compared with the more traditional two-step Friedel–Crafts acylation–Wolff–Kishner reduction procedure.[32] An analogous strategy was employed in the synthesis of



Scheme 4



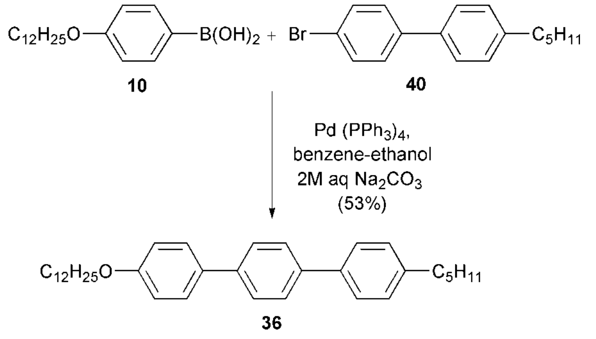
[a] Reagents used were 0.1M aq $PdCl_2$, 2M aq Na_2CO_3, acetone

Scheme 5

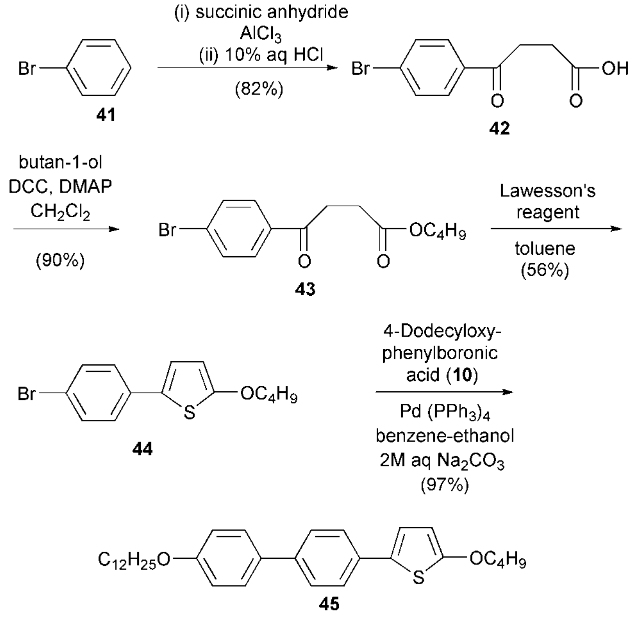
the laterally fluorinated biphenylboronic acids **12** and **19** (Schemes 3 and 4).

The key boronic acids **7**, **12**, **18** and **19** were then coupled with a variety of aryl bromides (**3**, **4** and **20**–**23**) under Suzuki coupling conditions[32] to afford the requisite liquid crystalline target compounds **24**–**35** and **37**–**39** (Scheme 5).

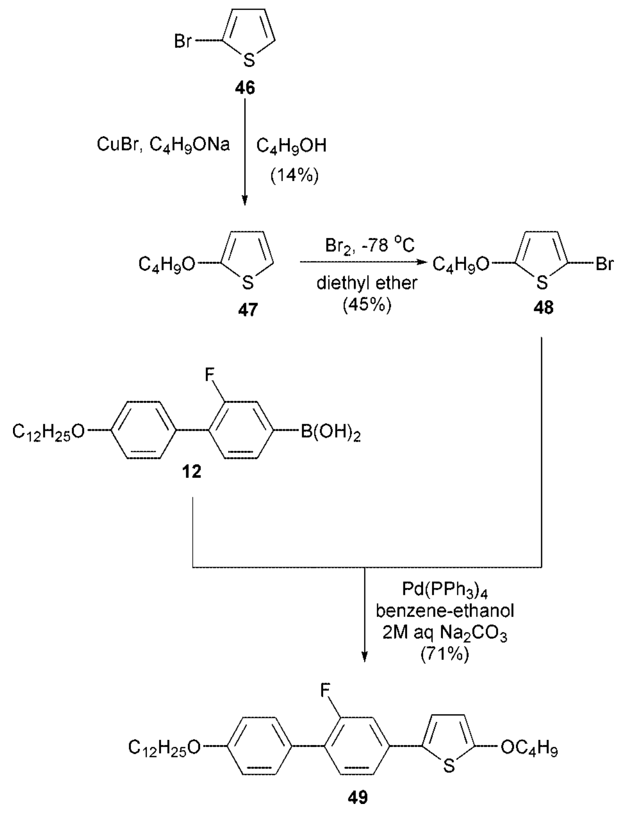
The synthesis of these aryl bromide building blocks is outlined below. The pivotal 1,1-difluoropentyl bromoaromatic building blocks **3** and **4** were efficiently prepared *via* fluoro-desulfurization of the corresponding dithiolanes **1** and **2**.[33] To obtain 2-bromo-5-pentylthiophene (**20**), thiophene was acylated with valeric anhydride, the resulting ketone was reduced using the Wolff–Kishner procedure[34] and the thiophene ring was finally brominated in the 5-position with NBS.[10,35] 2-Bromo-5-pentanoyl thiophene (**21**) was obtained by Friedel–Crafts acylation[36] of 2-bromothiophene with valeric anhydride.



Scheme 6



Scheme 7



Scheme 8

1-Bromo-4-pentylbenzene (**22**) was obtained by Friedel–Crafts acylation of bromobenzene using valeryl chloride followed by Wolff–Kishner reduction of the resulting ketone.[32] 1-Bromo-4-butoxybenzene (**23**) was obtained by etherification of 4-bromophenol with 1-bromobutane.[37]

The synthesis of terphenyl **36** was carried out *via* coupling of substituted phenylboronic acid **10** with bromobiphenyl building block **40** (Scheme 6).

The alkoxythiophene moiety in **45** (Scheme 7) was constructed by a novel ring closure methodology recently developed in our laboratory.[38–40] Friedel–Crafts acylation of bromobenzene with succinic anhydride followed by DCC–DMAP-mediated esterification[41] afforded γ-keto ester **43**, which was then cyclized[42] using Lawesson's reagent to obtain alkoxythiophene **44**. Finally, aryl bromide **44** was coupled with boronic acid **10** under Suzuki conditions to afford the desired alkoxythiophene-containing mesogen **45** in excellent yield.

It was recognized that acylation of 1-bromo-2-fluorobenzene might be compromised by side-product formation,[43] requiring us to employ a different approach for the construction of the laterally fluorinated alkoxythiophene mesogen **49** (Scheme 8). Thus, alkoxydebromination of 2-bromothiophene (**46**) using the method of Keegstra *et al.*[44,45] afforded alkoxythiophene **47** in 14% yield. Subsequent bromination of the highly reactive **47** with NBS or bromine at room temperature or reflux resulted in the competitive formation of significant amounts of 3,5-dibrominated product in addition to the desired monobrominated adduct **48**; however, this problem was largely overcome by performing this reaction at low temperatures. Suzuki cross-coupling of **48** with biphenylboronic acid **12** then afforded the target laterally fluorinated alkoxythiophene mesogen **49**.

The limited stability of liquid crystalline compounds having the 1,1-difluoropentyl side chain causes some purification problems, especially in the case of thiophene containing compounds **24**, **25**, **26** and **27**. These compounds decomposed to a substantial degree to the corresponding ketones while in prolonged contact with silica gel or acidic impurities in solvents. Therefore, flash chromatography using short silica columns was employed to avoid such decomposition. In contrast, the pure 1,1-difluoroalkyl mesogens **24**–**27** and **32**–**35** can be stored for a year without noticeable decomposition. Compounds **24** and **32**, having the highest clearing points, also show rapid decomposition while in the isotropic liquid or approaching the isotropic phase.

Results and discussion

Mesomorphic behavior

The transition temperatures for the mesogenic final products are given in Table 1.

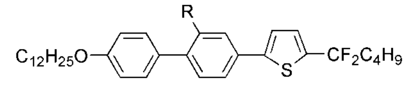
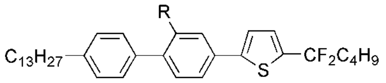
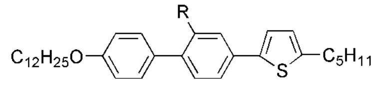
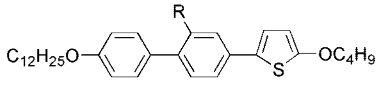
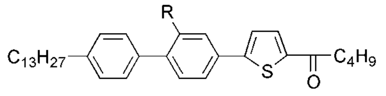
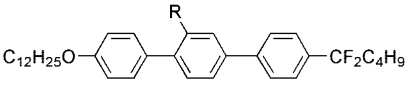
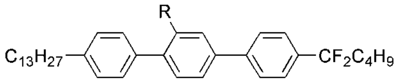
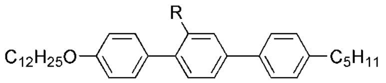
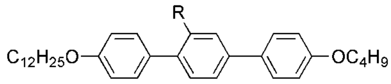
(i) Melting point trends. Upon examination of the melting points of the non-laterally fluorinated materials (R = H) some interesting conclusions may be drawn. The vast majority of liquid crystal literature pertaining to 2,5-disubstituted thienyl compounds clearly shows that thiophene-based materials are almost always lower melting than the corresponding phenyl analogs.[10,11,46–53] The reason often cited for this anomaly is the deviation from linearity brought about by such a substitution pattern on thiophene which gives rise to less efficient packing. In our study the pentyl (**28**) and butoxy (**45**) based thiophene materials are lower melting than the phenyl analogs **36** (13.3 °C difference in melting point) and **38** (27.8 °C difference in melting point) respectively. However, the non-laterally fluorinated 1,1-difluoropentylthienyl systems are much *higher* melting than the corresponding phenyl analogs [compare compounds **24** and **32** (51.4 °C difference in melting points) and compounds **26** and **34** (40.0 °C difference in melting points)] which is unprecedented in the liquid crystal literature. The 2-(1,1-difluoropentyl)thienyl mesogen **24** has a substantially higher melting point than that of the butoxy and pentyl analogs **45** and **28** (compare 155.9 °C to 92.2 °C and 92.3 °C respectively). The tridecyl side chain analog **26** also exhibits a high melting point (141.6 °C) approaching that of the corresponding ketone **30** (150.5 °C).

Lateral fluoro substitution has a very structure dependent and profound effect on melting point, mesomorphic stability and the types of mesophases exhibited by liquid crystalline compounds.[24,25,54,55] Lateral fluoro substitution generally causes a decrease in melting points when compared to the non-fluorinated derivatives and favors disordered and tilted mesophases, although the overall mesomorphic thermal stability is often variable.

By introducing fluorine into our new systems in an inter-annular position we expected to observe decreases in the melting and clearing points compared to the non-fluorinated analogs, and to suppress any higher-ordered smectic phases that might prove detrimental to mixture formulation for display use. Both of these expectations were realized in our compounds and we observed mesogens with broad phase ranges.

In all cases the introduction of lateral fluoro substitution led to the anticipated significant reduction in melting point. The thiophene-based materials showed the most dramatic depressions when a 1,1-difluoropentyl side chain was present at the 2-position of the thiophene ring [compare compounds **24** and **25** (85.0 °C reduction) and compounds **26** and **27** (90.7 °C reduction)]. A somewhat smaller effect was obtained with 2-pentanoyl, 2-butoxy and 2-pentyl side chains [compare compounds **30** and **31** (65.5 °C reduction), **45** and **49** (27.4 °C reduction) and compounds **28** and **29** (13.5 °C reduction)]. The terphenyl-based compounds showed a similar decrease in melting points [compare compounds **36** and **37** (44.9 °C reduction—pentyl chain), **32** and **33** (34.5 °C reduction—1,1-difluoropentyl chain), **34** and **35** (29.8 °C reduction—1,1-difluoropentyl chain) and compounds **38** and **39** (15.3 °C

Table 1 Transition temperatures/°C for the mesogenic final products as determined by polarizing optical microscopy (cooling rate of 5 °C)

Compound	R	No.	Cr	S_X	S_G	S_E	S_F	S_B	S_C	S_A	N	I
	H	**24**	• 155.9	—	—	—	• 160.4	—	—	• 172.4	—	•
	F	**25**	• 70.9	—	—	—	—	—	—	• 109.9	—	•
	H	**26**	• 141.6	—	—	—	—	—	—	• 151.9	—	•
	F	**27**	• 50.9	—	—	—	—	—	—	• 87.2	—	•
	H	**28**	• 92.3	—	—	—	—	—	—	• 178.7	—	•
	F	**29**	• 78.8	—	—	—	—	—	• 98.0	—	• 115.0	•
	H	**45**	• 92.2	—	• 148.8	—	—	—	• 166.3	• 181.4	—	•
	F	**49**	• 64.8	—	—	—	—	—	• 80.1	—	• 126.4	•
	H	**30**	• 150.5	—	—	—	• 180.2	—	—	• 219.6	—	•
	F	**31**	• 85.0	—	—	—	—	—	—	• 167.6	—	•
	H	**32**	• 104.5	• 190.1	—	—	—	• 193.5	—	• 197.2	—	•
	F	**33**	• 70.0	—	—	—	—	• 89.3	—	• 133.0	—	•
	H	**34**	• 101.6	—	—	—	—	• 168.2	—	—	—	•
	F	**35**	• 71.8	—	—	—	—	• 85.4	—	• 100.1	—	•
	H	**36**	• 105.6	—	• 186.5	—	—	• 202.6	—	• 206.9	—	•
	F	**37**	• 60.7	—	—	—	—	• 65.6	• 95.7	• 131.0	• 139.1	•
	H	**38**	• 120.0	• 187.2	—	• 228.2	—	—	—	• 235.0	—	•
	F	**39**	• 104.7	• (97.1)	—	—	—	—	• 137.6	• 162.4	• 170.7	•

reduction—butoxy chain)] except that the degree of melting point depression in the presence of the 1,1-difluoropentyl chain was much smaller than in the corresponding thiophene mesogens.

For materials with a 1,1-difluoropentyl chain, the identity of the other terminal chain (dodecyloxy or tridecyl) proved important as the melting points of the tridecyl materials were lower than for the analogous dodecyloxy derivatives [except for tridecyl derivative **35** which was observed to melt 1.8 °C higher than the dodecyloxy analog **33**]. Again it is notable that the thiophene compounds show the largest melting point reductions when substituting a tridecyl for a dodecyloxy terminal chain [compare compounds **24** and **26** (14.3 °C reduction) and compounds **25** and **27** (20.0 °C reduction)].

(ii) Clearing point trends. As was expected, significant lowering of the clearing points was also observed for all compounds upon lateral core fluorination as a result of increased molecular breadth and inter-annular twisting caused by the aromatic fluorine substituent.[25,56] Interestingly, the degree to which the clearing temperature was lowered (ΔT) does not seem to depend substantially on the nature of the linking group (-CF$_2$-, -O- or -CH$_2$- unit) [compare compounds **24** and **25** ($\Delta T = 62.5$ °C); **26** and **27** ($\Delta T = 64.7$ °C), **28** and **29** ($\Delta T = 63.7$ °C), **32** and **33** ($\Delta T = 64.2$ °C), **34** and **35** ($\Delta T = 68.1$ °C), **36** and **37** ($\Delta T = 67.8$ °C) and compounds **38** and **39** ($\Delta T = 64.3$ °C)]. Compounds with a ketone functionality had a somewhat lower value of ΔT [compare compounds **30** and **31** ($\Delta T = 52.0$ °C)] and alkoxythiophenes **45** and **49** showed an intermediate value of ΔT (55 °C).

(iii) Trends in mesomorphic phase range. In the case of the terphenyl core-containing materials, lateral fluoro substitution decreases the total mesomorphic phase range in all compounds [compare compounds **34** and **35** (38.3 °C depression), **32** and **33** (29.7 °C depression), **36** and **37** (22.9 °C depression) and compounds **38** and **39** (49 °C depression)]. In contrast, an opposite trend is sometimes observed with thiophene-containing materials. When the terminal chain on the thiophene ring is a pentyl or butoxy group, a reduction in total mesomorphic phase range is still seen upon lateral fluoro substitution [compare compounds **28** and **29** (50.2 °C depression) and compounds **45** and **49** (27.6 °C depression) respectively], but when the terminal chain is 1,1-difluoropentyl or pentanoyl, an *increase* in the total mesomorphic phase range is observed [compare compounds **24** and **25** (22.5 °C increase), **26** and **27** (26.0 °C increase) and compounds **30** and **31** (13.5 °C increase)].

(iv) Trends in S_C and other tilted mesophase stabilities. The tendency of lateral fluorine substituents to induce the S_C phase and other tilted mesophases and to eliminate/depress higher order smectic phases was observed to be highly structure dependent. None of the materials incorporating the 1,1-difluoromethylene unit exhibit the S_C phase. This may be attributed to a combination of the size of the difluoromethylene group or possibly the angle that the chain makes with the core. A study by one of the authors revealed a similar trend when oxygen in an alkoxy system was replaced by sulfur.[57] In such systems the oxygen-based materials exhibited a broad S_C phase range with associated S_C subphases whereas the analogous alkylsulfanyl materials had substantially depressed S_C phases with only the ferroelectric S_C phase being observed. A subsequent publication by Goodby[14] referencing these materials highlighted the importance of the angle that the terminal chains make with the core for materials to exhibit tilted phases. It is of note that the only 1,1-difluoropentyl-based material to exhibit a truly disordered tilted mesophase (S_F) is a thiophene-based system (**24**). The only other material in this class to exhibit a tilted phase is **32** which exhibits a quasi-crystalline S_X phase (probably a crystal J or a crystal G phase).

S_C phases are also observed in compounds **29** and **37** (pentyl-substituted thienyl and phenyl systems respectively) and compounds **45**, **49** and **39** (butoxy-substituted thienyl and phenyl systems). Once again it is noteworthy that the 2-pentylthienyl-based material **29** has a higher S_C phase thermal stability than the analogous phenyl based system **37** (2.3 °C higher). The thienyl-based system **45** also has a S_C phase unlike the analogous phenyl-based system **38**. Introduction of lateral fluorine in S_C-devoid terphenyl and thienyl-containing systems such as **36**, **38** and **28** results in formation of wide S_C phase ranges (20.0–32.9 °C) while eliminating higher ordered (S_G and S_X) smectic phases. No S_C phase was generated upon lateral fluoro substitution of compounds having the 1,1-difluoropentyl terminal chain.

(v) Trends in S_B and other orthogonal mesophase stabilities. The thermal stability of the S_B phase is greatly affected by the introduction of a lateral fluorine substituent. The thienyl-based compounds tend to exhibit much more disordered mesophases than the analogous phenyl systems with the exception of butoxy-based system **45**, which has a S_G phase. This increase in disorder for the thienyl-based compounds is likely to be a consequence of the non-linearity of the thienyl compounds, which give less efficient packing. With the exception of butoxy-based systems **38** (S_E and S_X phases) and **39** (S_X phase), all phenyl-based mesogens exhibit the orthogonal S_B phase. As expected, when lateral fluoro substitution is present these phases are dramatically depressed and, in the case of **39**, the S_E phase is completely eliminated. The decreases in thermal stabilities range from 82.8 °C (comparing compounds **34** and **35**) to 137.0 °C (comparing compounds **36** and **37**).

Conclusion

A series of 1,1-difluoropentyl-substituted biphenylthienyl and terphenyl liquid crystals have been synthesized and their mesogenic properties compared with analogs where the CF_2-C_4H_9 side chain was replaced by a pentyl, butoxy or pentanoyl moiety. The 1,1-difluoropentyl-based systems displayed significantly different mesomorphic behavior from the other systems and were characterized by high melting points and a tendency toward orthogonal phase behavior (S_A and S_B phases). Only in a single case was a disordered tilted phase (S_F) observed in such systems.

A number of the analogous alkoxythienyl and alkylthienyl mesogens display remarkably high S_C mesophase stabilities for ‘bent’ compounds and warrant further investigation as potential achiral ferroelectric host materials. Asymmetric analogs also deserve investigation as potential chiral, non-racemic ferroelectric dopants.

Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H (300 MHz, General Electric GN-300 FT NMR spectrometer), ^{13}C (75 MHz) and ^{19}F (470 MHz, Varian INOVA FT NMR spectrometer with VNMR version 5.3 software) NMR spectroscopy in $CDCl_3$ (tetramethylsilane was used as internal standard), unless another frequency and/or solvent are stated. IR spectra were recorded on a Biorad Excalibur FTS 3000 MX Mid-IR spectrophotometer. The content of carbon, hydrogen and sulfur in all final products was determined using a LECO Model CHNS-932 elemental analyzer (St. Joseph, MI).

The progress of reactions was monitored using either TLC [aluminium backed silica gel plates (Sigma-Aldrich, 200 μm layer thickness, 2–25 μm particle size and 60 Å pore size)] or GC [Shimadzu gas chromatograph GC-14A with a Restek™ RTX-5 capillary column (30 m) and Shimadzu class VP software].

Transition temperatures of the final products were measured using a Mettler FP82HT hot-stage and FP90 control unit in conjunction with a Leica Laborlux 12PolS polarizing microscope. All transitions are quoted from microscopic measurements and are given upon cooling at a rate of 5 °C per minute. The control unit was calibrated with three Merck standards (benzophenone, benzoic acid and caffeine). Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Differential Scanning Calorimeter 2920 at heating and cooling rates of 5 °C per minute with indium as internal standard.

The S_C phase was clearly identified by observation of the broken focal conic fan texture accompanied by the pseudo-homeotropic schlieren texture (see Fig. 1). The S_F phase was identified by both the mosaic texture obtained on cooling from the homeotropically aligned S_A phase and additionally from the ‘chunky’ focal conic texture (see Fig. 2) obtained on cooling from the focal conic fan texture of the S_A phase.

The ‘B’ phase in **32**, **33**, **34**, **35**, **36** and **37** is tentatively assigned as being S_B (hexatic). This assignment was based on the rounded shape of the focal conic domains (see Fig. 3) and the parabolic defects observed on reheating into the S_A phase (see Fig. 4). Transition bars were additionally observed at the transition point.

All chemicals were used without additional purification unless otherwise specified. Anhydrous dichloromethane was obtained by stirring and distillation from calcium hydride. Anhydrous ether and THF were obtained by distillation from benzophenone ketyl. All chromatographic separations were performed using flash column chromatography on silica gel [Fisher Davisil® silica gel (60 Å, 55–75 μm particle size, grade 1740)] unless otherwise stated.

The syntheses of compounds **22**, **23** and **40** are given in references 32, 58 and 59 respectively. Typical experimental procedures are provided below.†

2-Bromo-5-(1,1-difluoropentyl)thiophene (3)

To a pre-dried 50 mL plastic bottle charged with a magnetic stirrer was added nitrosonium tetrafluoroborate (0.543 g, 4.64 mmol) under dry argon. Anhydrous dichloromethane (10 mL) and pyridinium polyhydrogen fluoride (PPHF) (2 mL, 70% HF content) were injected into the bottle and the reaction mixture was cooled to 0 °C. A solution of dithiolane **1** (0.700 g, 2.17 mmol) in anhydrous dichloromethane (4 mL) was then added dropwise over a period of 3–5 min. The ice bath was removed and the reaction mixture was stirred for a further 2 min before being diluted with petroleum ether (80 mL) in a plastic cylinder. The upper (petroleum ether) layer was removed and the dark bottom layer was extracted with a

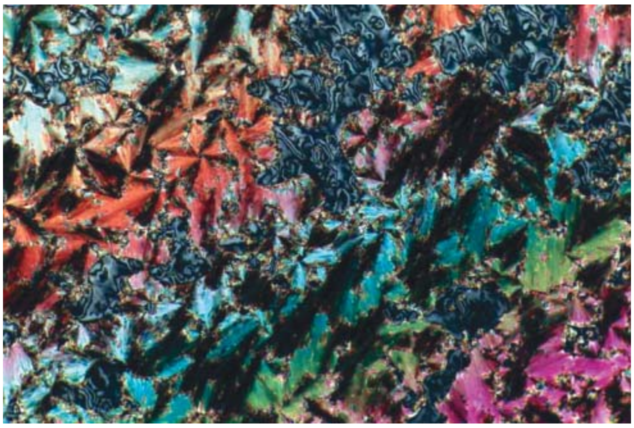


Fig. 1 S_C phase of compound **39** at 127.1 °C clearly showing broken focal conic domains accompanied by regions of pseudohomeotropic schlieren texture (100 × magnification).

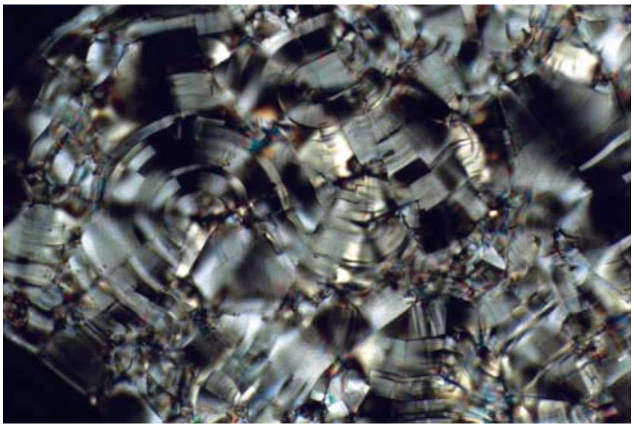


Fig. 2 S_F phase of compound **24** at 157.0 °C showing the paramorphotic 'chunky' focal conic texture obtained on cooling from the focal conic S_A texture (200 × magnification).

petroleum ether–dichloromethane mixture (3 : 1, 40 mL). The organic layers were combined and passed through a short silica plug (5 cm). The colorless filtrate was concentrated *in vacuo* to afford the title compound **3** as a colorless liquid (0.508 g, 87%). ^{1}H NMR δ 0.91 (t, $J = 6.9$ Hz, 3H), 1.33–1.52 (m, 4H), 2.17 (m, 2H), 6.95 (dt, $J = 3.6$ Hz, $J_{\text{H-F}} = 1.5$ Hz, 1H), 6.99 (dt, $J = 3.6$ Hz, $J_{\text{H-F}} = 0.9$ Hz, 1H); ^{13}C NMR δ 13.6, 22.2, 24.5, 38.3 (t, $J_{\text{C-F}} = 26.4$ Hz), 114.1, 120.5 (t, $J_{\text{C-F}} = 238.4$ Hz), 126.1 (t, $J_{\text{C-F}} = 5.7$ Hz), 129.5, 140.8 (t, $J_{\text{C-F}} = 32.0$ Hz); ^{19}F NMR δ -85.1(t, $J_{\text{F-H}} = 16.2$ Hz).

4-Bromo-4′-dodecyloxybiphenyl (6)

A mixture of 1-bromododecane (18.68 g, 0.075 mol), 4-bromo-4′-hydroxybiphenyl (15.0 g, 0.0602 mol) and potassium carbonate (31.0 g, 0.224 mol) in butan-2-one (120 mL) was heated under reflux for 24 h (GC revealed a complete reaction). After allowing to cool to room temperature, the potassium salts were filtered off. The solvent was removed *in vacuo* and the crude product was recrystallized from petroleum ether (bp 35–60 °C) to afford the title compound **6** as white crystals which were dried *in vacuo* (P_2O_5, 24 h) (22.2 g, 89%; purity (GC) > 99%); ^{1}H NMR δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.27–1.40 (m, 16H), 1.46 (m, 2H), 1.79 (quintet, $J = 6.6$ Hz, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.7$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H,); ^{13}C NMR δ 14.0, 22.6, 25.9, 29.2, 29.3, 29.5, 31.8, 68.0, 114.8, 120.6, 127.8, 128.1, 131.6, 132.1, 139.7, 158.9.

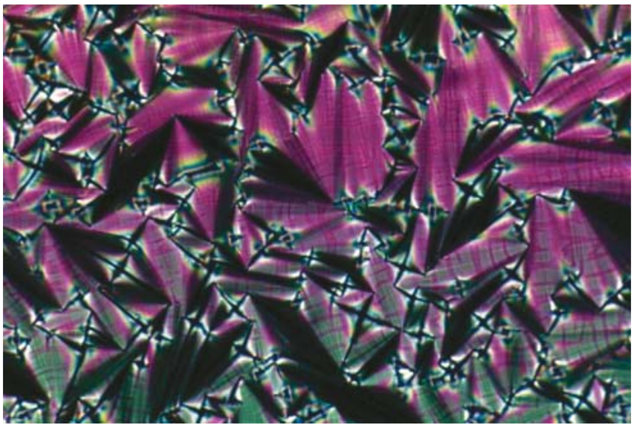


Fig. 3 S_B phase of compound **36** at 202.6 °C showing transition bars upon cooling from the S_A into the S_B phase. The rounded focal conic domains are clearly visible (320 × magnification).

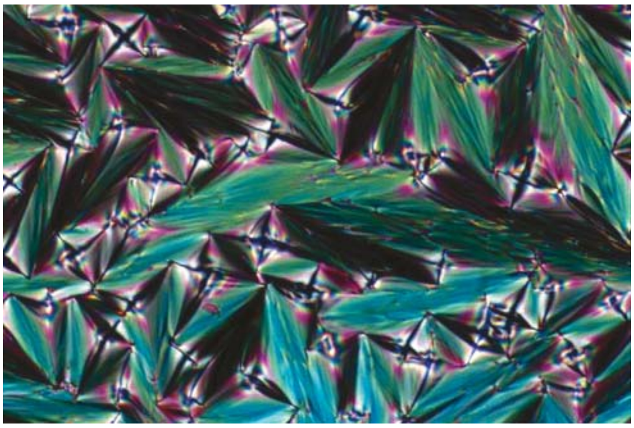


Fig. 4 S_A phase obtained on heating the S_B phase of compound **36** (203.5 °C). The parabolic defects inherently associated with a hexatic B phase are clearly visible (320 × magnification).

4′-Dodecyloxybiphenyl-4-ylboronic acid (7)

n-Butyllithium (1.6 mL, 10 M in hexanes, 0.016 mol) was added dropwise at -78 °C to a stirred, cooled (-78 °C) solution of bromobiphenyl **6** (4.17 g, 0.010 mol) in anhydrous THF (220 mL). The reaction mixture was maintained under these conditions for a further 2 h (GC revealed complete lithiation as a small reaction sample quenched with water did not contain any starting bromide) before previously cooled (0 °C) neat trimethyl borate (2.32 g, 0.0224 mol) was added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature (overnight) and was stirred for 45 min with hydrochloric acid (10%, 80 mL). The resulting mixture was extracted with diethyl ether (3 × 60 mL). The combined organic phases were washed with water (2 × 50 mL), a further aliquot of water (50 mL) was added and the organic solvent was evaporated from this biphasic mixture *in vacuo*. The white suspension was filtered and the resulting white solid was washed with petroleum ether and briefly dried on filter to afford the title compound **7** (3.82 g, 100%) which was used directly in the next step. ^{1}H NMR (DMSO-d_6) δ 0.87 (t, $J = 6.9$ Hz, 3H), 1.26–1.39 (m, 16H), 1.46 (m, 2H), 1.76 (quintet, $J = 6.6$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 6.96 (d, $J = 8.7$ Hz, 2H), 7.50–7.57 (m, 4H), 7.45 (d, $J = 8.7$ Hz, 2H), 8.09 (s, 2H).

4-Bromo-4′-dodecyloxy-2-fluorobiphenyl (11)

To a stirred biphasic mixture of 4-bromo-2-fluoro-1-iodobenzene (3.61 g, 12.0 mmol), tetrakis(triphenylphosphine)palladium(0)

(0.700 g, 0.606 mmol) in benzene (20 mL) and aqueous sodium carbonate (20 mL, 2 M, 40 mmol) under dry argon, was added phenylboronic acid **10** (4.59 g, 15.0 mmol) followed by ethanol (15 mL). The reaction mixture was heated under reflux for 72 h. The cooled mixture was diluted with water (50 mL) and extracted with dichloromethane (3 × 45 mL). The combined organic extracts were washed with water (50 mL) and brine (100 mL) before being dried (Na_2SO_4). The drying agent was filtered off and the filtrate was concentrated *in vacuo*. The resulting yellow solid was suspended in hexanes (250 mL) and was passed through a short silica plug (hexanes–dichloromethane 20 : 1). Concentration *in vacuo* followed by column chromatography on silica gel (hexanes) afforded the title compound **11** as a white solid (4.75 g, 91% yield). ^{1}H NMR δ 0.91 (3H, t, $J = 6.7$ Hz), 1.20–1.40 (m, 16H), 1.47 (quintet, $J = 7.2$ Hz, 2H), 1.85 (quintet, $J = 6.7$ Hz, 2H), 4.01 (t, $J = 6.5$ Hz, 2H), 6.98 (d, $J = 8.9$ Hz, 2H), 7.29–7.35 (m, 3H), 7.448 (d, $J = 8.8$ Hz, 1H), 7.454 (d, $J = 8.9$ Hz, 1H); ^{13}C NMR δ 14.3, 22.9, 26.2, 29.4, 29.6 (2), 29.8, 32.1, 68.1 (d, $J_{\text{C-F}} = 15.3$ Hz), 114.8, 119.8 (d, $J_{\text{C-F}} = 26.3$ Hz), 120.7 (d, $J_{\text{C-F}} = 9.1$ Hz), 127.0, 127.8 (d, $J_{\text{C-F}} = 3.4$ Hz), 129.6, 130.1 (d, $J_{\text{C-F}} = 2.9$ Hz), 131.6 (d, $J_{\text{C-F}} = 4.1$ Hz), 159.3, 159.6 (d, $J_{\text{C-F}} = 251.7$ Hz); ^{19}F NMR δ −115.7 (dd, $J_{\text{H-F}} = 10$, 7 Hz).

1-Bromo-4-tridecylbenzene (14)

To a stirred, cooled (0 °C) solution of [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.320 g, 0.437 mmol) and 1,4-dibromobenzene (52.0 g, 0.220 mol) in anhydrous THF (100 mL) under argon, a solution of Grignard reagent [prepared from magnesium (6.40 g, 0.263 mol) and 1-bromotridecane (63.7 g, 62.0 mL, 0.242 mol) in anhydrous ether (150 mL)] was added dropwise over a period of 30 min under dry argon. The reaction mixture was allowed to warm to room temperature and was stirred until completion of the reaction (monitored by GC). Methanol (2.5 mL) was added and the reaction mixture was diluted with hexanes (500 mL). The mixture was filtered through a short silica plug and the solvent was evaporated *in vacuo*. The residue was distilled to afford the title compound **14** as a low melting white solid (bp 170–172 °C/1.2 mmHg) (46.5 g, 62%). ^{1}H NMR δ 0.88 (t, $J = 6.6$ Hz, 3H), 1.27–1.46 (m, 20H), 1.57 (quintet, $J = 7.2$ Hz, 2H), 2.53 (t, $J = 7.8$ Hz, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR δ 14.0, 22.6, 29.1, 29.3, 29.4, 29.5, 29.6, 31.2, 31.9, 35.3, 119.1, 130.0, 131.1, 141.7.

2-Bromo-5-pentylthiophene (20)

2-Pentylthiophene[60] (13.8 g, 89.6 mmol) and *N*-bromosuccinimide (16.0 g, 90.0 mmol) in chloroform (20 mL) and acetic acid (20 mL) were gently heated under reflux for 45 min. The resulting black reaction mixture was diluted with water (30 mL) and extracted with dichloromethane (2 × 40 mL). The combined organic extracts were washed with water (2 × 40 mL), aqueous potassium hydroxide (5%, 30 mL) and dried ($MgSO_4$). The drying agent was filtered off and the residue was passed through a short silica plug (6 cm). Concentration *in vacuo* gave a yellow liquid (19.7 g, 94%) which was distilled under reduced pressure to afford the title compound **20** as a colorless liquid (bp 130–131 °C/1.5 mmHg) (13.8 g, 66%). ^{1}H NMR δ 0.92 (t, $J = 6.9$ Hz, 3H), 1.30–1.40 (m, 4H), 1.65 (quintet, $J = 7.4$ Hz, 2H), 2.75 (t, $J = 7.6$ Hz, 2H), 6.54 (d, $J = 3.7$ Hz, 1H), 6.85 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR δ 14.2, 22.6, 30.5, 31.3, 108.7, 124.5, 129.5, 147.8.

2-Bromo-5-pentanoylthiophene (21)

Iron(III) chloride (9.95 g, 0.0613 mol) was added in one portion to a stirred mixture of 2-bromothiophene (50.0 g, 0.307 mol) and valeric anhydride (65.7 g, 0.353 mol) under dry nitrogen at rt (a temperature rise to 100 °C was noted). The reaction mixture was stirred at rt for a further 2 h (TLC and GC analyses confirmed a complete reaction) and was then poured into water (300 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 50 mL). The combined organic extracts were washed with sodium carbonate (2 M, 2 × 200 mL) before being dried ($MgSO_4$). The drying agent was filtered off and the solvent was removed *in vacuo* to give a black liquid which was distilled to give the title compound **21** as a colorless liquid (bp 128–133 °C/0.5 mmHg) (62.4 g, 82%). ^{1}H NMR δ 0.94 (t, $J = 7.2$ Hz, 3H), 1.39 (sextet, $J = 7.5$ Hz, 2H), 1.70 (quintet, $J = 7.5$ Hz, 2H), 2.82 (t, $J = 7.2$ Hz, 2H), 7.09 (d, $J = 3.9$ Hz, 1H), 7.44 (d, $J = 3.9$ Hz, 1H); ^{13}C NMR δ 13.8, 22.6, 26.6, 38.3, 122.2, 130.5, 132.8, 145.9, 192.3.

2-(4′-Dodecyloxybiphenyl-4-yl)-5-(1,1-difluoropentyl)thiophene (24)

Palladium(II) chloride (0.1 M solution in water, 0.2 mL, 0.02 mmol) was added in one portion to a stirred mixture of biphenylboronic acid **7** (0.500 g, 1.30 mmol), bromothiophene **3** (0.210 g, 0.78 mmol) and sodium carbonate (2.0 M, 1.68 mL, 3.36 mmol) in acetone (10 mL) under dry argon. The reaction mixture was heated under reflux for 40 h and the cooled reaction mixture was diluted with hydrochloric acid (10%, 10 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed with water (100 mL) and dried (Na_2SO_4). The drying agent was filtered off and the extract was filtered through a column of silica gel (petroleum ether–dichloromethane, 3 : 1) before the solvent was removed *in vacuo*. The crude product was crystallized from ethyl acetate followed by petroleum ether (bp 35–60 °C) to afford the title compound **24** as a white solid, which was dried *in vacuo* (P_2O_5, paraffin wax, 24 h) (0.280 g, 72%). Transitions (°C) Cryst 155.9 S_F 160.4 S_A 172.4 Iso Liq; ^{1}H NMR δ 0.88 (t, $J = 6.9$ Hz, 3H), 0.93 (t, $J = 7.2$ Hz, 3H), 1.27–1.56 (m, 22H), 1.81 (quintet, $J = 6.6$ Hz, 2H), 2.25 (m, 2H), 4.00 (t, $J = 6.6$ Hz, 2H), 6.98 (d, $J = 9.0$ Hz, 2H), 7.17 (dt, $J = 3.9$ Hz, $J_{\text{H-F}} = 1.5$ Hz, 1H), 7.22 (dt, $J = 3.6$ Hz, $J_{\text{H-F}} = 1.2$ Hz, 1H), 7.54 (d, $J = 8.7$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 7.63 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR δ 13.7, 14.0, 22.2, 22.6, 24.6, 26.0, 29.2, 29.3 (2), 29.5, 31.8, 38.6 (t, $J_{\text{C-F}} = 26.5$ Hz), 68.0, 114.8, 121.2 (t, $J_{\text{C-F}} = 237.5$ Hz), 122.3, 126.2, 126.7 (t, $J_{\text{C-F}} = 4.8$ Hz), 127.0, 127.8, 131.8, 132.4, 138.2 (t, $J_{\text{C-F}} = 31.2$ Hz), 140.5, 145.6, 158.9; ^{19}F NMR δ −85.1(t, $J_{\text{F-H}} = 16.2$ Hz). Anal. calcd for $C_{33}H_{44}F_2OS$: C, 75.24; H, 8.42; S, 6.09; Found: C, 75.54; H, 8.62; S, 5.97%.

4-(4-Bromophenyl)-4-oxobutyric acid (42)

Anhydrous aluminium(III) chloride (27.0 g, 0.203 mol) was added in one portion to a mechanically stirred, cooled (0 °C) mixture of succinic anhydride (10.0 g, 0.100 mol) and bromobenzene (102 g, 0.650 mol). After 5 h at 0 °C, the reaction mixture was allowed to warm up to room temperature and was stirred for an additional 94 h. The reaction mixture was then poured into hydrochloric acid (450 mL, 10%), stirred for 1 h and the product was filtered, washed with water (1.0 L) and dried. The crude product was crystallized from toluene (250 mL) and dried under vacuum (P_2O_5, paraffin wax, 1.1 mmHg, 17 h) to afford the title compound **42** as a white solid (21.0 g, 82%, mp 146–149.5 °C). ^{1}H NMR (DMSO-d_6) δ 2.57 (t, $J = 6.2$ Hz, 2H), 3.23 (t, $J = 6.9$ Hz, 2H), 7.73 (d, $J = 8.7$ Hz, 2H), 7.90 (d, $J = 8.7$ Hz, 2H), 12.18 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 27.8, 33.1, 127.3, 129.9, 131.8, 135.4, 173.8, 197.7.

Butyl 3-(4-bromobenzoyl)propanoate (43)

To a solution of γ-keto acid **42** (10.3 g, 40.1 mmol) in anhydrous dichloromethane (600 mL) under dry argon at room temperature were added 4-(*N*,*N*-dimethylamino)pyridine

(1.84 g, 15.1 mmol), butan-1-ol (2.82 g, 38.1 mmol) and *N*,*N*'-dicyclohexylcarbodiimide (8.84 g, 42.9 mmol). The reaction mixture was stirred for 20 h and the resulting white precipitate was filtered off. The filtrate was washed with potassium hydroxide (5%, 2 × 200 mL), water (200 mL), acetic acid (5%, 200 mL), water (200 mL), brine (200 mL) and dried (Na_2SO_4). The drying agent was filtered off and the solvent was removed *in vacuo*. The crude semisolid was purified by column chromatography on silica gel (hexanes–ethyl acetate 9 : 1) to afford the title compound **43** as a white solid (11.3 g, 90%, mp 30–31 °C). ^{1}H NMR δ 0.89 (t, $J = 7.3$ Hz, 3H), 1.34 (sextet, $J = 7.4$ Hz, 2H), 1.58 (quintet, $J = 7.1$ Hz, 2H), 2.73 (t, $J = 6.6$ Hz, 2H), 3.24 (t, $J = 6.6$ Hz, 2H), 4.07 (t, $J = 6.7$ Hz, 2H), 7.57 (d, $J = 8.6$ Hz, 2H), 7.81 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR δ 13.8, 19.2, 28.3, 30.8, 33.5, 64.8, 128.5, 129.7, 132.1, 135.5, 172.9, 197.3.

2-(4-Bromophenyl)-5-butoxythiophene (44)

Lawesson's reagent (9.95 g, 24.6 mmol) was added in one portion to a stirred solution of γ-keto ester **43** (6.42 g, 20.5 mmol) in dry toluene (100 ml) under dry argon. The reaction mixture was heated under reflux for 16 h (GLC analysis revealed a complete reaction) before the reaction mixture was cooled to room temperature and the solvent was removed *in vacuo.* The crude product was purified thrice by column chromatography on silica gel [petroleum fraction (bp 40–60 °C)] and was dried *in vacuo* ($CaCl_2$, P_2O_5, 48 h) to afford the title compound **44** as a pale yellow solid (3.30 g, 56%, mp 74–75 °C, purity (GC) > 99%). ^{1}H NMR ($CDCl_3$) δ 0.95 (3H, t, $J = 7.3$ Hz), 1.50 (2H, sextet, $J = 7.3$ Hz), 1.80 (2H, quintet, $J = 7.3$ Hz), 4.20 (2H, t, $J = 7.3$ Hz), 6.15 (1H, d, $J = 4.0$ Hz), 6.95 (1H, d, $J = 4.0$ Hz), 7.35 (2H, d, $J = 8.7$ Hz), 7.50 (2H, d, $J = 8.7$ Hz); IR (KBr) ν_{max} 3080, 2868, 2265, 1892, 1585, 1551, 1500, 1465, 1390, 1271, 1202, 1112, 1070, 1031, 999, 979, 941, 904, 817, 773, 742, 711, 480 cm^{-1}.

2-Butoxythiophene (47)

Dry argon was bubbled through butan-1-ol (160 mL) for 30 min before sodium metal (6.35 g, 0.276 mol) was added in portions under dry argon. After the sodium had completely reacted, the solution was heated to reflux and 2-bromothiophene **46** (30.0 g, 0.184 mol) was added dropwise followed by copper(I) bromide (2.73 g, 0.0190 mol) in one portion. The reaction mixture was maintained under these conditions for a further 4 h before being allowed to cool to rt (overnight for convenience). The mixture was poured into a vigorously stirred solution of sodium cyanide (5.00 g, 0.102 mol) in water (200 mL) and was stirred for 1 h before separating the two layers. The aqueous layer was extracted with pentane (2 × 100 mL) and the combined organic washings were dried ($MgSO_4$). The crude product was purified twice by column chromatography on silica gel (hexanes) to afford a colorless liquid (4.16 g, 14%, purity (GC) > 99%). ^{1}H NMR δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.48 (sextet, $J = 7.4$ Hz, 2H), 1.76 (quintet, $J = 7.0$ Hz, 2H), 4.03 (t, $J = 6.5$ Hz, 2H), 6.20 (dd, $J = 3.8$, 1.5 Hz, 1H), 6.53 (dd, $J = 5.8$, 1.5 Hz, 1H), 6.70 (dd, $J = 5.8$, 3.7 Hz, 1H); ^{13}C NMR δ 13.9, 19.2, 31.4, 73.9, 104.8, 111.8, 124.8, 166.0.

2-Bromo-5-butoxythiophene (48)

Bromine (1.3 mL, 2.6 mmol) was added dropwise at −78 °C to a stirred, cooled (−78 °C) solution of butoxythiophene **47** (0.400 g, 2.56 mmol) in diethyl ether (5 mL). The yellow reaction mixture was stirred for 2 min at this temperature and was allowed to warm to rt. The clear yellow solution was diluted with petroleum ether (20 mL) and passed though a neutral alumina plug (7 cm long, 4 cm in diameter). The filtrate was concentrated *in vacuo* and the residue was subjected to column chromatography on silica gel (petroleum ether) to afford the title compound **48** as a clear liquid (0.270 g, 45%) and 2,4-dibromo-5-butoxythiophene (0.075 g, 9%): **48**: ^{1}H NMR δ 0.96 (t, $J = 7.3$ Hz, 3H), 1.46 (sextet, $J = 7.4$ Hz, 2H), 1.74 (quintet, $J = 7.0$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 5.97 (d, $J = 4.0$ Hz, 1H), 6.68 (d, $J = 4.0$ Hz, 1H); ^{13}C NMR δ 13.8, 19.1, 31.2, 74.1, 97.9, 105.5, 127.3, 165.5; 2,4-dibromo-5-butoxythiophene: ^{1}H NMR δ 0.97 (t, $J = 7.4$ Hz, 3H), 1.49 (sextet, $J = 7.4$ Hz, 2H), 1.77 (quintet, $J = 7.1$ Hz, 2H), 4.06 (t, $J = 6.5$ Hz, 2H), 6.73 (s, 1H); ^{13}C NMR δ 13.8, 19.1, 31.4, 76.4, 92.1, 99.2, 129.6, 158.0.

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