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REVIEW

Monosubstituted thermotropic ferrocenomesogens: an overview 1976–1999

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Research in the late 1940s in academic institutions, most notably the University of Hull in the UK, led to the development of liquid crystal display technology in the 1970s, which has subsequently had a large impact throughout the world. The liquid crystal technology is based on simple organic molecules. Since the late 1980s, some liquid crystal scientists have turned their attention to investigating the effect of introducing a metal atom into the systems. This review focuses on the major developments in the field of ferrocenyl-containing liquid crystals in which the organometallic group is situated in a terminal position with respect to the core of the molecule. Metallomesogens with terminal metal atoms are not very common, since it can be deduced from the theory of organic liquid crystals that bulky terminal groups would not be conducive to the stabilization of liquid crystal phases. Nevertheless, a terminal ferrocenyl group can stabilize a nematic liquid crystal phase and examples of this will be discussed in this review. Copyright © 2001 John Wiley & Sons Ltd.

Keywords: metallomesogens; liquid crystals; ferrocenomesogens; monosubstituted ferrocenes; nematic; smectic

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1 INTRODUCTION

1.1 Historical

Friedrich Reinitzer's observation in 1888 that molten cholesteryl benzoate appeared to exhibit two melting points[1] has resulted in him being widely acknowledged as the originator of organic liquid crystal chemistry. Vorlander described the first examples of thermotropic metallomesogens[2] in 1910 with the discovery that alkali-metal carboxylates formed classical lamellar phases. In 1923 Vorlander described the first examples of organometallic liquid crystals[3] based on diarylmercury derivatives.

The discovery of ferrocene in 1951 heralded a new era in the realm of organometallic chemistry.[4,5] The discovery can, in many respects, be compared to the more recent discovery of fullerene-60,[6] as both have opened up new horizons in chemistry. The events leading up to and shortly after the discovery of ferrocene are interesting.[7] The early years of research in ferrocene chemistry were primarily concerned with the reactivity of ferrocene and with the syntheses of new ferrocene derivatives. In 1974, Nesmeyanov and Kochetkova[8] published a thought-provoking paper entitled

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'Principal Practical Applications of Ferrocene and its Derivatives in which the authors described the potential use of ferrocenes in a range of applications. The applications covered included radiation absorbers, dyestuffs, combustion regulators, medicinal substances and electron-exchange resins. Surprisingly, the potential use of ferrocenes as liquid crystals was not mentioned and it was another 2 years before the first paper appeared on the subject of ferrocenyl-containing liquid crystals (now termed *ferrocenomesogens*).[9] During the last three decades of the 20th century, there has been a general renaissance in ferrocene chemistry, notably in the field of materials chemistry.[10]

This review covers work pertaining to the chemistry of new monosubstituted ferrocenomesogens in the period 1976–1999. It focuses primarily on ferrocenomesogens in which the ferrocenyl group is in a terminal position, since this is the area on which we have concentrated in our research and this aspect has not received much attention previously. Excellent reviews are available on the general subject of metallomesogens[11–13] and a monograph has appeared recently.[14]

1.2 Applications

An attempt to utilize liquid crystalline materials in weapons technology during the Second World War was largely unsuccessful and liquid crystals remained primarily of academic interest until the 1960s. It was at that time that scientists realized that the anisotropic physical properties of liquid crystals could be used in a flat optical display device by making use of the dynamic scattering effect. This presented a new challenge. Effective use of the dynamic scattering effect required materials with liquid crystal phases at or close to room temperature. This requirement was soon achieved, and organic liquid crystals took their place in device technology. The twisted nematic liquid crystal display was invented in the 1970s and since that time has found widespread use in electro-optic devices, such as watches, calculators and more recently in notebook and portable computers. Early work on liquid crystalline materials concentrated on organic compounds, with research on metallomesogens becoming significant only during the late 1980s. However, to date, there have been no major applications of metallomesogens in device technology. The incorporation of metals into liquid crystalline compounds combines the properties of the liquid crystal (fluidity) with the properties associated with metals (colour, electron density, magnetism and polarizability). The hope is that the symbiosis between the two may impart unique properties to the new liquid crystal materials.

1.3 Terminology

A liquid crystal or mesogenic molecule is one that forms a state of matter (termed the mesophase) that is intermediate between the solid and the liquid over a given temperature range. A metallomesogen is a mesogenic molecule that incorporates a metal atom, and if it incorporates a ferrocenyl moiety, we term it a ferrocenomesogen. Liquid crystalline compounds are anisotropic. This results from their shapes and may be ascribed to the significant difference in length of one molecular axis compared with the other two. The majority of ferrocenomesogens prepared to date, have been rod-shaped molecules, and liquid crystalline materials with this shape are known as calamitic liquid crystals. In calamitic liquid crystals, one molecular axis is considerably longer than the other two. Another class of liquid crystalline materials is known as discotics (generally molecules in this category are disc-shaped); in these molecules, one molecular axis is considerably shorter than the other two. Liquid crystalline materials can be further divided into two classes: the thermotropics and the lyotropics. The phase behaviour in thermotropic liquid crystals is temperature dependent, whereas lyotropic liquid crystal phases are formed by molecules in a solvent and are concentration dependent. For a thermotropic liquid crystal, during the heating cycle, the crystal phase changes to the first mesophase (if there is more than one) at a transition known as the melting point. The transition from the mesophase to the isotropic liquid is known as the clearing point. The mesophases can be either enantiotropic (thermodynamically stable) or monotropic (thermodynamically unstable). In the first the phase is observed on both the heating and cooling cycles whereas in the latter it is only observed on cooling.

The most common phases associated with monosubstituted ferrocenomesogens to date are the nematic (N) and, to a lesser extent, the smectic A (S_A). The nematic phase is the least ordered liquid crystal phase and is characterized by rod-like molecules lined up in approximately the same direction, but having negligible positional correlation. In the smectic phase, molecules have considerable directional and positional order. The introduction of a chiral centre into a molecule with either nematic or smectic phases gives rise to liquid

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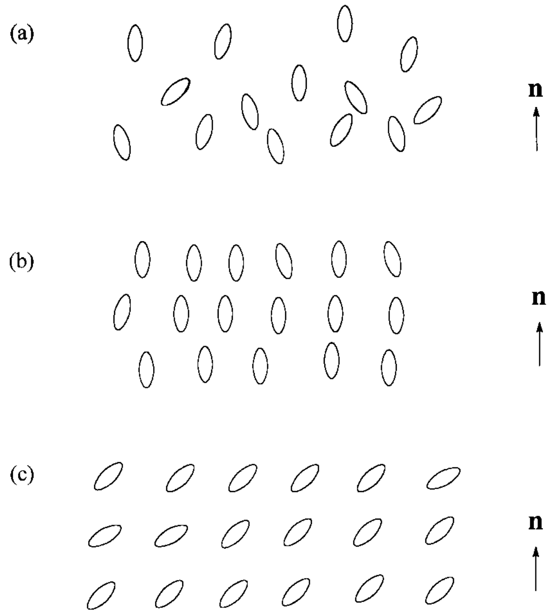


Figure 1 Schematic representation of molecules in (a) nematic phase (N) (b) smectic A phase (S_A and (c) smectic C phase (S_C).

crystals with the respective chiral phases. The chiral nematic phase (N*) is often termed the cholesteric phase, since it was first observed with derivatives of cholesterol. The chiral smectic C phase (S_C*) is currently receiving significant attention because of its usefulness in flat screen technology. The blue (BP) and twist-grain boundary (TGBA*) phases are examples of frustrated phases that occur only in chiral molecules. These phases are formed due to the reduction in symmetry resulting in unusual structural behaviour. The molecules are prevented from consistently adopting their preferred packing arrangement, resulting in the introduction of defects. The blue phase occurs at temperatures above the cholesteric and the TGBA* phase is the smectic analogue that is based on the smectic A phase. A schematic representation of the molecules in some of these phases is shown in Fig. 1. Far more in-depth discussion of definitions and concepts is given in Refs 14–16.

1.4 Structural requirements

Organometallic and metal–organic molecules that exhibit thermotropic properties usually have either a linear elongated shape (calamitics) or a disc-like shape (discotics). These particular shapes allow intermolecular interactions that favour alignment and which are critical for mesomorphic behaviour. The majority of ferrocenomesogens prepared so far are restricted to one of the structural types shown in Fig. 2. In monosubstituted ferrocenomesogens, the ferrocenyl unit is located at the terminus of the molecule, whereas in disubstituted ferrocenomesogens, and the majority of other metallomesogens, the metal is situated at the centre of the molecule. The incorporation of a ferrocenyl group in the terminal position in a long elongated molecule results in a monomolecular L-shape. In such cases the bulky ferrocenyl unit is expected to lead to repulsive steric effects, which would have an adverse effect on the intermolecular interactions. A possible way of minimizing the unfavourable steric effects would be to lengthen the mesogenic unit (mu) in order to improve the length:width ratio of the molecule. Alternatively, the metal unit can be situated at approximately the centre of a molecule and the chemistry of ferrocenomesogens based on 1,1′ and 1,3-disubstituted ferrocenes has been reviewed in a monograph by Deschenaux and Goodby in Ref 10.

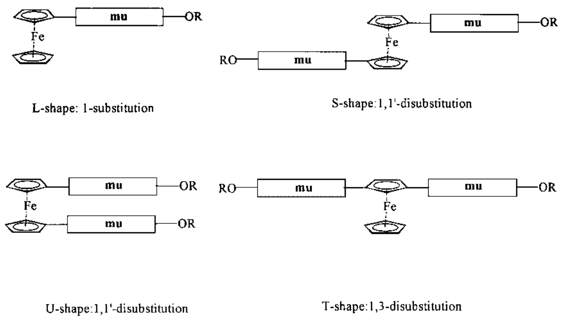


Figure 2 Most common structural geometrics of ferrocenomesogens (mu: mesogenic unit).

2 MONOSUBSTITUTED THERMOTROPIC FERROCENOMESOGENS

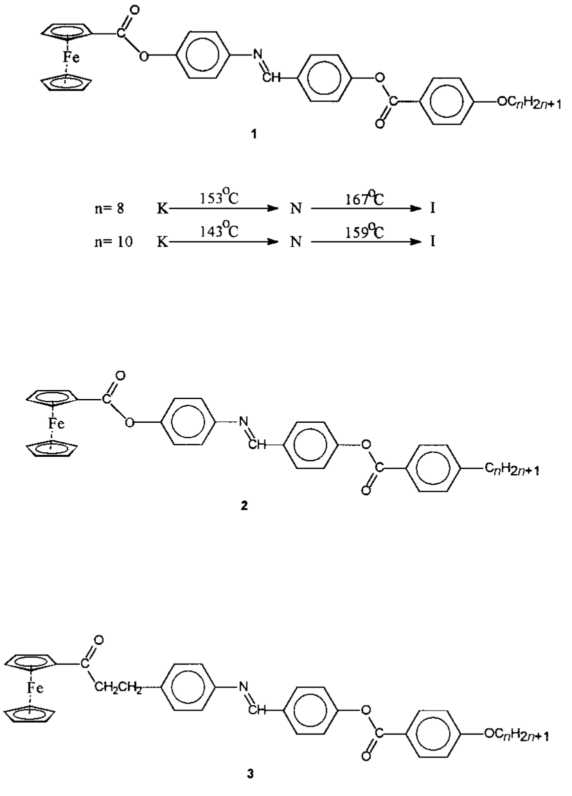
2.1 Early work

In 1957, Graham *et al.* reported that formylferrocene exhibited a liquid crystalline state between 45 °C and 124.5 °C.[17] Subsequent work utilizing optical polarizing microscopy,[18] X-ray diffraction[19] and Mössbauer spectroscopy[20] revealed that formylferrocene exhibits a plastic crystal phase and not a liquid crystal phase between the two temperatures. The structures of the crystal and plastic crystal states of formylferrocene have both been shown to be orthorhombic.

2.2 Rapid growth of new compounds

Malthête and Billard described the synthesis of the first examples of mesogenic ferrocene derivatives.[9] Compounds having three structural variations were synthesized (**1**–**3**, Fig. 3), and in each case, the ferrocenyl group was situated in a terminal position.

The compounds based on structure **1** displayed enantiotropic nematic liquid crystal phases characterized by their Schlieren textures using optical microscopy, but exhibited relatively short liquid crystal domains. Compounds based on structures **2** and **3** were monotropic nematogenics. The results of Malthête and Billard[9] were surprising, since it had been expected that monosubstituted ferrocenes would be poor compounds for stabilizing liquid crystalline phases owing to the bulky ferrocenyl group disrupting the overall linear shape of the molecule. It was only in 1993, however, that a publication by Loubser, *et al.* shed some light on the reason why the terminal ferrocenyl group could be tolerated in a liquid crystal.[21] They published the first X-ray crystal structure of a monosubstituted ferrocenomesogen (**4**).



1

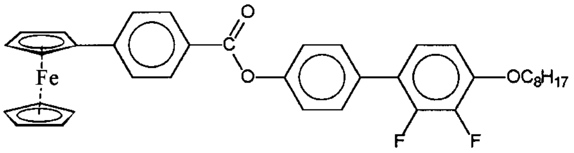
n= 8 $K \xrightarrow{153^\circ C} N \xrightarrow{167^\circ C} I$

n= 10 $K \xrightarrow{143^\circ C} N \xrightarrow{159^\circ C} I$

2

3

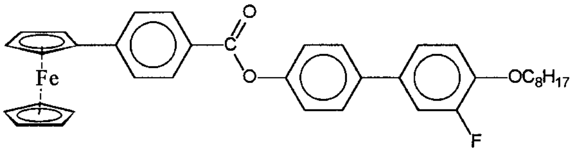
Figure 3 The first monosubstituted ferrocenomesogens.



4

$$K \xrightleftharpoons{115^\circ C} N \xrightleftharpoons{129^\circ C} I$$

Compound **4** which contains a terminal ferrocenyl group and laterally substituted fluorine atoms, exhibited an enantiotropic nematic phase with relatively low melting and clearing temperatures. Analysis of the molecular structure by single-crystal X-ray diffraction indicated that there was an intermolecular association between two molecules in neighbouring layers. This resulted in an overall extended S-shape with the ferrocenyl–phenyl units forming the “core” and the remainder of each pair of molecules extending in opposite but parallel directions. Since 1993, Imrie and co-workers[22] have determined the X-ray crystal structures of several other monosubstituted ferrocenomesogens, an example being the structurally related 4-octyloxy-3-fluorobiphenyl-4′-yl-ferrocenylbenzoate **5**. The packing diagram for compound **5** is shown in Fig. 4 and helps to illustrate many of the features already described for compound **4**. Again, the ferrocenyl groups of molecules in neighbouring layers are virtually interlocked giving rise to the formation of an extended S-shape.



5

$$K \xrightleftharpoons[80^\circ C]{131^\circ C} N \xrightleftharpoons[135^\circ C]{136^\circ C} I$$

One of the crystal structures determined by Imrie *et al.* provides evidence for the involvement of

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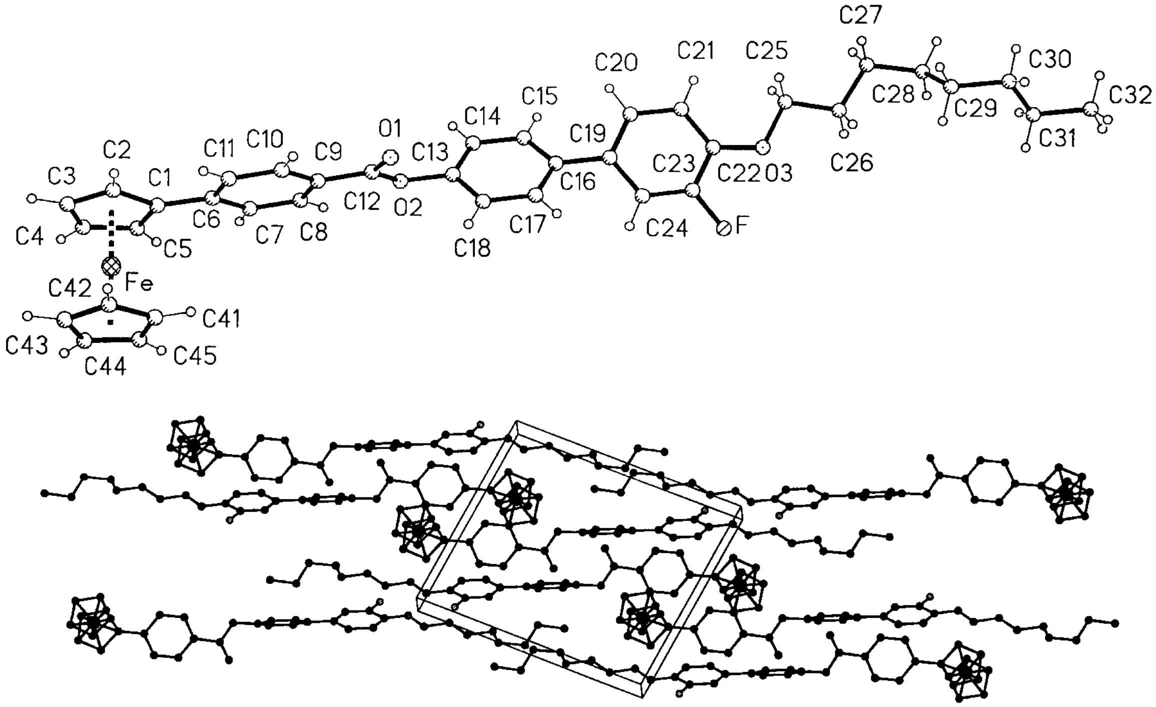

Figure 4 Ortep diagram with numbering and packing diagram for compound **5**.

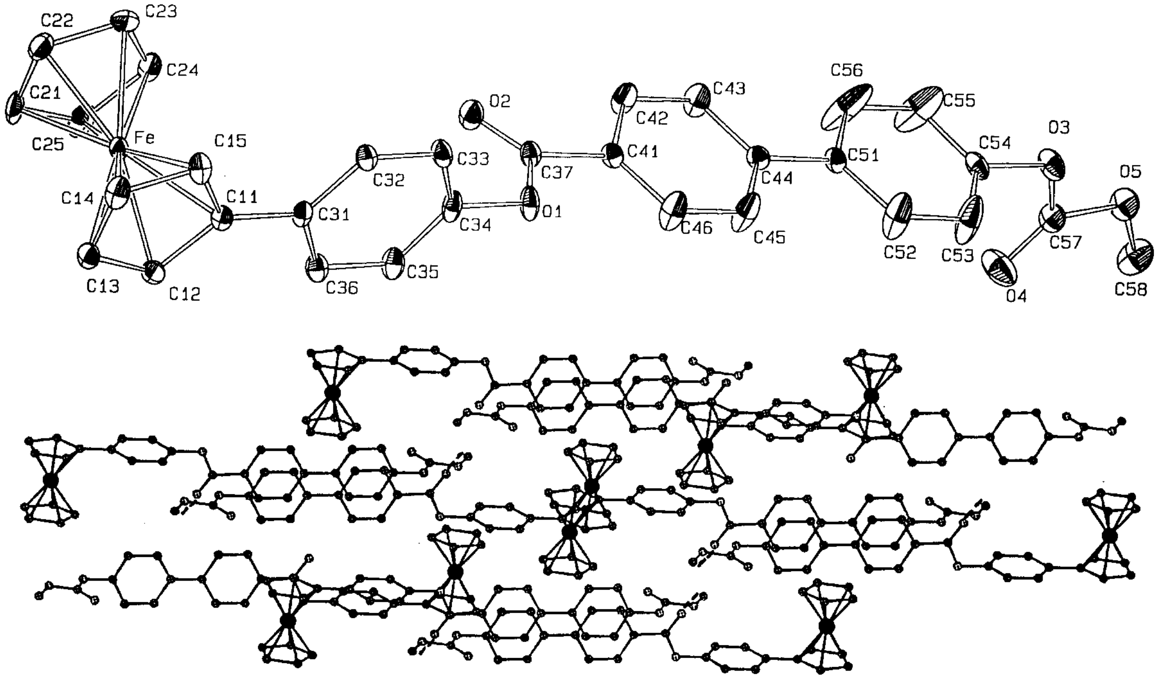

Figure 5 Ortep diagram with numbering and packing diagram for compound **6**.

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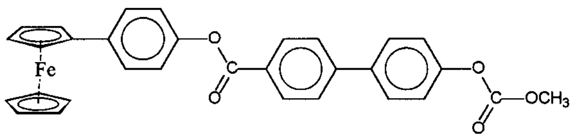
hydrogen bonding in the development of an extended molecular architecture.[22] The compound exhibiting this behaviour is 4-methoxycarboxyloxy-4′-biphenylcarboxyphenylferrocene **6**. A packing diagram for compound **6** is shown in Fig. 5 and highlights not only the hydrogen bonding interaction, but also the possibility of π–π stacking of the aromatic rings. An alternative to hydrogen bonding for building supramolecular structures is to use metal–organic coordination bonds to link the monomolecular units. Galyametdinov and co-workers have utilized such bonding to join monosubstituted monomolecular ferrocenomesogens together (Fig. 6).[23–25]



6

$$K \underset{124^{\circ}C}{\overset{162^{\circ}C}{\rightleftharpoons}} N \underset{192^{\circ}C}{\overset{194^{\circ}C}{\rightleftharpoons}} I$$

In the first instance, this Russian group reported on the synthesis of monoferrocenomesogens based on structure **7** minus the hydroxyl group. Ten compounds of this series varying between $n = 3$ and $n = 12$ were reported. This was the first instance of a series of monoferrocenomesogens in which the effects of structural variation on liquid crystal properties could be examined. All the compounds exhibited stable nematic mesophases, apart from where $n = 4$, and showed a reduction of their clearing temperatures as the terminal alkoxyl chain was lengthened. The compounds also exhibited the typical odd/even effect with relation to the clearing temperature and the number of carbon atoms in the alkoxyl chain. It is most notable from all the early examples of monoferrocenomesogens that a minimum of three phenyl groups and a terminal ferrocenyl group effectively stabilize the nematic liquid crystal phase. Introduction of a hydroxyl

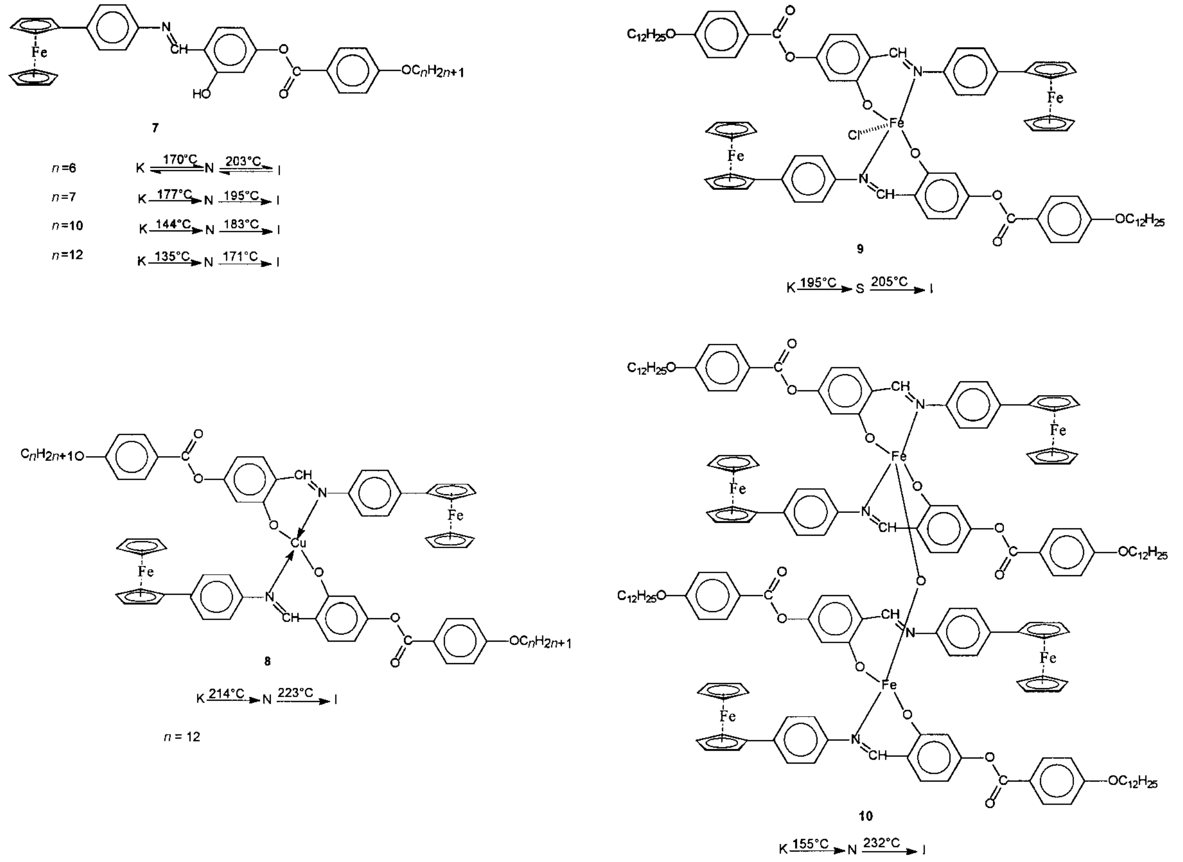


Figure 6 Ferrocenomesogens synthesized by Galyametdinov and co-workers.

group, as in compound **7**, led to the compounds having larger liquid crystal domains than their unsubstituted analogues. This resulted from a combination of lower melting and higher clearing temperatures; the higher clearing temperatures were explained in terms of the formation of a chelate ring involving an intramolecular hydrogen bond between the O-H group and the nitrogen atom of the imine group, which enlarged the conjugation pathway. Liquid crystals containing more than one transition metal ion in the monomolecular form are potentially interesting for future device technology, since manipulation of the various metals should allow for a refinement of the magnetic, electrical and optical properties of the bulk material. Galyametdinov and co-workers reported the first examples of heterometallic monoferrocenomesogens by complexation of **7** ($n = 12$) with various metal ions such as copper(II) (**8**),[23] nickel(II), VO(IV),[25] palladium(II)[25] and iron(III).[25] The complexes, such as **8**, **9** and **10** were characterized by a combination of elemental analysis, IR, magnetic susceptibility measurements and electron spin resonance (ESR) spectra. The heterometallic complexes exhibited nematogenic liquid crystal behaviour, apart from compound **9**, which was smectogenic, and the complex containing nickel(II), which was non-mesomorphic. Variation in mesomorphic behaviour according to the nature of the central metal atom was explained in terms of the different metal geometries. For example, the NiL_2 complex adopts a tetrahedral configuration and this provides a molecule with a length:width ratio that is too small to allow mesogenic behaviour. In all the other complexes, the configuration of the chelate centre is either planar or quasi-planar and the geometric anisotropy is large enough to allow mesogenic behaviour. ESR studies carried out by the authors on complex **9** provided significant results. The results suggest that, for complex **9**, the molecules can associate in two ways: either by forming molecular chains bonded through the chlorine atoms by weak antiferromagnetic exchange or by formation of dimers by bonding through oxygen atoms. Such associations would be conducive for packing of molecules in smectic layers.

The research group of Nakamura have endeavoured to elucidate the phase behaviour and multiple melting behaviour of monoferrocenomesgens compounds such as the series of monosubstituted ferrocenomesogens (**11** and **12**) (Fig. 7).[26–30] In the first series **11**, a terminal ferrocenylphenyl group was joined to a cholesteryl unit via ester groups linked by an alkyl chain of varying length.[26,27] The compounds of this series ($n = 2$, 4, 6, 9, 10, 11) exhibited monotropic smectic phases of an unidentified nature. In the second series **12**, the cholesteryl moiety was replaced by a 4-(4-methoxyphenoxycarbonyl)phenoxy group.[28] Compounds in this series ($n = 4$, 6, 10, 11) exhibited liquid crystal behaviour, but the phases were not specified. One of the most significant aspects of their results is that three of the compounds in series **12** ($n = 6$, 10, 11) exhibit liquid crystal phases around room temperature. These results are particularly significant when compared with those of the majority of monosubstituted ferrocenomesogens prepared to date (liquid crystal phases generally fall between 100–250 °C). In both series, the number of carbon atoms in the alkyl chain determined whether a compound exhibited a liquid crystal phase or not, and this suggests that the overall molecular shape of the molecule is a dominant factor in mesogenic behaviour.

The need had arrived for a systematic investigation into the structural limits in which the liquid-crystalline state can be generated and retained in monosubstituted ferrocenomesogens. Loubser and Imrie began such an investigation in 1993 and most of the initial results were published in 1997.[31] The authors synthesized a series of compounds based on the general structure (**13**) shown in Fig. 8. The size and shape of Z was modified by varying firstly the number of phenyl rings (j and i), secondly the linking group Y, thirdly, the lateral substitution X, and fourthly the number of carbon atoms n in the chain. It was found that a minimum of three phenyl rings in the substituent core (Z) stabilized the

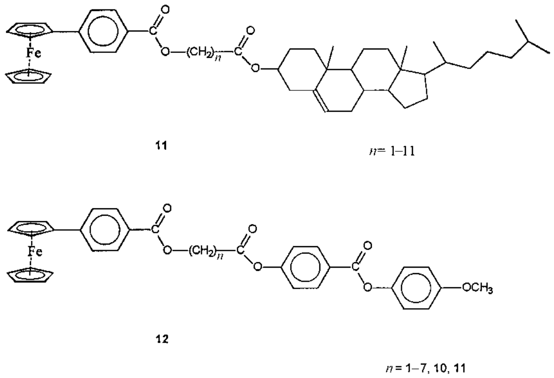
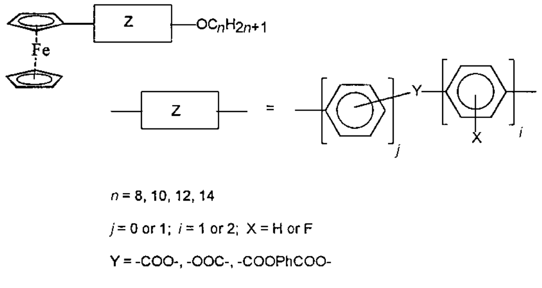


Figure 7 Ferrocenomesogens prepared by the Nakamura group.



13

Figure 8 General structure representing the compounds prepared by Loubser and Imrie.

nematic phase and addition of a fourth ring significantly enhanced nematic behaviour. The length of the alkoxyl chain was shown to be of some importance, but the general effect was similar to that observed earlier in the series synthesized by Galyametdinov and co-workers. The phase behaviour of some of their compounds is shown in graphical form in Fig. 9 and 10. The first highlights the effect of increasing the length of the chain *n*, and the second shows the effect of lateral substitution. Introduction of the highly electronegative fluorine atom is an ideal way of altering the properties of a liquid crystal (e.g. polarization, dipole moment) without disrupting the overall phase behaviour. A comparison of Fig. 9 and 10 shows that lateral fluorination leads to a lowering of the clearing points and melting points of the liquid crystals (the liquid crystal ranges are quite similar). Lateral fluorination supported nematic phase behaviour but suppressed smectic behaviour. It is also clear from Fig. 10 that the number and positions of the fluorine atoms on the core are important. An alteration in the shape of the core by movement of the carbonyloxy group from the 4- to the 3-position with respect to the ferrocenyl group resulted in a suppression of the nematic phase, owing to the

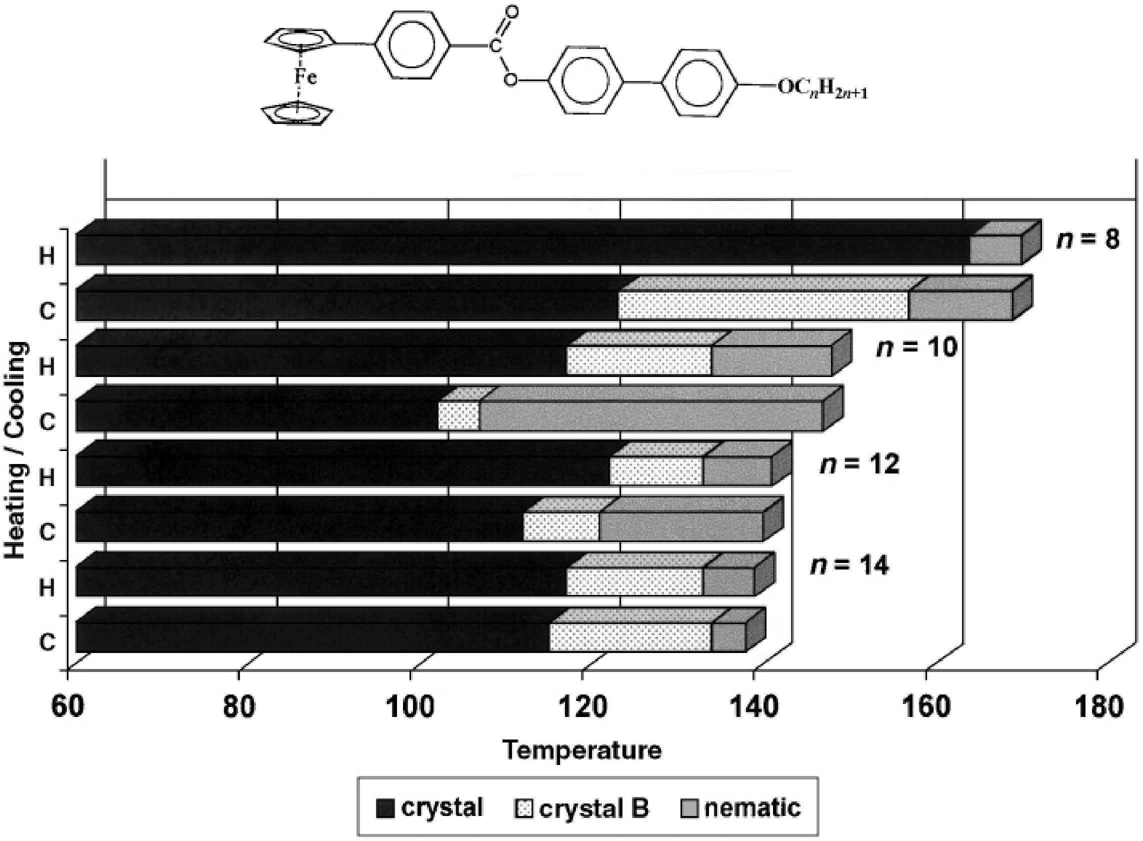


Figure 9 Phase behaviour of ferrocenomesogens prepared by Loubser and Imrie.

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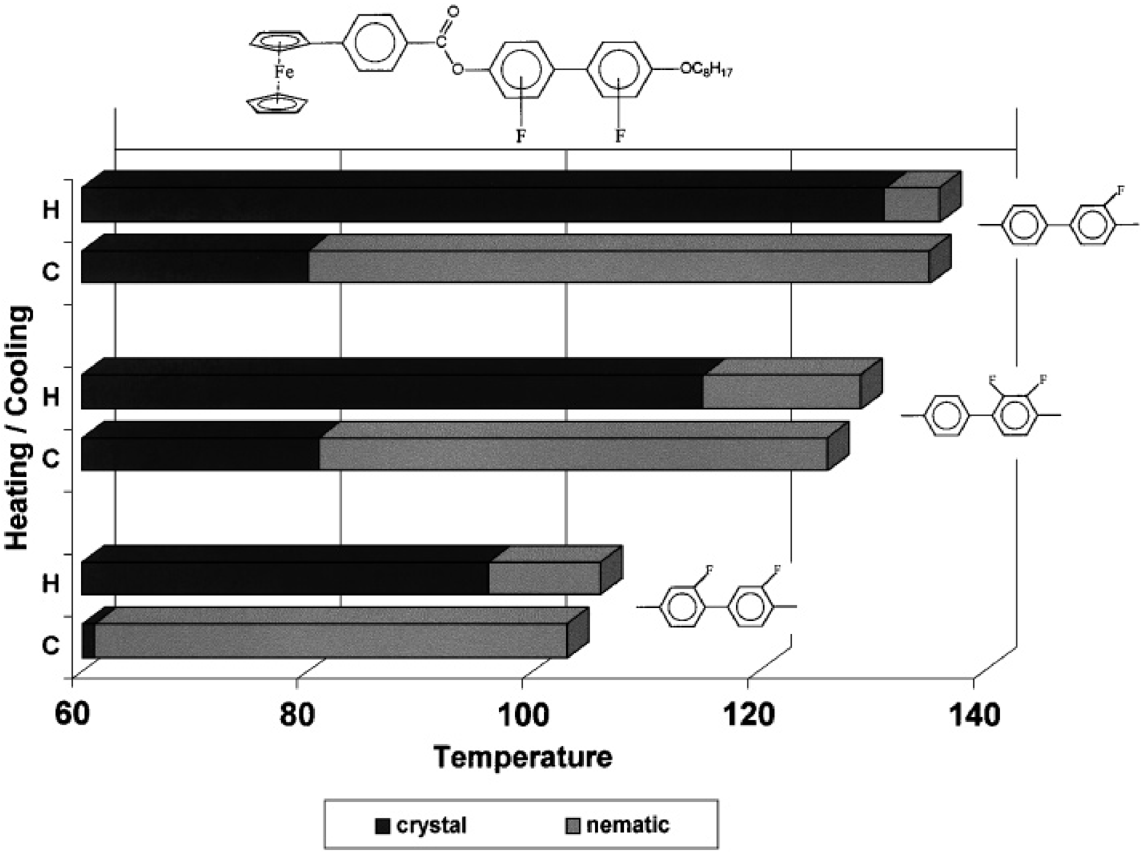
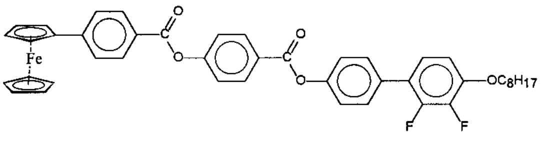


Figure 10 Phase behaviour of fluorinated ferrocenomesogens prepared by Loubser and Imrie.

introduction of a kink in the molecular structure which disrupts the overall linear structure.

The same authors also highlighted the importance of stability factors when designing new metallomesogens for commercial applications. It was shown that insertion of the relatively neutral phenyl group as a spacer between the ferrocenyl group and carbonyloxy link resulted in compounds that were less prone to hydrolysis. Such compounds are also expected to have greater thermal and photochemical stability than those in which the carbonyloxy link is directly attached to the ferrocenyl group. Extension of the molecular core from [**1Fc** + **3Ph**] groups to [**1Fc** + **4Ph**] groups provided a compound with a very wide nematic range (100 °C) (**14**).



14

$$\mathrm{K} \xrightarrow{132^{\circ}\mathrm{C}} \mathrm{N} \xrightarrow{252^{\circ}\mathrm{C}} \mathrm{I}\ (\mathrm{dec})$$

In a continuation of this systematic approach Imrie and co-workers[22] synthesized a series of potential ferrocenomesogens **15**–**19** (Fig. 11). The compounds of series **15** exhibited enantiotropic nematic phases with characteristic Schlieren textures (Fig. 12). As the length of the terminal chain was increased, smectic behaviour developed and the compounds where $n = 8$–10 exhibited monotropic smectic A phases and those with longer chains ($n = 12$, 14) enantiotropic smectic A and monotropic smectic C phases (Fig. 13). It is interesting to compare the phase behaviour of compounds in series **15** with those in series **13** ($j = 1$, $i = 2$, X = H, Y = COO), in which there has been a reversal of the carbonyloxy linkage. Aside from the different smectic behaviour, compounds in the two series have remarkably similar nematic

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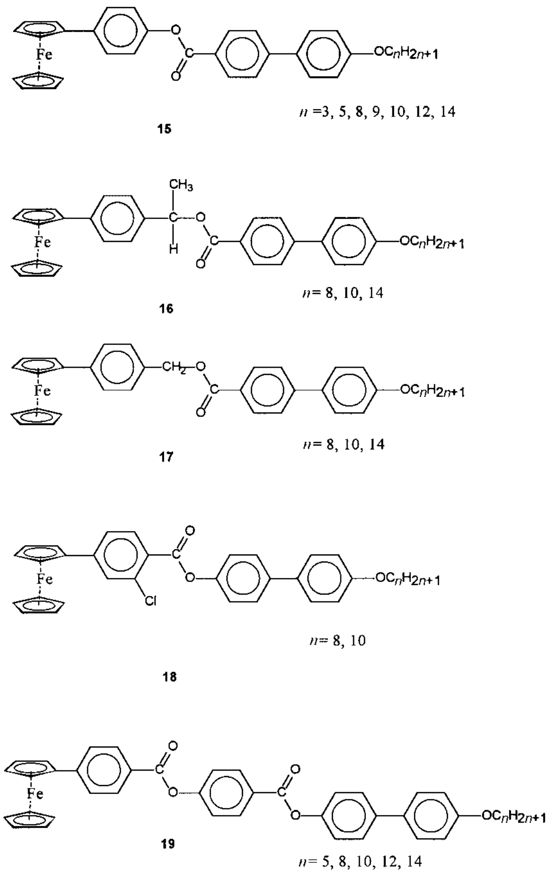
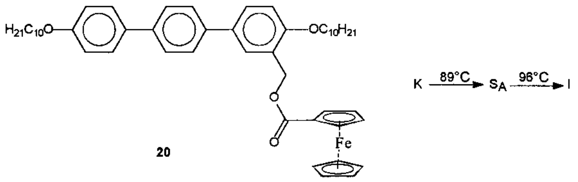


Figure 11 Compounds prepared by Imrie and co-workers.

behaviour and similar clearing temperatures. The authors also found that the insertion of an additional methylene (CH_2) and methylmethine ($CHCH_3$) spacer between the phenyl ring and carbonyloxy link resulted in non-mesogenic ferrocene derivatives (series **16** and **17**). The compounds of series **18** were synthesized in which a lateral chlorine atom was introduced on the benzene ring of the ferrocenyl–phenyl unit. The compounds exhibited low-temperature monotropic nematic phases. The phase behaviour of **18** was not totally unexpected, since a large lateral substituent such as a chlorine atom would lead to a substantial broadening of the molecular structure which would, in turn, lead to a decrease in the intermolecular forces between molecules. Lengthening of the linear rod-like shape through introduction of an additional phenyl group into the core, as in series **19**, provided compounds with very broad high-temperature nematic phases. For example, when $n = 12$, the nematic range was 104 °C (154–258 °C dec.). Some decomposition was evident for most of these compounds above 250 °C. Molecular modelling was used by the authors to investigate structure–activity relationships. The lowest energy conformations of the non-mesogenic ferrocene derivatives in most cases showed pronounced kinks in the molecular structures, whereas the mesogenic compounds were reasonably linear (Fig. 14).

In view of the effect of kinks introduced into the molecular structures of liquid crystal molecules through the inclusion of terminal ferrocenyl groups, the results reported by Andersch *et al.* are of interest.[32] The synthesis of **20** was reported in which the ferrocenyl group was connected in a lateral position to a rigid linear organic backbone. The molecule displayed a reasonably stable smectic A phase and, in fact, the ferrocenyl group was more stabilizing than a phenyl group in this system. The authors made a statement in their paper that 'there is an inherent mesophase stabilizing influence of the ferrocene unit', but, as pointed out, this is normally obscured by the unfavourable steric and conformational effects.

All the monosubstituted ferrocenomesogens described so far have been rod-like in shape and most of the research to date has concentrated on this shape. Cook *et al.* synthesized the first example of a disc-shaped monosubstituted ferrocenomesogen and this exhibits discotic liquid crystal properties.[33] Careful design of this compound was vital owing to the ease with which the bulky ferrocenyl group could disrupt columnar packing. The authors chose a phthalocyanine ring system that had a vacant site at one of the eight substitution positions. Space was thus specifically cleared in the columnar stack for the unsubstituted cyclopentadienyl rings of the ferrocenyl groups of neighbouring molecules. Compound **21** displayed a discotic columnar mesophase of hexagonal symmetry (D_{hd}) with disordered spacing within the column, which was characterized by a fan-type birefringent texture.



Seshadri and Haupt referred to the work of Loubser and Imrie[31] in the design of their monosubstituted ferrocenomesogens noting particularly the stabilizing effect of the group adjacent to the

Figure 12 Photomicrograph of a ferrocenomesogen with a characteristic nematic phase exhibiting a Schlieren texture.

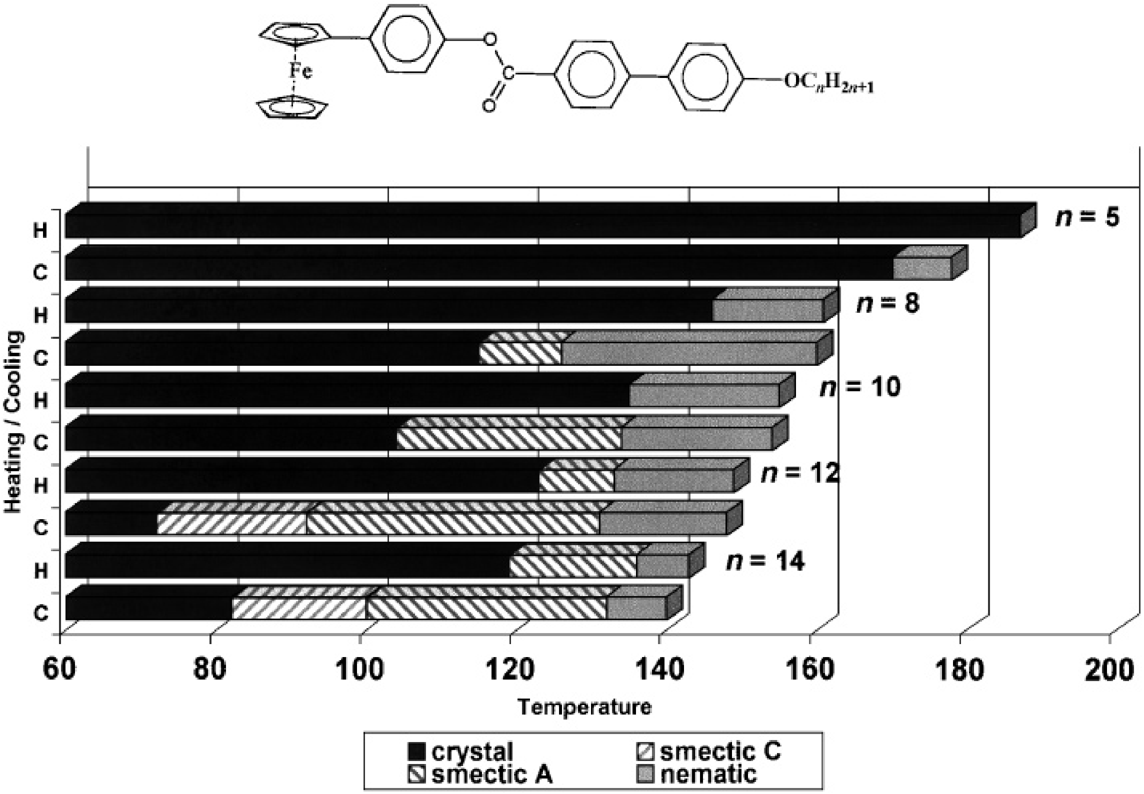


Figure 13 Phase behaviour of ferrocenomesogens (series **15**) prepared by Imrie and co-workers.

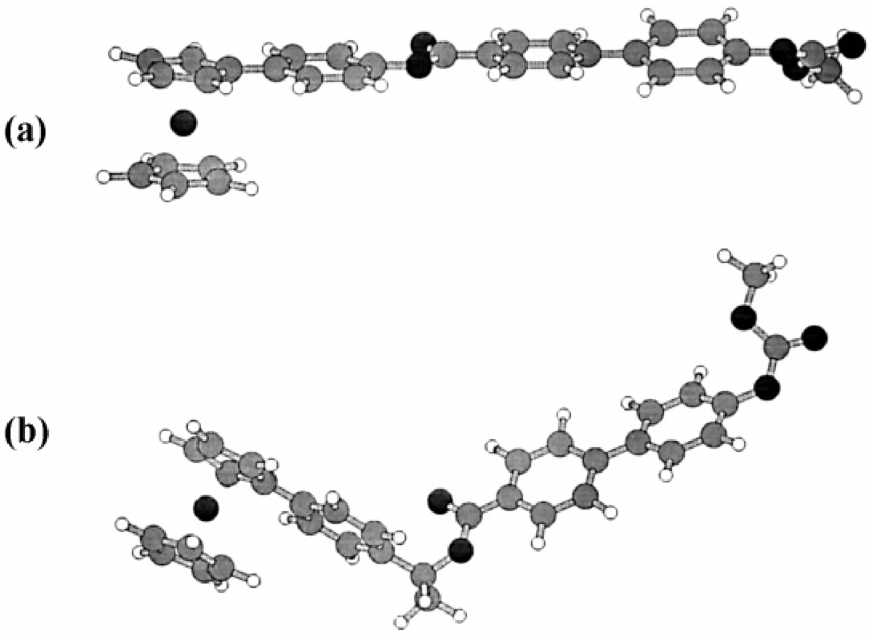
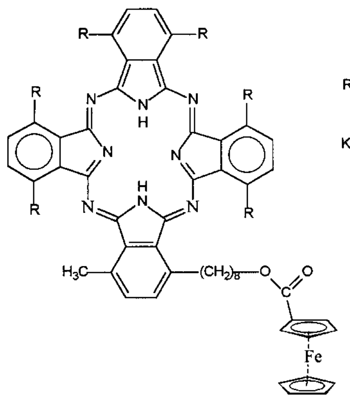


Figure 14 Lowest energy conformations of (a) mesogenic and (b) non-mesogenic ferrocenes.



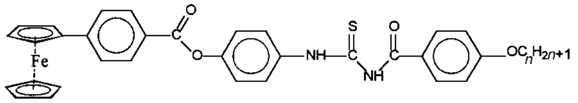
$R = C_8H_{17}$

$K \xrightarrow{60\,°C} D_{hd} \xrightarrow{133\,°C} I$

21

ferrocenyl group.[34] Accordingly, the authors designed some new molecules **22** containing [1Fc + 3Ph] groups with one of the phenyl groups placed between the ferrocenyl group and the carbonyloxy linkage. All four members of the series exhibited enantiotropic nematic phases with Schlieren textures and liquid crystalline domains were found to increase slightly with an increase in the length of the alkoxyl chain. On cooling, the nematic phase persisted below 0 °C for the compounds where $n = 8$, 12, and 16, whereas a monotropic nematic to smectic C transition was observed at 72 °C for the compound where $n = 18$.

The compounds in series **22** contain the *N*-benzoyl-*N*-arylthiourea fragment, and clearly these molecules may be envisaged as precursors of heterometallic ferocenomesogens at some later stage.



n=8, 12, 16, 18

22

$n=8$ $K \xrightarrow{160\,°C} N \xrightarrow{176\,°C} I$

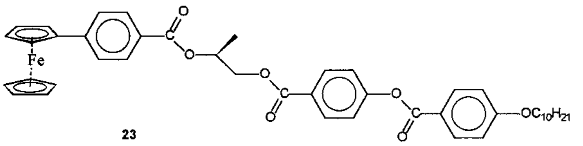
$n=12$ $K \xrightarrow{144\,°C} N \xrightarrow{157\,°C} I$

$n=16$ $K \xrightarrow{126\,°C} N \xrightarrow{146\,°C} I$

$n=18$ $K \xrightarrow{116\,°C} N \xrightarrow{139\,°C} I$

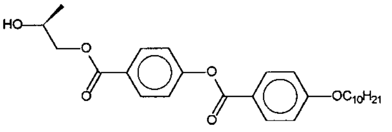
2.3 Chiral ferrocenomesogens

All of the compounds discussed so far, apart from the cholesteryl derivative synthesized by Nakamura *et al.*, have been achiral. The synthesis of chiral monosubstituted ferrocenomesogens has so far received very little attention, a surprising fact considering the strong interest in chiral organic liquid crystals. Imrie and Loubser reported the first synthesis of a chiral ferrocenomesogen (**23**) in 1994.[35] The chiral unit was based on *s*-ethyl lactate and was near the middle of the molecule.

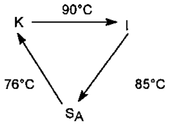


23

$$K \underset{<0°C}{\overset{83°C}{\rightleftharpoons}} S_{C^*} \underset{95°C}{\overset{99°C}{\rightleftharpoons}} I$$

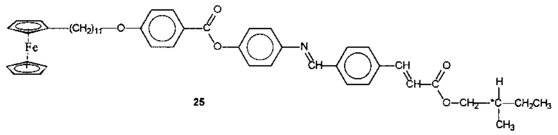


24



The alcohol precursor (**24**) of compound **23** exhibits a smectic A phase that is thermodynamically unstable. The effect achieved by attaching the 4-carboxylphenylferrocene group to **24** is therefore remarkable; the smectic A phase of **24** is replaced in **23** by a stable chiral smectic C phase, readily identified by its Schlieren texture. Upon cooling the isotropic liquid, the chiral smectic phase reappeared and when supercooled to room temperature it persisted for weeks.

Seshadri and Haupt have reported the only other known chiral monosubstituted ferrocenomesogen (**25**) and this compound exhibits an unusually rich mesogenic behaviour.[36] It not only exhibits an enantiotropic S_C^*, S_A and a cholesteric phase, but it is also the first metallomesogen to exhibit a twist grain boundary and a blue phase. Introduction of the flexible alkoxyl spacer was found to be of critical importance in providing the rich mesogenic behaviour, since the compound without this spacer exhibited only a cholesteric phase. The smectogenic character and favourable packing conditions for **25** were ascribed to the favourable co-planar arrangement of the benzene ring in the benzylidene–aniline unit, which led to an extended conjugation and a resultant enhanced polarizability. The authors speculated that compounds of this type may be useful in the preparation of ferroelectric smectic C* materials for fast switching electro-optic devices.



25

$$K \underset{77.9°C}{\overset{116°C}{\rightleftharpoons}} S_{C^*} \underset{132.6°C}{\overset{136°C}{\rightleftharpoons}} S_A \underset{141.2°C}{\overset{143.8°C}{\rightleftharpoons}} TGBA \underset{143.1°C}{\overset{144.9°C}{\rightleftharpoons}} N^* \underset{154.6°C}{\overset{158°C}{\rightleftharpoons}} BP \underset{157.2°C}{\overset{159.2°C}{\rightleftharpoons}} I$$

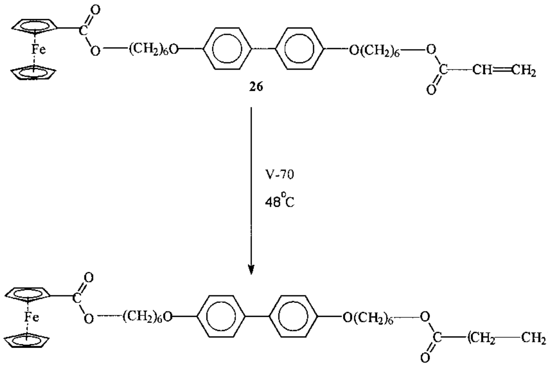


Figure 15 A polymeric ferrocenomesogen prepared by Tanaka and Hongo.

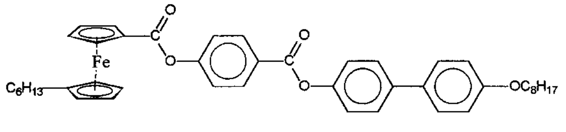
2.4 Polymeric ferrocenomesogens

Most of the work carried out to date in the area of ferrocenyl-containing liquid crystal polymers has been concerned with either 1,1′-disubstituted- or 1,3-disubstituted-ferrocenes.[37–41] However, Tanaka *et al.* have reported on the synthesis of polymeric ferrocenomesogens where the ferrocenyl substituents are situated in the terminal position.[42] In the example shown in Fig. 15, the monomer compound **26** exhibits a low-temperature smectic A phase, whereas the polymer **27** exhibits a smectic C phase below 97.9 °C that was maintained unchanged to 0 °C.

2.5 Miscellaneous compounds

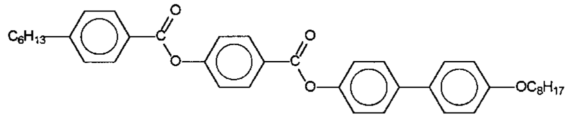
There are a number of examples in the literature of ferrocenomesogens in which the ferrocenyl unit is multi-substituted, but with only one of the substituents being an elongated group. These complexes are included under the category of miscellaneous compounds. Compound **28** is an example of a series of compounds synthesized by Thompson *et al.* with a view to investigating the effect of the ferrocene unit on mesomorphic properties.[43] In comparison with the 1,4-benzene analogue **29**, incorporation of the 1,1′-ferrocenyl unit leads to a substantial reduction in the clearing temperature of the molecule. This is a general trend observed in the results of Thompson *et al.*

Deschenaux *et al.* synthesized the oxidized persubstituted ferrocenomesogen **30**, and this represented the first example of a ferrocenium-containing liquid crystal.[44] Compound **30** exhibited a monotropic smectic A phase between 83 °C and 33 °C on cooling. The authors concluded that electrostatic interactions must play a critical role in the appearance of mesogenic behaviour since the unoxidized ferrocene precursor of **30** was non-mesogenic. It should be possible to exploit electron transfer in the control of supramolecular organization within the liquid crystalline state using the ferrocene-ferrocenium redox sysem. Deschenaux *et al*. have recently reported a more extensive study on mesomorphic compounds based on the ferrocene–ferrocenium redox system.[45] The ferrocenium derivative in their study was reported to have a monotropic columnar phase.



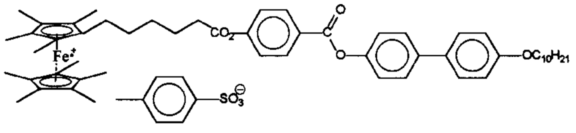
28

$$\begin{tikzcd}K \arrow[rr, "107°C"] & & I \arrow[dl, "63°C"] \\ & N \arrow[ul] & \end{tikzcd}$$



29

$$K \xrightarrow{138°C} S_C \xrightarrow{176°C} N \xrightarrow{280°C} I$$



30

3 CONCLUSION

It has now been firmly established that the ferrocenyl unit effectively stabilizes the liquid crystalline state (especially nematic) in monosubstituted ferrocenyl derivatives. A systematic investigation has been undertaken to determine the structural limits within which the liquid crystalline state can be generated and retained. A large number of compounds have been synthesized, some of which may prove useful in device technology at a later date. Some of the structural factors affecting transition temperatures and liquid crystal domains are reasonably well understood. Although significant progress in this field has been made, the search to find commercially viable ferrocenomesogens continues.

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