PERKIN 2

Thermal properties of monosubstituted ferrocene derivatives: a series of new ferrocenomesogens

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The preparation of a series of 1-substituted ferrocene derivatives is described. The structure of the substituent was varied systematically in order to determine the structural limits within which mesogenic behaviour is retained. The compounds are particularly useful for stabilizing the nematic phase, the range of which was increased substantially by extending the aromatic core of the substituent. Selective lateral fluorination was successfully used to lower the nematic temperatures as well as to suppress any smectic phases. Derivatives with no more than two rings in the core only display the crystal smectic B phase. The significance of substituents on the cyclopentadienyl rings is discussed with reference to their electronic properties and their effect on the stability of the compounds.

Introduction

Ferrocene behaves much like a three-dimensional arene and is useful for incorporating a metal atom into a molecule that requires a certain degree of structural rigidity, such as a liquid crystal. These three-dimensional units are not only useful for modifying the shape of a molecule—in addition the metal atom with its large electron density can be used to modify the physical properties (*e.g.* polarisability, colour) of a compound.

Following the publication in 1976 of the first attempt[1] to create a derivative of ferrocene with liquid-crystalline properties (type **A**, Fig. 1) and more notably since 1988 when the first liquid crystals based on disubstituted ferrocene were synthesized[2] (type **B**, Fig. 1), there has been a growing interest in these compounds amongst chemists.[3] The majority of ferrocenomesogens (as we have termed them) prepared to date are restricted to one of the structural types shown in Fig. 1 and this simply highlights the many unexplored structural possibilities waiting to be investigated. However, although the synthesis of derivatives with interesting new shapes continues to be exciting, a systematic approach which will allow meaningful predictions has become necessary.

Our choice fell upon derivatives of type **A** in which the ferrocenyl unit is pendent rather than being the 'centre-piece'. These compounds were not generally perceived to be conducive towards stabilizing the liquid-crystalline state due to their unfavourable molecular shape. For this reason they remain largely unexplored to date and, apart from the first imine derivatives,[1] two of which have enantiotropic nematic phases, only a few other unrelated examples have been prepared by different groups[4] (Fig. 2).

Disubstituted derivatives of type **B** are better known and many examples have been prepared to date. However, their thermal properties remain largely unpredictable as it is not possible to know which conformer(s) will predominate in the mesophase(s).[3,5] In terms of predictable properties some success has been achieved by either forcing an extended geometry[6] (type **C**, Fig. 1) or by preventing mutual rotation of the rings by employing a ferrocenophane unit.[7]

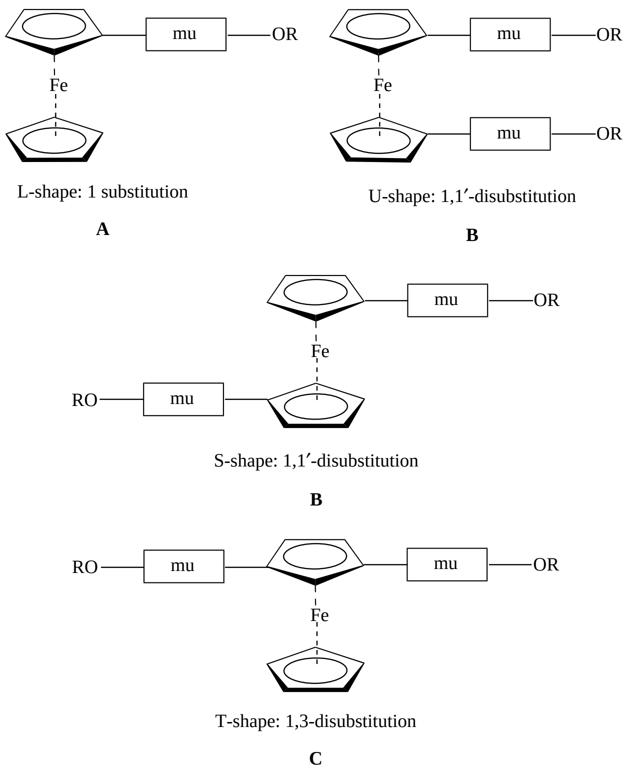

Fig. 1 General structural geometries of ferrocenomesogens (mu = mesogenic unit)

In the absence of any systematic information about derivatives of type **A**, the question that needs to be answered is: what are the structural limits within which the liquid-crystalline state can be generated and retained in these monosubstituted derivatives? Furthermore, is it possible to modify the ligand such that the effect of the bulky ferrocenyl unit is offset, in order to stabilize the mesogenic character of these derivatives? The results presented here form part of a systematic investigation into these structural factors and it is shown that a careful combination of structural elements can be used to produce potentially useful nematic ferrocenomesogens. A series of compounds represented by the general structure shown in Fig. 3 was synthesized. The size and shape of Z was modified by varying (*i*) the number of phenyl rings (*j* and *i*), (*ii*) the link Y, (*iii*) lateral substitution

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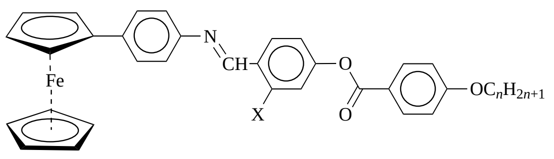
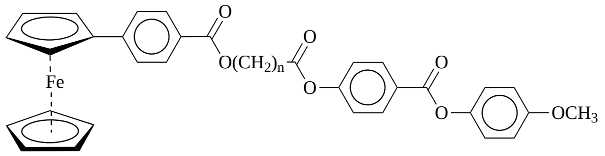

X = H, OH; n = 6, 10, 12 (Galyametdinov *et al.*[4a,e,f])


n = 1–7, 10, 11 (Hanasaki *et al.*[4c])

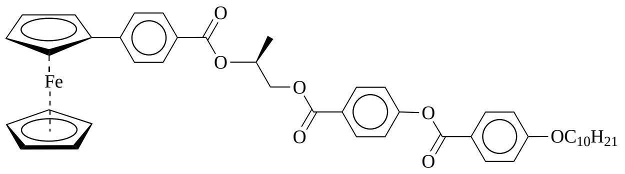
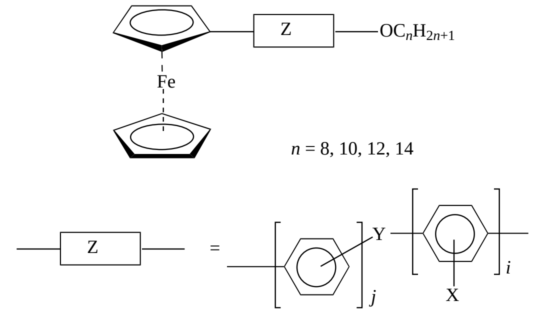

(Loubser and Imrie[4d])

Fig. 2 Recent examples of monosubstituted ferrocenomesogens prepared



j = 0 or 1; i = 1 or 2; X = H or F; Y = –COO–, –OOC–, –COOPhCOO–

Fig. 3 General structure representing the compounds prepared in this study

X and, to a limited extent, (*iv*) the number of carbon atoms, n, in the chain.

Another aspect worthy of attention in the design of metallomesogens is their stability, a requirement often disregarded in the quest for metallomesogens with novel molecular shapes and sizes. More specifically in the case of ferrocenomesogens, the nature of the group(s) immediately adjacent to the ferrocenyl moiety is important for the following reasons. In addition to its effect on the thermal behaviour of the bulk material, it is known that the electron-donating or -withdrawing ability of this group can have a profound influence on both the chemical and the thermal stability of ferrocene derivatives.[8] Our results will be discussed within the context of those obtained by other workers in an attempt to demonstrate the significance of the linking group.

Results and discussion

Mesomorphic properties and textures

All the compounds are listed in Table 1 together with their phases and transition temperatures. The temperatures shown are those obtained from DSC and optical microscopy, with the exception of some of the smectic–solid transitions which had to be obtained optically as they occur too slowly.

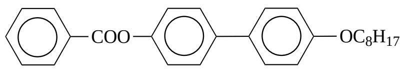
Compounds with a nematic phase. The nematic phase is characterized by the appearance of droplets immediately below the clearing point of the compound; on cooling, these droplets consolidate to display the characteristic marbled texture. The nematic texture of **25** is shown in Fig. 4 as a typical example.

The nematic phase of some of the fluorinated compounds exhibit the *schlieren* texture. On the whole, the series of compounds enable us to obtain a picture of the structural requirements necessary for nematic behaviour in monosubstituted ferrocene derivatives. The most important requirement is the presence of at least three rings in the core. The removal of any one of these rings invariably leads to the suppression of the nematic phase (compare *e.g.* **4** and **6** with **9**), while an additional ring (four rings in total as in **25**) greatly enhances the nematic character of the compounds (*vide supra*). The ability of the nematic phase to withstand an alteration of the shape of the core was also determined. This was done by moving the position of attachment of the carbonyloxy link from 4- to 3- (*e.g.* compare **10** with **14**). The nematic phase is completely suppressed in the compounds so produced. 3-Substitution is expected to introduce a 'bend' into the molecular structure and this appears to affect the mesophase behaviour adversely. However, a comparison of compounds **25** and **26** shows that the effect of the 'bent' core can at least to some extent be offset by extending the core by another ring to four rings—the nematic phase is retained although its range is much reduced. The effect of the number of carbon atoms in the terminal chain was investigated by extending the chain of one of the three-ring compounds, **9**. The result is shown in Fig. 5 where it can be seen that the length of the chain does not have a marked effect on the range of the nematic phase, although the phase is destabilized slightly with increasing n.

The final structural alteration that was investigated was lateral substitution. Hence, the structure of compound **9** was modified by replacing selected hydrogen atoms of the biphenyl group with fluorine atoms. It is well known that the relatively small size of the fluorine together with its high electronegativity makes fluorination the ideal way of altering the properties of a material without completely disrupting the phase transition temperatures[9] and there are many examples of fluorinated organic mesogens.[10] By comparison, fluorination has not yet found widespread use in metallomesogens, where it has met with mixed success, resulting in the complete suppression of the mesophases.[11]

Fluorination of some of our compounds proved interesting. Monofluorination of the biphenyl unit (compound **19**) lowers the clearing point by 34 °C, 2,3-difluorination of one of the rings as in **20** lowers it by an additional 7 °C, while two monofluorinated rings lead to a further reduction of 23 °C to 106 °C (compound **21**). An overall reduction of 64 °C was therefore achieved. This effect is illustrated in Fig. 6 where it can also be seen that a concurrent lowering of the respective melting points also occurs—fluorination therefore does not affect the nematic range of these compounds significantly. It is clear that it is not only the number of fluoro-substituents, but also their positions on the core that are important with respect to achieving a reduction in the transition temperatures. This is in agreement with the trend observed for fluorinated organic mesogens.[12]

On taking a closer look at the significance of these results, it is necessary to consider the thermal properties of the ligand itself. For this purpose compound **27** was prepared by removing the ferrocenyl unit of compound **9**.



$$\begin{tikzcd}
K \arrow[rr, "122"] & & S_C \arrow[r, "135"] \arrow[dl, "114"] & N \arrow[r, "136"] & I \\
& S_X \arrow[ul, "111"] & & &
\end{tikzcd}$$

27

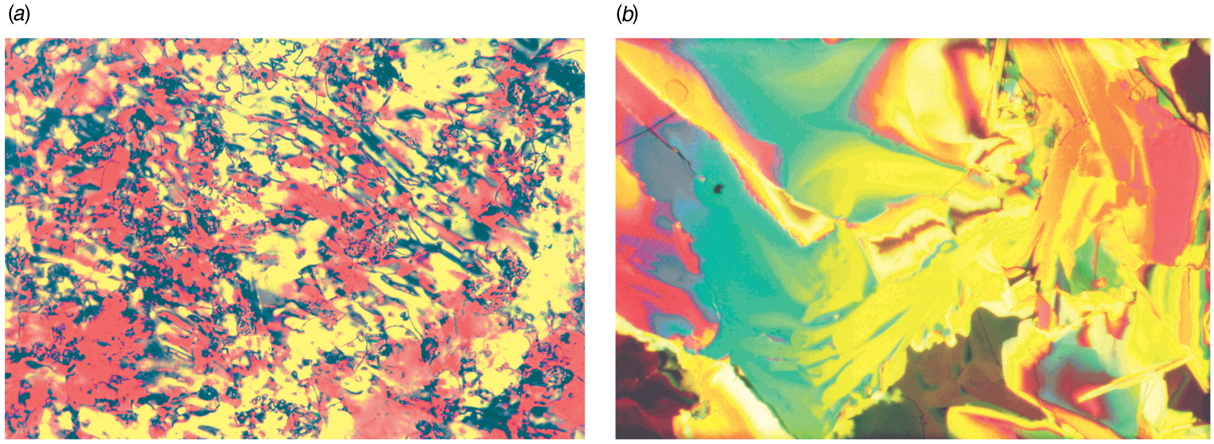


Fig. 4 Photomicrographs of (*a*) the marbled texture of the nematic phase of **25** and (*b*) the smectic B phase of **18**

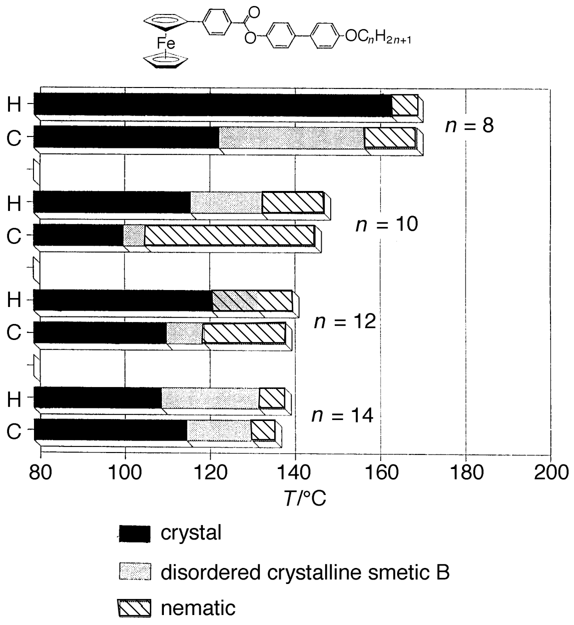


Fig. 5 The effect of increasing the length of the chain, *n*

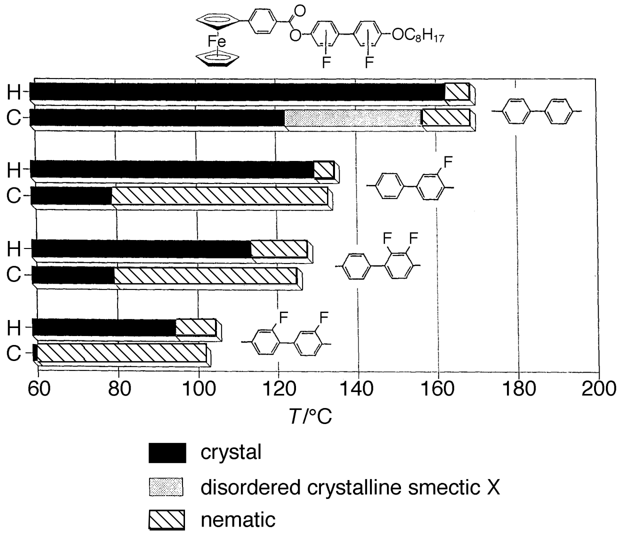


Fig. 6 The effect of lateral fluorination

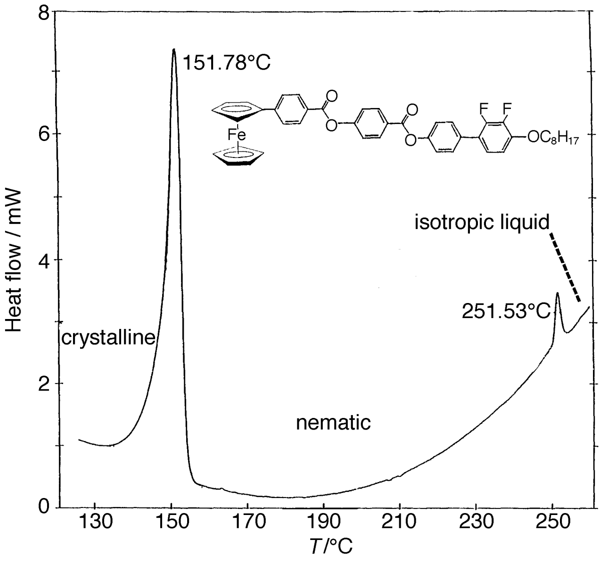


Fig. 7 DSC thermogram of **25** showing its wide nematic range (instrument: Perkin-Elmer DSC 7)

The effect of attaching the ferrocenyl unit to this ligand can now be appreciated; it raises the clearing temperature of **27** by 42 to 178 °C (compound **9**).‡ The ability of selected fluorination to counteract (and even improve upon) the adverse effect of the ferrocene is therefore not only remarkable but also extremely useful. On the other hand, it is interesting to note that the very short range unstable nematic phase of **27** is stabilized considerably by attachment of the ferrocenyl group, with the latter in itself acting as a lateral substituent which is (albeit to a lesser extent than fluorine) capable of discouraging the formation of smectic layers (compare **9** with **27**). However, complete suppression of the underlying highly ordered smectic phases can only be achieved by appropriate fluorination of the ligand core. It was mainly for this reason that our choice for core extension from three to four rings fell upon the fluorinated derivative **20**. Its core was extended by inserting a benzoate unit and this had the effect of greatly stabilizing the nematic phase by extending its range to nearly 100 °C (compound **25**). The DSC trace of **25** is shown in Fig. 7. The wide nematic range of **25** indicates that the use of a pendent ferrocene in conjunction with a larger core is particularly successful at stabilizing the nematic phase, much more so than 1,3-disubstituted ferrocenes[6] which in turn are perceived to nematically outperform their 1,1′-disubstituted counterparts. Unfortunately, **25** decomposes slowly above its clearing temperature. The attempt to combine lateral fluorin-

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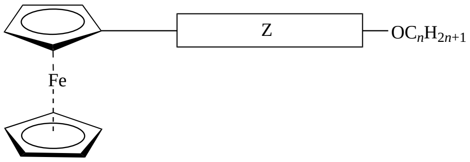
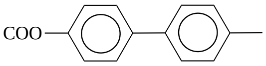
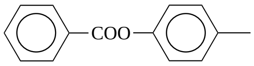
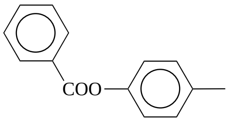
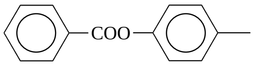
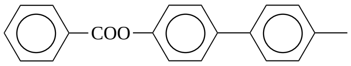
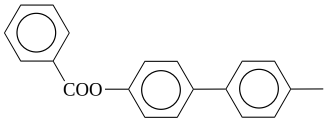
‡ Although such comparisons are often made by simply replacing the ferrocenyl unit with a phenyl group (N. Thompson, J. W. Goodby and K. Toyne, *Liq. Cryst.*, 1993, **13**, 381) this would not serve to illustrate our point, namely that the ferrocenyl group not only lengthens the core but also widens it.

Table 1 Phase transition temperatures of the ferrocenomesogens[a]



Compound no.	z	n	Phase transitions/°C
4		8	$\begin{tikzcd} K \arrow[rr, "143"] & & I \arrow[dl] \\ & K_x \arrow[ul] & \end{tikzcd}$
5		10	$\begin{tikzcd} K \arrow[rr, "120"] & & I \arrow[dl, "119"] \\ & K_x \arrow[ul, "116"] & \end{tikzcd}$
6		8	$K \underset{73}{\overset{110}{\rightleftharpoons}} K_B \underset{118}{\overset{119}{\rightleftharpoons}} I$
7		10	$K \underset{73}{\overset{92}{\rightleftharpoons}} K_B \underset{100}{\overset{102}{\rightleftharpoons}} I$
8		10	$\begin{tikzcd} K \arrow[rr, "74"] \arrow[rr, phantom, "\text{Fast}"', shift right=3] & & I \arrow[dl, "\text{73, slow}"] \\ & K_x \arrow[ul, "35"] & \end{tikzcd}$
16		8	$K \underset{64}{\overset{114}{\rightleftharpoons}} K_B \underset{122}{\overset{123}{\rightleftharpoons}} I$
17		10	$K \underset{65}{\overset{83}{\rightleftharpoons}} K_B \underset{102}{\overset{104}{\rightleftharpoons}} I$
18		12	$K \underset{61}{\overset{111}{\rightleftharpoons}} K_B \underset{116}{\overset{118}{\rightleftharpoons}} I$
9		8	$\begin{tikzcd} K \arrow[rr, "164"] & & N \arrow[dl, "157"] \arrow[r, "170", shift left] & I \arrow[l, "169", shift left] \\ & K_x \arrow[ul, "123"] & & \end{tikzcd}$
10		10	$K \underset{102}{\overset{117}{\rightleftharpoons}} K_B \underset{107}{\overset{134}{\rightleftharpoons}} N \underset{147}{\overset{148}{\rightleftharpoons}} I$
11		12	$K \underset{112}{\overset{122}{\rightleftharpoons}} K_B \underset{121}{\overset{133}{\rightleftharpoons}} N \underset{140}{\overset{141}{\rightleftharpoons}} I$
12		14	$K \underset{115}{\overset{117}{\rightleftharpoons}} K_B \underset{134}{\overset{133}{\rightleftharpoons}} N \underset{139}{\overset{139}{\rightleftharpoons}} I$
13		8	$\begin{tikzcd} K \arrow[rr, "102"] & & I \arrow[dl, "99"] \\ & K_x \arrow[ul, "83"] & \end{tikzcd}$
14		10	$K \underset{77}{\overset{82}{\rightleftharpoons}} K_B \underset{98}{\overset{100}{\rightleftharpoons}} I$

ation with a 'bent' molecule (3-substitution) in order to attempt to achieve a further reduction in transition temperatures was less encouraging as the nematic behaviour was suppressed completely in both of the examples prepared. In addition to this, an increase in clearing temperature also occurs in **22** (monofluorinated). Addition of a second fluoro-substituent (compound **23**) completely suppresses all mesogenic behaviour. However, extension of the 'bent' aromatic core by another ring does restore some of the nematic character (compound **26**).

Compounds with a crystal smectic phase. Compounds with no more than two aromatic rings in their core ($j + i < 3$ in Fig. 3) do not exhibit the nematic phase. The thermal behaviour of compounds **6**, **7** and **16**–**18** is similar (see Table 1) and that of compound **6** is described here as a typical example. On heating, the crystalline grain boundaries fade at 110 °C, but the texture remains essentially unchanged—this point coincides with the DSC endotherm at 110.27 °C and is taken to be the crystal–smectic transition. Clearing is observed at 119 °C. Subsequent cooling results in the formation of small highly birefringent platelets with well defined shapes (often elliptical or rectangular) in the isotropic melt. Slow cooling also leads to the observation of platelets shaped like clothes pegs, while faster cooling results in longer blades that slowly grow across the field of view. These platelets are highly characteristic[13] and led us to assign the phase as crystal smectic B.§ A photomicrograph of the fully developed texture of the phase is shown in Fig. 4(*b*). The graduality of formation of the crystal smectic B phase from the isotropic melt is reflected on the DSC thermogram from which the exotherm corresponding to this event is often absent (as is the case here). Crystallization of **6** commences below 80 °C and also occurs gradually. The thermal behaviour of **6** and its analogues is reproducible over at least three heating and cooling cycles (DSC).

In an attempt to confirm the disordered crystalline nature of the B phase, the phase was subjected to X-ray diffraction analysis. For practical reasons, compound **10** was chosen for this purpose. The complex diffraction pattern obtained for **10** con-

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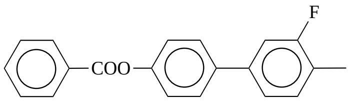
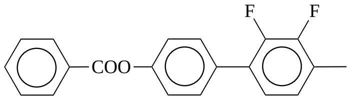
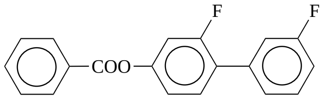
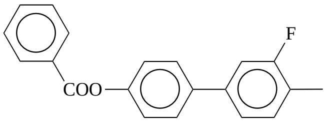
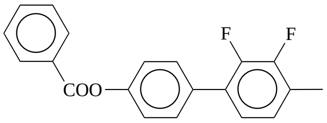
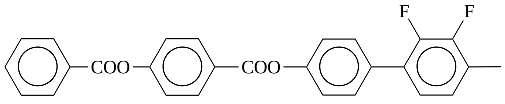
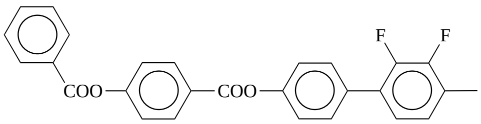
§ A 1,1′-dicholesteryl ferrocene derivative was recently shown to be the first ferrocenomesogen with a crystal smectic B phase.[14]

Table 1 *(continued)*

Compound no.	z	n	Phase transitions/°C
19		8	$K \underset{80}{\overset{131}{\rightleftharpoons}} N \underset{135}{\overset{136}{\rightleftharpoons}} \mathrm{I}$
20		8	$K \underset{81}{\overset{115}{\rightleftharpoons}} N \underset{126}{\overset{129}{\rightleftharpoons}} \mathrm{I}$
21		8	$K \underset{61}{\overset{96}{\rightleftharpoons}} N \underset{103}{\overset{106}{\rightleftharpoons}} \mathrm{I}$
22		8	$K \xrightarrow{115} \mathrm{I}$; $\mathrm{I} \xrightarrow{113} K_B \xrightarrow{70} K$
23		8	$K \xrightarrow{90} \mathrm{I}$
25		8	$K \xrightarrow{152} N \xrightarrow{252} \mathrm{I}$ (decomp.)
26		8	$K \underset{67}{\overset{100}{\rightleftharpoons}} N \underset{108}{\overset{108}{\rightleftharpoons}} \mathrm{I}$

[a] Abbreviations: K = crystalline, K_B = crystal smectic B phase, N = nematic phase, I = isotropic liquid, K_x = unidentified disordered crystalline phase.

firmed the phase to be of the disordered crystalline kind. The respective crystal smectic B phases of compound **10** and its homologues **9**, **11** and **12** are also mentioned in this section but they are formed from the nematic phase rather than directly from the liquid. The thermogram of **10** is shown in Fig. 8; the disordered crystalline smectic phase is unstable, but a sufficiently slow cooling rate revealed a microscopic texture quite similar to that of the compounds with two rings in their cores and it was also assigned as crystal smectic B. The exception in this series of homologues is compound **9** which exhibits a monotropic disordered crystalline smectic phase of an as yet unidentified nature.

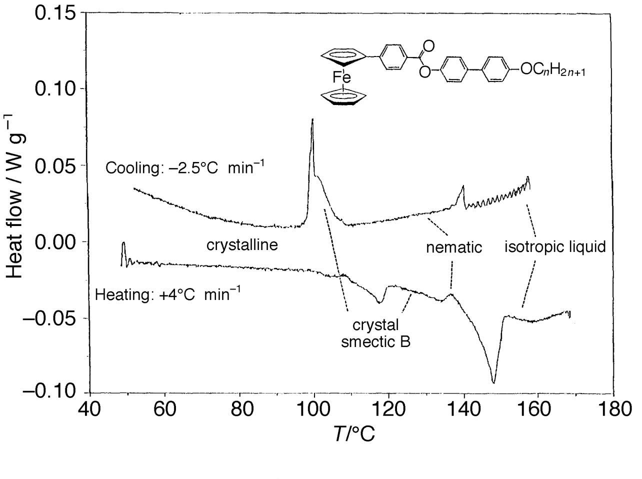
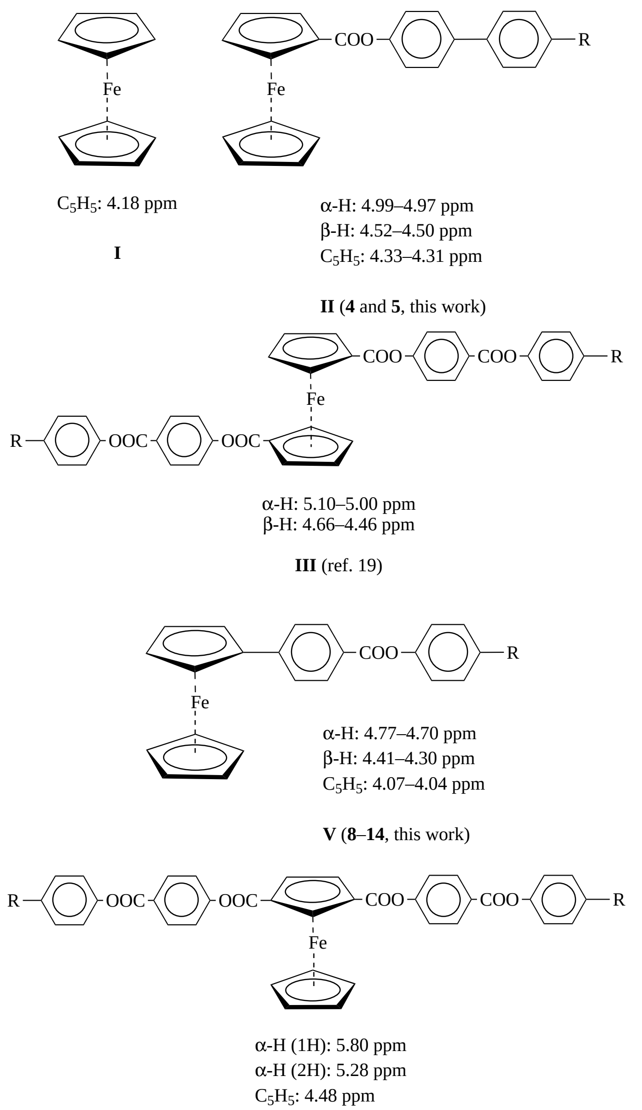


Fig. 8 DSC thermogram of **10**, see text (instrument: DSC V4.08 DuPont 2000)

The role of the cyclopentadienyl ring substituent(s)

An important criterion when designing materials for potential commercial use is that their constituent molecules should be sufficiently stable (photochemically, thermally, oxidatively and hydrolytically). More specifically in ferrocene chemistry, the effects of electron-donating or -withdrawing substituents on the stability of the compound need to be considered and additionally, in liquid crystals based on ferrocene, the size and shape of the group linking ferrocene with the remainder of the molecule also becomes important.

Ferrocenomesogens are commonly derived from ferrocenecarboxylic acid and ferrocene-1,1′-dicarboxylic acid as both are commercially available. Yet this approach, where the mesogenic group is attached to ferrocene *via* a carbonyloxy link, may not be the best one as the stability of these compounds should also be considered. In order to investigate the significance of these substituent effects compounds **4** and **5** were prepared by omitting the phenyl ring next to ferrocene from compounds **9** and **10** respectively. A comparison of **4** and **5** (Fc-COOR) with their respective isomers **6** and **7** (Fc-C_6H_4-COOR) reveals that the presence of the more flexible carbonyloxy link adjacent to the ferrocenyl group results in higher clearing temperatures (on average 20 °C higher). The temperature ranges of the smectic phases of these compounds are erratic and no meaningful comparison is therefore possible. In addition to its size, shape and flexibility, the electron-withdrawing nature of the carbonyloxy link is also important as it forms an extension of the conjugation of the C_5H_4 ring. The extent to which electron density is removed from the ferrocenyl group



C_5H_5: 4.18 ppm

I

α-H: 4.99–4.97 ppm
β-H: 4.52–4.50 ppm
C_5H_5: 4.33–4.31 ppm

II (**4** and **5**, this work)

α-H: 5.10–5.00 ppm
β-H: 4.66–4.46 ppm

III (ref. 19)

α-H: 4.77–4.70 ppm
β-H: 4.41–4.30 ppm
C_5H_5: 4.07–4.04 ppm

V (**8**–**14**, this work)

α-H (1H): 5.80 ppm
α-H (2H): 5.28 ppm
C_5H_5: 4.48 ppm

IV (ref. 6)

Fig. 9 Cyclopentadienyl ^{1}H chemical shifts of ferrocenylcarbonyloxy derivatives

manifests itself as a distinct trend in the way the ^{1}H chemical shifts of C_5H_4 change for the different kinds of derivatives. Selected values obtained from our work are given in Fig. 9 together with those of compounds prepared by others to illustrate the point. As the number of carbonyloxy substituents increases from one to two, first on ferrocene (compare **III** with **II**, Fig. 9) and then on a single cyclopentadienyl ring (compare **IV** with **II**, Fig. 9) a progressive downfield shift of both the α-H and β-H cyclopentadienyl resonances occurs as the ring(s) become more electron deficient. This deficiency will in turn cause a reduction in the Cp–Fe back donation of electron density with a consequent weakening of the metal–ligand bonds.[15]

In practice, hydrolysis was found to be a serious problem with compounds **4** and **5** and a significant degree of saponification was observed during work-up and purification, although this is rather surprising in view of the electron-donating nature of the ferrocenyl group.[16] Apart from these disadvantages, ferrocene derivatives with electron-withdrawing substituents (such as −COO−) on the cyclopentadienyl-rings or with any partial positive charge in the α-position are known to be photochemically unstable[17] and Nesmeyanov *et al.*[18] have demonstrated that ferrocene-1,1′-dicarboxylic acid is photochemically unstable.

Our solution to these problems was to insert a phenyl ring (which is neither strongly electron-withdrawing nor electron-donating[20]) as a spacer between ferrocene and the carbonyloxy link. The C_5H_4 ^{1}H chemical shifts that are given in Fig. 9 for **V** indicate a significantly reduced flow of electron density from the ferrocene group—the phenyl ring therefore is not only highly effective at quenching the influence that its substituent exerts on the substituted C_5H_4 ring, but also the effect on the unsubstituted C_5H_5 ring. Interestingly, an examination of the data of a previous comprehensive ^{1}H NMR study of small monoaryl ferrocenes reveals a trend similar to the one observed by us.[21] Compounds with the additional phenyl ring also appeared to have an improved thermal stability.

To summarize, although it is not yet possible to distinguish between structural contributions (size, shape and flexibility) on the one hand and electronic contributions by the carbonyloxy link on the other, it is clear that both of these need to be taken into account when new compounds are designed.

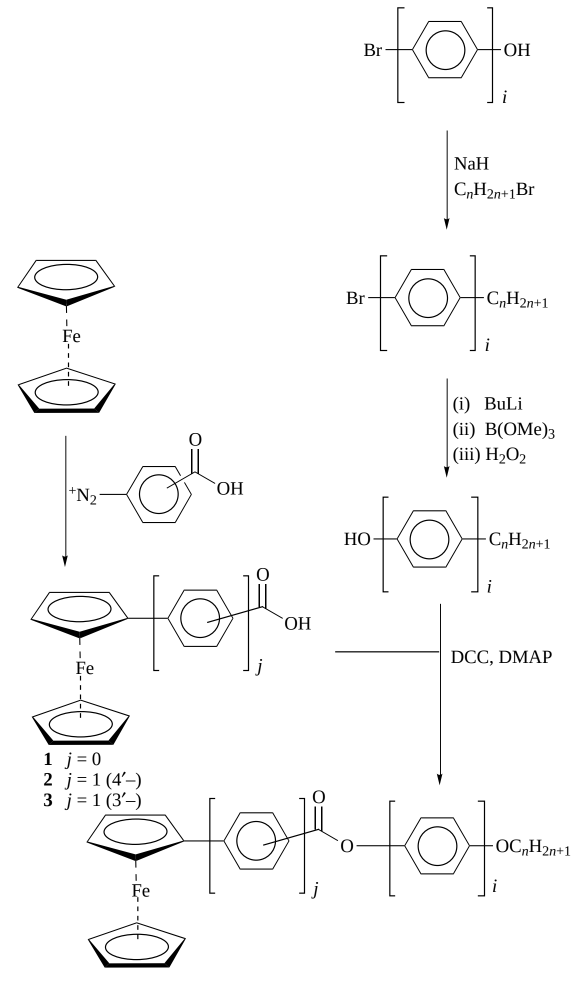
Experimental

Purification and characterization of the materials

The final products were purified by column chromatography over silica gel. Unless stated otherwise, they were recrystallized from dichloromethane and methanol sequentially until constant transition temperatures were obtained. All compounds were characterized by NMR, IR and mass spectrometry but to limit costs only some randomly selected compounds were submitted for microanalysis. ^{1}H NMR spectra were recorded on either a Varian VXR 200 or a Varian Gemini 200 spectrometer operating at 200 MHz as solutions in $CDCl_3$ unless otherwise stated. Selected ^{13}C and ^{19}F NMR spectra were recorded respectively on a Varian Gemini 200 spectrometer at 50.3 MHz and a Bruker AC300 instrument at 282.4 MHz (^{19}F externally referenced against $CFCl_3$). IR spectra were recorded on either a Perkin-Elmer 983 grating spectrometer or a Perkin-Elmer 1600 series FTIR spectrometer. Melting points of the intermediates in the synthesis of the metallomesogens were determined using an Electrotherm IA 9000 series digital melting-point apparatus and the values are uncorrected. Mass spectra were obtained on a VG 7070 H instrument (70 eV) or an AEI MS 902/MSS update (70 eV, probe-direct insertion). The textures of the mesophases were studied with a Reichert–Jung Thermovar polarizing microscope equipped with a Reichert–Jung hot stage and temperature control. Photomicrographs were recorded with a Nikon camera mounted on the microscope. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Dupont thermal analyst 2000 scanning calorimeter with the exception of compounds **25** that were investigated with a Perkin-Elmer DSC7 instrument (CSIR, Pretoria). The products were studied at various scanning rates (2.5, 5 or 10 °C min^{-1}) for the heating cycle and at 2.5 °C min^{-1} for the cooling cycle, after being encapsulated in aluminium pans. The calorimeter was calibrated with an indium standard. Microanalyses were performed by the Council for Scientific and Industrial Research, Pretoria.

Syntheses

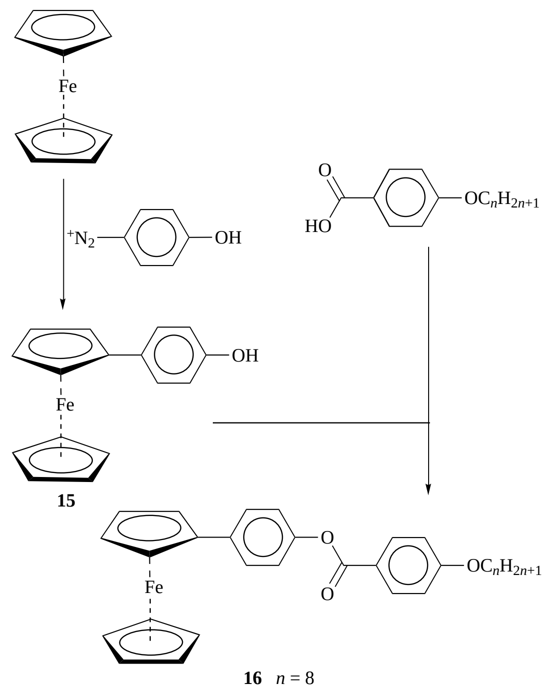
The general approach used in the synthesis of the ferrocene derivatives was to construct separately the organic phenol (or carboxylic acid) and to then attach this to the carboxylic acid (or phenol) containing the ferrocenyl moiety by way of a mild esterification step and the synthetic steps are shown in Schemes 1–4. The 4-alkyloxyphenols were synthesized by treating 4-bromophenol (after deprotonation with sodium hydride) with alkyl bromide, after which the aromatic bromide functionality was converted to the hydroxy group *via* the dihydroxyborane (Scheme 1). This method is an attractive ‘one pot’ route to phenols[22] since they are not readily obtained by electrophilic aromatic substitution. The biphenols were prepared in a similar fashion, but in this case the overall yield was found to be adversely affected by the reduced low-temperature solubility of the longer-chain intermediate aryllithium compound. The spectroscopic characteristics of the biphenols are in agree-



1 $j = 0$
2 $j = 1$ (4′–)
3 $j = 1$ (3′–)

4 $j = 0, i = 8, n = 8$
5 $j = 0, i = 2, n = 10$
6 $j = 1$ (4′–), $i = 1, n = 8$
7 $j = 1$ (4′–), $i = 1, n = 10$
8 $j = 1$ (3′–), $i = 1, n = 10$
9 $j = 1$ (4′–), $i = 2, n = 8$
10 $j = 1$ (4′–), $i = 2, n = 10$
11 $j = 1$ (4′–), $i = 2, n = 12$
12 $j = 1$ (4′–), $i = 2, n = 14$
13 $j = 1$ (3′–), $i = 2, n = 8$
14 $j = 1$ (3′–), $i = 2, n = 10$

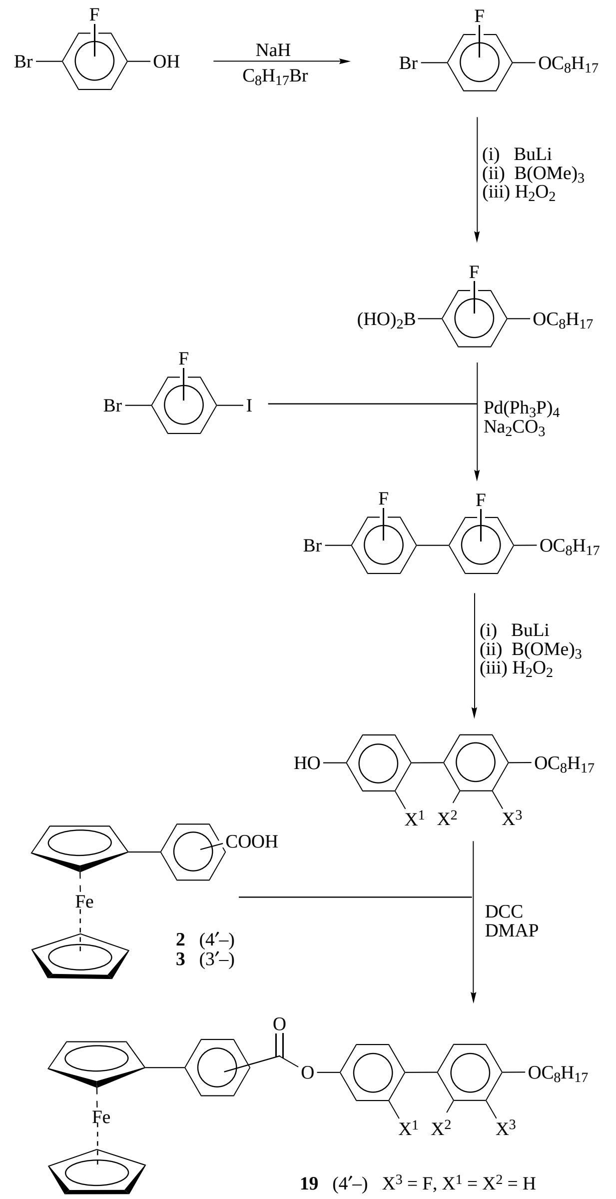
Scheme 1 General route to the non-fluorinated ferrocene derivatives



15

16 $n = 8$
17 $n = 10$
18 $n = 12$

Scheme 2 Reactions involving 4-hydroxyphenylferrocene

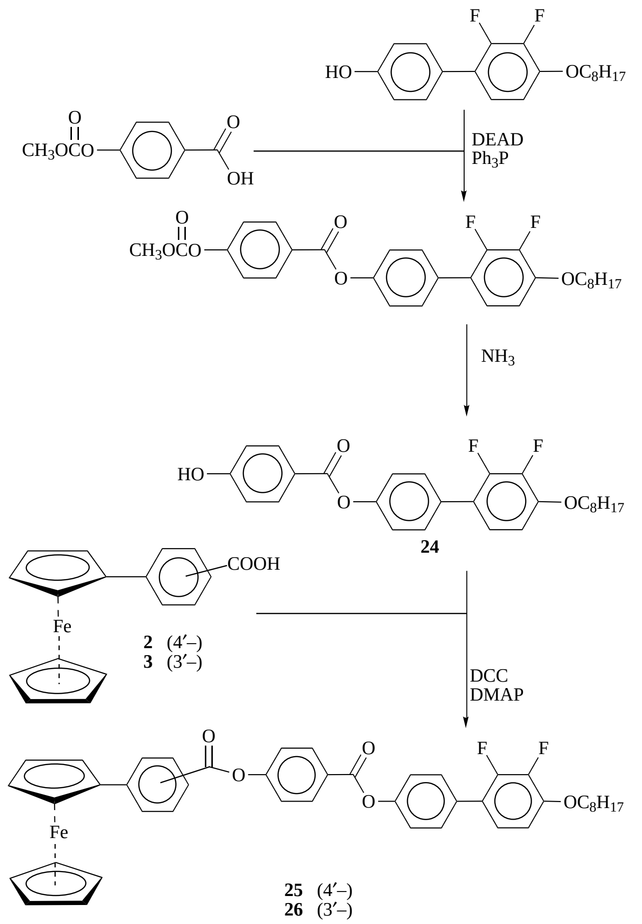


2 (4′–)
3 (3′–)

19 (4′–) $X^3 = F, X^1 = X^2 = H$
20 (4′–) $X^2 = X^3 = F, X^1 = H$
21 (4′–) $X^1 = X^3 = F, X^2 = H$
22 (3′–) $X^3 = F, X^1 = X^2 = H$
23 (3′–) $X^2 = X^3 = F, X^1 = H$

Scheme 3 General route to the fluorinated ferrocene derivatives

ment with those published previously.[23] The ferrocene and ferrocenecarboxylic acid that were used as starting materials were purchased from Aldrich (USA) and used without further purification. The arylferrocenes, 4-carboxyphenylferrocene **2**, 3-carboxyphenylferrocene **3** and 4-hydroxyphenylferrocene **15** were prepared by generating the diazonium salt of either 4- or 3-aminobenzoic acid (Scheme 1) or 4-aminophenol (Scheme 2) and reacting these with ferrocene.[24] The 4-alkyloxybenzoic acids (Scheme 2) were obtained from Frinton Laboratories (New Jersey, USA) and were recrystallized from toluene before use. The fluorinated biphenols were synthesized according to the sequence in Scheme 3, the key step being the construction of the biphenyl unit by Pd-catalysed cross-coupling of the fluorinated aryldihydroxyborane with the fluorinated 4-bromoiodobenzene in dimethoxyethane. This reaction was carried out under an inert atmosphere and was carefully monitored (TLC) to ensure an optimum yield of the biphenyl and to prevent subsequent coupling of this product with unreacted borane (which is added in slight excess) to give unwanted terphenyl. The fluorinated biaryl bromides (Scheme 3) were then converted to the corresponding phenols by treatment with



Scheme 4 Synthetic route to compounds **25** and **26**

butyllithium in tetrahydrofuran at −78 °C, followed by addition of trimethyl borate and subsequent oxidation using 10% hydrogen peroxide.[25]

Scheme 4 illustrates how the organic core of 4-octyloxy-2,3-difluoro-4′-hydroxybiphenyl was extended by esterification with 4-hydroxybenzoic acid (its hydroxy function protected as the methyl carbonate[26]) using diethylazodicarboxylate (DEAD) and triphenylphosphine in tetrahydrofuran (THF).[27] Subsequent removal of the protecting group was accomplished by stirring with aqueous ammonia in ethanol[26] to give the phenol **24**. The carboxyphenylferrocene was attached to this using dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP) to obtain the ferrocene derivatives. This method[28] was employed in the final step of the preparation of all the ferrocene compounds and the description of the preparation of 4-dodecyloxybiphenyl-4′-yl 4-ferrocenylbenzoate is representative thereof. Yields of the final products were not optimized and were in the range 45–60% (after purification).

4-Carboxyphenylferrocene (2). 4-Aminobenzoic acid (2.0 g, 14.6 mmol) was added to concentrated hydrochloric acid (2 ml) to which water (10 ml) was added. To this solution was added sodium nitrite (1.1 g, 15 mmol) in water (10 ml) at 0 °C. The cold solution was added slowly to a cold solution of ferrocene (4.65 g, 25 mmol) in diethyl ether (50 ml). The resulting solution was stirred at 0 °C for 8 h and then at room temp. for approximately 12 h. The ethereal layer was separated and the aqueous layer was extracted with diethyl ether (2 × 100 ml). The combined ethereal fractions were washed with water and dried over anhydrous sodium sulfate. The residue remaining after removing the solvent was subjected to chromatography on silica gel. Unreacted ferrocene was eluted using light petroleum (bp 40–60 °C) whilst the product was eluted using light petroleum–dichloromethane (1:1), mp 250 °C, lit.,[29] 255 °C (decomp.); δ_H(CDCl$_3$) (*J* in Hz) 8.00 (2 H, m, Ar), 7.51 (2 H, m, Ar), 4.70 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.38 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.02 (5 H, s, C$_5$H$_5$); ν_{max}(KBr)/cm^{-1} 3400–2700, 2866, 1681, 1604, 1423, 1284, 1179, 820; *m/z* 307 (17%), 306 (M$^+$, 100%), 186 (10%).

3-Carboxyphenylferrocene (3). This was prepared as for 4-carboxyphenylferrocene starting with 3-aminobenzoic acid, mp 174–177 °C (decomp.), lit.,[29] 166–169 °C; δ_H(CDCl$_3$) 8.20–7.36 (4 H, m, Ar), 4.73 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.35 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.08 (5 H, s, C$_5$H$_5$); ν_{max}(CHCl$_3$)/cm^{-1} 3400–2700, 3022, 1697, 1604, 1293, 1105, 819; *m/z* 307 (25%), 306 (M$^+$, 100%), 261 (2%), 260 (1%), 185 (5%).

4-Hydroxyphenylferrocene (15). This was prepared as for 4-carboxyphenylferrocene starting with 4-aminophenol, mp 164 °C, lit.,[29] 165–166 °C; δ_H(CDCl$_3$) 7.34 (2 H, m, Ar), 6.74 (2 H, m, Ar), 4.54 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.24 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.00 (5 H, s, C$_5$H$_5$); ν_{max}(KBr)/cm^{-1} 3511, 1606, 1525, 1266, 1208, 1178, 1102, 835, 813; *m/z* 280 (39%), 277 (81%), 276 (100%), 220 (10%), 213 (39%).

General method for the preparation of the ferrocenomesogens

The preparation of 4-dodecyloxybiphenyl-4′yl 4-ferrocenylbenzoate 11 as an example of the preparation of the final ferrocene derivatives. A catalytic amount of DMAP was added to a solution of 4-carboxyphenylferrocene (0.1 g, 0.33 mmol) and 4-*n*-dodecyloxy-4′-hydroxybiphenyl (0.104 g, 0.33 mmol) in dry dichloromethane (20 ml). To this was added a solution of DCC (0.082 g, 0.39 mmol) in dichloromethane (2 ml). The reaction was stirred at room temp. for 16 h. The *N*,*N*-dicyclohexylurea precipitate was filtered off and the filtrate evaporated to dryness. The crude product was subjected to flash chromatography on silica gel and was eluted with dichloromethane. Recrystallization from dichloromethane–methanol mixtures gave the product as an orange crystalline solid (yield 48%). δ_H(CDCl$_3$) 8.13 (2 H, d, *J* 8.3, Ar), 7.60 (4 H, 2 × d, *J* 8.3, Ar), 7.52 (2 H, d, *J* 8.3, Ar), 7.27 (2 H, d, *J* 8.3, Ar), 6.98 (2 H, d, *J* 8.3, Ar), 4.79 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.43 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.06 (5 H, s, C$_5$H$_5$), 4.00 (2 H, t, *J* 6.5, OCH$_2$), 1.81 (2 H, m, CH$_2$), 1.81 (2 H, m, CH$_2$), 1.57–1.20 (18 H, m, 9 × CH$_2$), 0.89 (3 H, t, CH$_3$); ν_{max}(KBr)/cm^{-1} 2918, 2847, 1729, 1604, 1494, 1465, 1262, 1215, 1181, 1166, 1086, 1070, 803; *m/z* 643 (M$^+$, 29%), 642 (63%), 354 (7%), 289 (99%), 261 (100%), 237 (18%), 186 (26%).

4-*Octyloxybiphenyl*-4′-*yl ferrocenylcarboxylate* **4**.—δ_H (CDCl$_3$) 7.59 (2 H, d, *J* 8.5, Ar), 7.52 (2 H, d, *J* 8.5, Ar), 7.24 (2 H, d, *J* 8.6, Ar), 6.99 (2 H, d, *J* 8.7, Ar), 4.99 (2 H, t, *J* 1.6, C$_5$H$_4$), 4.52 (2 H, t, *J* 1.5, C$_5$H$_4$), 4.33 (5 H, s, C$_5$H$_5$), 4.01 (2 H, t, *J* 6.6, OCH$_2$), 1.81 (2 H, m, CH$_2$), 1.33 (10 H, m, 5 × CH$_2$), 0.91 (3 H, t, CH$_3$); δ_C(CDCl$_3$) 172.2, 160.8, 151.8, 140,5, 134.8, 130.1, 129.7, 123.9, 116.8, 73.9 (Fc), 72.7 (Fc), quaternary C on substituted Cp ring not observed, 72.0 (Fc), 70.1, 33.8, 31.4, 31.3, 31.3, 28.1, 24.7, 16.1; ν_{max}(KBr)/cm^{-1} 2925, 2854, 1728, 1607, 1497, 1451, 1273, 1204, 1096; *m/z* 510 (M$^+$, 81%), 213 (100%), 185 (40%).

4-*Decyloxybiphenyl*-4′-*yl ferrocenylcarboxylate* **5**.—δ_H (CDCl$_3$) 7.57 (2 H, d, *J* 8.7, Ar), 7.50 (2 H, d, *J* 8.7, Ar), 7.22 (2 H, d, *J* 8.7, Ar), 6.96 (2 H, d, *J* 8.7, Ar), 4.97 (2 H, t, *J* 2.0, C$_5$H$_4$), 4.50 (2 H, t, *J* 2.0, C$_5$H$_4$), 4.31 (5 H, s, C$_5$H$_5$), 3.99 (2 H, t, *J* 6.6, OCH$_2$), 1.80 (2 H, m, CH$_2$), 1.56–1.20 (14 H, m, 7 × CH$_2$), 0.88 (3 H, t, CH$_3$); ν_{max}(KBr)/cm^{-1} 2918, 2849, 1724, 1604, 1493, 1471, 1449, 1371, 1272, 1247, 1212, 1201, 1164, 1104, 1094, 1027, 1011, 998, 909, 828, 787; *m/z* 539 (M$^+$, 28%), 538 (73%), 213 (100%), 185 (43%).

4-*Octyloxyphenyl* 4-*ferrocenylbenzoate* **6**.—δ_H(CDCl$_3$) 8.10 (2 H, d, *J* 8.6, Ar), 7.57 (2 H, d, *J* 8.6, Ar), 7.12 (2 H, d, *J* 8.6, Ar), 6.93 (2 H, d, *J* 8.6, Ar), 4.74 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.41 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.05 (5 H, s, C$_5$H$_5$), 3.96 (2 H, t, *J* 6.6, OCH$_2$), 1.78 (2 H, m, CH$_2$), 1.58–1.20 (10 H, m, 5 × CH$_2$), 0.89 (3 H, t, CH$_3$); ν_{max}(KBr)/cm^{-1} 2922, 2851, 1726, 1605, 1592, 1505, 1469, 1270, 1251, 1191, 1180, 1085, 1070, 1014, 885, 821; *m/z* 512 (4%), 511 (M$^+$, 20%), 508 (4%), 290 (16%), 289 (74%), 262 (21%), 261 (100%), 260 (8%) (Found: C, 72.87; H, 6.73. C$_{31}$H$_{34}$FeO$_3$ requires C, 72.9; H, 6.7%).

4-*Decyloxyphenyl-4-ferrocenylbenzoate* **7**.—δ_{H}($CDCl_3$) 8.11 (2 H, d, *J* 8.6, Ar), 7.58 (2 H, d, *J* 8.6, Ar), 7.13 (2 H, d, *J* 8.6, Ar), 6.94 (2 H, d, *J* 8.6, Ar), 4.75 (2 H, t, *J* 1.9, C_5H_4), 4.42 (2 H, t, *J* 1.9, C_5H_4), 4.06 (5 H, s, C_5H_5), 3.97 (2 H, t, *J* 6.7, OCH_2), 1.80 (2 H, m, CH_2), 1.59–1.20 (14 H, m, 7 × CH_2), 0.90 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2925, 2849, 1728, 1605, 1503, 1469, 1269, 1248, 1192, 1181, 1085, 1070, 821; *m/z* 540 (5%), 539 (M^+, 24%), 538 (60%), 289 (80%), 262 (22%), 261 (100%), 260 (7%), 259 (71%) (Found: C, 73.75; H, 7.19. $C_{33}H_{38}FeO_3$ requires C, 73.6; H, 7.1%).

4-*Decyloxyphenyl* 3-*ferrocenylbenzoate* **8**.—δ_{H}($CDCl_3$) 8.26 (1 H, t, *J* 1.4, Ar), 8.02 (1 H, dt, *J* 7.8, *J* 1.3, Ar), 7.73 (1 H, dt, *J* 7.8, *J* 1.3, Ar), 7.42 (1 H, t, *J* 7.7, Ar), 7.15 (2 H, d, *J* 9.0, Ar), 6.95 (2 H, d, *J* 9.0, Ar), 4.73 (2 H, t, *J* 1.9, C_5H_4), 4.37 (2 H, t, *J* 1.9, C_5H_4), 4.06 (5 H, s, C_5H_5), 3.97 (2 H, t, *J* 6.6, OCH_2), 1.80 (2 H, m, CH_2), 1.55–1.20 (14 H, m, 7 × CH_2), 0.89 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2919, 2846, 1738, 1598, 1500, 1461, 1293, 1231, 1186, 1104, 1097, 1064, 1031, 1017, 1006, 995, 816, 750, 688; *m/z* 540 (6%), 539 (M^+, 57%), 538 (50%), 289 (7%), 262 (27%), 261 (100%), 260 (13%), 205 (3%).

4-*Octyloxybiphenyl*-4′-*yl* 4-*ferrocenylbenzoate* **9**.—δ_{H}($CDCl_3$) 8.13 (2 H, t, *J* 8.6, Ar), 7.60 (2 H, t, *J* 8.6, Ar), 7.59 (2 H, t, *J* 8.6, Ar), 7.52 (2 H, t, *J* 8.6, Ar), 7.27 (2 H, t, *J* 8.6, Ar), 6.98 (2 H, t, *J* 8.6, Ar), 4.76 (2 H, t, *J* 1.9, C_5H_4), 4.43 (2 H, t, *J* 1.9, C_5H_4), 4.07 (5 H, s, C_5H_5), 4.01 (2 H, t, *J* 6.7, OCH_2), 1.82 (2 H, m, CH_2), 1.58–1.20 (10 H, m, 5 × CH_2), 0.90 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2986, 2922, 2849, 1729, 1605, 1495, 1285, 1266, 1209, 1180, 1165, 1085, 1071, 805; *m/z* 587 (52%), 586 (M^+, 21%), 298 (6%), 290 (23%), 289 (72%), 262 (17%), 261 (100%), 186 (31%), 185 (7%) (Found: C, 75.6; H, 6.4. $C_{37}H_{38}FeO_3$ requires C, 75.8; H, 6.5).

4-*Octyloxybiphenyl*-4′-*yl* 3-*ferrocenylbenzoate* **13**.—δ_{H} ($CDCl_3$) 8.29 (1 H, t, *J* 1.8, Ar), 8.05 (1 H, dt, *J* 7.7, *J* 1.6, Ar), 7.75 (1 H, dt, *J* 7.8, *J* 1.8, Ar), 7.62 (2 H, d, *J* 8.7, Ar), 7.53 (2 H, d, *J* 8.7, Ar), 7.45 (1 H, t, *J* 7.7, Ar), 7.30 (2 H, d, *J* 8.5, Ar), 6.98 (2 H, d, *J* 8.7, Ar), 4.75 (2 H, t, *J* 1.9, C_5H_4), 4.38 (2 H, t, *J* 1.9, C_5H_4), 4.07 (5 H, s, C_5H_5), 4.01 (2 H, t, *J* 6.6, OCH_2), 1.82 (2 H, m, CH_2), 1.60–1.20 (10 H, m, 5 × CH_2), 0.91 (3 H, t, CH_3); δ_{C}($CDCl_3$) 160.8, 151.9, 142.4, 140.8, 134.7, 133.0, 131.7, 130.6, 130.1, 129.7, 129.5, 123.9, 116.8, 98.1, 85.9 (Fc), 71.7 (Fc), 71.4 (Fc), 70.1 (Fc), 68.7, 33.9, 31.7, 31.4, 31.3, 28.1, 24.7, 16.1; *m/z* 586 (M^+, 41%), 262 (21%), 261 (100%), 260 (15%), 203 (11%), 185 (10%); ν_{max}(KBr)/cm^{-1} 2949, 2919, 2845, 1725, 1605, 1493, 1470, 1288, 1264, 1247, 1231, 1201, 1163, 1080, 1012, 995, 832, 814, 797, 750 (Found: C, 75.6; H, 6.9. $C_{37}H_{38}FeO_3$ requires C, 75.8; H, 6.5%).

4-*Decyloxybiphenyl*-4′-*yl* 4-*ferrocenylbenzoate* **10**.—δ_{H} ($CDCl_3$) 8.13 (2 H, d, *J* 8.8, Ar), 7.60 (2 H, d, *J* 8.8, Ar), 7.59 (2 H, d, *J* 8.7, Ar), 7.51 (2 H, d, *J* 8.8, Ar), 7.27 (2 H, d, *J* 8.8, Ar), 6.97 (2 H, d, *J* 8.7, Ar), 4.76 (2 H, t, *J* 1.8, C_5H_4), 4.43 (2 H, t, *J* 1.8, C_5H_4), 4.07 (5 H, s, C_5H_5), 4.00 (2 H, t, *J* 6.6, OCH_2), 1.82 (2 H, m, CH_2), 1.55–1.21 (14 H, m, 7 × CH_2), 0.90 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2919, 2846, 1729, 1604, 1495, 1464, 1286, 1262, 1181, 1086, 1070, 803; *m/z* 614 (M^+, 2%), 431 (7%), 430 (100%), 290 (9%), 262 (3%), 261 (10%), 186 (17%), 185 (34%) (Found: C, 76.4; H, 6.9. $C_{39}H_{42}FeO_3$ requires C, 76.2; H, 6.9%).

4-*Decyloxybiphenyl*-4′-*yl* 3-*ferrocenylbenzoate* **14**.—δ_{H} ($CDCl_3$) 8.29 (1 H, t, *J* 1.8, Ar), 8.05 (1 H, dt, *J* 7.7, *J* 1.6, Ar), 7.75 (1 H, dt, *J* 7.8, *J* 1.8, Ar), 7.62 (2 H, d, *J* 8.7, Ar), 7.53 (2 H, d, *J* 8.7, Ar), 7.45 (1 H, t, *J* 7.7, Ar), 7.30 (2 H, d, *J* 8.7, Ar), 6.99 (2 H, d, *J* 8.7, Ar), 4.74 (2 H, t, *J* 1.9, C_5H_4), 4.38 (2 H, t, *J* 1.9, C_5H_4), 4.08 (5 H, s, C_5H_5), 4.01 (2 H, t, *J* 6.6, OCH_2), 1.82 (2 H, m, CH_2), 1.58–1.20 (14 H, m, 7 × CH_2), 0.90 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2945, 2920, 2844, 1725, 1604, 1493, 1470, 1288, 1266, 1246, 1232, 1201, 1163, 1081, 1011, 814; *m/z* 614 (M^+, 100%), 613 (32%), 587 (3%), 290 (3%), 289 (5%), 262 (22%), 261 (80%), 259 (7%), 237 (6%), 203 (6%) (Found: C, 76.3; H, 6.9. $C_{39}H_{42}FeO_3$ requires C, 76.2; H, 6.9).

4-*Tetradecyloxybiphenyl*-4′-*yl* 4-*ferrocenylbenzoate* **12**.—δ_{H} ($CDCl_3$) 8.13 (2 H, d, *J* 8.6, Ar), 7.60 (4 H, 2 × d, *J* 8.6, Ar), 7.52 (2 H, d, *J* 8.6, Ar), 7.27 (2 H, d, *J* 8.6, Ar), 6.98 (2 H, d, *J* 8.6, Ar), 4.76 (2 H, t *J* 1.9, C_5H_4), 4.43 (2 H, t, *J* 1.9, C_5H_4), 4.07 (5 H, s, C_5H_5), 4.01 (2 H, t, OCH_2), 1.81 (2 H, m, CH_2), 1.58–1.20 (22 H, m, 11 × CH_2), 0.89 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2916, 2846, 1729, 1604, 1494, 1464, 1287, 1262, 1215, 1181, 1166, 1086, 1070, 802; *m/z* 671 (50%), 670 (M^+, 96%), 474 (96%), 289 (89%), 261 (100%), 186 (46%).

4-*Ferrocenylphenyl* 4-*octyloxybenzoate* **16**.—δ_{H}($CDCl_3$) 8.15 (2 H, d, *J* 8.6, Ar), 7.52 (2 H, d, *J* 8.6, Ar), 7.14 (2 H, d, *J* 8.6, Ar), 6.98 (2 H, d, *J* 8.6, Ar), 4.63 (2 H, t, *J* 1.9, C_5H_4), 4.32 (2 H, t, *J* 1.9, C_5H_4), 4.07 (5 H, s, C_5H_5), 4.05 (2 H, t, *J* 6.6, OCH_2), 1.83 (2 H, m, CH_2), 1.59–1.20 (10 H, m, 5 × CH_2), 0.90 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2922, 2849, 1732, 1602, 1517, 1505, 1450, 1312, 1257, 1196, 1160, 1101, 1050, 1004, 846, 817, 762; *m/z* 512 (16%), 511 (M^+, 77%), 508 (11%), 410 (3%), 279 (11%), 278 (59%), 277 (29%), 234 (17%), 233 (100%).

4-*Ferrocenylphenyl* 4-*decyloxybenzoate* **17**.—δ_{H}($CDCl_3$) 8.15 (2 H, d, *J* 8.6, Ar), 7.51 (2 H, d, *J* 8.6, Ar), 7.13 (2 H, d, *J* 8.6, Ar), 6.97 (2 H, d, *J* 8.6, Ar), 4.62 (2 H, t, *J* 1.9, C_5H_4), 4.31 (2 H, t, *J* 1.9, C_5H_4), 4.06 (5 H, s, C_5H_5), 4.05 (2 H, t, *J* 6.5, OCH_2), 1.82 (2 H, m, CH_2), 1.60–1.20 (14 H, m, 7 × CH_2), 0.88 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2919, 2846, 1733, 1601, 1517, 1504, 1450, 1312, 1255, 1196, 1159, 1101, 1053, 1003, 846, 817, 762; *m/z* 539 (M^+, 28%), 538 (100%), 279 (8%), 278 (35%), 277 (21%), 262 (11%), 261 (47%), 186 (5%).

4-*Ferrocenylphenyl* 4-*dodecyloxybenzoate* **18**.—δ_{H}($CDCl_3$) 8.15 (2 H, d, *J* 8.7, Ar), 7.51 (2 H, d, *J* 8.7, Ar), 7.13 (2 H, d, *J* 8.6, Ar), 6.98 (2 H, d, *J* 8.6, Ar), 4.62 (2 H, t, *J* 1.8, C_5H_4), 4.30 (2 H, t, *J* 1.8, C_5H_4) 4.06 (5 H, s, C_5H_5), 4.05 (2 H, t, *J* 6.6, OCH_2), 1.83 (2 H, m, CH_2), 1.58–1.20 (18 H, m, 9 × CH_2), 0.89 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2920, 2848, 1726, 1603, 1517, 1504, 1450, 1311, 1253, 1195, 1159, 1102, 1063, 1003, 843, 819, 762; *m/z* 566 (M^+, 100%), 539 (2%), 538 (1%), 290 (5%), 289 (16%), 278 (17%), 262 (1%), 261 (1%) (Found: C, 74.02; H, 7.41. $C_{35}H_{42}FeO_3$ requires C, 74.2; H, 7.5).

4-*Octyloxy*-2,3-*difluorobiphenyl*-4′-*yl* 4-*ferrocenylbenzoate* **20**.—δ_{H}($CDCl_3$) 8.11 (2 H, d, *J* 8.6, Ar), 7.55 (4 H, m, Ar), 7.29 (2 H, d, *J* 8.6, Ar), 7.09 (1 H, dt, *J* 7.9, *J* 1.6, Ar), 6.79 (1 H, dt, *J* 7.9, *J* 1.6, Ar), 4.74 (2 H, t, *J* 1.9, C_5H_4), 4.41 (2 H, t, *J* 1.9, C_5H_4), 4.07 (2 H, t, *J* 6.6, OCH_2), 4.05 (5 H, s, C_5H_5), 1.83 (2 H, m, CH_2), 1.48 (2 H, m, CH_2), 1.30 (8 H, m, 4 × CH_2), 0.88 (3 H, t, CH_3); δ_{C}($CDCl_3$) 165.2, 150.6, 148.9 ($^1J_{\mathrm{CF}}$ 249.1), 147.9, 146.2, 142.3 ($^1J_{\mathrm{CF}}$ 247.0), 132.6, 130.4, 129.9, 129.8, 126.5, 125.8, 123.6, 122.2, 121.9, 109.7, 83.1 (Fc), 70.0 (Fc), 69.9 (Fc), 69.8 (Fc), 67.0, 31.8, 29.3, 29.2, 29.1, 25.9, 22.7, 14.1; δ_{F}($CDCl_3$) −146.1 (1 F, d, $^3J_{\mathrm{FF}}$ 19.3), −162.9 (1 F, d, $^3J_{\mathrm{FF}}$ 19.3); ν_{max}(KBr)/cm^{-1} 2922, 1728, 1603, 1499, 1469, 1264, 1209.

4-*Octyloxy*-2,3-*difluorobiphenyl*-4′-*yl* 3-*ferrocenylbenzoate* **23**.—δ_{H}($CDCl_3$) 8.29 (1 H, t, *J* 1.6, Ar), 8.05 (1 H, dt, *J* 7.9, *J* 1.6, Ar), 7.76 (1 H, dt, *J* 7.9, *J* 1.6, Ar), 7.59 (2 H, d, *J* 8.7, Ar), 7.45 (1 H, t, *J* 7.7, Ar), 7.33 (2 H, d, *J* 8.7, Ar), 7.12 (1 H, td, J_{HF} 8.8, *J* 2.4, Ar), 6.82 (1 H, td, J_{HF} 8.9, *J* 1.9, Ar), 4.74 (2 H, t, *J* 1.9, C_5H_4), 4.38 (2 H, t, *J* 1.9, C_5H_4). 4.09 (2 H, t, *J* 6.6, OCH_2), 4.07 (5 H, s, C_5H_5), 1.85 (2 H, m, CH_2), 1.57–1.20 (10 H, m, 5 × CH_2), 0.90 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2924, 2852, 1731, 1627, 1502, 1470, 1312, 1289, 1233, 1203, 1167, 1104, 1085, 1013, 869, 823, 809, 794, 746; *m/z* 622 (M^+, 100%), 289 (3%), 261 (62%), 259 (6%), 255 (3%), 222 (7%) (Found: C, 71.4; H, 5.8. $C_{37}H_{35}FeF_2O_3$ requires C, 71.4; H, 5.8%).

4-*Octyloxy*-3-*fluorobiphenyl*-4′-*yl* 4-*ferrocenylbenzoate* **19**.—δ_{H}($CDCl_3$) 8.10 (2 H, d, *J* 8.4, Ar), 7.57 (2 H, d, *J* 8.4, Ar), 7.56 (2 H, d, *J* 8.6, Ar), 7.32–7.24 (4 H, m, Ar), 7.00 (1 H, t, *J* 8.6, Ar), 4.73 (2 H, t, *J* 1.9, C_5H_4), 4.41 (2 H, t, *J* 1.9, C_5H_4), 4.05 (2 H, t, *J* 6.6, CH_2), 4.04 (5 H, s, C_5H_5), 1.83 (2 H, m, CH_2), 1.59–1.20 (10 H, m, alkyl), 0.88 (3 H, t, *J* 6.6, CH_3); δ_{F}($CDCl_3$) −138.5; ν_{max}(KBr)/cm^{-1} 2927, 1731, 1605, 1498, 1384, 1267, 1208, 1179, 1087, 801; *m/z* 605 (M^+, 100%), 604 (7%), 492 (1%), 290 (49%), 287 (18%), 263 (8%), 262 (78%), 260 (30%).

4-*Octyloxy*-3-*fluorobiphenyl*-4′-*yl* 3-*ferrocenylbenzoate* **22**.—δ_H(CDCl$_3$) 8.29 (1 H, t, *J* 8.6, Ar), 8.04 (1 H, dt, *J* 7.7, *J* 1.6, Ar), 7.75 (1 H, dt, *J* 7.7, *J* 1.6, Ar), 7.60 (2 H, d, *J* 8.6, Ar), 7.44 (1 H, t, *J* 8.6, Ar), 7.39–7.24 (4 H, m, Ar), 7.03 (1 H, t, *J* 8.6, Ar), 4.74 (2 H, t, *J* 1.9, C_5H_4), 4.38 (2 H, *J* 1.9, C_5H_4), 4.08 (2 H, t, *J* 6.7, OCH_2), 4.07 (5 H, s, C_5H_5), 1.85 (2 H, m, CH_2), 1.59–1.20 (10 H, m, 5 × CH_2), 0.89 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2949, 2917, 2846, 1729, 1494, 1470, 1288, 1277, 1261, 1243, 1231, 1202, 1164, 1132, 1076, 1012, 872, 814, 795, 749; *m/z* 605 (2%), 604 (M$^+$, 100%), 493 (1%), 290 (1%), 289 (2%), 261 (67%), 259 (6%), 246 (5%), 204 (8%), 205 (6%) (Found: C, 73.4; H, 6.2. $C_{37}H_{38}FeFO_3$ requires C, 73.4; H, 6.3%).

4-*Octyloxy*-2′,3-*difluorobiphenyl*-4′-*yl* 4-*ferrocenylbenzoate* **21**.—δ_H(CDCl$_3$) 8.08 (2 H, d, *J* 8.6, Ar), 7.57 (2 H, d, *J* 8.5, Ar), 7.42 (1 H, t, *J* 8.3, Ar), 7.25 (2 H, m, Ar), 7.09 (2 H, m, Ar), 7.01 (1 H, t, *J* 8.6, Ar), 4.74 (2 H, t, *J* 1.9, C_5H_4), 4.41 (2 H, t, *J* 1.9, C_5H_4), 4.06 (2 H, t, *J* 6.6, CH_2), 4.04 (5 H, s, C_5H_5), 1.83 (2 H, m, CH_2), 1.51–1.20 (10 H, m, alkyl), 0.88 (3 H, t, *J* 6.8, CH_3); δ_F(CDCl$_3$) −119.42, −138.75; *m/z* 624 (3%), 623 (2%), 622 (M$^+$, 31%), 290 (13%), 289 (63%), 262 (22%), 261 (100%).

Preparation of 4-octyloxy-2,3-difluorobiphenyl-4′-yl 4-hydroxybenzoate (24). A suspension of compound **27** (1.35 g, 2.64 mmol) in a mixture of ethanol (30 ml) and aqueous ammonia (35%, 30 ml) was stirred at room temp. for 3.5 h or until TLC showed the reaction to be complete. The volatile components were removed under reduced pressure to give a colourless solid which was further dried *in vacuo* (P_2O_5). Yield 1.17 g (97%), mp 145 °C; δ_H(CDCl$_3$) 8.13 (2 H, d, *J* 8.5, Ar), 7.55 (2 H, d, *J* 8.5, Ar), 7.27 (2 H, d, *J* 8.5, Ar), 7.09 (1 H, td, *J* 8.9, *J* 2.4, Ar), 6.92 (2 H, d, *J* 8.5, Ar), 6.80 (1 H, td, *J* 8.9, *J* 2.3, Ar), 5.04 (1 H, s, Ar), 4.07 (2 H, t, *J* 6.6, OCH_2), 1.84 (2 H, m, CH_2), 1.48–1.21 (10 H, m, 5 × CH_2), 0.89 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 3320, 2960, 2930, 2760, 1734, 1705, 1610, 1509, 1475, 1294, 1215, 1200, 1171, 1104, 1082, 800, 765; *m/z* 454 (M$^+$, 6%), 334 (25%), 222 (61%), 117 (100%).

4-*Octyloxy*-2,3-*difluorobiphenyl*-4′-*yl* 4-(4-*ferrocenylbenzoyloxy*)*benzoate* **25**.—δ_H(CDCl$_3$) 8.29 (2 H, d, *J* 8.6, Ar), 8.11 (2 H, d, *J* 8.6, Ar), 7.58 (2 H, d, *J* 8.6, Ar), 7.56 (2 H, d, *J* 8.6, Ar), 7.39 (2 H, d, *J* 8.6, Ar), 7.27 (2 H, d, *J* 8.6, Ar), 7.09 (1 H, td, J_{HF} 9.6, *J* 2.4, Ar), 6.79 (1 H, td, J_{HF} 9.6, *J* 1.8, Ar), 4.75 (2 H, t, *J* 1.9, C_5H_4), 4.42 (2 H, t, *J* 1.9, C_5H_4), 4.06 (2 H, t, *J* 6.6, OCH_2), 4.05 (5 H, s, C_5H_5), 1.83 (2 H, m, CH_2), 1.48–1.20 (10 H, m, 5 × CH_2), 0.88 (3 H, t, CH_3); δ_F(CDCl$_3$) −146.06 (1 F, d, $^3J_{FF}$ 20), −162.94 (1 F, d, $^3J_{FF}$ 20); ν_{max}(KBr)/cm^{-1} 2930, 2857, 1735, 1604, 1503, 1472, 1263, 1201, 1180, 1163, 1067, 796; *m/z* 742 (M$^+$, 66%), 741 (99%), 558 (4%), 334 (6%), 289 (84%), 262 (20%), 261 (100%), 225 (26%).

4-*Octyloxy*-2,3-*difluorobiphenyl*-4′-*yl* 4-(3-*ferrocenylbenzoyloxy*)*benzoate* **26**.—δ_H(CDCl$_3$) 8.31 (2 H, d, *J* 8.6, Ar), 8.29 (2 H, d, *J* 8.6, Ar), 8.05 (1 H, dt, *J* 7.9, *J* 1.2, Ar), 7.79 (1 H, dt, *J* 7.9, *J* 1.2, Ar), 7.58 (2 H, d, *J* 8.6, Ar), 7.43 (2 H, d, *J* 8.6, Ar), 7.35 (2 H, d, *J* 8.6, Ar), 7.12 (1 H, td, J_{HF} 9.6, *J* 2.4, Ar), 6.82 (1 H, td, J_{HF} 9.6, *J* 1.8, Ar), 4.75 (2 H, t, *J* 1.9, C_5H_4), 4.39 (2 H, t, *J* 1.9, C_5H_4), 4.09 (2 H, t, *J* 6.6, OCH_2), 4.08 (5 H, s, C_5H_5), 1.83 (2 H, m, CH_2), 1.48–1.20 (10 H, m, 5 × CH_2), 0.88 (3 H, t, CH_3); ν_{max}(KBr)/cm^{-1} 2920, 2850, 1731, 1627, 1600, 1500, 1469, 1404, 1311, 1274, 1228, 1198, 1160, 1103, 1075, 1013, 894, 882, 797, 756, 745; *m/z* 742 (M$^+$, 56%), 741 (100%), 622 (6%), 560 (8%), 334 (4%), 289 (16%), 262 (4%), 261 (20%), 225 (50%) (Found: C, 71.4; H, 5.5. $C_{44}H_{40}F_2FeO_5$ requires C, 71.2; H, 5.4%).

Summary and conclusion

A series of new monosubstituted ferrocene derivatives was synthesized in which selected structural features were varied systematically. The size and shape of the aromatic core of the substituent on ferrocene is found to play an important role in determining the thermal properties of these compounds. It was established that a minimum of three rings in the substituent core are necessary for stabilizing the nematic phase, but that four rings vastly enhance the nematic behaviour. The usefulness of lateral fluorination with respect to both the reduction of the nematic phase temperatures and the suppression of smectic phases has been demonstrated. ^{1}H NMR chemical shifts were shown to provide an indication of the extent to which electron-withdrawing substituents (such as COO) affect the Fe–Cp bonding and the advantages of inserting a phenyl ring between ferrocene and the carbonyloxy link were pointed out. It is concluded that ferrocene derivatives with a pendent ferrocene group do have potential as useful materials although the work presented here should be considered a starting point.

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