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Ferrocene-containing liquid crystals

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Abstract. The review concerns liquid-crystalline mono- and disubstituted ferrocenes, systems based on ferrocenophane, heteronuclear complexes with ferrocene-containing ligands, ferrocene-based polymers and dendrimers, as well as mixed systems based on ferrocene derivatives. It is shown that liquid-crystalline ferrocene exhibits unique physical properties. The state of the art in the title field and prospects for the development of research on such liquid crystals are outlined and the present and possible fields of their application are discussed. The bibliography includes 131 references.

I. Introduction

Ferrocene is a unique compound from the standpoint of its structure, chemical and thermal stabilities, and the possibility of being immediately used in various organic reactions. This is due to the sandwich structure of ferrocene representing a three-dimensional (3D) aromatic system. The discovery of ferrocene in 1950 (Ref. 1) was followed by two or three decades of rapid progress in ferrocene chemistry, especially in the studies of researchers from the scientific school headed by A N Nesmeyanov.[2,3] Investigations on ferrocene included many applied aspects, such as application of ferrocene derivatives as pharmaceuticals,[4] additives to motor fuels and oils,[4] catalysts in fine organic synthesis[5–7] and polymeric materials.[6–8] Paramagnetic[9,10] and ferromagnetic systems based on ferrocene,[10,11] ferrocene derivatives with nonlinear optical properties,[12,13] luminescent systems,[14] ferrocene compounds for flash photolysis,[15] ferrocene – ferricinium redox systems and analytical sensors based on them,[16] *etc*. are of great fundamental and practical interest. Taking into account intensive research in the field, it is surprising that liquid-crystalline ferrocene derivatives have been obtained relatively recently.

The term 'liquid crystal' (or 'mesomorphic state') denotes a specific type of structural organization of matter, which combines typical properties of conventional isotropic liquids, such as fluidity, viscosity, dissolving power, *etc*., and anisotropic properties typical of crystalline solids. The anisotropic properties mean physical properties that depend on a specified direction; examples are provided by the refractive index, dielectric permittivity, electrical and thermal conductivities, elasticity, *etc*. The anisotropy of liquid crystals is due to their partial molecular ordering, *viz*., the nematic phase is the most disordered, its properties are the closest to those of conventional liquids; the properties of the more ordered types of structural organization resemble those of conventional crystals (Fig. 1).

Usually, liquid crystals represent rod-like or disk-shaped organic molecules with pronounced geometric anisotropy, or anisometry. Such molecules are also characterized by high polarizability anisotropy, which in turn leads to anisotropy of intermolecular interactions. The structures of molecules that can form liquid-crystalline mesophases include rigid fragments based on aromatic rings which are connected to one another directly or through some bridges, *e.g*., carboxyl, azomethine, ethylidene, azo groups, *etc*., as well as conformationally flexible terminal groups, usually, hydrocarbon, polysiloxane or polyoxyethylene chains. Thus, the formation of mesophases is mainly due to pronounced anisotropy of the molecular structure. Also, taking into account asymmetry on the molecular level, more

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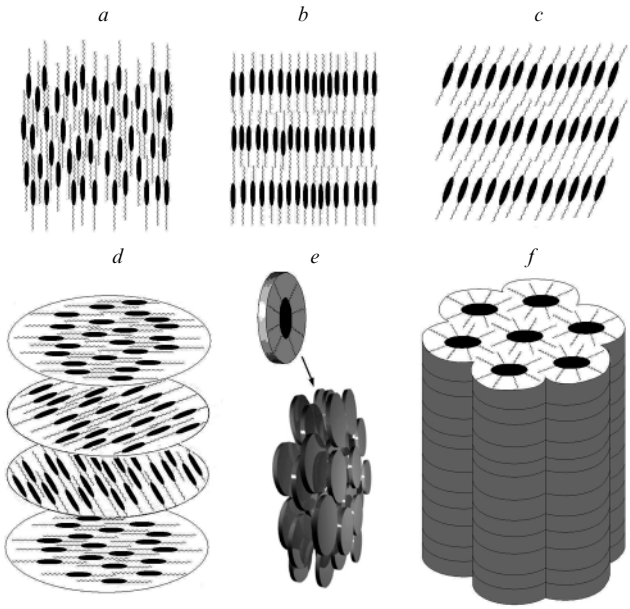


Figure 1. Some types of ordering in thermotropic liquid crystals. Nematic packing: orientationally ordered rod-like molecules with no positional ordering (*a*); layered smectic A structure with no positonal ordering (*b*); smectic C structure: unlike smectic A structure, the rod-like molecules are slightly tilted with respect to the plane of the layer (*c*); chiral nematic (cholesteric) structure: the preferred orientation direction of rod-like molecules moves along a helical line on going from one layer to another (*d*); discotic nematic structure formed by disk-shaped molecules (*e*); and hexagonal columnar phase with stacked disk-shaped molecules (*f*).

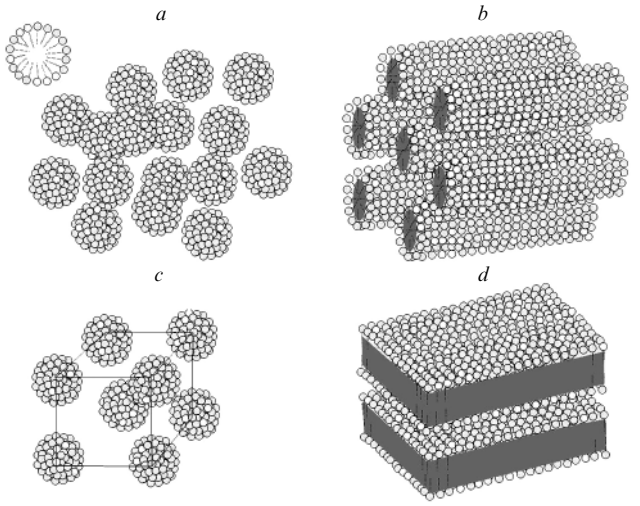


Figure 2. Some types of supramolecular organization in lyotropic liquid crystals.
Micellar (*a*), hexagonal (*b*), micellar cubic (*c*) and lamellar mesophase (*d*).

complex mesophases with chiral structural organization, *i.e.*, cholesteric liquid crystals (see Fig. 1) can be formed based on such compounds.

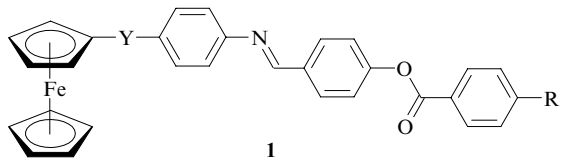
From the standpoint of transition to the mesomorphic state, liquid crystals are divided into two main groups. Thermotropic liquid crystals (or liquid-crystalline phases) are formed upon heating a mesomorphic substance and separated from the crystalline state, from one another and from the isotropic liquid state by first-order phase transitions (with rare exceptions where close types of mesophases are separated by second-order phase transitions). This also concerns liquid crystals based on high-molecular-mass compounds with characteristic features of the structure of polymer chains, as well as supramolecular liquid crystals. In the last-mentioned case, supramolecular aggregates containing a finite number of molecules are used as elements of liquid-crystalline packing instead of molecules. Generally, liquid crystals can be treated as a kind of supramolecular organization of matter. This particularly holds for the second group of liquid-crystalline systems.

Lyotropic liquid crystals (Fig. 2) are formed in mixtures of mesogens with solvents. Amphiphilic molecules in polar and nonpolar solvents are prone to form lyotropic mesophases. It is believed that lyotropic liquid-crystalline structures are abundant in biological systems, *e.g.*, cell membranes.

At present, there are more than 20 structural types of thermotropic mesophases. Some of them are thermodynamically unstable, *i.e.*, they are formed only in supercooled melts. Such mesophases cannot be obtained by direct melting of crystals; therefore, they are called monotropic in contrast to thermodynamically stable enantiotropic mesophases. In this review, we present structural formulas of compounds that form liquid-crystalline mesophases. Different phase states are denoted as follows: K is crystal; L is liquid; S_x and Col_x are smectic and columnar mesophases of undetermined type, respectively; the letters A, B and C denote the types of smectic mesophases; T denotes a tetrahedral mesophase; N is a nematic mesophase and 'i' is isotropic liquid; chiral mesophases are asterisked, *e.g.*, S_C^* is chiral smectic C phase; ('d') denotes decomposition; numbers near the letter denote the phase transition temperatures in °C; information in square brackets refers to monotropic phase transitions. In some specific cases, corresponding notations are given in Notes.

The liquid-crystalline state is mainly studied by the following physicochemical methods: variable-temperature polarizing microscopy, differential scanning calorimetry (DSC), X-ray powder diffraction (both SAXS and WAXS techniques), electron and atomic force microscopies, thermal phase analysis of mixtures, NMR spectroscopy, circular dichroism spectroscopy, *etc*. In most cases, primary identification of mesophases is performed by polarizing microscopy. Owing to optical anisotropy, optical birefringence and defects in the molecular packing, liquid crystals give various multicoloured textures observed in a polarizing microscope; each type of mesophases exhibits a characteristic texture. Indirect information on the types of mesophases can be obtained by DSC from the thermal effects of phase transitions. X-Ray and neutron diffraction techniques provide information on the interlayer spacings in lamellar mesophases and on the packing parameters of columnar and cubic mesophases (the latter are optically isotropic and give no characteristic textures in a polarizing microscope). Additional in-plane ordering causes peaks in the diffraction patterns to appear also in the wide-angle region. X-Ray diffraction analysis also provides information on the character of molecular packing in liquid crystals through the determination of the conformational structure of a single crystal-precursor of mesophases.

Taking into account the uniqueness of ferrocene moiety and first of all the fact that ferrocene readily and reversibly goes to the oxidized state with one unpaired electron, it was of interest to incorporate a ferrocene molecule into the liquid crystal molecule to obtain materials with specific electrophysical and magnetophysical properties. A number of ferrocene-containing liquid crystals **1** were for the fisrt time synthesized in 1976 to be used as labels in Mössbauer spectroscopy studies of the order parameter of liquid crystals.[17] However, despite the presence of a bulky ferrocene moiety, the compounds synthesized formed nematic mesophases only in a narrow temperature range; in some cases, only monotropic mesophases formed.



1

Y	R	Mesophases	Y	R	Mesophases
C(O)O	OC_8H_{17}-n	K153N167i	C(O)	n-C_8H_{17}	K[135N]152i
C(O)O	$OC_{10}H_{21}$-n	K143N159i	$C(O)(CH_2)_2$	OC_8H_{17}-n	K[112N]137i

It has been accepted for long that bulky ferrocene, as a terminal group of a rod-like molecule, favours destabilization of the liquid-crystalline state. More recently, 1,1′-disubstituted ferrocenes with more stable mesophases were synthesized [18] and also tested as Mössbauer labels.[19–21] In this connection, mention may be made that Mössbauer spectroscopy provides the most correct information on the structure, orientational and dynamic properties of liquid crystals. Studies on ferrocene-containing liquid-crystalline compounds published in the late 1980s – early 1990s demonstrate the appearance of interest in these systems.[22–25]

Ferrocene-containing liquid crystals belong to a large class of metal-containing liquid crystals, or metallomesogens, that have been described in detail in many reviews;[26–34] however, ferrocene compounds have not been always considered thoroughly.

There is a number of liquid-crystalline ferrocene derivatives representing molecular compounds, supramolecular structures and polymers. Molecular compounds of ferrocene can conditionally be divided into mono- and polysubstituted ones. A review [35] of monosubstituted liquid-crystalline ferrocene derivatives generalizes the results of studies carried out from 1976 to 1999. A comprehensive review on liquid-crystalline polymers with ferrocene moieties carried out up to 2006 is available.[36] The data reported in other reviews [37–39] of the earlier studies of liquid-crystalline ferrocene derivatives are to a great extent fragmentary.

The aim of this review is to generalize the publications not surveyed previously and to describe recent advanves in the synthesis and studies on mesomorphic ferrocene derivatives. We will discuss the structural features and the phase behaviour and types of mesophases formed by this class of compounds. Most studies analyzed in the reviews [37–39] are left out of consideration, although some interesting studies are included to provide a complete picture. Considerable attention is paid to heteronuclear complexes with ferrocene-containing ligands, [3]ferrocenophane compounds and to 1,1′-disubstituted ferrocenes with unusual tetrahedral packing of mesophases, because it is these investigation lines that have been the focus of recent scientific research of the authors of this review.

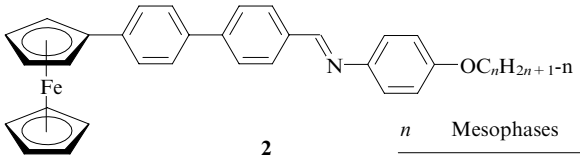
II. Monosubstituted liquid-crystalline ferrocenes

The steric effect of bulky 3D structure of ferrocene as terminal group precludes a favourable molecular packing and leads to a noticeable anisotropy of intermolecular interactions in the liquid-crystalline phase.[35] Enlargement of the rigid fragment (core) of a rod-like molecule due to the introduction of additional benzene rings allows one to avoid this difficulty but is followed by a significant increase in the phase transition temperatures. Manifestation of mesomorphism requires the presence of not only a ferrocene moiety, but also at least three aromatic rings in the molecular core. Attempts to synthesize ferrocene-containing liquid crystals with smaller number of benzene rings gave either no liquid-crystalline phase [40, 41] or a highly ordered smectic B phase [41] corresponding to plastic crystals. The exceptions are the structures containing a *trans*-cyclohexane moiety instead of benzene rings,[42] fused polycyclic moieties,[43–45] as well as recently obtained compounds containing a ferrocene moiety separated from the rigid rod-like fragment comprised of two benzene rings by a long hydrocarbon chain.

The other group of compounds mainly includes ferrocene derivatives with cholesteryl group as rigid core. Mesomorphic compounds with cholesteryl group are structurally different from most liquid-crystalline structures containing typical elements of the rigid part of the molecule. This also influences their phase (thermal) behaviour; therefore, mono- and disubstituted ferrocenes containing cholesteryl group will be considered in a separate Section.

The properties of liquid crystals formed by monosubstituted ferrocenes are affected by not only the number of benzene rings, but also the length of the hydrocarbon chain in the terminal group, the presence of lateral substituents in the aromatic system and the nature of linker groups in the rigid molecular core. Replacement of benzene rings by other poly- and heterocyclic aromatic systems also changes the properties. Here, we will discuss the results obtained for monosubstituted liquid-crystalline ferrocene derivatives since 2000. Most recent studies in the field are concerned with variations of the phase behaviour of monosubstituted ferrocenes depending on the chemical structure.

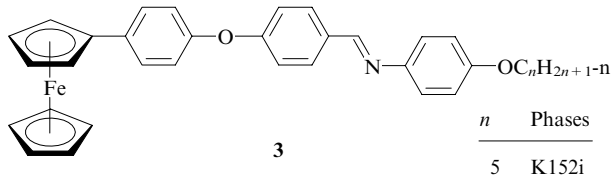
Imrie *et al.*[46] synthesized a number of liquid-crystalline compounds **2** based on biphenylferrocene.



2

n	Mesophases
5	K[208N]215i
8	K177S_x183N201i
14	K146S_x164N182i

The introduction of an ether bond between two benzene rings in biphenyl (structure **3**) causes the loss of liquid-crystalline properties. This is due to unfavourable geometry with a kink at the midpoint of the rigid fragment, as was shown using quantum chemical models.

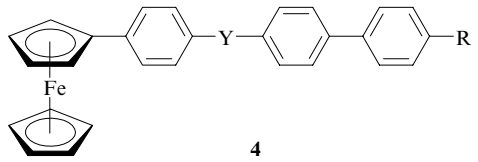


3

n	Phases
5	K152i
14	K127i

Researchers from this group also demonstrated[47] the effect of the nature of linker groups, terminal groups and the number of benzene rings on the properties of monosubstituted ferrocene derivatives **4**–**6** they have synthesized.

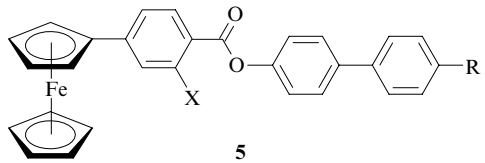
Considering compounds **4**, one can trace how terminal groups and the nature of the linker groups influence the liquid-crystalline properties. Namely, in the case of alkoxy terminal group, elongation of the hydrocarbon chain enhances the ability of a compound to form smectic mesophases and the thermodynamic stability of the liquid-crystalline state, while decreasing the phase transition temperatures. A more branched and more polar terminal group favours the formation of a nematic phase; no terminal alkyl chains no liquid-crystalline state; replacement of a carboxyl linker group by more flexible carboxyalkyl groups also leads to suppression of the liquid-crystalline state.



4

Y	R	Mesophases
C(O)O	OC_3H_7-n	K229i
	OC_5H_{11}-n	K[178N]187i
	OC_8H_{17}-n	K[126S_A]146N161i
	OC_9H_{19}-n	K[104S_C][130S_A]127N157i
	$OC_{10}H_{21}$-n	K[134S_A]135N155i
	$OC_{12}H_{25}$-n	K[92S_C]123S_A133N149i
	$OC_{14}H_{29}$-n	K[100S_C]119S_A136N143i
	OC(O)OMe	K166N194i
	OH	K275i (d)
$H_2CC(O)O$	OC_8H_{17}-n	$K_1$66$K_2$91i
MeCHC(O)O	$OC_{10}H_{21}$-n	$K_1$66$K_2$97i
	$OC_{14}H_{29}$-n	$K_1$76$K_2$99i

Compounds **5** with terminal carboxyalkyl and cyano groups form nematic phases. Branching of the carboxyalkyl substituent causes no mesomorphism. The compound with the polar Cl atom as the lateral substituent and alkoxyl terminal group forms a monotropic nematic phase at low temperatures.

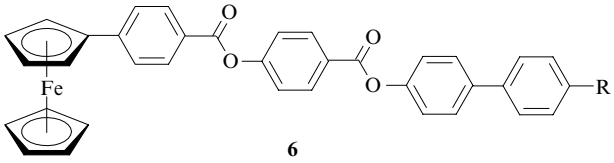


5

X	R	Mesophases	X	R	Mesophases
H	C(O)OC_8H_{17}-n	K[106N]165i	H	CN	K238N248i
H	C(O)OCH(Me)C_6H_{13}-n	K122i	Cl	$OC_{10}H_{21}$-n	K[??N]122i

'??' means that no exact monotropic transition temperature was specified in the original study.

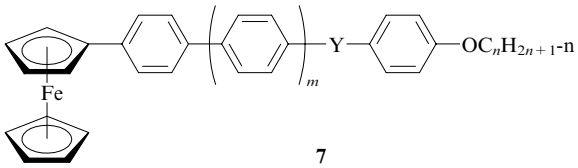
An increase in the number of benzene rings (compounds **6**) leads to a noticeable extension of the temperature range of mesophase existence; however, the phase transition temperatures also significantly increase.



6

R	*n*	Mesophases
OC_nH_{2n+1}-n	5	$K_1$178$K_2$192N291i (d)
	8	$K_1$163$K_2$191N275i (d)
	9	K172N268i
	10	K200N262i
	12	K147S_A154N258i
	14	K141S_C150N232i
CN	–	K258N304i (d)

Compounds **7** with biphenylene and terphenylene rigid fragments adjacent to the ferrocene moiety were reported by Makarov *et al.*[48,49]

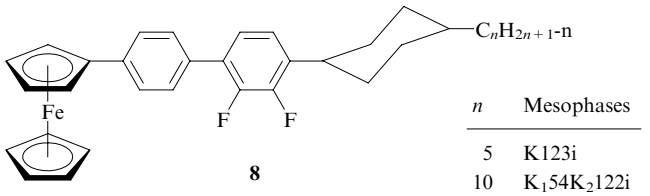


7

Y	*m*	*n*	Mesophases	Y	*m*	*n*	Mesophases
OC(O)	1	6	K186i	N=CH	1	6	K204i
	1	8	K154N161i		1	10	K180i
	1	10	K148N155i		1	14	K178i
	1	12	K133N148i	OC(O)	2	10	K204N270i (d)
C(O)O	1	10	K[151N]172i		2	12	K202N262i (d)
	1	12	K138N141i	N=CH	2	12	K255N292i (d)

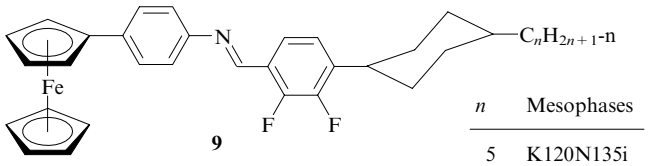
A comparison of the properties of the biphenylene and terphenylene derivatives showed that the introduction of an additional benzene ring undoubtedly extends the temperature range of mesophase existence, but the lower temperature limit of mesophase existence considerably increases, as should be expected. Also, it is of interest to monitor the influence of the orientation of bridging groups in the rigid core. The introduction of an azomethine bridge suppresses mesomorphism in the biphenylene derivatives, although analogous compounds with other orientations of the azomethine group contained nematic and smectic phases.[46] This was explained by a greater extent of delocalization of electrons of oxygen atom in the terminal alkoxy group owing to more efficient conjugation with the electron-accepting bridging group through the aromatic system in the case of connection to the electrophilic group. The same effect is clearly seen at different positions of the carboxyl bridge. (Unsymmetric 1,1′-disubstituted structure with alkyl group at the second cyclopentadienyl ring will be discussed below.)

In recently obtained liquid-crystalline ferrocene derivatives **8**–**10**, one benzene ring in the rigid core of the rod-like molecule is replaced by the cyclohexane moiety.[42] An undoubtful advantage of this structural type is a decrease in the phase transition temperatures and in the viscosity of mesophases. These properties can play an important role in the search for possible fields of practical applications of liquid-crystalline ferrocene derivatives in the future.



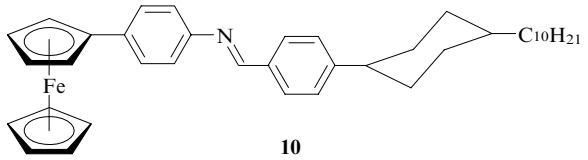
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n	Mesophases
5	K123i
10	$K_1$54$K_2$122i



9

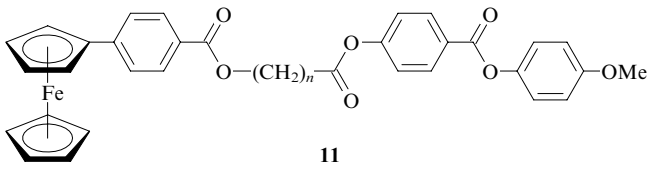
n	Mesophases
5	K120N135i
10	K109N117i



10

Mesophase is K[134N]143i

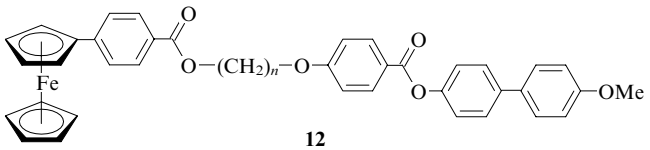
Nakamura *et al.*[50–58] carried out a series of X-ray diffraction studies of liquid-crystalline monosubstituted ferrocenes **11** that form the smectic C and nematic mesophases (this was established earlier).



11

The ferrocene derivatives **11** with short hydrocarbon linker groups were reported in the early studies.[50–54] More recently,[55–58] the packing of molecules in the crystalline phases of the derivatives with $n = 9-11$ was studied. The aim of these investigations was to determine the structural features of the liquid crystal precursor, which predetermine manifestation of mesomorphism. It was found that packing of anisotropic molecules corresponds to somewhat bent rod-like structures in which the orientation of carbonyl groups is favourable for effective lateral intermolecular interaction that stabilizes smectic mesophases. Compounds with short chains ($n = 1-3$, 5 and 7) demonstrated no mesomorphism because they do not exactly meet the conditions for geometric anisotropy of molecules and polarizability anisotropy owing to a large angle between the benzene ring planes. In spite of this, the structures with $n = 9$ and 11 are mesomorphic because the negative factors mentioned above are eliminated with an increase in the length of the molecule and, as a consequence, its shape anisotropy.

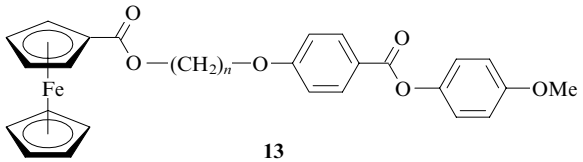
Compounds **12** containing a biphenylene moiety in the rigid core and structurally similar to the derivatives **11** were studied.



12

These structures are characterized by greater geometric anisotropy.[59] The number, *n*, of carbon atoms in the central hydrocarbon linker chain varied from 6 to 10. Compared to compounds **11**, the temperature ranges of nematic mesophase existence for compounds **12** increase while the smectic C mesophase is not formed. This increase is due to an increase in the temperature of transition to the isotropic liquid state. An enantiotropic nematic phase is observed only with the short linker group ($n = 6$); at $n = 7-10$, the phase transitions are monotropic. The observed even–odd alternation of the phase transition temperatures can be explained by the fact that at even *n* values, the rigid mesogenic core and the ferrocene moiety provide a more linear molecular shape; the thermal stability of mesophases at even *n* values increases compared to the odd-*n* homologues of compounds **11** and **12**.

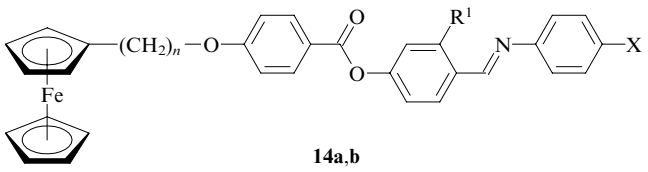
Yet another study carried out by this research group concerned mesomorphic ferrocene derivatives **13** with two benzene rings in the rigid core of the rod-like molecule and no phenylene substituent at the ferrocene moiety.[60]



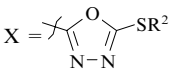
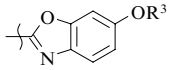
13

At $n = 9-12$, these ferrocene derivatives form monotropic nematic and smectic mesophases.

The introduction of heterocyclic fragments into the rigid core is also of some interest, because such compounds may exhibit luminescent and nonlinear optical properties. Majumdar *et al.*[61] reported the synthesis of a number of rod-like ferrocene derivatives **14a** containing an oxadiazole unit. S-Alkyl chains were used as terminal groups while hydrocarbon chains played the role of flexible bridges between the ferrocene moiety and the rigid mesogenic core. Also, lateral substituents in the oxadiazole ring were varied. All compounds synthesized and studied by Majumdar *et al.* exhibited enantiotropic smectic C and nematic mesophases. In one case, only the enantiotropic smectic C phase with no transition to the nematic phase was observed. Ferrocene derivatives **14b** containing benzoxadiazole units form a smectic C phase.[62]



14a,**b**

X =  (**14a**),  (**14b**)

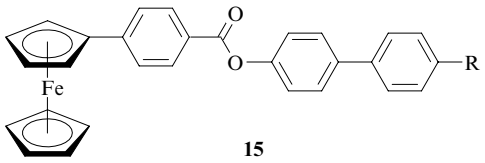
Compound	R^1	*n*	R^2	R^3	Mesophases
14a	H	6	n-$C_{12}H_{25}$	–	K123S_C171N187i
	H	6	n-$C_{14}H_{29}$	–	K120S_C170N184i
	OH	6	n-$C_{12}H_{25}$	–	$K_1$104$K_2$132S_C194N203i
	OH	6	n-$C_{14}H_{29}$	–	K149S_C195N200i
	H	11	n-$C_{12}H_{25}$	–	K111S_C175N180i
	H	11	n-$C_{14}H_{29}$	–	K101S_C173N177i
	OH	11	n-$C_{12}H_{25}$	–	K128S_C195N197i
	OH	11	n-$C_{14}H_{29}$	–	K120S_C149i
14b	H	6	–	n-$C_{14}H_{29}$	$K_1$116$K_2$126S_C201i
	H	6	–	n-$C_{16}H_{33}$	K118S_C201i
	H	6	–	n-$C_{18}H_{37}$	$K_1$116$K_2$127S_C202i
	H	11	–	n-$C_{14}H_{29}$	K111S_C199i
	H	11	–	n-$C_{16}H_{33}$	$K_1$116$K_2$126S_C198i
	H	11	–	n-$C_{18}H_{37}$	K112S_C196i

Cârlescu *et al.*[63–65] synthesized and studied ferrocene derivatives **15**–**19** containing azo and azomethine bridging groups. These investigations again confirmed the previously known general structural requirements for manifestation of mesomorphism of ferrocene derivativess, such as the presence of at least three benzene rings, orientation of carboxyl groups and the nature of terminal groups. The thermochemical and thermophysical properties of the compounds synthesized were studied in detail.[66]

Using experimental data[63–66] and molecular design software, Lisa *et al.*[67,68] developed a method for theoretical prediction of liquid-crystalline properties of ferrocene derivatives. Essentially, the method requires the design of a database for quantitative molecular descriptors of the liquid-crystalline properties calculated using computer simulation methods, for elements of the chemical structure and the use of neural network techniques for the molecular design of ferrocene derivatives with specified properties. Neural models optimized using relevant algorithms allow one to quite correctly evaluate the thermal stability and to predict parameters of the liquid-crystalline state of ferrocene derivatives.

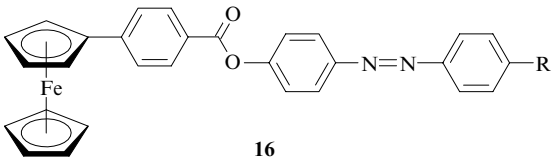
Seshadri *et al.*[69] synthesized and studied thiourethane derivatives **20** and **21** and imine derivatives **22** and **23** with flexible hydrocarbon linkers connecting the ferrocene moiety to the other part of the molecule. It was reported that cholesteric phases in chiral compounds **22** and **23** are prone to undergo a glass transition on cooling with conservation of liquid-crystalline order; therefore, they can be used to construct devices for full colour recording media.

Lai and co-workers[70] obtained ferrocene-based liquid-crystalline compounds **24** and **25** containing pyrazole ring in the rigid molecular core. These compounds were studied by powder X-ray diffraction and single-crystal X-ray diffraction of the initial crystals. Changes in the liquid-crystalline properties of compounds depending on the hydrocarbon



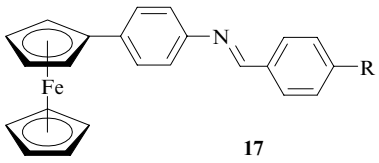
15

R	Mesophases
OC(O)C$C_{17}H_{35}$-n	K129N137i
$OC_{18}H_{37}$-n	K[132N]136i



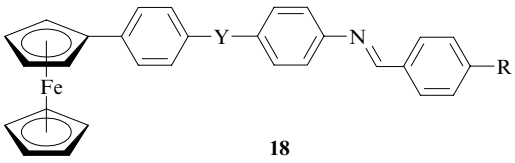
16

R	Mesophases
OC(O)$C_{17}H_{35}$-n	K128N145i
$OC_{18}H_{37}$-n	K[135N]136i



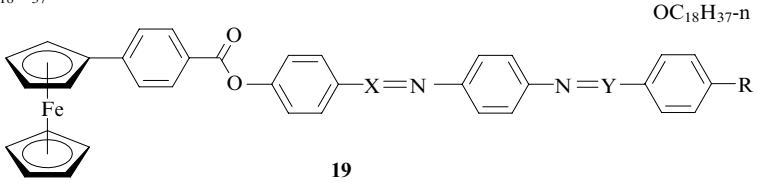
17

R	Phases
OC(O)$C_{17}H_{35}$-n	K115i
$OC_{18}H_{37}$-n	K112i



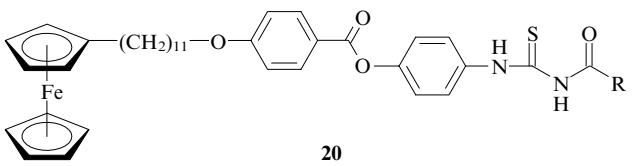
18

Y	R	Mesophases	Y	R	Mesophases
C(O)O	OC(O)$C_{17}H_{35}$-n	K126N153i	OC(O)	OC(O)$C_{17}H_{35}$-n	K129N155i
	$OC_{18}H_{37}$-n	K133N144i		$OC_{18}H_{37}$-n	K114N145i



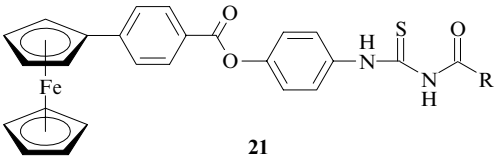
19

X	Y	R	Mesophases	X	Y	R	Mesophases
CH	N	OH	K300i	N	CH	$OC_{18}H_{37}$-n	K129N155i
	N	$OC_{18}H_{37}$-n	K133N144i		CH	OC(O)$C_{17}H_{35}$-n	K151N154i
	N	OC(O)$C_{17}H_{35}$-n	K130N168i				



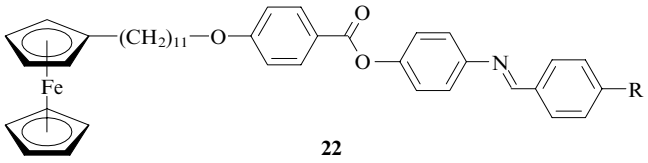
20

R	Mesophases
$C_6H_4OC_nH_{2n+1}$-n-4	K104N147i
	$K110S_C112N145i$
	$K117S_C119N145i$
	$K112S_C117N144i$
	$K113S_C[129S_B]129N138i$
$C_6H_2(OC_{10}H_{21}\text{-n})_3$-3,4,5	K59i



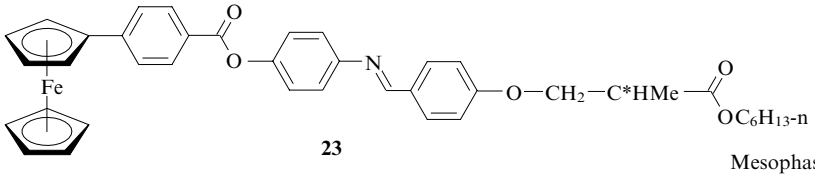
21

R	Mesophases
$C_6H_4OC_{10}H_{21}$-n-4	K144N157i
$C_6H_2(OC_{10}H_{21}\text{-n})_3$-3,4,5	K72i



22

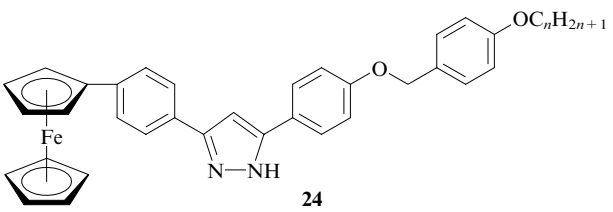
R	Mesophases
$OCH_2C^*HMeC(O)OC_6H_{13}$-n	K120N*122i
$HC{=}CHC(O)OC^*HMeC(O)OC_6H_{13}$-n	K88N*99i



23

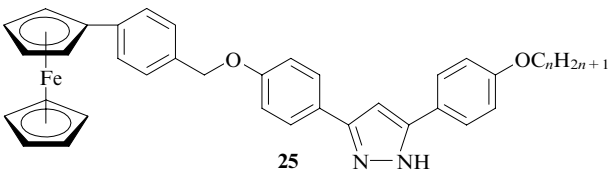
Mesophase is K161N*168i

chain length and on the position of pyrazole ring were studied and compared with the properties of a similar structure containing no ferrocene. It was shown that the liquid-crystalline properties somewhat deteriorate in the presence of ferrocene moiety. In our opinion, of particular interest is the possibility of comparing structures **24** and **25**. As the pyrazole ring responsible for the kink of the rigid molecular core moves away from the ferrocene moiety, structure **25** exhibits several types of mesophases (liquid-crystalline polymorphism); the temperature range of mesophase existence is somewhat wider compared to that for structure **24**.



24

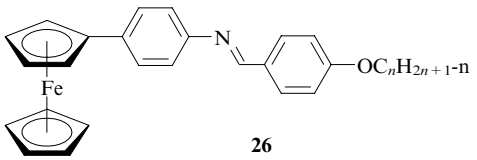
n	Mesophases	*n*	Mesophases
6	K[179N]186i	12	$K175S_A183i$
8	K[178N]189i	14	$K_1147K_2173S_A187i$
10	$K[178S_A]182i$	16	$K_1146K_2172S_A183i$



25

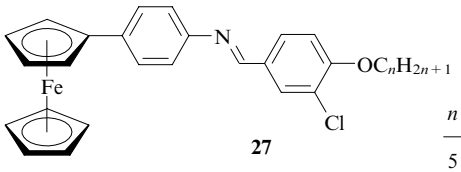
n	Mesophases	*n*	Mesophases
6	$K_1115K_2[174S_C]196N197i$	12	$K_168K_2168S_C181N1188i$
8	$K_1158K_2177S_C192N193i$	14	$K_170K_2168S_C183S_A186i$
10	$K_1133K_2175S188N192i$	16	$K_182K_2168S_C182S_A184i$

Zhao *et al.*[45] reported the synthesis of ferrocene derivatives **26** and **27**. It should be noted that many properties of mesophases and the phase transition temperatures are inconsistent with the data obtained by other research groups. For instance, based on analysis of numerous studies on monosubstituted liquid-crystalline ferrocene derivatives, Imrie *et al.*[35] concluded that for this structure, two benzene rings in the rigid rod-like molecular core are insufficient for manifestation of mesomorphism.



26

n	Mesophases	*n*	Mesophases
4	K173S186i	10	K103S107i
6	K145S149i	12	K76S106i
8	K118S131i	14	$K_150S54N76i$



27

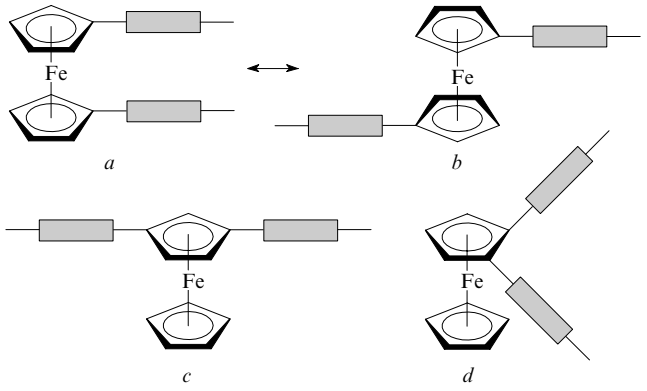
n	Mesophases
5	K114N121i
9	K122N139i

III. Ferrocene derivatives with two substituents in cyclopentadienyl moieties

Homoannular and heteroannular disubstituted ferrocenes allow one to better use the advantages of the 3D ferrocene system to obtain variously shaped mesogenic molecules

compared to monosubstituted analogues. Often, the second substituent makes it possible to eliminate unfavourable effect of bulky ferrocene moiety owing to more 'natural' incorporation of ferrocene into the molecular structure. Also, the first and second substituents can be varied to form unsymmetrically substituted structures that can influence not only the shape of mesogenic molecules, but also the 3D supramolecular organization of corresponding mesophases (see below). Possible isomers of disubstituted ferrocenes are shown in Scheme 1. Usually, 1,2-disubstituted ferrocenes (see Scheme 1 *d*) do not show liquid-crystalline properties owing to wedge-like shape which disturbs the molecular anisometry.

Scheme 1



1. 1,3-Disubstituted ferrocenes

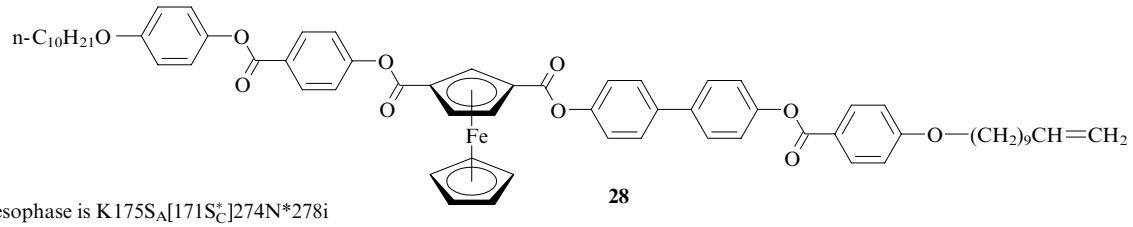
Ferrocene derivatives with two substituents in the same cyclopentadienyl moiety are rare. The known 1,3-disubstituted ferrocenes (see Scheme 1 *c*) have been reviewed [37–39] and therefore we will not dwell on them here. Mention may be made only that this type of substitution allows one to better alleviate unfavourable influence of the bulky ferrocene moiety because both substituents lie in the same plane and form a rigid rod with no steps and kinks at the midpoint unlike the 1,1′-disubstituted analogues (see Scheme 1 *a*). Other structural features of these compounds include planar asymmetry and the possibility of formation of mesophases whose chiralities are due to the ferrocene moiety *per se* provided that enantiomers can be separated. Such a separation is a nontrivial task and the development of novel synthetic routes to planar unsymmetrically substituted liquid-crystalline ferrocene derivatives remains topical. In this case, chiral smectic phases can exhibit the properties of ferroelectrics. In addition to a previously synthesized ferroelectric liquid crystal based on planar-chiral ferrocene,[71] Deschenaux and co-workers [72] obtained planar unsymmetrically substituted liquid-crystalline monomers **28** and **29** and polymers based on them (see below).[72]

Unsymmetrically substituted ferrocene derivatives were separated as follows.[71] Replacement of one acid group in the initial ferrocene-1,3-dicarboxylic acid was followed by transformation of a mixture of optical isomers of planar unsymmetrically substituted monoester to a mixture of diastereomeric ammonium salts using optically active (+)-phenylethylamine. Diastereoselective crystallization and subsequent reduction of the initial monoester made it possible to separate optical isomers to an enantiomeric purity of 98%. The absolute configurations of the optical isomers of intermediate ferrocenedicarboxylic acid monoester were determined from circular dichroism spectra. The monomers **28** and **29** formed chiral nematic (cholesteric) mesophases as well as smectic C* mesophases. The last-mentioned mesophase is first of all interesting from the standpoint of possibility of bulk electrical polarization of a material or the appearance of ferroelectricity. The possibility for these compounds to be used in nematic twist cells as twisting agents was studied.[71]

2. Symmetrical 1,1′-disubstituted ferrocenes

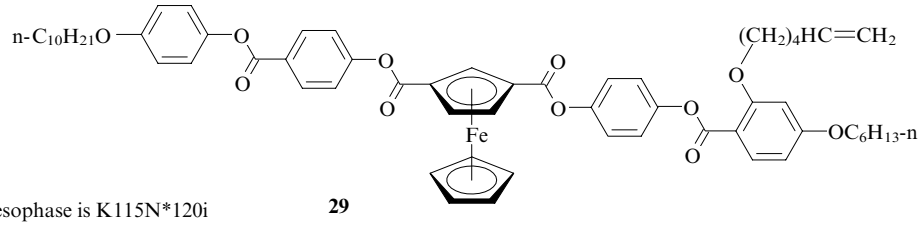
Most studies of symmetrically substituted ferrocenes were carried out before the 2000s and they were reviewed.[37–39] Therefore, we will dwell only on some general moments and recent studies.

The synthesis of disubstituted as well as homoannular disubstituted ferrocenes may be complicated by, *e.g.*, low yields and by the need for separation of isomers and products of further substitution reactions. The second substituent in the substitution reactions in the ferrocene unit can be introduced not only into positions 2 and 3 of the same cyclopentadienyl ring, but also into different cyclopentadienyl moieties. In the vast majority of cases the role of intermediates was played by ferrocenedicarboxylic acids, which can be obtained quite readily. We also used diacetylferrocene hydrazones [73] and 1,1′-diarylferrocenes.[74] In the latter compounds, conjugation of benzene rings with cyclopentadienyl rings and free rotation of the rings relative to



28

Mesophase is K175S_A[171S_C^*]274N*278i



Mesophase is K115N*120i **29**

each other may lead to an interesting internal organization of mesophases (see below).

Unlike monosubstituted ferrocenes, in 1,1′-substituted analogues unfavourable effect of bulky ferrocene unit is alleviated due to its location at the centre of the rigid molecular core. This underlies the formation of various mesophases; the number of benzene rings in the rigid molecular core can be minimum (one per substituent in the cyclopentadienyl rings).[75]

The geometry of such ferrocene derivatives is complicated by the possibility of free rotation of cyclopentadienyl rings relative to each other about the axis passing through the iron atom. First, this to some extent destabilizes the liquid-crystalline state due to the appearance of a kink at the midpoint of the rigid fragment of the molecule; second, one deals with uncertainty, namely, what is the possible configuration adopted by mesophases? Therefore, X-ray diffraction studies of crystalline precursors to mesophases and powder X-ray diffraction studies of liquid-crystalline phases become of particular importance in this case.

Based on the results of such studies, it was concluded that liquid-crystalline ferrocene dicarboxylates adopt a *trans*-conformation (S-configuration).[23] However, X-ray diffraction studies of crystalline precursors to mesophase for ferrocene diazine derivatives revealed a *cis*-conformation (U-configuration) of the molecules.[76] Therefore, the molecular geometry of 1,1′-disubstituted liquid-crystalline ferrocenes depends strongly on their chemical structure. In this case, intermediate conformations may also exist (see below).

Nakamura *et al.*[77–82] reported thorough X-ray diffraction studies of liquid-crystalline 1,1′-disubstituted ferrocenes **30** (Fig. 3).

This type of compounds exhibited liquid-crystalline polymorphism; mesophases were identified by polarizing microscopy, DSC and powder X-ray diffraction.[77] At $n = 2$ and 4, no mesomorphism was observed. At $n = 3$, a nematic mesophase was identified in the temperature range 19–35 °C. At $n = 5–10$, a nematic and two smectic mesophases were found in the temperature range from −6 to 65 °C. Low transition temperatures deserve particular attention. In most cases, the compounds under study crystallize at higher temperatures upon transition to the isotropic liquid state; this indicates a complex phase behaviour and metastable character of the liquid-crystalline state. Based on the X-ray diffraction data and on the assumption of *trans*-configuration of the molecules, the following was concluded:

— these compounds exhibit the lamellar smectic C mesophase with deep interpenetration of layers into one another, which is due to ordering of S-shaped molecules (see Fig. 3);

— the other type of the smectic phase belongs to more organized types, *viz.*, smectic F or smectic I phase.

Nevertheless, according to X-ray diffraction data, crystalline precursors to mesophases in the compounds **30** with $n = 3, 9, 10$ (see Refs 78–82) have an U-shaped configuration, whereas at $n = 5$ one deals with packing of the molecules with S-shaped configuration.[81] At the same time, X-ray data showed that the compound with $n = 2$ has a different configuration of the Z-type,[82] which demonstrates no rod-like shape anisotropy. In this connection, the lack of mesomorphism seems to be quite logical.

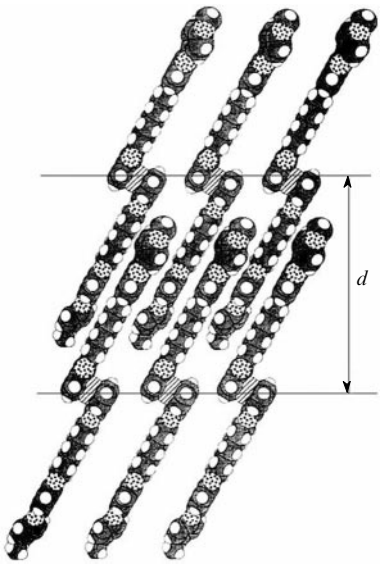


Figure 3. Molecular packing in the smectic C phase of 1,1′-disubstituted ferrocene **30** with $n = 7$ according to Nakamura *et al.*[77] *d* is the interlayer spacing.

Thus, the role of conformational interconversions in 1,1′-disubstituted ferrocenes is significant for manifestation of mesomorphism. A study of compounds **31** also revealed more complex types of organization of tetrahedral mesophases. Here, the bent conformation occupying intermediate position between the S- and U-conformations is stabilized through the formation of molecular dimers

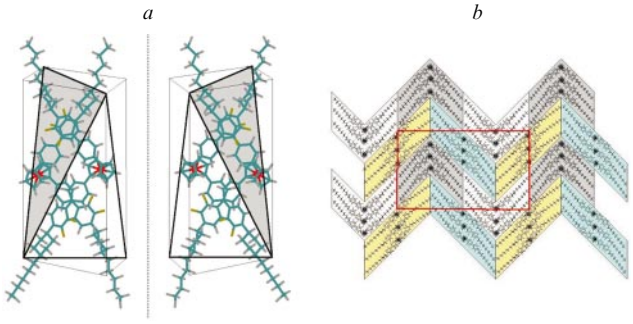
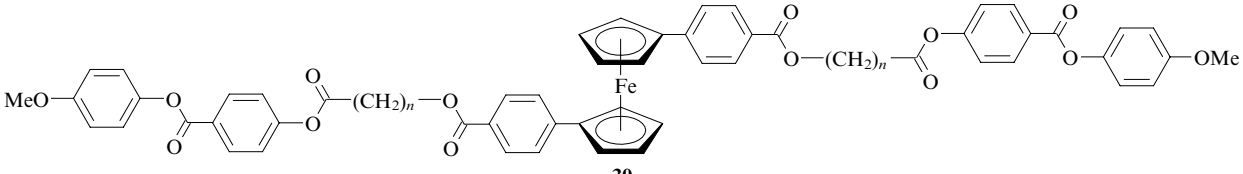
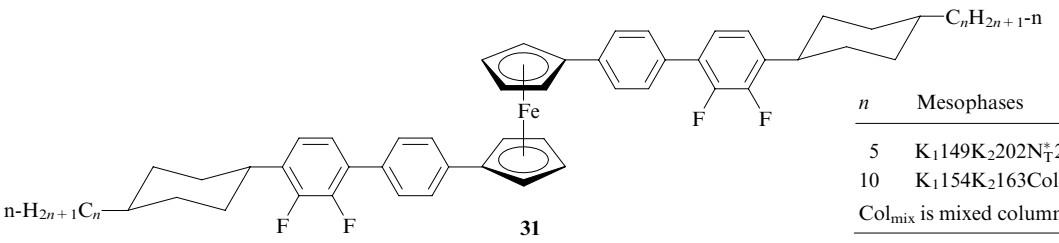


Figure 4. Dimers of bent conformers in tetrahedral nematic (N_T^*) and smectic A (S_A^*) mesophases (*a*) and a columnar mesophase with mixed packing of S-shaped and bent conformers of compound **31** (*b*).[83]



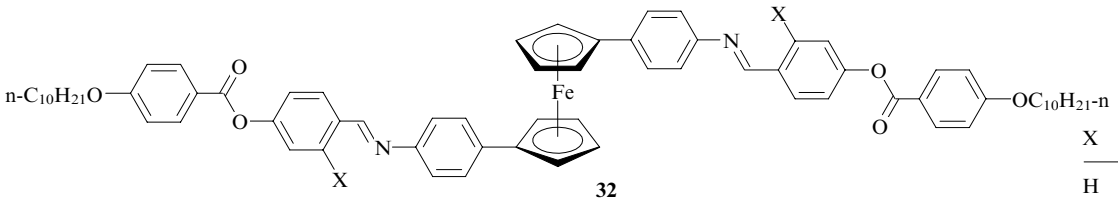
$n = 2–10$

30



n	Mesophases
5	$K_1149K_2202N_T^*253i$
10	$K_1154K_2163Col_{mix}181S_{AT}^*225N_T^*228i$

Col_{mix} is mixed columnar mesophase



X	Mesophases
H	K250N303i (d)
OH	K250N (d)

(Fig. 4).[83] In addition, mixed packing of the S-conformers and bent intermediate conformers leads to unusual columnar mesophase exhibiting characteristic optical textures. The structures of tetrahedral mesophases were confirmed by the results of analysis of optical textures by polarizing microscopy, by X-ray diffraction data and by the results of molecular simulation. Surprisingly, this type of structural organization of mesophases was not observed in the variety of ferrocene dicarboxylate and diazine derivatives.

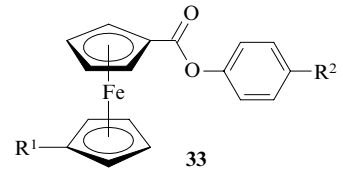
One can assume that the ferrocene unit in 1,1′-diaryl derivatives is included in the common system of conjugated aromatic fragments in which the benzene rings lie in the same plane with the cyclopentadiene rings. Therefore, the dimerized conformers form a stable molecular system with effective interplanar interaction between their π-electron systems. This was also confirmed by quantum chemical calculations of molecular models. Lateral substituents, in particular, fluorine atoms, which induce a large dipole moment oriented perpendicular to the long axis of the molecule, can also play some role in the formation of dimers. Analogous diaryl derivatives **32** are characterized by very high temperatures of transition to the mesophase (~250 °C); therefore, observation and investigations of the liquid-crystalline state was precluded by their thermal degradation.[74]

A method was developed[84,85] for quantum chemical calculations of large molecular ensembles comprising about 1000 mesogenic molecules in order to predict the transition temperatures and to reveal specific features of phase transitions of nematic and smectic systems upon temperature variation, changes in the substrate shape, as well as the chemical composition and molecular structure. The method was tested on compounds **31**. According to the results of molecular dynamics simulation with no boundary conditions, liquid-crystalline clusters of 1,1′-disubstituted ferrocene undergo conformational rearrangements upon temperature variation; this is consistent with experimental data.[83]

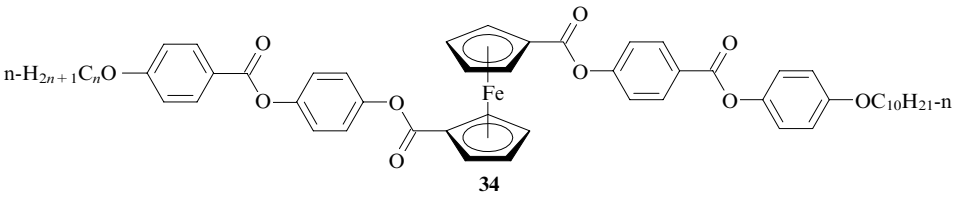
Summing up, it is believed that bulky ferrocene unit in 1,1′-disubstituted ferrocenes is more 'naturally' incorporated into the rod-like structure of the mesogenic molecules. However, unambiguous determination of the molecular packing in the liquid-crystalline phase is often difficult due to free rotation of cyclopentadienyl rings relative to each other. It is clear that the number of benzene rings in substituents necessary to produce a desired anisotropy of molecules with the *cis*-configuration is larger than for the *trans*-configuration. Also, an increase in the number of benzene rings often leads to an increase in the transition temperatures. A possible way of decreasing the transition temperatures is to introduce flexible hydrocarbon chains between the ferrocene unit and the rigid mesogenic core. However, in this case, the compounds under study may show a complex thermal behaviour with subsequent crystallization of isotropic melts. Another method to improve the thermal properties of mesophases is to violate the symmetry of substituents in the ferrocenyl group (see below).

3. Unsymmetrical 1,1′-disubstituted ferrocenes

To study the effect of ferrocenyl group in the molecular cores and to compare with the analogues containing benzene and cyclohexane moieties, Thompson *et al.*[86] synthesized a number of unsymmetrically substituted ferrocene derivatives **33**. They exhibited nematic liquid-crystalline phases which often showed monotropic behaviour at negative temperatures. Some ferrocene derivatives form enantiotropic nematic phases with rather low transition temperatures.



R^1	R^2	Mesophases
Bu^n	n-C_7H_{15}	L
	OC_6H_{13}-n	L
	$OC(O)C_6H_4OC_5H_{11}$-n-4	K77i
	$N{=}CHC_6H_4[OC(O)C_6H_4OC_8H_{17}$-n-4]-4	K96N127i
n-C_6H_{13}	Ph	K[−85N]73i
	C_6H_4Br-4	K[−20N]78i
	$C(O)OC_6H_4OC_8H_{17}$-n-4	K[−6N]54i
	$C(O)OC_6H_4[C_6H_4OC_8H_{17}$-n-4]-4	K[63N]107i
	{[$C_6H_4OC(O)$(cyclo-C_5H_4)]-4}. . Fe(cyclo-$C_5H_4C_6H_{13}$-n)	K[−28N]84i
n-C_9H_{19}	C_6H_4CN-4	K[−25N]78i
	$C_6H_4OC_{10}H_{21}$-n-4	K67i
	$N{=}CHC_6H_4[OC(O)C_6H_4OC_8H_{17}$-n-4]-4	K83N115i
	$OC(O)$(cyclo-C_5H_4)Fe(cyclo-$C_5H_4C_9H_{21}$-n)	K35i

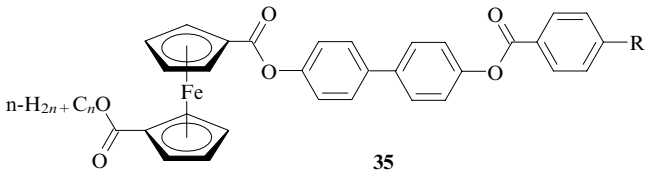


34

n	Mesophases
11	K144S_A149i
12	K[134S_C]143S_A150i
13	K140S_C144S_A151i
14	K135S_C142S_A152i
15	K132S_C145S_A151i
16	K132S_C148S_A153i

Deschenaux *et al.*[87] synthesized unsymmetrically substituted ferrocenes **34**. A distinctive feature of these compounds is that they form smectic A and C mesophases. Also, they have lower transition temperatures compared to the symmetrically substituted analogues.

Hanasaki *et al.*[88] synthesized a series of compounds **35**. The data presented here can be used to follow changes in the liquid-crystalline properties and transition temperatures depending on the structural features of this group of unsymmetrically substituted ferrocene derivatives. Most compounds form nematic phases that are stable at relatively low temperatures.

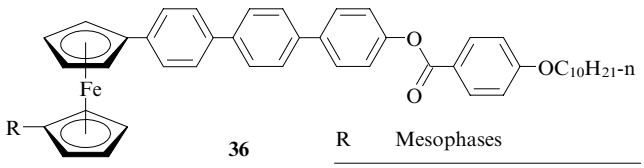


35

n	R	Mesophases	*n*	R	Mesophases
10	H	K131i	8	OC_7H_{15}-n	K82N94i
10	CN	K[117LC][129N]143i	9	OC_7H_{15}-n	K82N98i
10	CF_3	K[95S_A]131i	10	OC_7H_{15}-n	K85N93i
10	OMe	K[79LC_1][81LC_2][88N]120i	12	OC_7H_{15}-n	K82N91i
10	OBu^n	K102N103i	13	OC_7H_{15}-n	K89N91i
10	OC_6H_{13}-n	K99N100i			

LC is the liquid-crystalline mesophase whose type was not determined.

Using this approach, Dyadchenko and co-workers[48] succeeded in considerably reducing the temperatures of transition of the ferrocene derivatives **36** with terphenyl substituent to the liquid-crystalline phase.



36

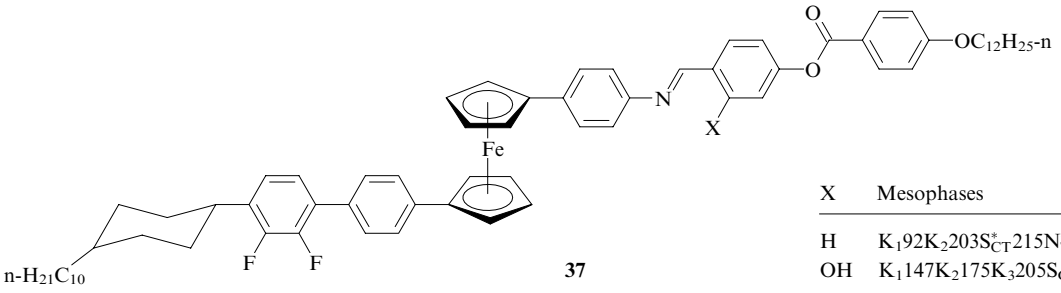
R	Mesophases
Et	$K_1136K_2145S_x159N250$ (d)
Bu^n	K120S_x161N238i

Compounds **36** with alkyl group introduced into the second cyclopentadiene ring can form a nematic and a smectic mesophase.

Similarly to the symmetric derivatives **31**, the unsymmetrically substituted ferrocene derivatives **37** and **38** exhibited mesophases with unusual tetrahedral packing of their molecules (Fig. 5).[89] A characteristic feature of the S^*_{CT} and N^*_T tetrahedral mesophases is spontaneous separation into large optically active regions, which is due to chiral supramolecular organization provided that the molecule contains no chiral centres. This is accompanied by the formation of randomly distributed large areas of the plane of polarization of light with both signs of rotation. In addition, there are some indications of optical biaxiality in the tetrahedral nematic N^*_T mesophase.

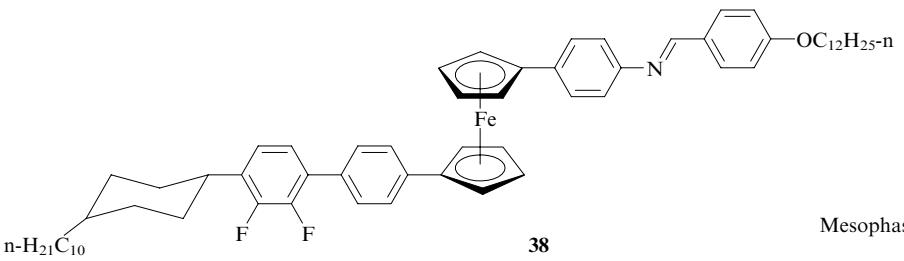
The S^*_{CT} mesophase also contains helical supramolecular structures, while the N^*_T mesophase in polarized light between crossed polarizers is mainly a dark field (unlike colourful textures of conventional nematic mesophase). The X-ray diffraction patterns of these mesophases are complicated, being atypical of the known mesophases.

Zhao *et al.*[90] reported the synthesis of unsymmetrically substituted ferrocenes **39**. An attractive feature of these



37

X	Mesophases
H	$K_192K_2203S^*_{CT}215N^*_T272i$
OH	$K_1147K_2175K_3205S_C225S^*_{AT}279N^*_T287i$



38

Mesophases are $K_1113K_2195S^*_{AT}205N^*_T206i$

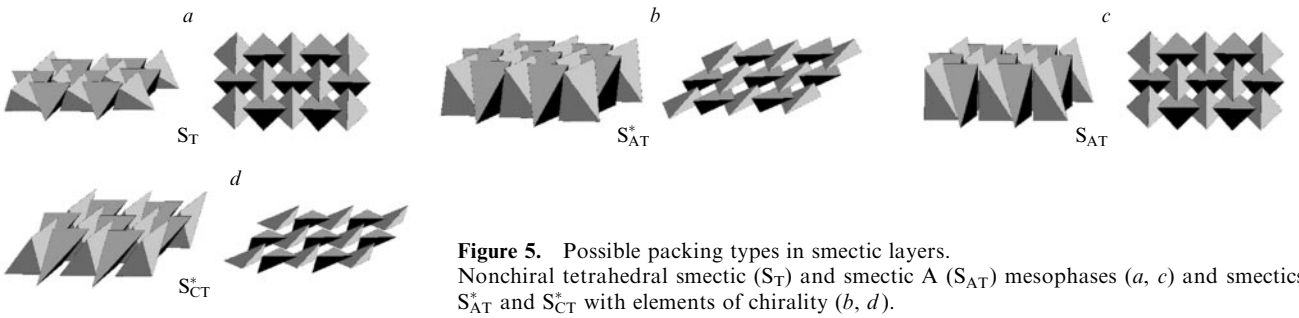
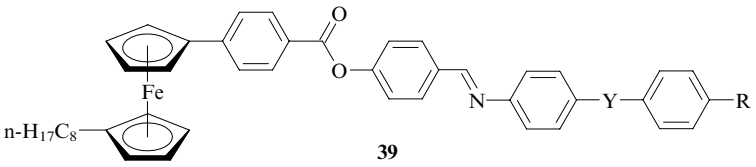


Figure 5. Possible packing types in smectic layers.
Nonchiral tetrahedral smectic (S_T) and smectic A (S_{AT}) mesophases (*a*, *c*) and smectics S^*_{AT} and S^*_{CT} with elements of chirality (*b*, *d*).



39

Y = O(O)C: R = H or OC_nH_{2n+1} (n = 2, 4, 6, 8);
Y = N═N: R = Cl, Br, Me

compounds consists in manifestation of liquid-crystalline properties at moderate temperatures.

IV. Mono- and 1,1′-disubstituted liquid-crystalline ferrocenes based on mesogenic cholesteryl group

The cholesteryl group is a convenient mesogenic core to be introduced into various molecular structures. Simultaneously, elements of chirality are introduced into the liquid-crystalline molecule to obtain optically active mesophases, which are of importance in various applied areas.[91,92] Therefore, interest of researchers in the synthesis of liquid-crystalline compounds containing ferrocene and cholesteryl group is logical.

Nakamura *et al.*[43,44,93–97] synthesized ferrocene derivatives **40** containing a cholesteryl group and studied their phase behaviour by polarizing microscopy, DSC and X-ray diffraction. Compounds with n = 2, 4, 6, 8, 9, 10 and 11 form monotropic smectic C mesophase that appears from the supercooled liquid.

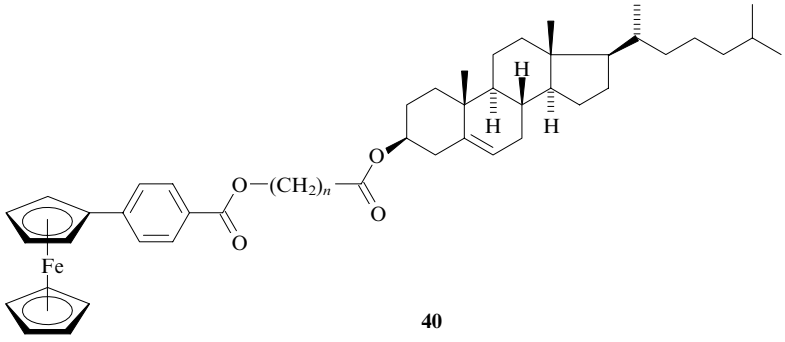
Another study reported by Nakamura's group concerned the viscoelastic properties of compounds **40**.[98] It was found that these liquid-crystalline ferrocene derivatives to a great extent manifest viscous rather than elastic properties in the smectic state, unlike most other compounds exhibiting the smectic phase. This was attributed to a weaker association of molecules in the compounds under study. High dynamic elastic moduli were also noted, which are to some extent retained even in the isotropic liquid state. It is assumed that this is a consequence of retention of a weak short-range local order even after transition to isotropic liquid. X-Ray diffraction studies of compounds **40** showed[96] that the appearance of the smectic C mesophases is due to the peculiar features of molecular packing in the crystalline precursor, namely, antiparallel packing with some displacement of the molecules relative to one another along the long axis of the molecule.

The simplest cases of addition of cholesteryl group to ferrocene unit were reported by Deschenaux *et al.*[99] The derivative **41** showed no mesomorphism, whereas 1,1′-disubstituted ferrocene **42** formed a crystalline smectic B mesophase at relatively high temperatures (265–276 °C).

Monosubstituted ferrocene **43** with attached cholesteryl group showed a cholesteric mesophase (chiral nematic) in a rather wide temperature range (119–171 °C).[69]

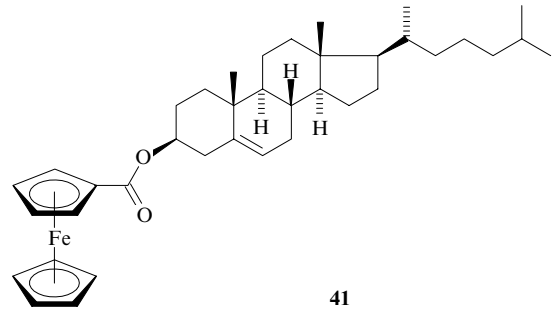
Structures with two rigid mesogenic cores linked by a flexible hydrocarbon chain are suitable for the synthesis of liquid crystals with bulky fragments. Majumdar *et al.*[100] obtained a series of compounds **44**, **45** with quite interesting properties. A number of dimers synthesized exhibited not only the expected cholesteric mesophase, but also the twisted grain boundary (TGB) and smectic A mesophases.

It is interesting to compare ferrocene compounds **46**, **47** containing cholesteryl group[101] with analogous compounds **48**.[102] These groups of cholesterol- and ferrocene-containing mesomorphic compounds were studied by polarizing microscopy and DSC. In the former case, the ferrocenyl group is separated from the other part of the mesogenic molecular core by a flexible hydrocarbon chain. Compounds **46** and **48** exhibited a cholesteric mesophase,

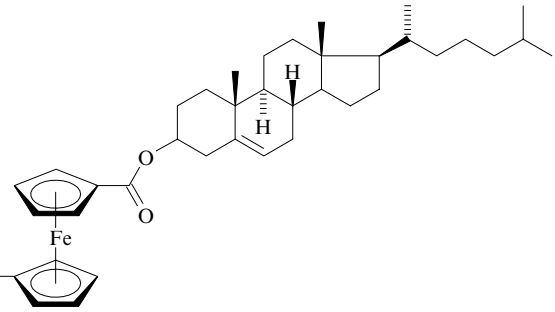


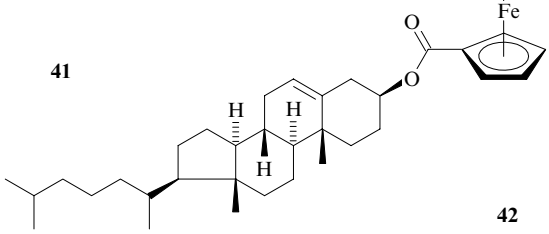
n = 1–11

40

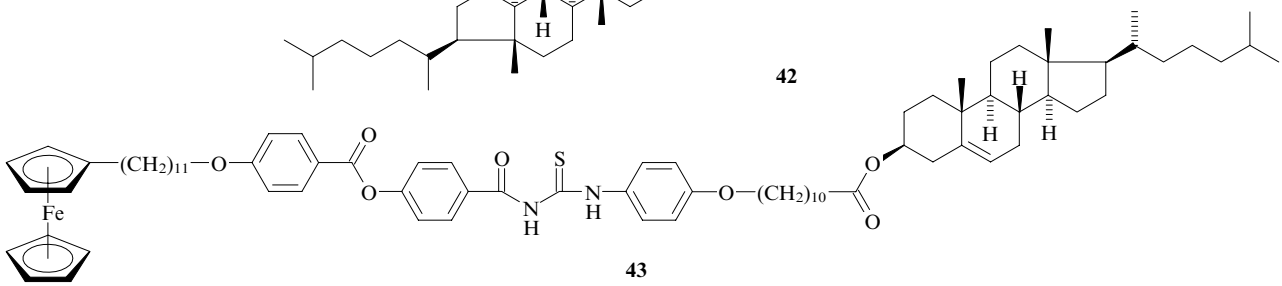


41

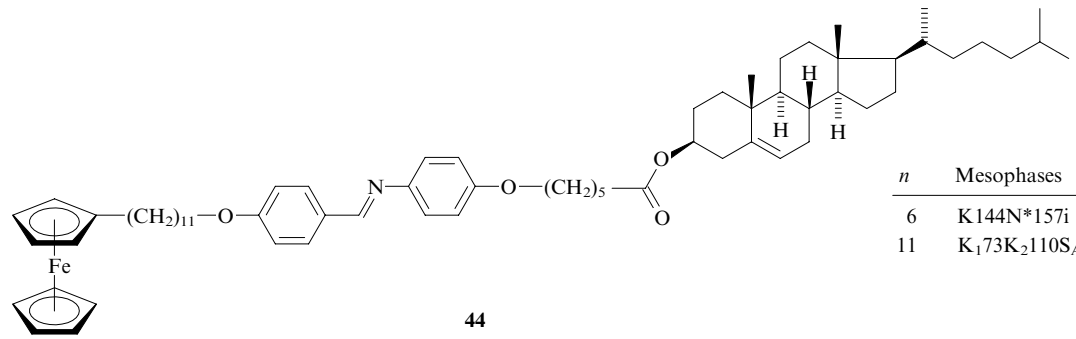




42

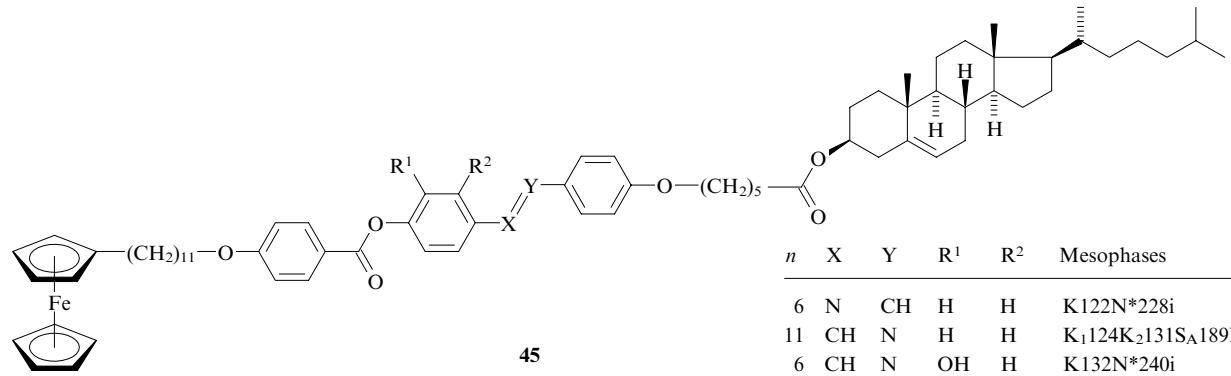


43



n	Mesophases
6	K144N*157i
11	$K_1$73$K_2$110S_A152TGB153N*155i

44



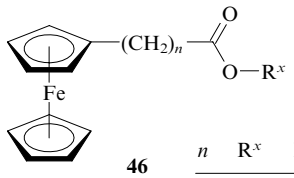
n	X	Y	R^1	R^2	Mesophases
6	N	CH	H	H	K122N*228i
11	CH	N	H	H	$K_1$124$K_2$131S_A189N*218i
6	CH	N	OH	H	K132N*240i
6	CH	N	H	NO_2	K90N*192i

45

although no liquid-crystalline properties were observed in the absence of the rigid core or in the presence of a kink between the cholesteryl group and other molecular fragments. Mesophases of compounds **48** were found at lower temperatures. Cholesteric mesophases and, in some cases, a conventional and chiral smectic A phase were identified by both methods. Both types of compounds are promising for the synthesis of systems with photoswitchable properties owing to the presence of azo group, which can undergo reversible *cis-trans*-isomerization on exposure to light and thus change some parameters of the cholesteric phase, *e.g.*, the pitch of the cholesteric helix (it is responsible for colour) or lead to optically isotropic liquid.

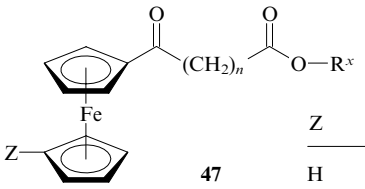
Then, the thermal stabilities of compounds **47**, **48** were studied by thermogravimetry.[103, 104] In most cases, the first phase of thermal degradation of these compounds began above 310 °C. It was shown that liquid crystals with ferrocenyl group are rather stable towards thermal degradation.

Monosubstituted ferrocene **49** exhibited a monotropic cholesteric mesophase on cooling from isotropic melt at 137 °C.[45]



46

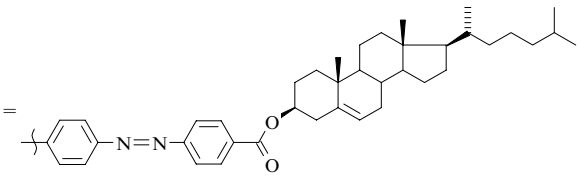
n	R^x	Mesophases
3	R^1	$K_1149K_2161N*287$ (d)
3	R^2	K132i
3	R^3	K155i
4	R^1	$K_1127K_2139N*201i$



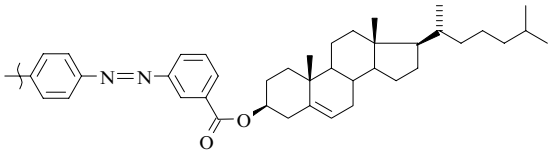
47

Z	*n*	R^x	Mesophases
H	2	R^1	$K_163K_2163N*249$ (d)
H	2	R^2	K97i
H	2	R^3	K130i
H	3	R^1	$K_185K_2181K_3193N*265$ (d)
n-$C_{17}H_{35}C(O)$	2	R^1	K98N*175i

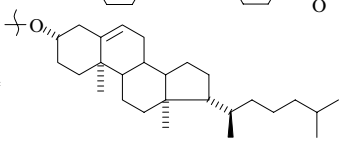
46, **47**: R^1 =



R^2 =

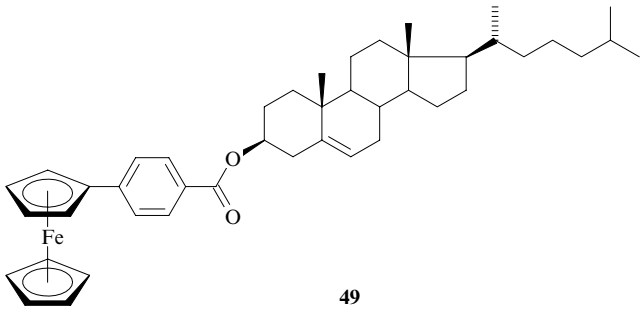


R^3 =



48

X	Y	Z	Mesophases
–	C(O)O	C(O)O	$K[154S_A]152N*178i$
–	N=CH	O	$K[176S^*_A]177N*214i$
C(O)O	N=CH	O	K179N*220i



49

V. Liquid-crystalline systems based on ferrocenophane

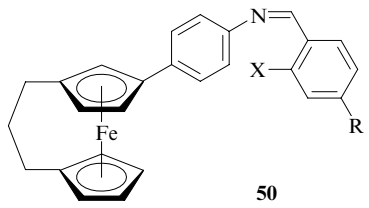
Liquid crystals containing a ferrocenyl group with alkyl bridge were for the first time obtained by Werner and Friedrichsen.[105] Such compounds can exhibit the smectic C and nematic mesophases.

Intermediates for the synthesis of ferrocenophane-containing mesomorphic compounds were obtained by arylation of ferrocenophane using diazonium salts and then structurally characterized.[106] More recently, they were used to synthesize a number of mono- and disubstituted ferrocenophane **50**–**54** with different substituents.[107]

Monosubstituted ferrocenophanes **51** with the mesogenic substituent in position adjacent to the alkyl bridge are less prone to form mesophases owing to unfavourable molecular geometry, although elongation of the rigid core may lead to the appearance of thermodynamically unstable monotropic nematic phase. If the third carbon atom (numeration is given relative to the alkyl bridge) bears a substituent, a common conjugated aromatic system including the cyclopentadiene ring can form again. In addition, in this case the alkyl bridge is in position that favours extension of the long axis of the molecule. Compound **50** containing two benzene rings exhibits monotropic mesomorphism unlike corresponding ferrocene structures. In this case, the formation of a columnar mesophase can be explained by the formation of clusters comprised of a few molecules, which are then packed into columns. As the geometric anisotropy of substituents increases, this type of ferrocenophanes exhibits enantiotropic nematic mesomorphism similarly to the ferrocene analogues.

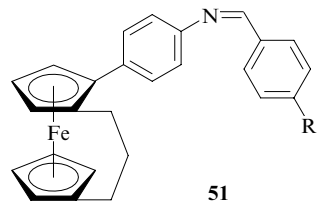
Disubstituted ferrocenophanes **52** with substituents in neighbouring positions of the same ring, exhibit no mesomorphism due to their V-shaped geometry and steric hindrances to formation of a common conjugation system of aromatic rings. Analogous ferrocene-based systems containing no alkyl bridge are also non-mesogenic.[37–39] The molecule of compound **53** with substituents in different cyclopentadiene rings also has a wedge-like shape, but in this case effective conjugation of the ferrocene moiety with the aromatic substituent is possible and the system exhibits mesomorphism. Interestingly, compound **53** with the short substituents exhibits an enantiotropic nematic mesophase, whereas the system with the long ones exhibits only an unidentified monotropic smectic mesophase. Chain extension in substituents leads to stronger 'wedging' of their ends and to a decrease in the overall geometric anisotropy.

Compound **54** with aminovinyl ketone substituent demonstrated a complicated thermal behaviour with subsequent crystallization of melts upon transition to the isotropic liquid state. Rapid cooling leads to formation of thermodynamically unstable monotropic nematic and smectic C mesophases.



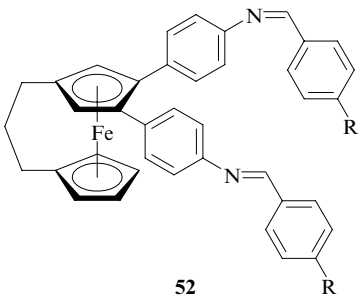
50

X	R	Mesophases
H	$OC_{12}H_{25}$-n	K[65Col]116i
OH	$OC_{12}H_{25}$-n	K52i
H	$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K138N172i
OH	$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K130N163i



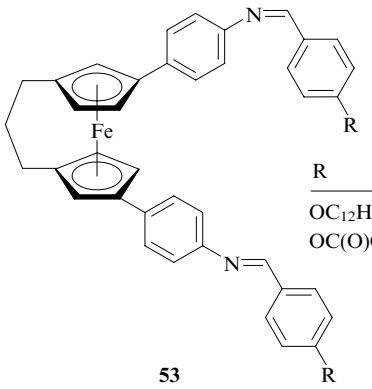
51

R	Mesophases
$OC_{12}H_{25}$-n	K105i
$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K[66N]153i



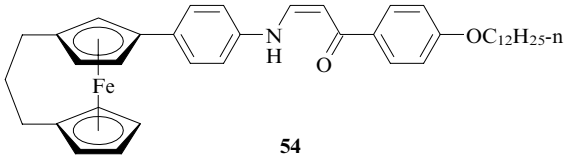
52

R	Mesophases
$OC_{12}H_{25}$-n	K60i
$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K121i



53

R	Mesophases
$OC_{12}H_{25}$-n	K112N116i
$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K[155S_x]178i

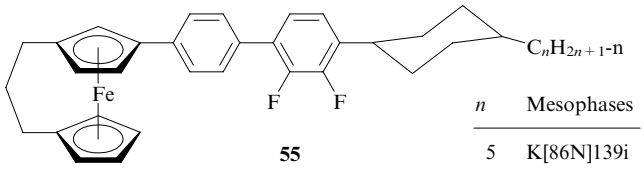


54

Mesophases are K_{1T}[118S_C][124N]135K_{2T}[152i(K_{1T})]192i(K_{2T})

Many ferrocenophane derivatives were then used for the synthesis of heteronuclear liquid crystals (see below).

Liquid-crystalline ferrocenophane derivatives **55** and **56** with the cyclohexane moiety in the rigid rod-like fragment of the molecule were synthesized.[42] Compounds **55** can form a nematic mesophase unlike their analogues **8** based on ferrocene with no alkyl bridge. Compound **56** with a different melt-grown crystalline form exhibits enantiotropic nematic mesomorphism.



55

n	Mesophases
5	K[86N]139i
10	K[83N]125i

Summing up, ferrocenophane is a valuable structural fragment for the synthesis of ferrocene-containing liquid crystals.

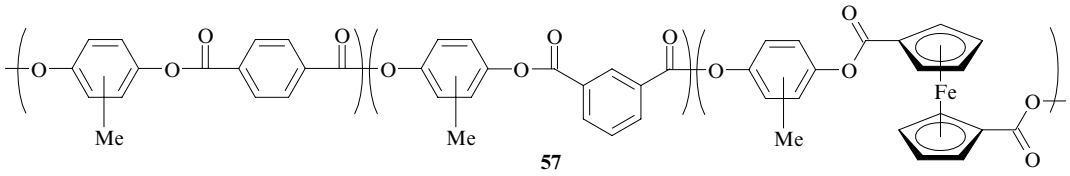
VI. Liquid-crystalline polymers and dendrimers based on ferrocene†

Ferrocene-containing liquid-crystalline polymers belong to a large family of macromolecular compounds whose representatives were considered in a review.[36] In side-chain liquid-crystalline polymers, the ferrocene unit can be either in the backbone, thus significantly improving the thermal stability of the material, or in lateral substituents. Studies on the redox properties of ferrocene and on the possibility of interaction between metal centres to obtain new optical, electrical, magnetic switchable properties in liquid-crystalline polymers are of considerable interest. Investigations of the first liquid-crystalline polymers **57** with ferrocene units in the backbones showed that ferrocene can favour the formation of mesophases.[24]

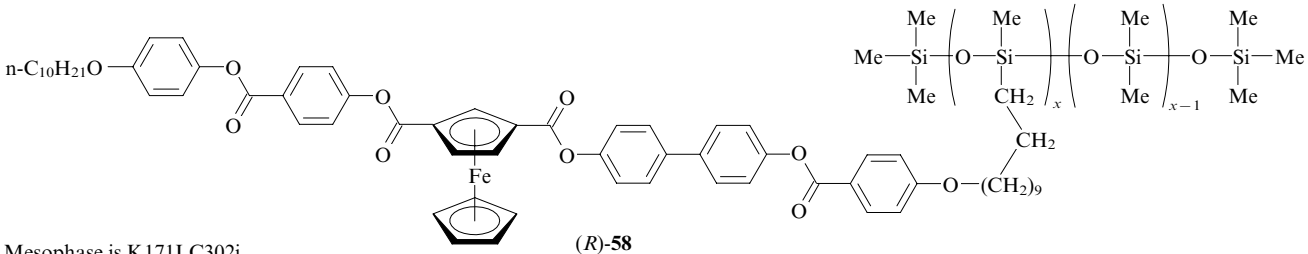
The variety of ferrocene-containing liquid-crystalline polymers is due to the introduction of different linker groups into the polymer structure and to the use of different patterns of substitution in the ferrocene unit. Many of these ways have already been used in the synthesis of high-molecular-mass ferrocene-containing mesomorphic compounds.[36]

Among this class of materials, liquid-crystalline polymers with siloxane linker groups are of particular interest. Polysiloxanes exhibit a number of unique properties. High chain flexibility and weak chain–chain interactions underlie high solubility, low melting points and low surface energy. These properties allow the compounds in question to be used as coatings. Loose structure and increased adsorption capacity of polysiloxanes are attractive for their application as membranes and catalyzing agents. Polysiloxanes also have high thermal and chemical stabili-

† Unfortunately, researchers working in this field not always provide information on the degree of polymerization, molecular mass distribution, rheological, mechanical and other properties, *i.e.*, the properties of polymers; they mainly restrict themselves to investigations of the liquid-crystalline properties by optical polarizing microscopy, DSC, analysis of phase transformations, powder X-ray diffraction, thermogravimetry and study of the chemical structure. Therefore, in this review the emphasis is placed on correlations between the structures of ferrocene-containing polymers and their liquid-crystalline properties. This is of particular importance for targeted molecular desing of such structures. Ferrocene-containing liquid-crystalline dendrimers are compounds with exactly specified molecular composition and relatively high molecular masses. They are studied by the same methods as those used to investigate low-molecular-mass compounds, *viz.*, various spectroscopic methods including NMR, MALDI-TOF mass spectrometry, elemental analysis, *etc.*

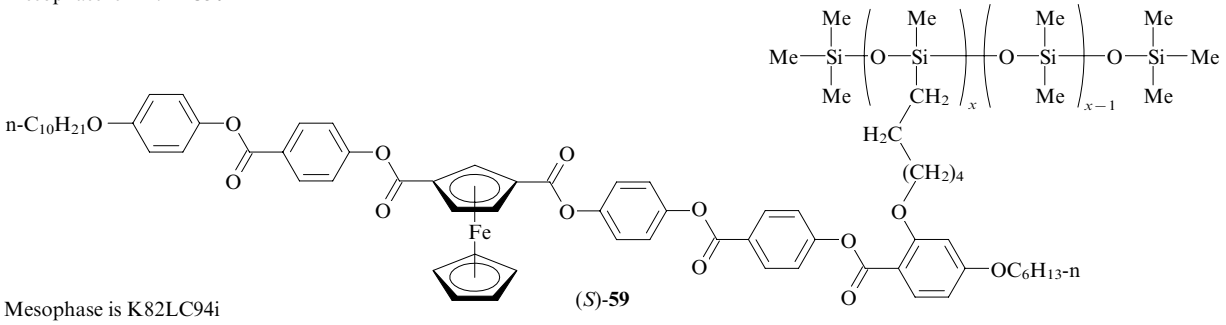


57



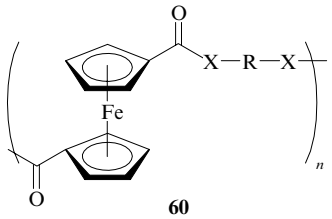
(*R*)-**58**

Mesophase is K171LC302i



(*S*)-**59**

Mesophase is K82LC94i



60

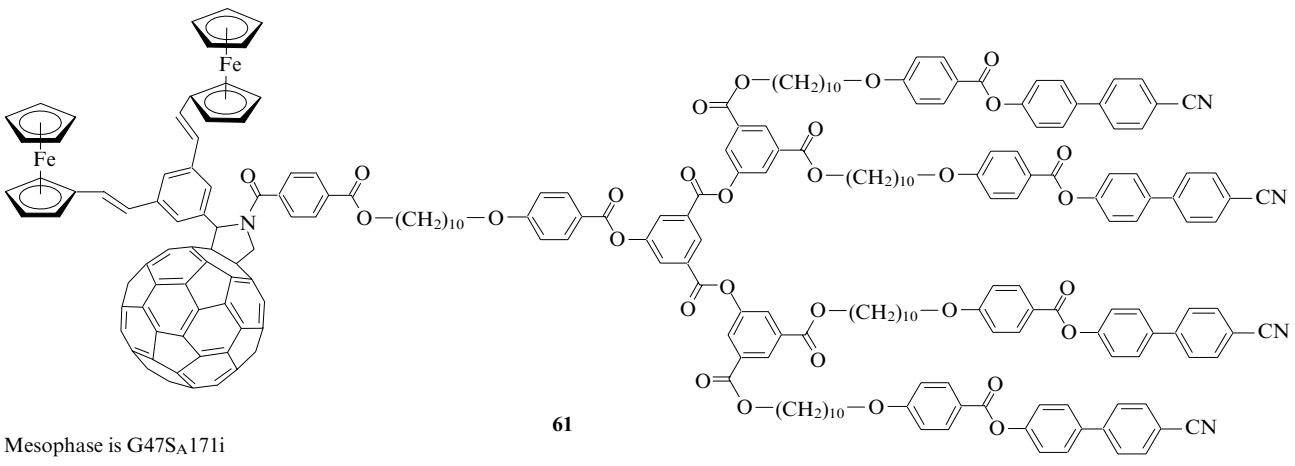
X	R	Mesophases
NH	$(CH_2)_3SiMe_2OSiMe_2(CH_2)_3$	K65G120LC175i
	$(CH_2)_3(SiMe_2OSiMe_2)_x(CH_2)_3$	W
O	$(CH_2)_3SiMe_2OSiMe_2(CH_2)_3$	L
	4-$C_6H_4CH{=}N(CH_2)_3SiMe_2OSiMe_2$. .$(CH_2)_3N{=}CHC_6H_4$-4	K50G75M108i

G is glass and W is the wax-like phase.

ties,being stable to daylight. Many ferrocene-containing polysiloxanes were sythesized and studied by Deschenaux and co-workers.[72] For instance, polydimethylsiloxanes **58**, **59** with planar chiral ferrocene units [72] are of considerable interest. They can be used as twisting agents in nematic twist cells.

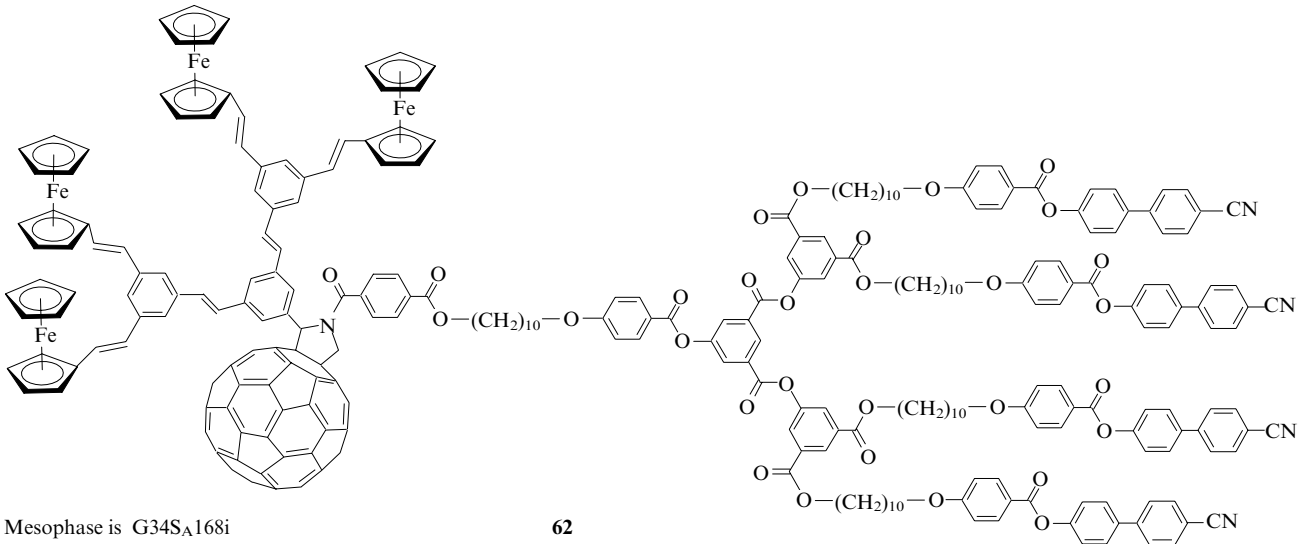
Cazacu *et al.*[108] synthesized a series of ferrocene-containing polyamides and polyesters of the general formula **60** and their copolymers with di- and oligosiloxanes, with the ferrocene fragment being a constituent of the polymer backbone. These materials show liquid-crystalline properties, are redox active and can be used as modifiers in electrode systems.

In a continuation of their earlier studies, Deschenaux and co-workers [109, 110] synthesized a number of new ferrocene–fullerene liquid-crystalline dendrimers **61**–**63**. This type of materials is interesting because electronic transitions

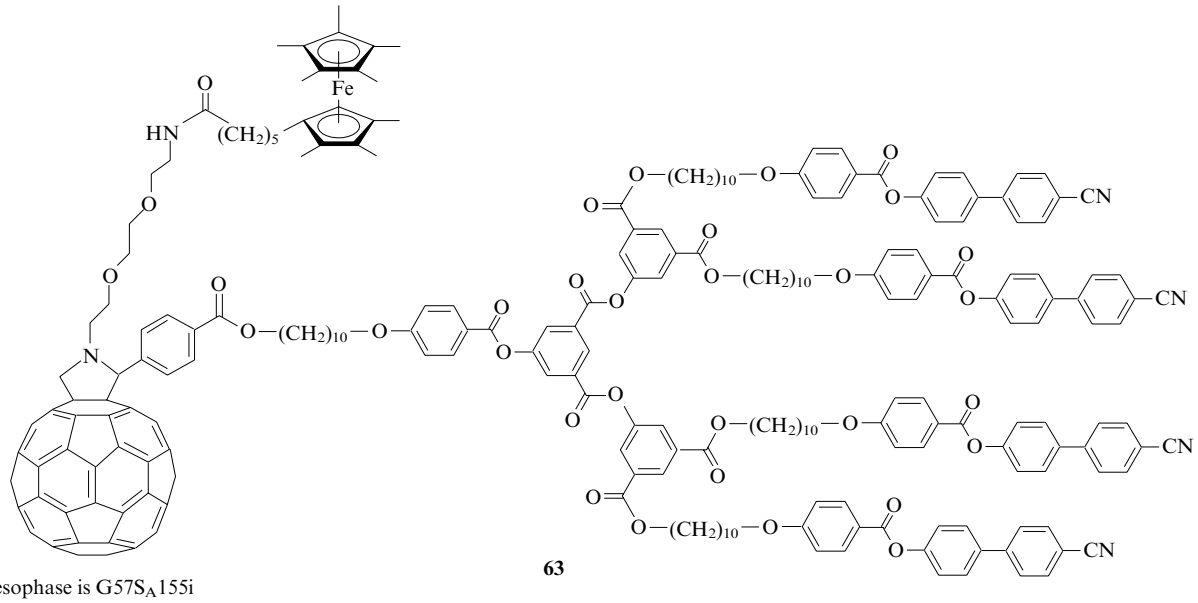


61

Mesophase is G47S_A171i



Mesophase is G34S_A168i **62**



Mesophase is G57S_A155i **63**

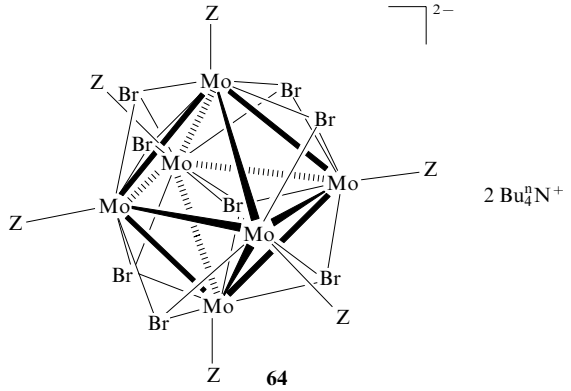
between two types of structural units can occur in them. Also, they should possess quite interesting photophysical properties. Spectroscopic studies revealed a complete quenching of fluorescence owing to the presence of two types of structural fragments in the molecule; *i.e.*, such compounds can be used as light-harvesting antennas. Although bulky, the dendrimeric systems synthesized formed smectic A phases with good thermal parameters.

Thus, the ferrocene unit can successively be incorporated into polymers and dendrimers either as a constituent of the backbone or a lateral substituent. Owing to electron transfer in them, such systems can exhibit interesting electrical and optical properties. Note also that the oxidized form of ferrocene exhibits magnetic properties. All these features are of interest for the design of various switches.

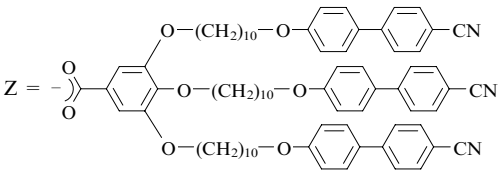
VII. Heteronuclear liquid-crystalline complexes with ferrocene-containing ligands

Atoms of several metals introduced into a liquid-crystalline molecule may undergo exchange interactions, giving rise to unusual electrical, magnetic and optical properties. We synthesized such systems for the first time in 1990.[25] At present, unusual properties of di- and polynuclear metallomesomorphic compounds (including heteronuclear ones) still attract the attention of researchers. For instance, a polynuclear system **64** based on molybdenum clusters was synthesized.[111] It forms a smectic mesophase showing a typical fan-shaped confocal texture at room temperature and brightly luminesces in the red and near-IR regions.

Ferrocene-containing mesogenic structures show some features of conventional organic molecules owing to aromaticity of the ferrocene complex and can therefore be successfully used as ligands in coordination compounds with retention of the sandwich structure. This leads to mesomorphic compounds with a number of metal centres. Researchers at the Kazan National Research Technological University work in this field using various ferrocene derivatives as ligands in order to optimize the liquid-crystalline properties. For instance, symmetry violation in mixed-ligand organometallic complexes causes a significant decrease in the temperatures of transition to the mesophase. Taking compounds **65**–**68** as examples, it was shown that symmetric complexes **65** (Refs 112 and 113) and organopalladium dimer **66** (Ref. 113) have rather high transition



64



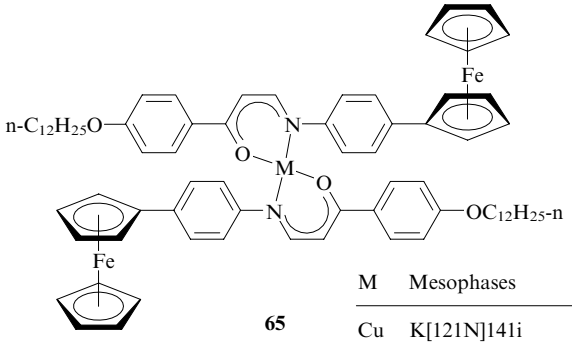
Mesophase is G23S$_x$103i

temperatures, whereas those of mixed-ligand palladium complexes **67** and **68** are relatively low.

Bekeshev *et al.*[114] reported a Mössbauer spectroscopy study of complexes **69** (see Ref. 115) containing six iron atoms of different nature. The spectra exhibit three quadrupole doublets that are well resolved at low temperatures (Fig. 6). One doublet corresponds to the iron atom in the ferrocene unit. The major contribution to the spectrum comes from the paramagnetic doublet of ^{57}Fe atoms linked through an oxygen atom. Yet another, less intense, paramagnetic doublet with similar quadrupole splitting suggests that some ^{57}Fe atoms are in different chemical environment.

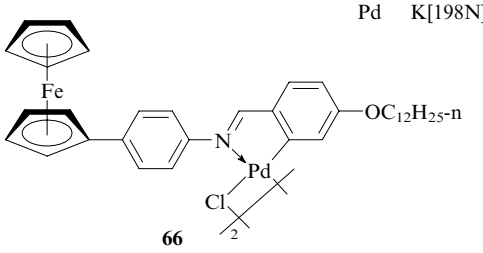
Organopalladium complexes have a greater potential for fine modification of the chemical structure and, thus, improvement of the thermal properties of mesophases. Therefore, they were used in a continuation of our studies on heteronuclear systems[116] with ferrocenophane derivatives as ligands. Complexes **70**–**72** form stable nematic phases at rather low temperatures corresponding to transition to the mesophase and in a rather wide temperature range. Two favourable factors effected here, *viz.*, strong violation of the molecular symmetry and the presence of a flexible alkyl bridge in the ferrocene moiety.

Mesophases formed by complexes **73** and **74** with ferrocenophane ligands[117] also exhibit improved properties compared to those of the mesophases formed by analogous complexes based on ferrocene-containing ligands.[115]



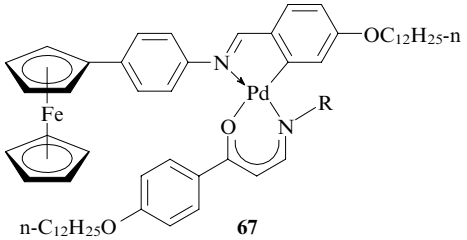
65

M	Mesophases
Cu	K[121N]141i
Pd	K[198N][196S$_C$]208i



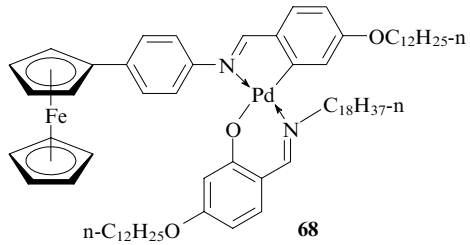
66

Mesophases are K$_1$220K$_2$238S$_A$248i (d)



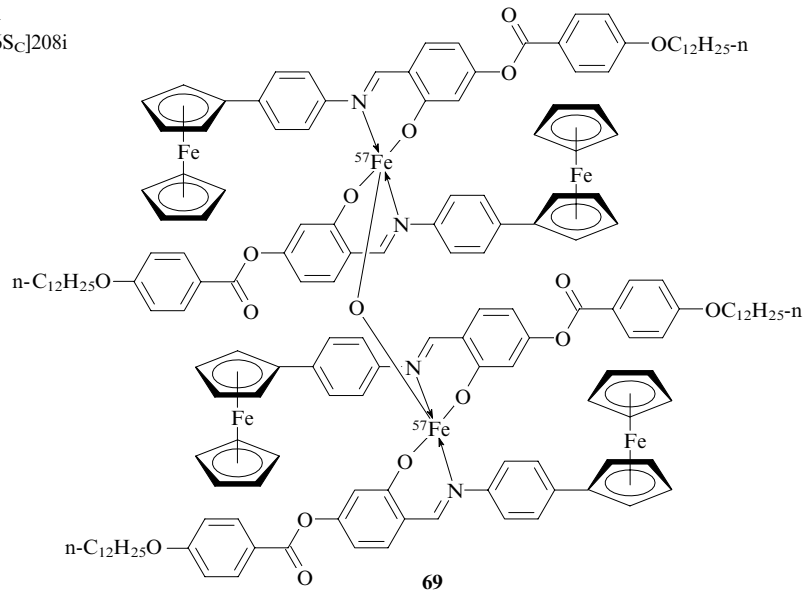
67

R	Mesophases
C$_6$H$_4$[(cyclo-C$_5$H$_4$)Fe(cyclo-C$_5$H$_5$)]-4	K$_1$144K$_2$[138S$_A$]174i
n-C$_{18}$H$_{37}$	K48S$_A$115i



68

Mesophase is K39S$_A$75i



69

Mesophase is K$_1$220K$_2$238S$_A$248i (d)

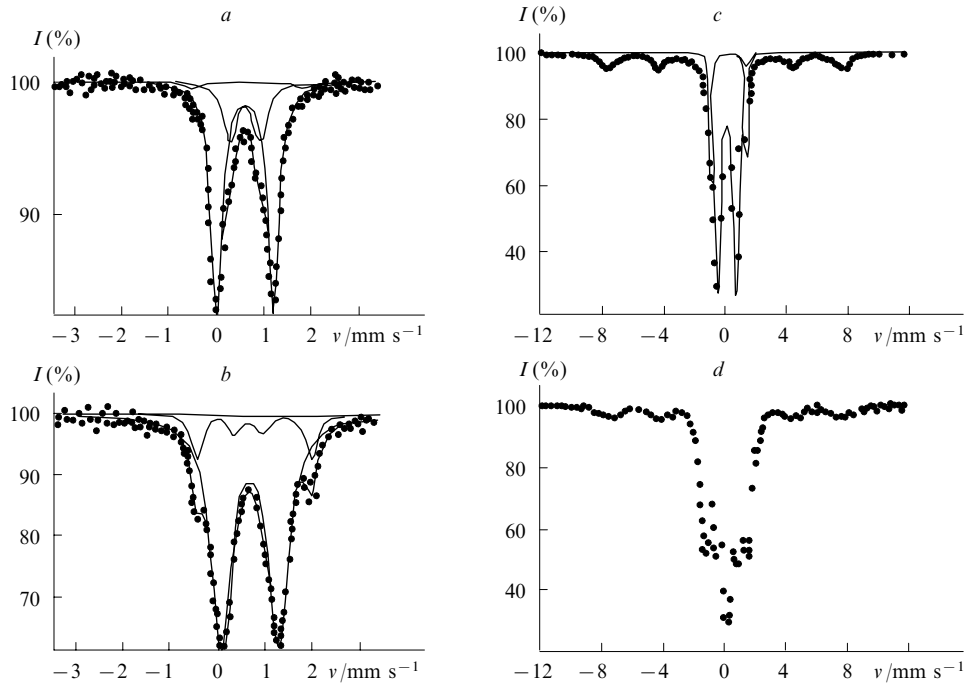
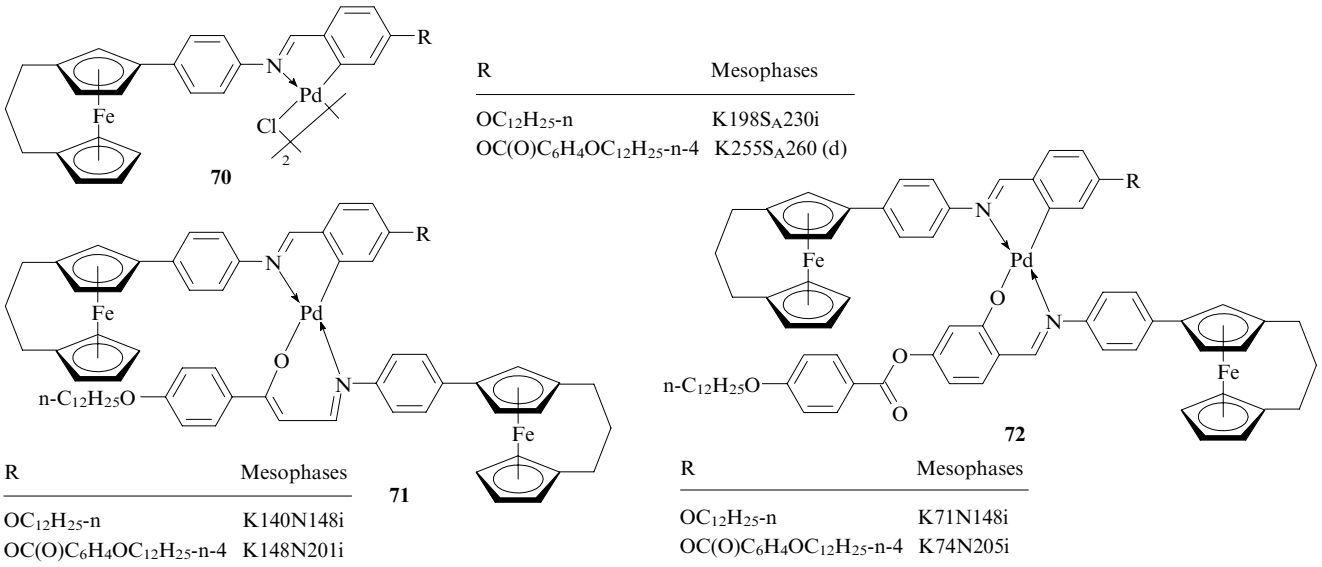


Figure 6. Mössbauer spectra of complex **69** at 293 (*a*), 80 (*b*), 4.2 (*c*) and 4.0 K (*d*).[114]



R	Mesophases
$OC_{12}H_{25}$-n	K198S_A230i
$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K255S_A260 (d)

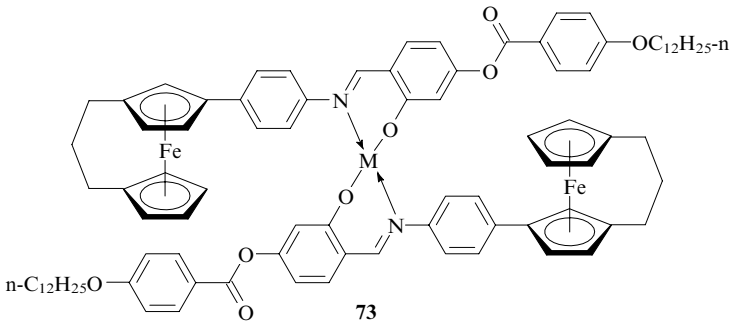
R	Mesophases
$OC_{12}H_{25}$-n	K140N148i
$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K148N201i

R	Mesophases
$OC_{12}H_{25}$-n	K71N148i
$OC(O)C_6H_4OC_{12}H_{25}$-n-4	K74N205i

It should be noted that an analogous vanadyl complex forms an enantiotropic nematic phase; the temperature range of mesophase existence becomes somewhat wider. However, heteronuclear complexes **73** and **74** have more symmetrical structures compared to mixed-ligand organopalladium compounds (*e.g.*, **67** and **68**) and, as a consequence, higher transition temperatures.

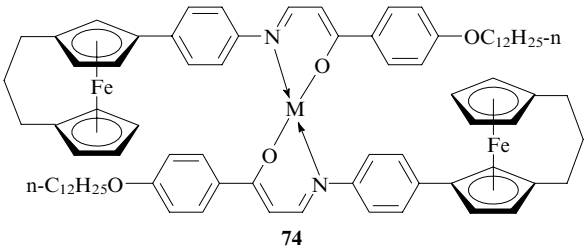
Copper and palladium complexes with aminovinyl ketone, in which the ferrocene moiety is adjacent to the chelate centre, are interesting from the standpoint of possible exchange interactions between metal atoms. We synthesized a series of metal chelates **75**.[118] The initial ferrocene-containing ligands were non-mesogenic. Heteronuclear complexes based on these ligands exhibited only monotropic mesomorphism. Probably, bulky ferrocene moieties in the complexes **75** preclude the formation of ordered states.

Thus, ferrocene derivatives show a great potential for the synthesis of heteronuclear liquid-crystalline structures. Using known methods of chemical modification of metal-containing systems one can attain rather low temperatures of transition tom the liquid-crystalline state and wide temperature ranges of mesophase existence.



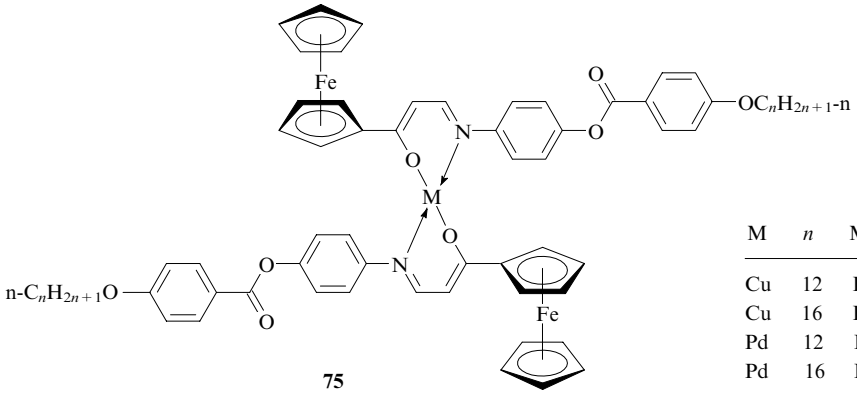
73

M	Mesophase	M	Mesophases
Cu	K199N230i	Pd	K257N277i
Ni	K225i	VO	K217N242i



74

M	Mesophases
Cu	K[131N]134i
Pd	$K_1$172K_2[184S_C][188N]207i



75

M	*n*	Mesophases
Cu	12	K_1[107LC]150$K_2$164i
Cu	16	K[120LC]145i
Pd	12	K_1[140S_C]183$K_2$221i
Pd	16	K[136S_C]201i

VIII. Mixed systems based on ferrocene derivatives

Ferrocene derivatives exhibit various types of mesomorphic states. In addition to the nematic, smectic and columnar mesophases described above and their chiral subtypes, some other types of phase organization are possible. For instance, hexacatenar ferrocene-containing liquid crystals **76** exhibit an optically isotropic cubic mesophase (Bicontinuous Cubic, BCC),[119] which undergoes transformation to the hexagonal columnar (Col_h) phase with an increase in the chain length of hydrocarbon terminal groups (Fig. 7).

Earlier, Deschenaux *et al.*[120] studied an interesting type of columnar phase organization from hydrogen-bonded tetracatenar molecular self-assembling structures, namely, compounds **77**–**79**. In the ferrocene-containing compounds **79** with $n = 8$ and $m = 6$ a decrease in the number of units in terminal hydrocarbon chains causes a lamellar organization of mesophases.

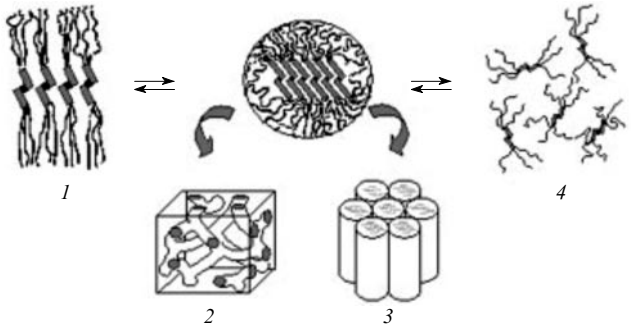
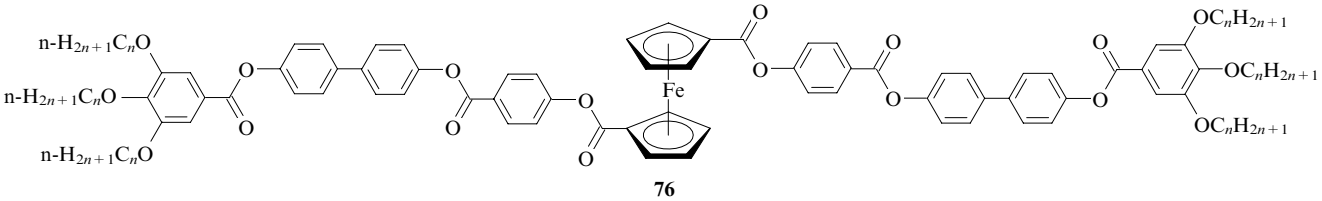
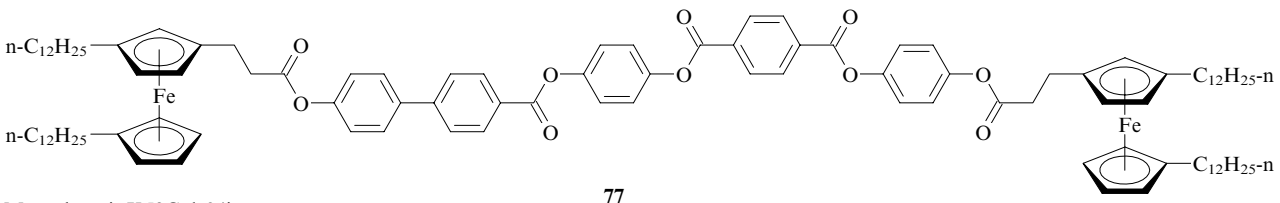


Figure 7. Scheme illustrating transition from cubic phase to hexagonal columnar structure upon elongation of terminal hydrocarbon chains in ferrocene-based hexacatenar liquid crystals. Crystal (*1*), cubic phase (*2*), hexagonal columnar structure (*3*) and isotropic liquid (*4*).



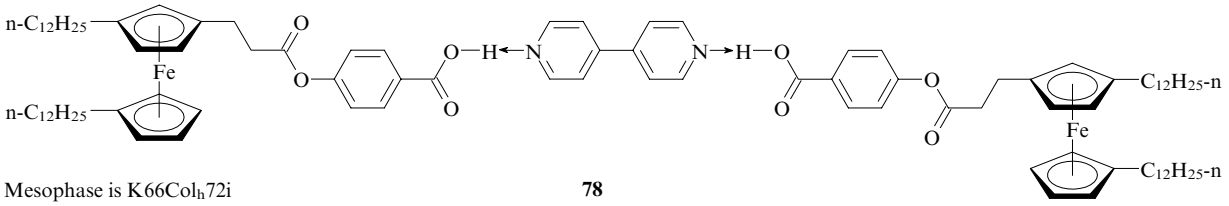
76

n	Mesophases	*n*	Mesophases	*n*	Mesophases	*n*	Mesophases
6	K200i	10	K126BCC175i	14	K113Col_h171i	18	K121Col_h173i
8	K163BCC173i	12	K117Col_h171i	16	K120Col_h172i	20	K118i



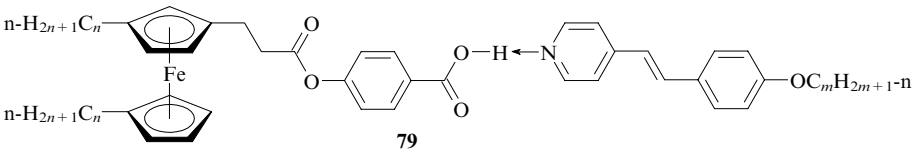
77

Mesophase is K52Col$_h$84i



78

Mesophase is K66Col$_h$72i

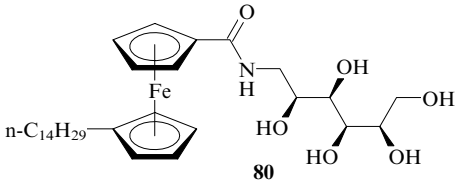


79

n	*m*	Mesophases
6	6	K55S$_C$73S$_A$101i
10	6	K20BCC[72S$_C$]76S$_A$89i
12	6	K65BCC78S$_A$(90–95)i
8	10	K61BCC88i
10	10	K69BCC87i
12	10	K76BCC88i

More recently,[121] the thermotropic behaviour of supramolecular liquid crystals **79** with different-length hydrocarbon chains was studied in more detail by calorimetry, polarizing microscopy and powder X-ray diffraction. As the chain length in terminal hydrocarbon groups increases, the layered packing becomes curved and a complex supramolecular organization with cubic symmetry appears (cubic mesophase).

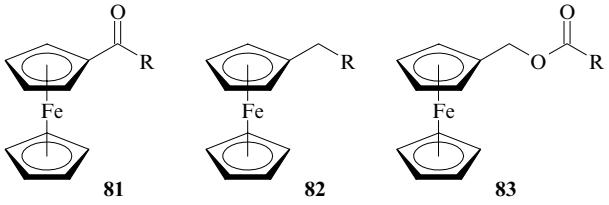
Hydrogen bonds are a powerful tool for the design of various supramolecular structures. In particular, a relatively small molecule **80**



80

with alkyl chain and a residue of modified D-sorbitol self-organizes to a rather complex supramolecular structure owing to intermolecular hydrogen bonds.[122] When heated to 98 °C, compound **80** goes to the S_A phase. Smectic bilayers are formed by segregation of amphiphilic molecules in accordance with their hydro- and lipophilic fragments and by additional linking of hydrophilic fragments of the sorbitol residue by a network of hydrogen bonds. At 137 °C, the thermotropic liquid-crystalline system goes to the isotropic liquid state. The addition of water (solvent) to compound **80** leads to the formation of a lamellar lyotropic liquid crystal, which in turn undergoes structural transformations on heating to the Krafft temperature and subsequent cooling. Thus, ferrocene can be used in the design of redox active lyotropic liquid-crystalline systems for biological applications.

Ferrocene derivatives **81**–**83** were incorporated[123] into lipid systems based on hexadeca-7-ene to develop electrochemical biosensors.

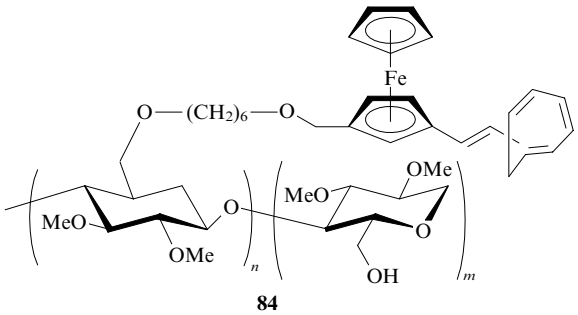


81 **82** **83**

R = $(CH_2)_6CH{=}CHC_8H_{17}$-n

Ferrocene derivatives with alkene groups used as additives caused transformations and interconversions between different types of lyotropic lipid mesophases.

An interesting example of incorporating ferrocene structures into natural polysaccharides was reported by Vill and co-workers.[124] A polymer with a chromophore ferrocene fragment (structure **84**) exhibited the properties of a liquid crystal in the temperature range from room temperatue to 122 °C.

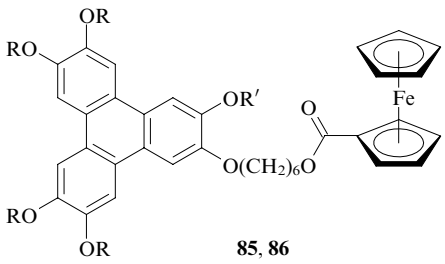


84

Lyotropic systems methylene chloride–compound **84** also contained an anisotropic mesophase.

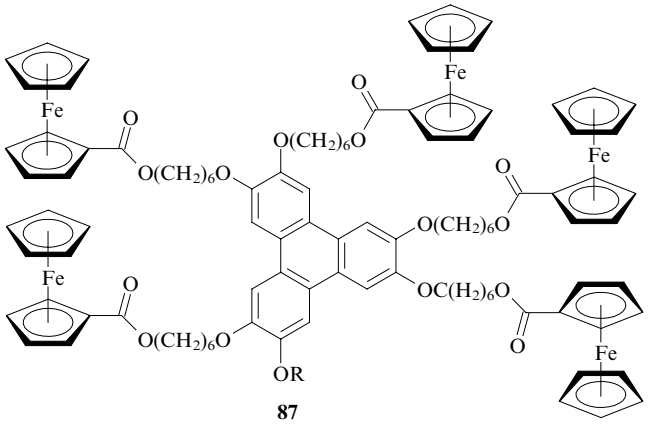
An attempt to synthesize discotic systems based on triphenylene ferrocene derivatives has failed.[125] Compounds **85**–**87** were synthesized, which are expected to have the properties of liquid crystals. Columnar packing of discs is interesting from the standpoint of design of anisotropic

molecular conductors, especially if the system contains groups suitable for charge transfer, *e.g.*, ferrocene.



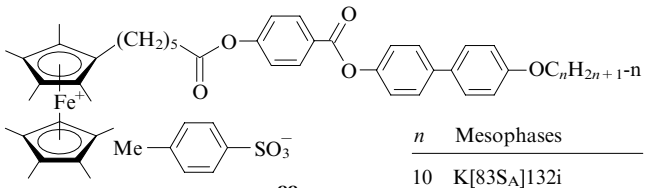
85, **86**

85: R = R′ = n-C_6H_{13}; **86**: R = n-C_6H_{13}, R′ = Me



87

The ability of ferrocene to form charge-transfer complexes is of importance for the formation of smectic and columnar mesophases in compounds **88**.[126, 127]



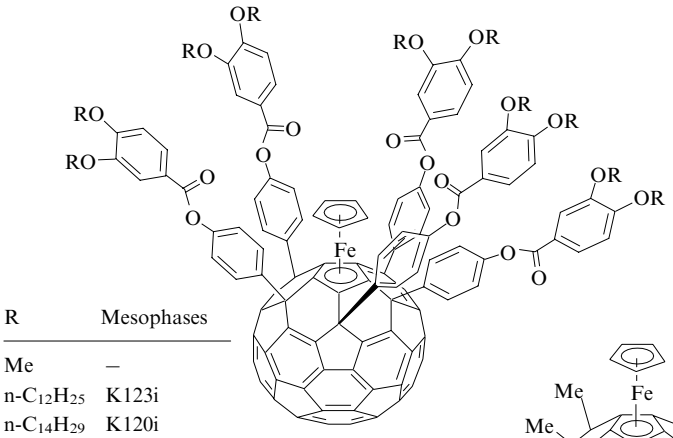
88

n	Mesophases
10	K[83S_A]132i
18	K[101Col_{rect}]123i

Col_{rect} is the rectangular columnar mesophase.

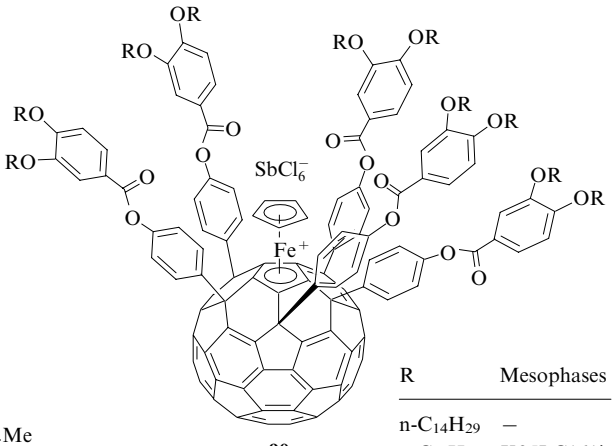
An interesting feature of complexes **88** is that the initial ferrocene derivative was non-mesogenic before the interaction with the acceptor of electron density. In this case, electron transfer is a tool for generating liquid-crystalline ordering of molecules. Another feature consists in the formation of paramagnetic centres on the ferrocene unit upon complexation. The Mössbauer spectra exhibit a singlet line from ferricinium cation (or a doublet with a small splitting at low temperatures), while the doublet characteristic of ferrocene was very weak; this indicates efficient formation of a charge transfer complex. Magnetic susceptibility measurements for the synthesized compounds revealed no exchange interactions due to the liquid-crystalline ordering of magnetic species.

Complex liquid-crystalline structures **89**–**91** combining ferrocene units and fullerene C_{60} moieties were reported.[128–130] According to X-ray diffraction data, molecules of compounds **89** and **90** have columnar packing and contain anisotropic liquid phases in the case of long hydrocarbon chains (according to polarizing microscopy and DSC data). An EPR study of the paramagnetic properties of compounds **91** gave $g_{||} = 3.75$ and $g_{\perp} = 1.70$ at 4 K. The reversible redox potentials of these systems were determined by cyclic voltammetry. According to X-ray diffraction data,



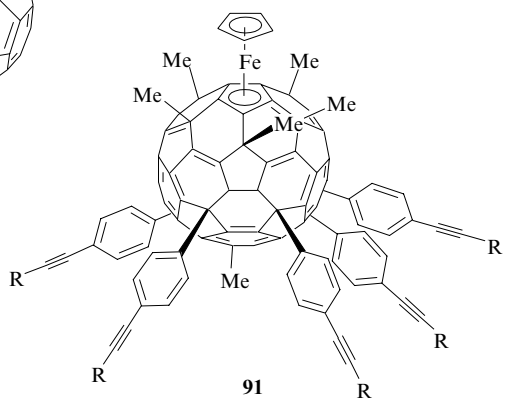
89

R	Mesophases
Me	–
n-$C_{12}H_{25}$	K123i
n-$C_{14}H_{29}$	K120i
n-$C_{16}H_{33}$	K(−3)LC123i
n-$C_{18}H_{37}$	K21LC120i



90

R	Mesophases
n-$C_{14}H_{29}$	–
n-$C_{18}H_{37}$	K25LC161i



91

R	Mesophases
$SiMe_2C_{12}H_{25}$-n	K55LC230i
$SiMe_2C_{18}H_{37}$-n	LC189i

compounds **91** exhibited[130] 3D ordering in liquid-crystalline phases; mesophases were observed in very wide temperature intervals starting with near-room temperatures.

Using low electric fields, one can control the orientation of nematic liquid crystals on a gold electrode treated with sulfoalkylated ferrocene.[131] Under the action of electric potential or some chemical action, ferrocene goes to the oxidized form and causes the surface layers of a supported or twisted nematic to move. This principle can underlie the design of electrical and chemical transducers that change their colour or transparency under the action of external factors.

IX. Conclusion

Ferrocene unit can be successfully incorporated into mesogenic molecules. The possibility of polysubstitution and structural isomerism of ferrocene compounds lead to a great variety of shapes and types of supramolecular organization and, in some cases, to the appearance of new types of liquid-crystalline phases. By modifying the chemical structure one can significantly improve some parameters of mesophases, *e.g.*, reduce the transition temperatures and extend the temperature range of mesophase existence. Peculiar features of the chemical structure of ferrocene predetermine the appearance of unusual properties of ferrocene-based liquid crystals, such as photochromism, reversible redox switching, paramagnetism, nonlinear optical properties, charge transfer, *etc*. The possibility of combining ferrocene moiety with liquid-crystalline polymers, various metal complexes and with fullerenes makes the fabrication of nanostructured materials with novel properties more probable. We believe a possible promising route is to design novel ferrocene-containing liquid-crystalline materials with magnetic centres, molecular switches and ferroelectrics.

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