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Thermotropic properties of ferrocene derivatives bearing a cholesteryl unit: structure–properties correlations

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The synthesis and structural characterization of new liquid-crystalline compounds containing ferrocene, azo-aromatic and cholesteryl groups are reported. Taking into account the advantage brought by chirality, ferrocene and azo units, these structures could be good precursors for obtaining materials capable of responding to magnetic and electric fields or to UV-light exposure. The influence of each structural unit (ferrocene, cholesterol, azo aromatic core and flexible chain length) has been studied by comparing analogous compounds possessing the same structure but without the element being analyzed. Ferrocene is a three-dimensional bulky unit, so that, regardless of the substituents' nature, this unit could cause steric repulsions with neighboring molecules. These interactions could lead to a decrease of the transition temperature domain. Surprisingly, a decrease in the clearing point was not observed for the compounds discussed. This behavior was possible because ferrocene is connected to the mesogen via a flexible unit. As a consequence, both phenyl analogues and ferrocene derivatives presented liquid-crystalline properties with similarly high clearing points, but above the thermal stability of derivatives with azo groups. Their melting points depend on the way the molecules are packed, with different crystalline states being detected in the case of ferrocene derivatives.

In order to explain the liquid-crystalline behavior of the compounds synthesized, molecular simulations were performed using the Hyperchem program.

KEYWORDS: liquid crystals; ferrocenomesogens; cholesteryl esters; azo-aromatic compounds

INTRODUCTION

In the last decade, intensive research on ferrocene-containing liquid crystals has been performed with the hope to combine the properties of liquid crystals (fluidity) with the properties associated with metals (color, electron density, magnetism and polarizability). Moreover, the ferrocene unit was used extensively for functionalized materials synthesis, especially because of its active redox properties and the planar chirality of the 1,3-asymmetrically substituted derivatives.[1–30]

The combination of different structural units in such molecules brings special physical properties, which are important when materials with potential applicability are requested. For technical use, the compound should not only have the necessary molecular shape for liquid-crystalline behavior at a certain temperature, but also an appropriate combination of physical properties. The factors involved in the molecular unit are varied and include core units, connecting groups, terminal groups, lateral groups, lengths of flexible chains, etc. Generally, the first aim is the mesophase type, then an acceptable mesomorphic

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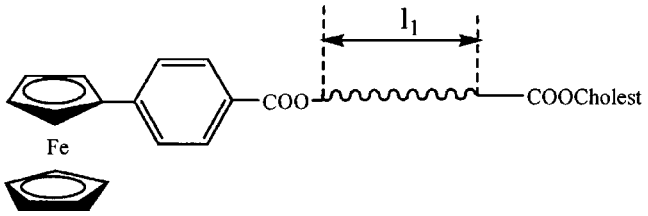


Figure 1. Ferrocene derivatives synthesized by Nakamura.

domain, viscosity (usually low), and dielectric and optical properties. All these structural factors affect the nature of interactions between liquid-crystalline molecules and are very important for obtaining adequate mesomorphic behavior. As a consequence, even small changes of the shape and structure of the molecules could have an important influence over the mesophase type and transition temperature domain.

Although chiral liquid crystals are especially studied because of their particular advantages (fast response on switching, high birefringence and the presence of physical colors), only a few examples of chiral ferrocene liquid crystals could be found in the literature. Nakamura and coworkers had tried to elucidate the mesomorphic behavior of a few derivatives incorporating cholesterol.[31–35] The series contains a terminal ferrocenyl-phenyl unit, connected to the cholesteryl unit by a flexible chain, with various lengths l_1 (Fig. 1). These compounds were found to present monotropic chiral smectic phases of an unidentified nature.

Taking into account the advantages brought about by the presence of both chirality and a ferrocene unit, our experimental study is focused on the synthesis and characterization of new liquid-crystalline compounds containing ferrocene, azo-aromatic and cholesteryl groups that are capable of responding to magnetic and electric fields or to UV-light exposure. For this purpose, different kinds of cholesteryl ferrocene derivatives were synthesized and investigated, the cholesteryl and ferrocene units being rigidly connected or by a flexible spacer. The general structure of the compounds synthesized is presented in Fig. 2. Such a molecular architecture is based on a number factors.

First, studies on monosubstituted ferrocene liquid crystals showed that, for inducing mesomorphic properties, the mesogenic unit should contain at least three aromatic rings in conjugated systems with ferrocene. These structures are necessary to compensate for the bulkiness of ferrocene, which reduces the interactions between molecules through its repulsive steric effects.[12] We considered that the connection of ferrocene through a flexible unit might reduce this negative influence of ferrocene. Second, the flexible chain also balances rigidity with flexibility of the molecule with a direct effect concerning the temperature transition values. Third, the presence of the cholesteryl unit induces chiral mesophases, which are known to have a fast response on switching and are highly birefringent. On the other hand, the presence of

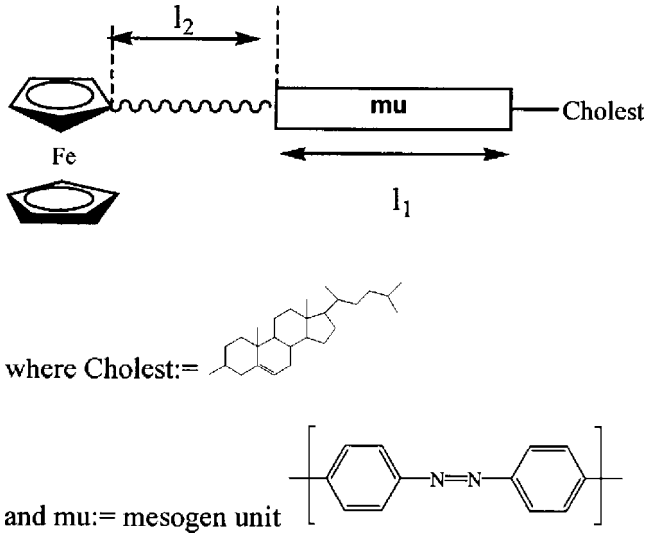


Figure 2. General structure of the synthesized compounds.

azobenzenic moieties can induce photo-responsive properties in the system (due to the capacity to generate cis–trans isomerization under UV–VIS irradiation).[36]

As is well known, cholesteric liquid crystals have the molecules organized in helical ordered structures, whose helical pitch determines the wavelength of the reflected light. The two important properties of chiral liquid crystals, mainly determined by the helical structure, are high optical activity and the presence of physical colors. Helical pitch is dependent on the temperature, electric field, nature and concentration of the impurities. If a cholesteric liquid crystal also presents a photo-controllable unit such as an azo-aromatic group, then the liquid crystal color could be controlled by UV light stimulation.[37–42] Owing to the azo group presence, one could anticipate photochemical changes of the cholesteric pitch by isomerization, process reversibility (taking into account the reversible reaction of isomerization of an azo compound) and physical color modifications, with potential use of these compounds in rewritable color recording.

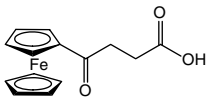
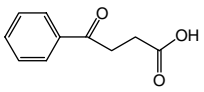
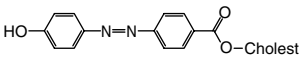
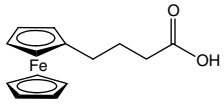
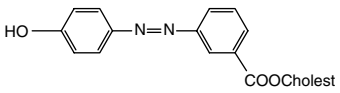
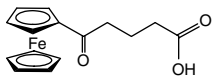
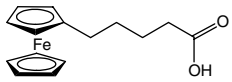
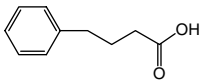
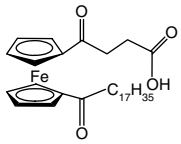
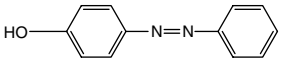
RESULTS AND DISCUSSION

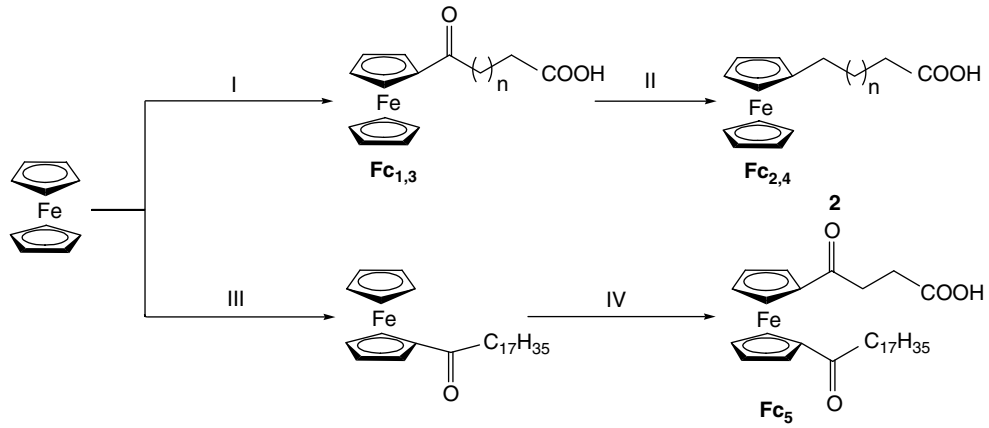
For the study of the molecular structure influence upon mesomorphic properties, namely the influences of the ferrocene, the flexible chain length, the connecting position of the cholesteric unit and influence of cholesterol, four mesogens (M_{1-4}), five ferrocene acids (Fc_{1-5}) and two phenyl analogues ($Ph_{1,2}$) were chosen (Table 1).

The ferrocene acids' synthesis involved a typical Friedel–Crafts acylation[43,44] and a Clemmensen reaction[45] (Scheme 1).

Mesogens M_1 and M_2, bearing a cholesteryl unit, were synthesized in four steps (according to Scheme 2), whereas M_3 and M_4 were purchased from Aldrich Company.

Table 1. Ferrocene derivatives and phenyl analogues bearing a cholesteryl unit

No.	Ferrocene acids (Fc_{1-5})	Phenyl analogues ($Ph_{1,2}$)	Mesogens (M_{1-4})	Esters (FcM; PhM)
1				Fc_1M_1; Ph_1M_1 Fc_1M_2 Fc_1M_3 Fc_1M_4
2				Fc_2M_1; Ph_2M_1 Fc_2M_2 Fc_2M_3 Fc_2M_4
3			HO–Cholest	Fc_3M_1
4				Fc_4M_1
5				Fc_5M_1



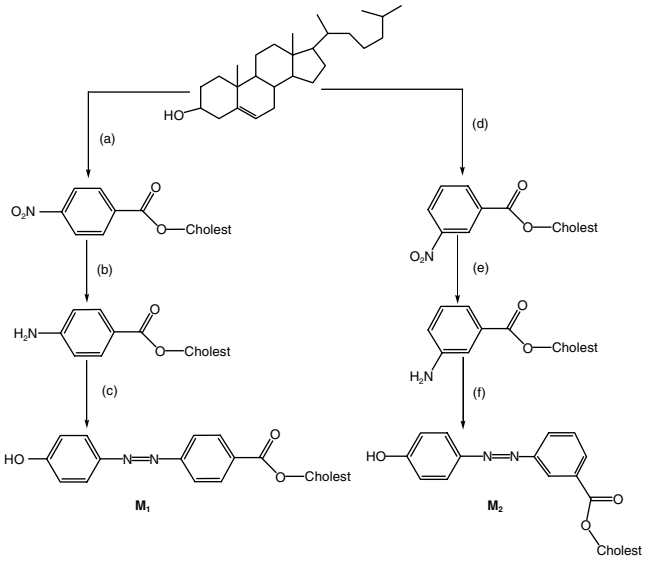
I. succinic or glutaric anhydride/$AlCl_3$/CH_2Cl_2,n=1,2; II. Zn/$HgCl_2$/HCl; n=1,2; III. stearoyl chloride/$AlCl_3$/CH_2Cl_2; IV. succinic anhydride/$AlCl_3$/CH_2Cl_2

Scheme 1. Synthesis of ferrocene acids: (I) succinic or glutaric anhydride/$AlCl_3/CH_2Cl_2$, $n = 1, 2$; (II) $Zn/HgCl_2$/HCl; $n = 1,2$; (III) stearoyl chloride/$AlCl_3/CH_2Cl_2$; (IV) succinic anhydride/$AlCl_3/CH_2Cl_2$.

The final ferrocene derivatives were obtained by esterification of ferrocene acids with mesogens with 1,3-dicyclohexylcarbodiimide (DCC)–4-(dimethylamino)pyridine (DMAP) (dichloromethane, room temperature).

Mesomorphic properties and textures

Seven of the compounds synthesized presented liquid-crystalline properties, with a wide mesomorphic domain, due to the strong interactions between cholesteryl units. The mesophases are stable up to around 240 °C, when degradation processes begin, before clearing. For this reason, the differential scanning calorimetry (DSC) curves were recorded in two stages: first by heating up to 200 °C and the then by heating up to 300 °C with a rate of 10 °C min^{-1}. For the majority of ferrocene derivatives, DSC curves revealed the property of polymorphism, resulting from the different arrangements of the ferrocene in the solid state. As is well known, conformational polymorphism occurs when a molecule is able to adopt different shapes, due to internal degrees of freedom (ferrocene is connected to the mesogen by a flexible chain).[46] Besides that, the two cyclopentadienyl rings of the ferrocene may be easily reoriented by small



Scheme 2. Synthesis of azo mesogens bearing a cholesteryl unit: (a) 4-nitrobenzoic acid, DMAP, DCC, CH_2Cl_2, RT; (b) $SnCl_2$, ethanol, refluxing; (c) (i) tetrahydrofuran (THF), HCl, $NaNO_2$, 0–5 °C, (ii) phenol, sodium acetate/water, 0–5 °C; (d) 3-nitrobenzoic acid, DMAP, DCC, CH_2Cl_2, RT; (e) activated zinc, CH_2Cl_2, formic acid, RT; (f) (i) dimethylformamide (DMF), HCl, $NaNO_2$, 0–5 °C, (ii) phenol, sodium acetate/, 0–5 °C.

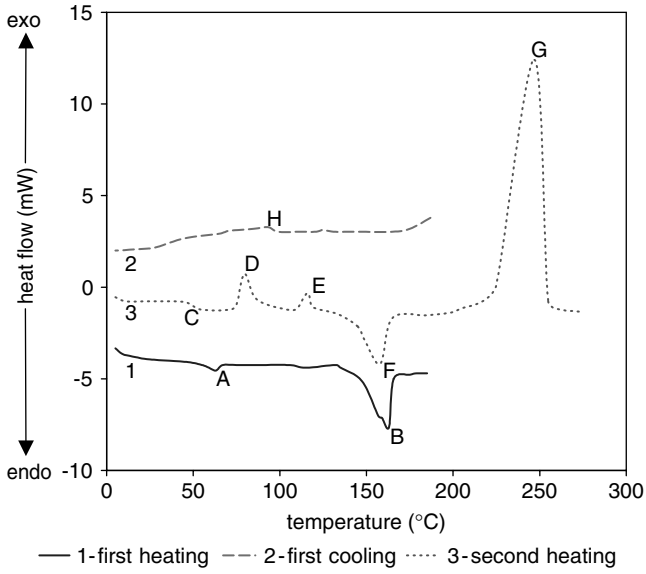
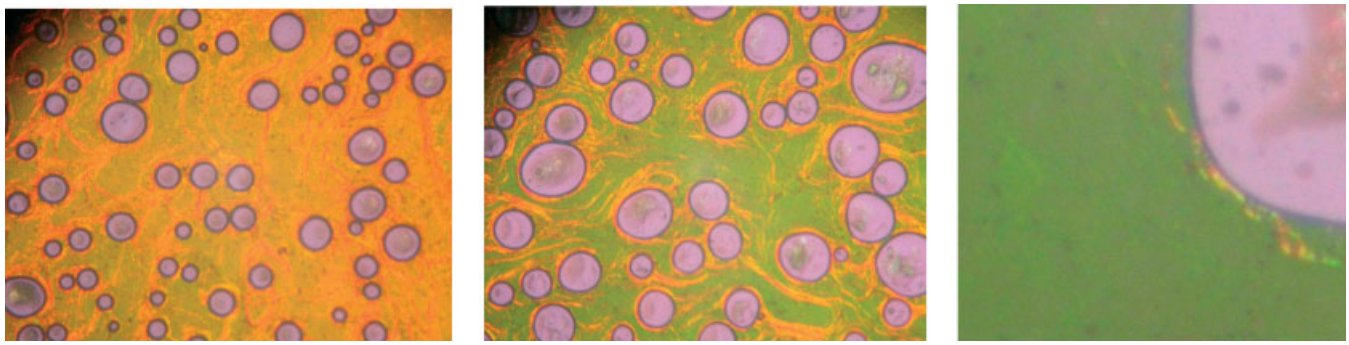


Figure 3. DSC curves of Fc_1M_1.

rotations of the rings, even in the solid state, with a low energy requirement.[16]

Figure 3 shows the DSC curves of Fc_1M_1. On the first heating, the two endothermic peaks A and B, at 63 °C and 163 °C respectively, are observed. Owing to the typical shape, the first peak corresponds to a second-degree transition and the second peak to the melting point. On the first cooling, a very broad peak, H, was observed at around 95 °C. On the second heating, from 0 °C to 300 °C, five peaks (C, D, E, F and G) were observed. The peak C, at 52 °C, corresponds to a second-degree transition of the material. The sample crystallized at 79 °C (peak D) and transformed to another crystalline state at 116 °C (peak E). The crystals melted at 158 °C (peak F), at about the same temperature as for the first heating. Finally, the last peak, F (249 °C), corresponds to the beginning of the degradation process. The study of this sample by optical polarized microscopy reveals a non-crystalline plastic material that melts between 158 and 163 °C. Although the sample is colored, no orientation has been detected in this temperature domain, the material being very slimy and viscous. Above 163 °C, a grainy liquid crystalline texture has been observed up to 210 °C, after which the typical cholesteric oily streaks and planar texture appear (Fig. 4). The sample is very fluid and remains in the mesophase up to 223 °C. Above this temperature the degradation process begins. As a consequence, on cooling, the mesophase could be observed only for the non-degraded areas.

The DSC curves for Fc_2M_1 are shown in Fig. 5. On the first heating the sample showed two endothermic peaks (A and B, at 149 °C and 161 °C respectively). On cooling from



(a) 173 °C (b) 183 °C (c) 201 °C

Figure 4. Textures of the sample Fc_1M_1 (second heating, heating rate 10 °C min^{-1}).

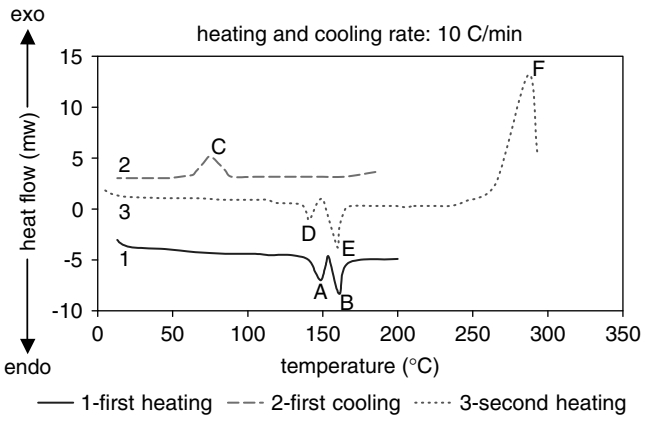


Figure 5. DSC curves of Fc_2M_1.

200 °C, one exothermic peak (C, at 76 °C) corresponding to a liquid–solid transition was observed. Because of the high viscosity, the sample crystallizes very slowly, at a lower temperature. On the second heating, the two endothermic peaks D and E appear at 141 °C and 160 °C respectively. The exothermic peak F, at 287 °C, corresponds to the degradation process. Using polarized-light optical microscopy (POM), at the second heating, the sample initially appears non-crystalline, as a vitreous film, which crystallizes at 85 °C in a grainy texture (Fig. 6, Ia and Ib); in non-polarized light the sample evidenced very small crystals). At 114 °C the crystalline textures changes into a bright one, showing large crystals (Fig. 6, Ic). At 149 °C, the crystals begin to melt, until around 154 °C, when a new change of the crystalline state was observed. The sample melts into a mesophase at 161 °C. The material easily forms homeotropic phases, and on touching responds with flickering. The mesophase is viscous until 205 °C, when an intense reorganization of the molecules into a mesophase was observed. Different textures were detected on cooling from 209 °C (Fig. 6, IIa, IIb).

For decomposition reasons, the sample was only heated to 210 °C. At around 185 °C a classical fan-shaped texture appeared, which remained until the sample froze at 92 °C. The DSC curves for Fc_3M_1 are shown in Fig. 7. Three endothermic peaks were observed on the first heating: one (A, at 85 °C) was very broad and two (B, at 181 °C; C, at 193 °C) were sharp. On cooling from 200 °C, one exothermic peak (F), corresponding to crystallization, was observed at 153 °C. On the second heating, only one endothermic peak (D) appears at 184 °C and an exothermic peak (E) at 265 °C, corresponding to the degradation process. On the first heating, the sample observed using POM appears semi-crystalline and enters into a mesophase at 193 °C. The texture is very similar, comprising oily streaks; on touching, the sample changes color from light red to a yellow–gold. On cooling from 220 °C the texture appears similar, and the sample crystallizes at 154 °C. On the second heating, the sample melts from the crystalline state into a mesophase at 184 °C. This difference appeared because the sample is crystalline, and so was in a different state than the previous time.

The DSC curves for Fc_4M_1 are shown in Fig. 8. On the first heating the sample showed two endothermic peaks (A and B, at 127 °C and 139 °C respectively). On cooling from 200 °C, one exothermic peak (G), corresponding to crystallization, was observed at 114 °C. On the second heating,

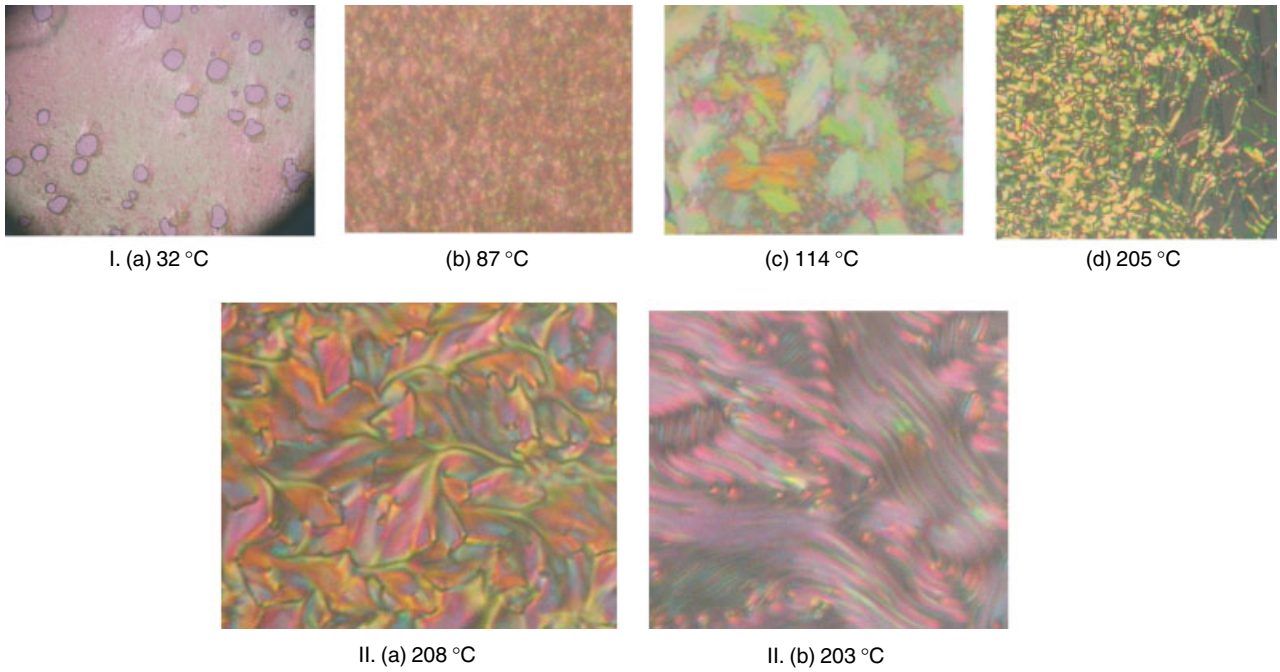


Figure 6. Textures of the Fc_2M_1 sample, observed on the POM.

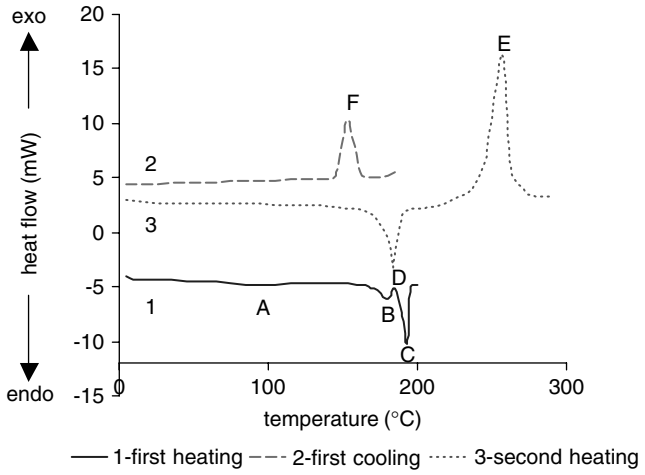


Figure 7. DSC curves for Fc_3M_1.

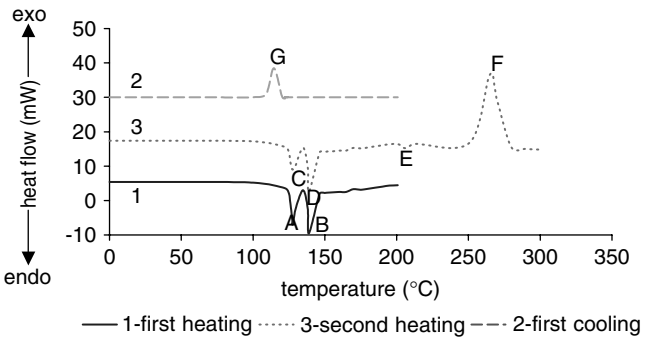


Figure 8. DSC curves for Fc_4M_1.

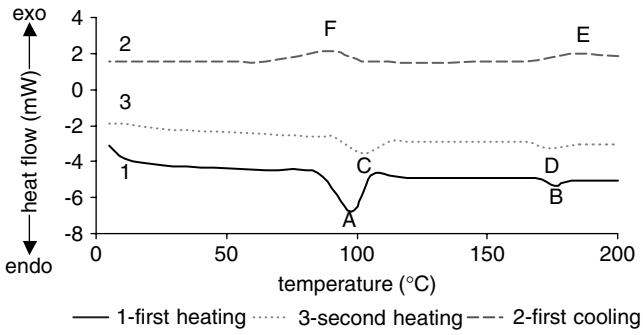


Figure 9. DSC curves for Fc_5M_1.

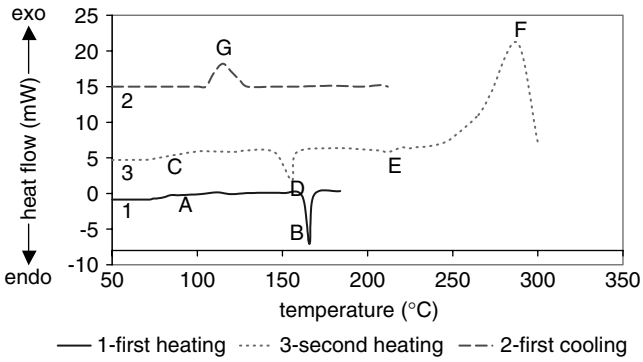


Figure 10. DSC curves for Ph_1M_1.

the endothermic peaks C, D and E appear, at 127 °C, 138 °C and 201 °C respectively. The exothermic peak F corresponds to the degradation process.

In order to decrease both melting and clearing temperatures, a long acyl chain of 18 carbon atoms was attached to the Fc_1M_1 structure. The behavior of the new Fc_5M_1 compound could be the consequence of the increased flexibility of the molecule, which also changes the interactions between neighboring molecules. The DSC curves from Fig. 9, uphold the above observation. On first heating, two endothermic peaks were detected: A at 98 °C, corresponding to the melting point, and B, at 175 °C, corresponding to the clearing point. Owing to the high molecular weight, the crystallization tendency is very small; on cooling, the two very broad exothermic peaks E and F are detected, at 180 °C and 89 °C respectively. On the second heating, two endothermic peaks appeared, one at 102 °C and the other at 174 °C (C and D respectively).

Under a polarizing microscope the sample appears semi-crystalline and starts to melt at 98 °C. Up until 165 °C the material is very viscous, and reacts on touching by changing color from red to green. The texture is homogeneous and appears planar. On looking at the glass plate without a microscope the sample appears fluorescent, with the colors changing depending on the hot-plate temperature. The material becomes isotropic at 175 °C. On cooling, the sample organizes in the same manner as on heating, and freezes at 89 °C without changing the liquid-crystalline texture.

Taking into account the large influence played by physical interactions on the type of mesophase and the temperature domain, the experimental study was also focused on determining the structural parameters necessary for inducing liquid-crystalline properties. For this purpose, compounds with similar length but with small changes of their structures have been synthesized. In order to investigate the influence of a ferrocene unit upon the mesomorphic properties, the Ph_1M_1 and Ph_2M_1 phenyl analogues were prepared by reacting the corresponding acids with mesogen M_1. The DSC curves for Ph_1M_1 are shown in Fig. 10. Two peaks were detected on the first heating: A, at 76 °C, was very broad and corresponds to a second-degree transition; B, at 166 °C, corresponds to the melting point. The broad peak G was detected at 115 °C on the first cooling, and corresponds to a liquid–solid transition. On the second heating, the DSC curve presents two endothermic peaks, at 156 °C (D, sharp) and 212 °C (E, broad), and an exothermic peak (F), corresponding to the

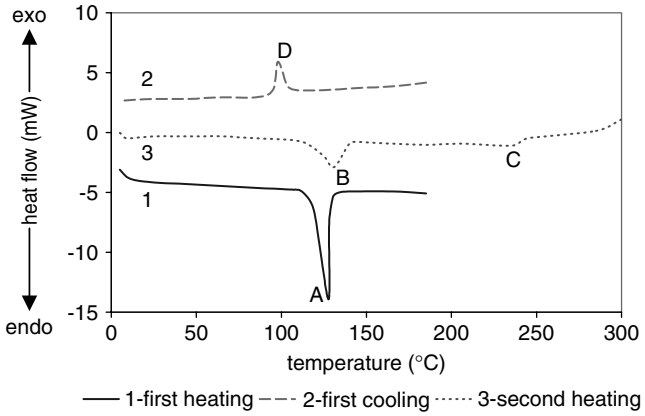


Figure 11. DSC curves of sample Ph_2M_1.

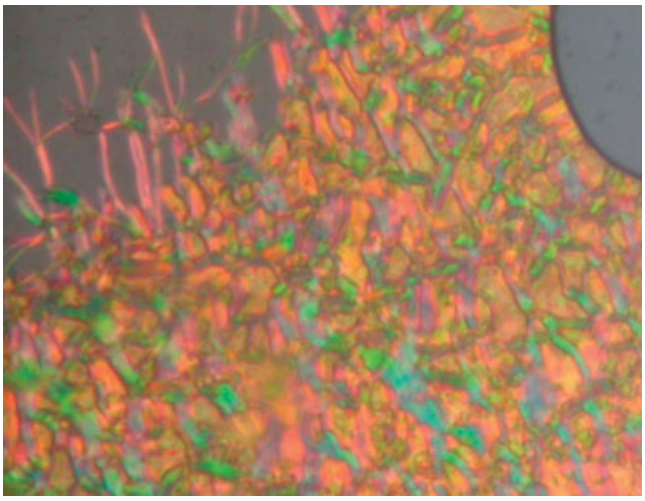


Figure 12. Photomicrograph of sample Ph_2M_1 at 200 °C.

degradation process. Observations using POM showed that the sample melts into a mesophase at 166 °C, with a grainy texture, up to 211 °C, whereupon an oily streak texture was detected. On heating up to 245 °C the compound is still in the mesophase, but the sample borders become black, which is a sign that decomposition has started.

The DSC curves for Ph_2M_1 are shown in Fig. 11. On the first heating the sample shows one endothermic peak, A, at 127 °C. On cooling from 200 °C, the exothermic peak D, corresponding to a liquid–solid transition, was observed at 98 °C. On the second heating, the two endothermic peaks D and E appeared, at 132 °C and 235 °C respectively. Using POM, the sample appears very viscous and plastic between 110 and 115 °C and, on pressing, spreads on the glass plate. At around 125 °C the sample becomes very fluid and organizes into a mesophase with a grainy texture. Upon touching, the sample forms a homeotropic arrangement in small regions at 185 °C. At 200 °C, a changing texture is observed, with a spontaneous arrangement into a mesophase (Fig. 12). On cooling, the sample partially crystallizes and partially freezes at 102 °C.

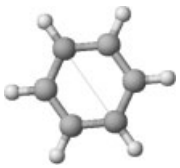
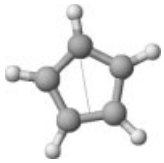
Structure–properties correlations on ferrocene derivatives

Influence of ferrocene

To the estimate the influence of the ferrocene unit upon the mesomorphic properties, the synthesis of compounds with the same core length, but incorporating other units (with similar length) to replace the ferrocene was required. This kind of unit could be the phenyl unit (Table 2).

Ferrocene is a three-dimensional bulky unit; thus, regardless of the substituents' nature, this unit could cause steric repulsions with neighboring molecules. These interactions could lead to a decrease in the transition temperature domain. Surprisingly, for the previously mentioned compounds, a decrease in the clearing point has been not observed. This behavior is possible because ferrocene is connected to the mesogenic unit through a flexible spacer. As a consequence,

Table 2. Comparison of the geometries for phenyl and pentadienyl units

Unit	Phenyl	Pentadienyl
Geometry		
Diagonal length (Å)	2.81	2.16

both the phenyl and ferrocene derivatives presented liquid-crystalline properties with similarly high clearing points, but above the thermal stability of derivatives with azo groups. The melting points depend on the way the molecules are packed; in the case of ferrocene derivatives, different crystalline states are detected. In order to obtain information regarding the liquid-crystalline behavior of the compounds synthesized, conformational theoretical studies were performed. The geometries of the liquid-crystalline compounds investigated are presented in Fig. 13.

Although the geometries of these compounds seem to be very similar, since only small changes in their structures have been made, the simulated properties reveal very different values of the dipole moment (Table 3).

The dipole moments differ not only with regard to their absolute values, but also concerning their distribution about the axes. The differences between the polarities of these compounds affect the interaction nature between molecules and, as a consequence, the mesophase type and its stability. According to Table 3, Fc_3M_1 has the greatest dipole moment value, which induces strong interactions between molecules in the solid state, as shown by the highest value of the melting point (184 °C).

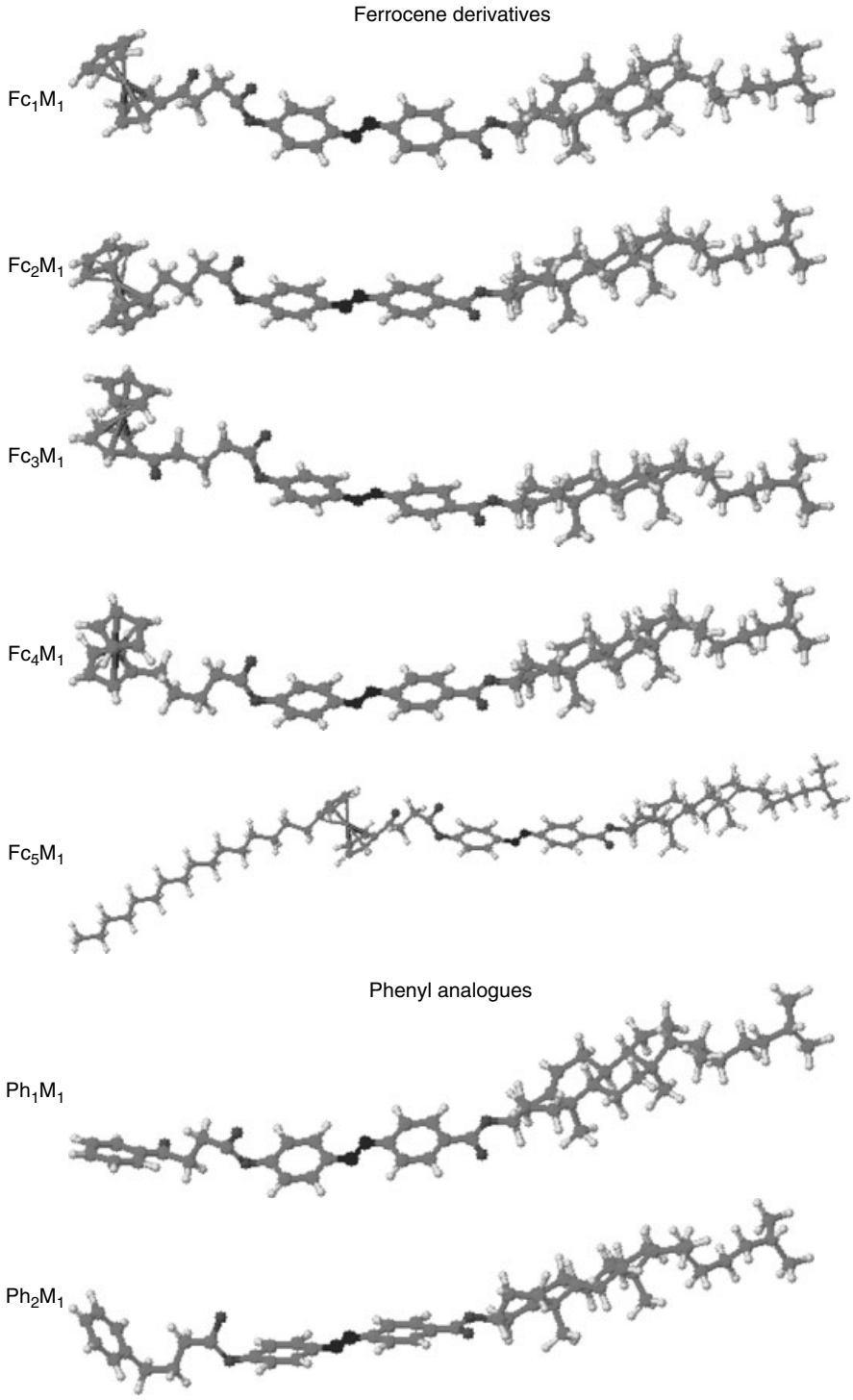


Figure 13. Geometries of the liquid crystalline compounds.

Influence of the flexible chain length

The compounds studied contain a number of two, three or four carbon atoms in the flexible segment that are connected to the ferrocene directly or via a carbonyl link (compounds Fc_iM_1; $i = 1–4$). In the case of Fc_2M_1 and Fc_4M_1, both have similar dipole moment values, so that the length of the flexible chain is responsible for their behavior. The slight increase in the flexible chain length results in a decrease in the melting point, from 160 °C to 138.5 °C, a fact that has been previously mentioned in the literature.[48] Regarding samples Fc_1M_1 and Fc_2M_1, the most important factor that affects their behavior is the different dipole moment values, which has been discussed

Table 3. Simulated properties of the compounds

Sample code	Dipole moment (Debye)			
	Total	*X* axis	*Y* axis	*Z* axis
Fc_1M_1	1.67	−1.27	−0.59	0.89
Fc_2M_1	2.56	1.22	−1.52	1.65
Fc_3M_1	5.22	2.18	−3.60	3.08
Fc_4M_1	2.41	1.06	−1.38	1.65
Fc_5M_1	1.89	−1.48	−0.28	1.14
Ph_1M_1	1.40	−0.03	−1.15	−0.79
Ph_2M_1	2.53	1.01	−1.33	1.89

previously. For none of the compounds did these structural changes affect the clearing points, which are higher than their thermostability. To decrease both the melting and clearing points, a long acyl chain was attached to the ferrocenyl unit of Fc_1M_1 compound. As expected, the melting point of the Fc_5M_1 compound decreased, from 161 °C to 98 °C. The influence upon the clearing point is much greater, the decrease being significant (down to 175 °C). This behavior is due to the much more flexible structure, determined by the increase of the flexible : rigid ratio. On cooling, the high molecular weight induces a very small tendency to crystallization and an increased viscosity.

Influence of the cholesterol connecting position

The influence of the connecting position for the cholesterol unit has been studied by comparing the properties of compounds with cholesterol connected in the third and fourth positions of the phenylene unit.

The results show that the introduction of a bend in the molecular structure, determined by the substitution in the third position of the benzene nucleus (compounds Fc_1M_2 and Fc_2M_2), affects the organization in liquid-crystalline structures negatively, with the liquid-crystalline phase being completely suppressed (Fig. 14). The sample melts into a very viscous and slimy liquid phase and crystallizes very slowly on cooling. Besides this, the increased diameter of the molecules induced a higher viscosity, so that orientation could be very difficult.

Influence of cholesteryl and azo aromatic core

In order to investigate the influence of the cholesteryl unit upon the mesomorphic properties, the compounds Fc_1M_4 and Fc_2M_4 were synthesized by reaction of the ferrocene acids Fc_1 and Fc_2 with 4-phenylazo-phenol in the presence of DCC and DMAP. As expected, mesogenic behavior disappeared for both of them. This is partly because cholesterol, owing to the strong interactions between hydrogen atoms of the aliphatic core, is the most important promoter of liquid-crystalline behavior, and partly because the molecule is too short to generate a mesophase, the length of the rigid core being 10.1 ´Å, compared with 22.3 ´Å, the length of the liquid-crystalline compounds' rigid core $Fc_iM_1 (i = 1–4)$. The

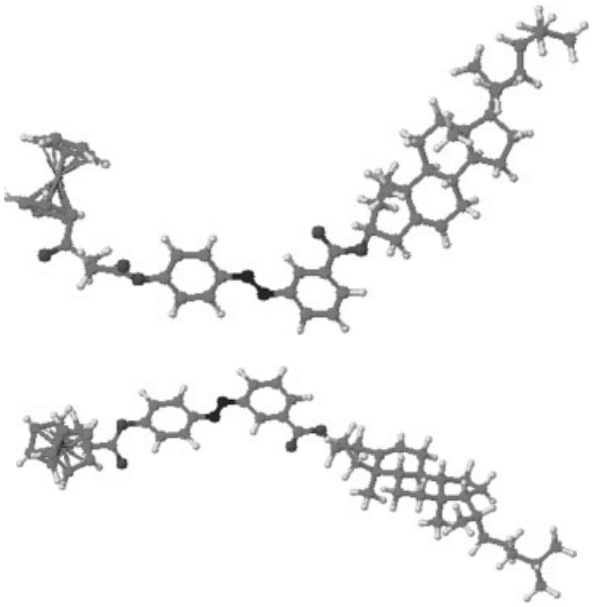


Figure 14. Geometries of the Fc_1M_2 and Fc_2M_2 samples.

synthesis of compounds Fc_1M_3 and Fc_2M_3, by reaction of ferrocene acids Fc_1 and Fc_2 with cholesterol (M_3), under the same conditions as for the previously mentioned esters, led to the conclusion that the molecules are too flexible to give liquid-crystalline properties. Beside this, the azo aromatic unit contributes significantly to the increase of the rigid core length and polarity, as a consequence of the electronic delocalization in the aromatic conjugate system.

EXPERIMENTAL

Materials

All reactions involving DCC and DMAP were performed under a dry atmosphere of nitrogen. Silica gel 60 (Merck) or Al_2O_3 (active, neutral, Merck) were used for column chromatography. Thin-layer chromatography (TLC) was performed on silica gel or Al_2O_3 plates (Merck, silicagel F_{254}, aluminum oxide F_{254}). Dichloromethane was distilled over P_2O_5 prior to use. Ferrocene (Merck), dicyclohexylcarbodiimide (Merck), 4-*N*,*N*-dimethylamino-pyridine (Fluka), cholesterol (Aldrich), 4-nitrobenzoic acid (Merck), 3-nitrobenzoic acid (Merck), aluminum chloride (Merck), succinic anhydride (Aldrich) and glutaric anhydride (Merck) were used as received. 3-Benzoylpropionic and 4-phenylbutyric acids were prepared following literature procedures.[49,50]

Techniques

Confirmation of the structures of the intermediates and the final products was obtained by ^{1}H NMR and ^{13}C NMR spectroscopy using a Jeol ECA 600 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer

(NaCl crystal window). Mass spectra were recorded on a Jeol JMS-AX 505 mass spectrometer using the FAB^+ method for ionization. Elemental analysis was performed on a Fisons EA1108 CHN, and melting points were recorded on a Boetius Karl Zeiss Jena microscope. Transition temperatures and textures were determined and recorded using a Linkam heating stage PU 1500 unit, in conjunction with a Nikon polarizing optical microscope and a Nikon Coolpix 4500 video camera. The DSC analysis was undertaken on a Seiko Instrument SSC 5200H and a thermal analysis station TAS 100, Rigaku thermoflex TG 8110. Heating and cooling cycles were run at rate of 10 °C min^{-1}, under nitrogen atmosphere, with samples measured in closed-lid aluminum pans. Mesophase type was assigned by visual comparison (under microscope) with known phase standards. The molecular simulations were performed using the Hyperchem 4.5 program (Hypercube Inc.). The initial molecular conformation of the simulated products was optimized using an MM+ field force and the value of the total potential energy of the single molecule was obtained. In order to determine the real value for minimum energy (not a local minimum), the conformation obtained was followed by a molecular dynamics cycle and re-minimized. The criterion of energy convergence was to obtain a residual root-mean-square force in the simulated system of less than 0.05 kJ mol^{-1} $Å^{-1}$. Minimization was performed using the steepest-descent and conjugate-gradient algorithm (The conjugate-gradient algorithm is known as Fletcher–Reeves algorithm and is used in hyperchem modeling).

Ferrocene acids synthesis

General procedure for ketoacids synthesis

To a stirred solution containing ferrocene and anhydride in anhydrous dichloromethane, cooled to about 5 °C, anhydrous $AlCl_3$ was added in small portions, the temperature being kept under 10 °C. The reaction mixture was maintained at room temperature, under stirring, for an additional 7 h. The mixture was then poured on iced water and the organic layer was separated. The acid was extracted from dichloromethane with sodium hydroxide solution (5%) and precipitated with dilute hydrochloric acid. The purity of the ketoacid (based on TLC) was good enough not to require further purification.

4-Oxo-4-ferrocenyl-butyric acid (Fc_1). Quantities: ferrocene (10.0 g, 0.053 75 mol), succinic anhydride (5.3752 g, 0.053 75 mol), anhydrous dichloromethane (225 ml), anhydrous $AlCl_3$ (7.8923 g, 0.059 13 mol). Yield: 43.5% (6.7126 g); m.p.: 166.5–167.5 °C (dec.). IR (KBr/cm^{-1}): 3082 (very broad, –OH), 2927, 2916 (C–H), 1714 (>C═O, carboxylic), 1658 (>C═O, ketonic), 1454, 1379, 1259, 1168, 935, 827, 480, 457. ^{1}H NMR δ_H (DMSO): 12.13 (s, 1H, –COOH), 4.80 (t, 2H, ferrocene), 4.54 (t, 2H, ferrocene), 4.27 (s, 5H, ferrocene), 3.36 (s, 2H, $-CH_2-$), 2.99 (s, 2H, $-CH_2-$). ^{13}C NMR δ_C (DMSO): 201.66, 173.92, 78.52, 71.87, 69.54, 68.88, 33.77, 27.42. *m/z*: 285 $[M-1]^+$.

5-Oxo-5-ferrocenyl-pentanoic acid (Fc_3). Quantities: ferrocene (4 g, 0.021 75 mol), glutaric anhydride (2.4516 g, 0.021 75 mol), anhydrous dichloromethane (100 ml), anhydrous $AlCl_3$ (3.4446 g, 0.0261 mol). Yield: 3.0484g (47%); m.p.: 131–134 °C. IR (KBr/cm^{-1}): 3130.4–2607.75 (very broad, –OH), 2966.51, 2908.65 (C–H), 1708.93 (>C═O, carboxylic), 1668.42 (>C═O, keto). ^{1}H NMR δ_H (DMSO): 12.09 (s, 1H, –COOH), 4.77 (s, 2H, ferrocene), 4.54 (s, 2H, ferrocene), 4.21 (s, 5H, ferrocene), 2.77 (t, 2H, $-CH_2-$), 2.30 (t, 2H, $-CH_2-$), 1.79 (qv, 2H, $-C-CH_2-C-$). ^{13}C NMR δ_C (DMSO): 202.91, 174.21, 78.87, 71.95, 69.47, 68.92,, 37.76, 32.84, 19.24. *m/z*: 299 $[M-1]^+$.

General procedure for ketoacid reduction

In a two-necked flask, 0.1148 mol of zinc and 0.002 74 mol of $HgCl_2$ in 15 ml of water were stirred for 5 min. Concentrated hydrochloric acid (1 ml) was slowly added and the mixture was stirred for another 5 min. The freshly prepared amalgam was decanted and 50 ml of water, 11 ml of concentrated HCl and 250 ml of toluene containing 0.017 419 mol of ketoacid acid were added. The mixture was refluxed, under stirring, for 7 h; 1 ml of concentrated HCl was added every hour. The completion of reduction was monitored using TLC (2:1 chloroform : ethyl ether). The organic layer was separated and washed several times with water. The reduced ketoacid was extracted with sodium hydroxide solution (5%) and precipitated with a 20% HCl solution.

4-Ferrocenyl-butyric acid (Fc_2). Quantities: zinc (7.50 g, 0.1148 mol), $HgCl_2$ (1.014 g, 0.002 74 mol), 4-oxo-4-ferrocenyl-butyric acid (5 g, 0.017 419 mol). Yield: 3.5 g (73%); m.p.: 85–85.8 °C. IR (KBr/cm^{-1}): 3093 (very broad, –OH), 2953, 2914 (C–H), 1708 (>C═O, carboxylic), 1433, 1409, 1330, 1267, 1219, 1186, 1101, 1001, 908, 817, 702, 487, 416. ^{1}H NMR δ_H($CDCl_3$): 12.25 (very broad, 1H, –COOH), 4.10 (s, 5H, ferrocene), 4.05 (m, 4H, ferrocene), 2.37 (m, 4H, $-CH_2-$groups), 1.84 (qv, 2H, $C-CH_2-C$); ^{13}C NMR δ_C($CDCl_3$): 179.95, 87.87, 68.48, 68.06, 67.23, 33.64, 28.83, 25.89. *m/z*: 271 $[M-1]^+$.

5-Ferrocenyl-pentanoic acid (Fc_4). Quantities: zinc (1.4366 g, 0.0219 mol), $HgCl_2$ (0.194 g, 0.000 71 mol), 5-oxo-5-ferrocenyl-pentanoic acid (1 g, 0.0033 mol). Yield: 0.7 g (73.42%); m.p.: 102–105 °C. IR (KBr/cm^{-1}): 3093 (very broad, –OH), 2953, 2914 (C–H), 1708 (>C═O, carboxylic), 1433, 1409, 1330, 1267, 1219, 1186, 1101, 1001, 908, 817, 702, 487, 416; ^{1}H NMR δ_H($CDCl_3$): 12.25 (very broad, 1H, COOH), 4.10 (s, 5H, ferrocene), 4.05 (m, 4H, ferrocene), 2.35 (m, 4H, $-CH_2-$groups), 1.66 (qv, 2H, $C-CH_2-C$), 1.54 (qv, 2H, $C-CH_2-C$); m/z: 285 $[M-1]^+$.

1-(3-Carboxypropionyl)-1′-stearoyl-ferrocene (Fc_5).

(a) Synthesis of stearoyl-ferocene: to a solution containing ferrocene (5 g, 0.028 mol) and stearoyl chloride (8.1415 g, 0.0268 mol) in anhydrous dichloromethane (200 ml), cooled to around 5 °C, anhydrous $AlCl_3$ (3.935 g, 0.0308 mol) was added in small portions, the temperature being kept under 10 °C. The reaction mixture was left

at room temperature, under stirring, for an additional 10 h. The crude product was poured on iced water and the organic layer was separated, washed several times with water, dried and concentrated. Stearoyl-ferrocene was purified by column chromatography on Al_2O_3 (1 : 1 dichloromethane : hexane). Yield: 92.9% (11.3 g); m.p.: 42–47 °C. IR (KBr/cm^{-1}): 2914, 2850 (C–H), 1670 (>C=O, ketonic), 1473, 1458, 1408, 1265, 1107, 1001, 817, 713, 532, 476. ^{1}H NMR δ_H($CDCl_3$): 4.77 (t, 2H, ferrocene), 4.47 (t, 2H, ferrocene), 4.18 (s, 5H, ferrocene), 2.68 (t, 2H, –$COCH_2$), 1.69 (m, 2H, –CO–CH_2C–), 1.34–1.25 (28H, aliphatic protons), 0.87 (t, 3H, –CH_3).

(b) Synthesis of 1-(3-carboxypropionyl)-1′-stearoyl-ferrocene (Fc_5): the synthesis was accomplished using the Friedel–Crafts reaction, with a large excess of $AlCl_3$, in a 1: 1: 5 molar ratio of stearoyl-ferrocene : succinic anhydride : $AlCl_3$. After 12 h of stirring, the reaction mixture was poured onto iced water. The organic layer was dried and concentrated and the crude product was purified on silica (1: 5 dichloromethane : ethyl acetate). Yield: 25%, (0.48 g); m.p.: 123 °C. Anal. Found: C, 69.53; H, 8.74. Calc. for $C_{32}H_{48}FeO_4$: C, 69.56; H, 8.76%. IR (KBr/cm^{-1}): 3130 (very broad, –OH), 2916, 2850 (C–H), 1710 (>C=O, carboxylic), 1666 (>C=O, ketonic), 1629 (>C=O, ketonic), 1456, 1401, 1381, 1342, 1286, 1257, 1170, 1083, 889, 833, 480. ^{1}H NMR δ_H($CDCl_3$): 4.82 (t, 2H, ferrocene), 4.79 (t, 2H, ferrocene), 4.53 (t, 2H, ferrocene), 4.49 (t, 2H, ferrocene), 3.01 (t, 2H, –CH_2–COO), 2.75 (t, 2H, CO–CH_2–), 2.63 (t, 2H, –$COCH_2$), 1.66 (qv, 2H, C–CH_2–C), 1.28–1.17 (28H, aliphatic protons), 0.87 (t, 3H, –CH_3). m/z: 552 $[M-1]^+$.

Phenol mesogens' preparation (M_1 and M_2)

Cholesteryl nitrobenzoates synthesis

To a solution containing 3- or 4-nitrobenzoic acid, cholesterol and a catalytic amount of DMAP in anhydrous CH_2Cl_2, under stirring, a solution of DCC solved of dried CH_2Cl_2 was added. After 18 h of stirring, the dicyclohexyl urea was filtered off and the solution was concentrated. The solid residue was purified by column chromatography on Al_2O_3 to provide pure nitrobenzoates as white solids.

Cholesteryl 4-nitrobenzoate. Quantities: 4-nitrobenzoic acid (5 g, 29.94 mmol), cholesterol (11.5769 g, 29.94 mmol), a catalytic amount of DMAP in anhydrous CH_2Cl_2 (150 ml), DCC (6.7952 g, 32.93 mmol) in anhydrous CH_2Cl_2 (50 ml). Purification: column chromatography on neutral Al_2O_3 (3 : 1 CH_2Cl_2:hexane). Yield: 79% (12.67 g); m.p. (liquid crystal): 179 °C (K/Ch); 264 °C (Ch/I). IR (KBr/cm^{-1}): 2939.51, 2864.29 (C–H), 1720.5 (>C=O, ester), 1604.77, 1527.62, 1463.97, 1344.38, 1271.09, 1107,14, 1002.98, 968.26, 846.75, 715.59, 505.35. ^{1}H NMR δ_H ($CDCl_3$): 8.27 (d; 2H, aromatic); 8.19 (d, 2H, aromatic), 5.40 (d, 1H, –C=CH–, cholesteryl), 4.88 (m, 1H, COO–CH–), 2.46 (d, 2H, cholesteryl), 2.01–0.83 (41H, aliphatic protons), 0.67 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 164.00, 150.42, 139.22, 136.20, 130.61, 123.40, 123.14, 75.77, 56.67, 56.15, 50.04, 42.31, 39.71, 39.50, 38.09, 36.96, 36.61, 36.18, 35.77, 31.91, 31.85, 28.21, 27.99, 27.80, 24.27, 23.83, 22.79, 22.54, 21.05, 19.32, 18.71, 11.85. m/z: 534 $[M-1]^+$.

Cholesteryl 3-nitrobenzoate. Quantities: 3-nitrobenzoic acid (3.2255 g 19.30 mmol), cholesterol (7.4627 g, 19.30 mmol), a catalytic amount of DMAP in anhydrous CH_2Cl_2 (100 ml), DCC (4.3805 g, 32.93 mmol) in anhydrous CH_2Cl_2 (40 ml). Purification: column chromatography on neutral Al_2O_3 (1 : 1 CH_2Cl_2 : hexane). Yield: 86.04% (8.8974 g), m.p. (liquid crystal): 128 °C (K/Ch); 170 °C (Ch/I). IR (KBr/cm^{-1}): 2939.51; 2872 (C–H), 1726.29.5 (>C=O, ester), 1614.42, 1533.41, 1467.83, 1440.82, 1348.24, 1259.51, 1138, 1074.35, 995.27, 829.39, 717.52. ^{1}H NMR δ_H ($CDCl_3$): 8.84 (s, 1H, aromatic); 8.40 (d, 1H, aromatic), 8.36 (d, 1H, aromatic) 7.64 (t, 1H, aromatic), 5.42 (d, 1H, –C=CH–), 4.89 (m, 1H, COO–CH–), 2.46 (m, 2H), 2.02–0.84 (41H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 163.78, 148.25, 139.27, 135.25, 132.60, 129.45, 121.15, 124.49, 127.16, 124.50, 123.11, 75.76, 56.68, 56.16, 50.05, 42.31, 39.73, 39.51, 38.10, 36.97, 36.63, 36.19, 35.78, 31.93, 31.86, 28.21, 27.99, 27.81, 24.28, 23.84, 22.79, 22.54, 21.05, 19.34, 18.71, 11.85. m/z: 534 $[M-1]^+$.

Cholesteryl aminobenzoates

Cholesteryl 4-aminobenzoate. Cholesteryl 4-nitrobenzoate (2 g, 3.73 mmol) and 8 equivalents of $SnCl_2{\cdot}2H_2O$ (6.739 g, 29.84 mmol) were refluxed in ethanol (100 ml) for 6 h. After cooling, the mixture was poured over iced water and the pH value was adjusted to 7–8 using a 5% NaOH solution. The mixture was extracted with dichloromethane, washed several times with water and dried over anhydrous $MgSO_4$. After solvent removal, the white solid was purified by column chromatography (Al_2O_3, 3 : 1 dichloromethane : hexane). Yield: 63.2% (1.2 g); m.p. (liquid crystal): 241 °C (K/Ch), decomp. IR (KBr/cm^{-1}): 3489.22, 3369.63, (–NH_2), 2953, 2864 (C–H), 1683.85 (>C=O), 1629.85, 1604.77, 1273, 1168, 1118, 839, 771.52. ^{1}H NMR δ_H ($CDCl_3$): 7.84 (d, 2H, aromatic), 6.62 (d, 2H, aromatic), 5.40 (d, 1H, –C=CH–), 4.79 (m, 1H, COO–CH–), 4.02 (s, 2H, –NH_2), 2.43 (d, 2H, cholesteryl), 2.02–0.85 (41H, aliphatic protons), 0.67 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 166.04, 150.59, 139.88, 131.53, 122.53, 120.48, 113.73, 73.82, 56.68, 56.11, 50.03, 42.30, 39.73, 39.50, 38.32, 37.05, 36.64, 36.17, 35.78, 31.91, 31.87, 28.22, 27.99, 27.95, 24.28, 23.81, 22.80, 22.54, 21.03, 19.37, 18.70, 11.84.

Cholesteryl 3-aminobenzoate. Activated zinc (with 20% solution of HCl and washed three times with water and methanol) (1.098 g, 16.8 mmol) was added over a solution containing cholesteryl 3-nitrobenzoate (3 g, 5.6 mmol) in dichloromethane (100 ml). Under vigorous stirring, formic acid 80% (2.79 ml) was poured in a single portion. The reaction evolves with an exothermic effect and powerful foaming. After 15 min of stirring, the reaction was complete and the inorganic compounds were filtered off. The organic solvent was washed several times with a 10% Na_2CO_3 solution and water and dried over $MgSO_4$. The crude product was purified

on silica gel (15 : 1 dichloromethane : ethyl acetate). Yield: 47.7% (1.35 g); m.p.: 184–186 °C. IR (KBr/cm^{-1}): 3489.22, 3369.63, (–NH_2), 2953, 2864 (C–H), 1683.85 (>C=O), 1629.85, 1604.77, 1273, 1168, 1118, 839, 771.52. ^{1}H NMR δ_H ($CDCl_3$): 7.42 (dd, 1H, aromatic); 7.34 (s, 1H, aromatic), 7.19 (t, 1H, aromatic), 6.83 (dd, 1H, aromatic), 5.40 (d, 1H, –C=CH–), 4.82 (m, 1H, COO–CH–), 3.76 (s, 2H, –NH_2), 2.43 (d, 2H, cholesteryl), 2.04–0.85 (41H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 166.08, 146.37, 139.66, 131.81, 129.12, 122.70, 119.66, 119.16, 115.72, 74.43, 56.67, 56.13, 50.03, 42.03, 39.73, 39.50, 38.19, 37.02, 36.63, 36.18, 35.78, 31.91, 31.86, 28.21, 27.98, 27.86, 24.27, 23.83, 22.79, 22.54, 21.03, 19.35, 18.71, 11.84. m/z: 504 $[M-1]^+$.

Azo-cholesteryl mesogens (M_1, M_2)

Cholesteryl 4-(4-hydroxyphenylazo)benzoate (M_1). To a solution of cholesteryl 4-aminobenzoate (2 g, 3.96 mmol) in THF (30 ml), hydrochloric acid (0.3 ml, 32%) was added. The mixture was cooled on an ice bath to 0 °C and a solution containing $NaNO_2$ (0.3 g, 5.1 mmol) in H_2O (2ml) was slowly dropped, under stirring, keeping the temperature under 5 °C. The diazonium salt was maintained at 5 °C for an additional 30 min. The diazonium salt was added dropwise over a solution containing phenol (0.37 g, 3.96 mmol) and $CH_3COONa{\cdot}3H_2O$ (1.07 g, 7.86 mmol), in water (5 ml), at 5 °C. After 3 h, the azo derivative was passed over cold water. The orange precipitate was filtered off and washed several times with water. Yield: 84% (2.03 g); m.p. (liquid crystal): 190 °C (K/Ch); 265 °C (Ch/I) decomp. Anal. Found: C, 78.63; H, 8.90; N, 4.57. Calc. for $C_{40}H_{54}N_2O_3$: C, 78.65; H, 8.91; N, 4.59%. IR (KBr/cm^{-1}): 3419.78 (broad, –OH), 2945.3, 2866.21 (C–H), 1681.92 (>C=O, ester), 1597.06, 1290.38, 1134.14, 1008.77, 860.25, 839.03, 773.45, 694.37, 613.36, 542. ^{1}H NMR δ_H ($CDCl_3$): 8.16 (d, 2H, aromatic), 7.90 (d, 2H, aromatic), 7.88 (d, 2H, aromatic), 6.96 (d, 2H, aromatic), 5.98 (s, 1H, –OH), 5.42 (d, 1H, –C=CH–), 4.88 (m, 1H, COO–CH–), 2.48 (d, 2H, cholesteryl), 2.01–0.85 (41H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR: 164.86, 159.14, 155.26, 153.44, 151.11, 139.58, 131.86, 130.55, 125.40, 122.90, 122.30, 115.94, 74.98, 56.70, 56.16, 50.06, 42.33, 39.75, 39.53, 38.25, 37.06, 36.68, 36.20, 35.80, 31.90, 28.24, 28.02, 27.91, 24.30, 23.86, 22.82, 22.56, 21.07, 19.39, 18.73, 11.87. m/z: 609 $[M-1]^+$.

Cholesteryl 3-(4-hydroxyphenylazo)benzoate (M_2). To a solution of cholesteryl 3-aminobenzoate (0.5 g, 0.988 mmol) dissolved in DMF (10 ml), hydrochloric acid (0.6 ml, 32%, 2.66 mmol) was added. The mixture was cooled on an ice bath to 0 °C and a solution containing $NaNO_2$ (0.07 g, 1.1 mmol) in H_2O (0.3 ml) was slowly dropped, under stirring, keeping the temperature under 5 °C. The diazonium salt was maintained at 5 °C for an additional 30 min. The diazonium salt was added dropwise over a solution containing phenol (0.09 g, 0.988 mmol) and anhydrous sodium acetate (1.0 g, 7.35 mmol), in water (4 ml), at 5 °C. After 3 h, the azo derivative was passed over cold water. The orange precipitate was filtered off and washed several times with water. Yield: 50% (0.3 g); m.p.: 193 °C. Anal. Found: C, 78.64; H, 8.89; N, 4.56. Calc. for $C_{40}H_{54}N_2O_3$: C, 78.65; H, 8.91; N, 4.59%. IR (KBr/cm^{-1}): 3415.93 (broad, –OH), 2943.37, 2866.21 (C–H), 1720.05 (>C=O, ester), 1593.2, 1465.9, 1438.89, 1273.02, 1143.79, 999.12, 840.96, 756.09, 682.8, 493.78. ^{1}H NMR δ_H ($CDCl_3$): 8.54 (s, 1H, aromatic), 8.14 (d, 1H, aromatic), 8.06 (d, 1H, aromatic), 7.75 (d, 2H, aromatic), 7.58 (t, 1H, aromatic), 6.95 (d, 2H, aromatic), 5.98 (s, 1H, –OH), 5.42 (d, 1H, –C=CH–), 4.82 (m, 1H, COO–CH–), 3.76 (s, 2H, –NH_2), 2.43 (d, 2H, cholesteryl), 2.04–0.85 (41H, aliphatic protons), 0.68 (s, 3H, cholesteryl). m/z: 609 $[M-1]^+$.

General procedure for preparing ferrocene-containing liquid crystals

To a stirred solution containing the ferrocene acid, phenol mesogen (1 : 1 molar ratio) and a catalytic amount of DMAP in anhydrous CH_2Cl_2 a solution of DCC in CH_2Cl_2 was added (1 : 1 : 1.1 final molar ratio of acid : phenol : DCC). After 24 h of stirring, dicyclohexyl urea was filtered off and the solution was concentrated. The purification of the ester was made using column chromatography on silica gel.

Cholesteryl 4-[4-(3-ferrocenoylpropionyloxy) phenylazo]benzoate (Fc_1M_1)

Quantities: 4-oxo-4-ferrocenyl-butyric acid (0.2 g, 0.69 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate (0.425 494 g, 0.69 mmol), DMAP, dichloromethane (27 ml) and DCC (0.22 g, 1.06 mmol). Column chromatography, 3 : 1 dichloromethane : hexane. Yield: 69% (0.4229 g). Anal. Found: C, 73.77; H, 7.56; N, 3.16. Calc. for $C_{54}H_{66}FeN_2O_5$: C, 73.79; H, 7.57; N, 3.19%. IR (KBr/cm^{-1}): 2935.65, 2864.29 (C–H), 1759.08 (>C=O, ester), 1712.78 (>C=O, ester), 1662.64 (>C=O, keto), 1539.2, 1494.83, 1458.18, 1371.39, 1274.94, 1195.86, 1132.21, 1004.91, 858.32, 821.67, 771.52, 692.44, 532.35, 480.27. ^{1}H NMR δ_H ($CDCl_3$): 8.17 (d, 2H, aromatic), 7.99 (d, 2H, aromatic), 7.92 (d, 2H, aromatic), 7.32 (d, 2H, aromatic), 5.42 (d, 1H, –C=CH–), 4.87 (m, 1H, COO–CH–), 4.84 (t, 2H, ferrocene), 4.52 (2H, t, ferrocene), 4.24 (s, 5H, ferrocene), 3.20 (t, 2H, $-CH_2-$), 2.97 (t, 2H, $-CH_2-$), 2.48 (d, 2H, cholesteryl), 2.04–0.85 (41H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 201.78, 171.42, 165.40, 154.93, 153.33, 150.13, 139.56, 132.52, 130.55, 124.39, 122.87, 122.55, 122.40, 78.16, 74.96, 72.35, 69.96, 69.21, 56.68, 56.13, 50.04, 42.32, 39.73, 39.51, 38.21, 37.03, 36.66, 36.18, 35.79, 34.17, 31.94, 31.88, 28.23, 28.14, 28.01, 27.89, 24.29, 23.83, 22.82, 22.56, 21.05, 19.38, 18.71, 11.86. m/z: 878 $[M-1]^+$.

Cholesteryl 4-[4-(4-Ferocenylbutyryloxy) phenylazo]benzoate (Fc_2M_1)

Quantities: 4-ferrocenyl-butyric acid (0.2 g, 0.732 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate (0.4468 g, 0.732 mmol), DMAP, dichloromethane (15 ml) and DCC (0.166 24 g, 0.805 mmol). Column chromatography, 1 : 1 dichloromethane : hexane. Yield: 72% (0.4565 g). Anal. Found: C, 74.97; H, 7.90; N, 3.23. Calc. for $C_{54}H_{68}FeN_2O_4$: C, 74.98; H, 7.92; N, 3.24%. IR (KBr/cm^{-1}): 2935.65, 2866.21 (C–H), 1759.08

(>C═O, ester), 1712.78 (>C═O, ester), 1597.06, 1494.83, 1463.97, 1411.89, 1369.46, 1276.87, 1222.87, 1195.86, 1116.78, 1008.77, 864.11, 815.89, 771.52, 690.51, 543.92, 484.13, 445.56. ^{1}H NMR δ_H ($CDCl_3$): 8.18 (d, 2H, aromatic), 7.98 (d, 2H, aromatic), 7.92 (d, 2H, aromatic), 7.25 (d, 2H, aromatic), 5.43 (d, 1H, –C═CH–), 4.88 (m, 1H, COO–CH–), 4.12 (s, 5H, ferrocene), 4.10 (s, 2H, ferrocene), 4.07 (s, 2H, ferrocene), 2.61 (t, 2H, $-CH_2-$), 2.48 (m, 4H, $-CH_2-$and cholesteryl), 2.03–0.86 (43H, aliphatic protons), 0.69 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 171.61, 165.37, 154.89, 153.20, 150.09, 139.56, 132.56, 130.55, 124.36, 122.87, 122.56, 122.29, 87.72, 74.96, 68.54, 68.14, 67.33, 56.68, 56.13, 50.03, 42.31, 39.73, 39.51, 38.21, 37.02, 36.65, 36.18, 35.78, 33.90, 31.94, 31.87, 28.93, 28.23, 28.00, 27.88, 26.11, 24.29, 23.83, 22.82, 22.56, 21.05, 19.38, 18.71, 11.86. m/z: 864 $[M-1]^+$.

Cholesteryl 4-[4-(4-ferrocenoylbutiryloxy) phenylazo]benzoate (Fc_3M_1)

Quantities: 5-oxo-5-ferrocenyl-pentanoic acid (0.2 g, 0.709 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate (0.4069 g, 0.709 mmol), DMAP, dichloromethane (20 ml) and DCC (0.1512 g, 0.78 mmol). Column chromatography, 15 : 1 dichloromethane : ethyl acetate. Yield: 57% (0. 3476 g). Anal. Found: 73.96; H, 7.67; N, 3.12. Calc. for $C_{55}H_{68}FeN_2O_5$: C, 73.98; H, 7.68; N, 3.14%. IR (KBr/cm^{-1}): 2931.79, 2868.14 (C–H), 1762.93, 1710.86 (C═O, ester), 1668.42 (C═O, keto), 1593.2, 1494.83, 1458.18, 1381.03, 1273.02, 1132.21, 1089.78, 1006.84, 862.18, 813.96, 694.37, 487.99. ^{1}H NMR δ_H ($CDCl_3$): 8.17 (d, 2H, aromatic), 7.98 (d, 2H, aromatic), 7.92 (d, 2H, aromatic), 7.28 (d, 2H, aromatic), 5.42 (d, 1H, –C═CH–), 4.89 (m, 1H, COO–CH–), 4.81 (t, 2H, ferrocene), 4.51 (t, 2H, ferrocene), 4.20 (s, 5H, ferrocene), 2.89 (t, 2H, $-CH_2-$), 2.75 (t, 2H, $-CH_2-$), 2.48 (d, cholesteryl), 2.17 (qv, 2H, C–CH_2–C), 2.03–0.85 (41H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 205.02, 171.44, 165.35, 154.89, 153.15, 150.12, 139.56, 132.58, 130.54, 124.37, 122.85, 122.55, 122.28, 78.82, 74.96, 72.30, 69.79, 69.28, 56.68, 56.14, 50.05, 42.31, 39.73, 39.51, 38.21, 38.16, 37.02, 36.65, 36.18, 35.78, 33.54, 31.93, 31.88, 28.21, 27.99, 27.88, 24.28, 23.83, 22.80, 22.54, 21.05, 19.41, 19.37, 18.71, 11.85. m/z: 891 $[M-1]^+$.

Cholesteryl 4-[4-(5-ferrocenylpentanoyloxy-phenylazo]benzoate (Fc_4M_1)

Quantities: 5-ferrocenyl-pentanoic acid (0.2 g, 0.699 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate (0.4269 g, 0.699 mmol), DMAP, dichloromethane (20 ml) and DCC (0.1586 g, 0.769 mmol). Column chromatography, dichloromethane. Yield: 43.88% (0.2696 g); m.p. 139 °C Anal. Found: C, 75.14; H, 8.99; N, 3.18. Calc. for $C_{55}H_{70}FeN_2O_4$: C, 75.15; H, 8.03; N, 3.19%. IR (KBr/cm^{-1}): 2931.79, 2864.29 (C–H), 1762.93, 1712.76 (C═O, ester), 1597.06, 1494.83, 1463.97, 1373.31, 1273.02, 1195.86, 1112.92, 1006.84, 862.8, 817.82, 771.52, 694.37, 543.92, 484.13. ^{1}H NMR δ_H ($CDCl_3$): 8.16 (d, 2H, aromatic), 7.97 (d, 2H, aromatic), 7.92 (d, 2H, aromatic), 7.24 (d, 2H, aromatic), 5.42 (d, 1H, –C═CH–), 4.88 (m, 1H, COO–CH–), 4.09 (s, 5H, ferrocene), 4.07 (s, 2H, ferrocene), 4.05 (s, 2H, ferrocene), 2.60 (t, 2H, $-CH_2-$), 2.48 (d, 2H, cholesteryl), 2.41 (t, 2H, $-CH_2-$), 2.03–0.85 (45H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 205.02, 165.39, 154.96, 153.26, 150.42, 139.60, 132.59, 130.56, 124.36, 122.29, 122.67, 122.08, 95.84, 74.98, 68.49, 68.07, 67.18, 56.71, 56.16, 50.07, 42.33, 39.76, 36.68, 36.20, 35.79, 31.95, 31.90, 30.58, 29.69, 29.30, 28.23, 28.01, 27.90, 24.75, 24.30, 23.84, 22.55, 22.38, 21.33, 21.07, 19.38, 18.72, 11.87, 11.83. m/z: 877 $[M-1]^+$.

1-{Cholesteryl 4-[4-(3-ferrocenoylpropionyloxy) phenylazo]benzoate}-1′-stearoyl-ferrocene (Fc_5M_1)

Quantities: 1-(3-carboxypropionyl)-1′-stearoyl-ferrocene (0.1 g, 0.181 mmol), (0.1105 g, 0.181 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate, DMAP, 20 ml dichloromethane and 0.041 g (0.199 mmol) DCC. Column chromatography, 20 : 1 dichloromethane : ethyl acetate. Yield: 57% (0.118 g). Anal. Found: C, 75.48; H, 8.79; N, 2.43. Calc. for $C_{72}H_{100}FeN_2O_6$: C, 75.50; H, 8.80; N, 2.45%. IR (KBr/cm^{-1}): 2926.01, 2852.71 (C–H), 1761.01 (C═O, ester), 1714.71 (C═O, ester), 1668.42 (C═O, keto), 1597.06, 1492.9, 1460.11, 1375.24, 1273.02, 1215.15, 1199.72, 1120.64, 1006.84, 885.32, 831.32, 769.6, 694.37, 543.92, 482.2. ^{1}H NMR δ_H ($CDCl_3$): 8.18 (d, 2H, aromatic), 7.99 (d, 2H, aromatic), 7.92 (d, 2H, aromatic), 7.32 (d, 2H, aromatic), 5.43 (d, 1H, –C═CH–), 4.88 (m, 1H, COO–CH–), 4.84 (t, 2H, ferrocene), 4.81 (t, 2H, ferrocene), 4.54 (t, 2H, ferrocene), 4.51 (t, 2H, ferrocene), 3.14 (t, 2H, $-CH_2-$), 2.98 (t, 2H, $-CH_2-$), 2.63 (t, 2H, $-CH_2-$), 2.48 (d, 2H, cholesteryl), 2.03–0.85 (74H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 204.02, 203.07, 173.99, 165.41 (C═O). m/z: 1144 $[M-1]^+$.

Cholesteryl 3-[4-(3-ferrocenoylpropionyloxy) phenylazo]benzoate (Fc_1M_2)

Quantities: 4-oxo-4-ferrocenyl-butyric acid (0.1 g, 0.348 mmol), cholesteryl 3-(4-hydroxyphenylazo)benzoate (0.2127 g, 0.348 mmol), DMAP, 20 ml dichloromethane and DCC (0.11 g, 0.382 mmol). Column chromatography, dichloromethane. Yield: 74% (0.2267 g); m.p.: 96–97 °C. Anal. Found: C, 73.77; H, 7.55; N, 3.17. Calc. for $C_{54}H_{66}FeN_2O_5$: C, 73.79; H, 7.57; N, 3.19%. IR (KBr/cm^{-1}): 2937.58, 2866.21 (C–H), 1762.93 (C═O, ester), 1716.64 (C═O, ester), 1668.42 (C═O, keto), 1591.27, 1458.18, 1369.46, 1269.16, 1213.22, 1193.93, 1130.28, 1078.21, 999.12, 910.4, 881.47, 821.67, 758.02, 731.02, 680.87, 482.2. ^{1}H NMR δ_H ($CDCl_3$): 8.54 (t, 1H, aromatic), 8.14 (d, 1H, aromatic), 8.06 (d, 1H, aromatic), 7.99 (d, 2H, aromatic), 7.57 (t, 1H, aromatic), 7.31 (d, 2H, aromatic), 5.42 (d, 1H, –C═CH–), 4.90 (m, 1H, COO–CH–), 4.84 (t, 2H, ferrocene), 4.52 (t, 2H, ferrocene), 4.24 (s, 5H, ferrocene), 3.20 (t, 2H, $-CH_2-$), 2.97 (t, 2H, $-CH_2-$), 2.49 (d, 2H, cholesteryl), 2.03–0.85 (41 H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 202.01, 171.84, 165.57, 153.20, 152.64, 150.21, 142.00, 139.78, 136.99, 132.25, 129.27, 126.48, 124.42, 123.07, 122.45, 87.93, 75.20, 68.73, 68.34, 67.52, 56.89, 56.33, 50.25, 42.52, 39.94, 39.71, 38.42, 37.24, 36.86, 36.38, 34.10, 32.08, 29.89, 29.13, 28.19, 24.48, 24.02, 23.00, 22.75, 21.25, 19.58, 18.91, 12.05. m/z: 878 $[M-1]^+$.

Cholesteryl 3-[4-(4-ferrocenylbutyryloxy) phenylazo]benzoate (Fc_2M_2)

Quantities: 4-ferrocenyl-butyric acid (0.1 g, 0.366 mmol), cholesteryl 3-(4-hydroxyphenylazo)benzoate (0.2236 g, 0.366 mmol), DMAP, 20 ml dichloromethane and DCC (0.0831 g, 0.402 mmol). Column chromatography, dichloromethane. Yield: 72% (0.2281 g); m.p.: 130–132 °C. Anal. Found: C, 74.97; H, 7.90; N, 3.23. Calc. for $C_{54}H_{68}FeN_2O_4$: C, 74.98; H, 7.92; N, 3.24%. IR (KBr/cm^{-1}): 2927.94, 2852.71 (C–H), 1759.08 (C═O, ester), 1716.64 (C═O, ester), 1589.34, 1463.97, 1438.89, 1375.24, 1298.09, 1271.09, 1215.15, 1118.71, 1074.35, 999.12, 912.33, 846.75, 815.89, 756.09, 678.94, 557.43, 484.13. ^{1}H NMR δ_H ($CDCl_3$): 8.54 (t, 1H, aromatic), 8.14 (d, 1H, aromatic), 8.06 (d, 1H, aromatic), 7.98 (d, 2H, aromatic), 7.58 (t, 1H, aromatic), 7.25 (d, 2H, aromatic), 5.42 (d, 1H, –C═CH–), 4.90 (m, 1H, COO–CH–), 4.12 (s, 5H, ferrocene), 4.10 (s, 2H, ferrocene), 4.08 (s, 2H, ferrocene), 2.61 (t, 2H, –CH_2–), 2.48 (m, 4H, –CH_2–and cholesteryl), 2.03–0.85 (43H, aliphatic protons), 0.68 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 171.68, 165.39, 153.02, 152.46, 150.03, 139.59, 132.07, 131.45, 129.24, 129.09, 124.43, 124.24, 122.89, 122.26, 87.75, 75.02, 68.55, 68.15, 67.34, 56.70, 56.15, 50.07, 42.33, 39.76, 39.53, 38.24, 37.06, 36.68, 36.20, 35.80, 33.92, 31.90, 29.71, 28.95, 28.24, 28.01, 26.13, 24.30, 23.84, 22.82, 22.56, 21.07, 19.39, 18.72, 11.87. m/z: 864 $[M-1]^+$.

Cholesteryl 3-ferrocenoylbutyrate (Fc_1M_3)

Quantities: 4-oxo-4-ferrocenyl-butyric acid (0.2 g, 0.696 mmol), cholesterol (0.2694 g, 0.696 mmol), DMAP, 25 ml dichloromethane and DCC (0.1581 g, 0.7656 mmol). Column chromatography, dichloromethane. Yield: 52% (0.2439 g); m.p.: 129–130 °C. Anal. Found: C, 75.19; H, 8.90. Calc. for $C_{41}H_{58}FeO_3$: C, 75.21; H, 8.93%. IR (KBr/cm^{-1}): 2926.01, 2854.64 (C═H), 1734 (C═O, ester), 1672.28 (C═O, keto), 1460.11, 1404.17, 1379.1, 1222.87, 1205.51, 1172.72, 1089.78, 1026.13, 1002.98, 885.32, 821.67, 522.71, 480.27, 457.13. ^{1}H NMR δ_H ($CDCl_3$): 5.36 (d, 1H, –C═CH–), 4.80 (t, 2H, ferrocene), 4.64 (m, 1H, COO–CH–), 4.49 (t, 2H, ferrocene), 4.23 (s, 5H, ferrocene), 3.05 (t, 2H, –CH_2–), 2.65 (t, 2H, –CH_2–), 2.34 (d, 2H, cholesteryl) 2.00–0.84 (41H, aliphatic protons), 0.66 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 202.10, 172.45, 139.67, 122.54, 78.44, 74.14, 72.12, 69.86, 69.16, 56.65, 56.08, 49.98, 42.27, 39.69, 39.47, 38.06, 36.95, 36.56, 36.13, 35.74, 34.21, 31.86, 31.81, 29.65, 28.26, 28.17, 27.96, 27.73, 24.23, 23.78, 22.76, 22.52, 20.98, 19.29, 18.67, 11.81. m/z: 654 $[M-1]^+$.

Cholesteryl 4-ferrocenylbutyrate (Fc_2M_3)

Quantities: 4-ferrocenyl-butyric acid (0.3 g, 1.09 mmol), cholesterol (0.4248 g, 1.09 mmol), DMAP, 30 ml dichloromethane and DCC (0.2493 g, 1.199 mmol). Column chromatography, dichloromethane. Yield: 62.7% (0.4424 g); m.p.: 153–155 °C. Anal. Found: C, 76.83; H, 9.42. Calc. for $C_{41}H_{60}FeO_2$: C, 76.85; H, 9.44%. IR (KBr/cm^{-1}): 2935.65, 2843.07 (C–H), 1728.22 (C═O, ester), 1463.97, 1379.1, 1286.52, 1240.23, 1170.79, 1128.35, 1026.13, 1001.05, 825.53, 804.31, 736.81, 594.07, 497.63, 484.13, 443.63. ^{1}H NMR δ_H ($CDCl_3$): 5.36 (d, 1H, –C═CH–), 4.60 (m, 1H, COO–CH–), 4.09 (s, 5H, ferrocene), 4.06 (s, 2H, ferrocene), 4.04 (s, 2H, ferrocene), 2.35 (t, 2H, –CH_2–), 2.30 (m, 4H, –CH_2–), 1.81 (qv, 2H, C–CH_2–C), 2.01–0.84 (43 H, aliphatic protons), 0.66 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 172.94, 139.6, 122.62, 88.17, 73.79, 68.47, 68.47, 68.09, 67.17, 56.68, 56.14, 50.03, 42.31, 39.73, 39.51, 38.19, 37.00, 36.60, 36.19, 35.78, 34.28, 31.90, 31.87, 28.92, 28.21, 28.00, 27.84, 26.30, 24.28, 23.83, 22.80, 22.55, 21.03, 19.32, 18.71, 11.85. m/z: 640 $[M-1]^+$.

4-Oxo-4-ferrocenyl-butyric acid 4-phenylazo-phenyl ester (Fc_1M_4)

Quantities: 4-oxo-4-ferrocenyl-butyric acid (0.3 g, 1.045 mmol), 4-phenylazophenol (0.2069 g 1.045 mmol), DMAP, 30 ml of dichloromethane and DCC (0.2372 g, 1.149 mmol). Column chromatography, dichloromethane. Yield: 29% (0.14 g); m.p.: 185 °C. Anal. Found: C, 66.94; H, 4.75; N, 5.99. Calc. for $C_{26}H_{22}FeN_2O_3$: C, 66.97; H, 4.76; N, 6.01%. IR (KBr/cm^{-1}): 2927.94, 2852.71 (C–H), 1755.22 (C═O, ester), 1658.78 (C═O, keto), 1589.34, 1490.97, 1452.4, 1361.74, 1188.15, 1132.21, 1074.35, 881.47, 819.74, 765.74, 686.66, 526.57, 478.35. ^{1}H NMR δ_H ($CDCl_3$): 7.96 (d, 2H, aromatic), 7.90 (d, 2H, aromatic), 7.51 (t, 2H, aromatic), 7.48 (t, 1H, aromatic), 4.83 (t, 2H, ferrocene), 4.52 (t, 2H, ferrocene), 4.24 (s, 5H, ferrocene), 3.20 (t, 2H, –CH_2–), 2.97 9t, 2H, –CH_2–); ^{13}C NMR δ_C ($CDCl_3$): 200.75, 170.47, 151.81, 151.54, 149.21, 130.00, 128.06, 123.05, 121.82, 121.28, 77.17, 71.31, 68.95, 68.19, 27.12, 24.59.

4-Ferrocenyl-butyric acid 4-phenylazo-phenyl ester (Fc_2M_4)

Quantities: 4-ferrocenyl-butyric acid (0.5 g 1.831 mmol), 4-phenylazo-phenol (0.3625 g, 1.831 mmol), DMAP, 40 ml of dichloromethane and DCC (0.4156 g, 2.0143 mmol). Column chromatography, 1 : 1 dichloromethane : hexane. Yield: 79% (0.6553 g); m.p.: 88–90 °C. Anal. Found: C, 69.02, H, 5.34, N, 6.18. Calc. for $C_{26}H_{24}FeN_2O_2$: C, 69.04, H, 5.35, N, 6.19%. IR (KBr/cm^{-1}): 2926.01, 2870.07, 2837.28 (C–H), 1749.43 (C═O, ester), 1587.41, 1487.11, 1409.96, 1382.96, 1220.94, 1203.58, 1147.64, 1136.07, 1099.42, 1006.84, 997.2, 854.46, 810.1, 865.74, 742.59, 682.8, 549.71, 487.99, 430.13, 403.12. ^{1}H NMR δ_H ($CDCl_3$): 7.96 (d, 2H, aromatic), 7.52 (t, 2H, aromatic), 7.47 (t, 1H, aromatic), 7.25 (d, 2H, aromatic), 4.12 (s, 5H, ferrocene), 4.10 (s, 2H, ferrocene), 4.08 (s, 2H, ferrocene), 2.61 (t, 2H, –CH_2–), 2.48 (2H, –CH_2–), 1.98 (qv, 2H, C–CH_2–C). ^{13}C NMR δ_C ($CDCl_3$): 171.66, 152.64, 150.14, 130.99, 129.03, 124.00, 122.79, 122.15, 87.72, 68.50, 68.11, 67.29, 33.87, 28.89, 26.09. m/z: 452 $[M-1]^+$.

Phenyl analogues' preparation

Cholesteryl 4-[4-(4-oxo-4-phenylbutyryloxy) phenylazo]benzoate (Ph_1M_1)

Quantities: 4-oxo-4-phenyl-butyric acid (0.1 g, 0.561 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate (0.3427 g, 0.561 mmol), DMAP, 20 ml dichloromethane and DCC (0.1273 g, 0.617 mmol). Column chromatography, 15 : 1

dichloromethane : ethyl acetate. Yield: 85% (0.3677 g). Anal. Found: C, 77.86; H, 8.07; N, 3.60. Calc. for $C_{50}H_{62}N_2O_5$: C, 77.89; H, 8.10; N, 3.63%. IR (KBr/cm^{-1}): 2935.65, 2866.21 (C–H), 1761.01 (C═O, ester), 1712.78 (C═O, ester), 1687.71 (C═O, keto), 1598.98, 1494.83, 1465.9, 1409.96, 1369.46, 1274.94, 1220.94, 1199.72, 1136.07, 10 008.77, 864.11, 771.52, 690.51, 543.92. ^{1}H NMR δ_H ($CDCl_3$): 8.17 (d, 2H, aromatic), 8.01 (d, 2H, aromatic), 7.98 (d, 2H, aromatic), 7.92 (d, 2H, aromatic), 7.59 (t, 1H, aromatic), 7.49 (t, 2H, aromatic), 7.30 (d, 2H, aromatic), 5.43 (d, 1H, –C═CH–), 4.88 (m, 1H, COO–CH–), 3.46 (t, 2H, –CH_2–), 3.05 (t, 2H, –CH_2–), 2.50 (d, 2H, cholesteryl), 2.05–0.86 (41H, aliphatic protons), 0.70 (s, 3H, cholesteryl). ^{13}C NMR δ_C ($CDCl_3$): 198.78, 179.71, 165.40, 154.92, 153.26, 150.15, 140.84, 139.58, 136.38, 133.41, 130.55, 128.69, 128.07, 124.36, 122.87, 122.56, 122.33, 75.12, 56.82, 56.26, 50.16, 42.47, 39.85, 39.62, 38.21, 36.67, 36.29, 35.79, 35.14, 33.41, 32.04, 31.89, 29.79, 28.51, 28.23, 28.01, 27.89, 24.62, 24.30, 24.03, 23.83, 22.81, 22.56, 21.05, 19.38, 18.72, 11.87. m/z: 770 $[M-1]^+$.

Cholesteryl 4-[4-(4-phenyl-butyryloxy) phenylazo]benzoate (Ph_2M_1)

Quantities: 4-phenyl-butyric acid (0.1 g, 0.609 mmol), cholesteryl 4-(4-hydroxyphenylazo)benzoate (0.3719 g, 0.609 mmol), DMAP, 20 ml dichloromethane and DCC (0.138 23 g, 0.669 mmol). Column chromatography, 3 : 1 dichloromethane: hexane. Yield: 87.0% (0.4036 g). Anal. Found: C, 79.29; H, 8.49; N, 3.67. Calc. for $C_{50}H_{64}N_2O_4$: C, 79.33; H, 8.52; N, 3.70%. IR (KBr/cm^{-1}): 2933.72, 2863.11 (C–H) 1761.01 (C═O, ester), 1714.71 (C═O, ester), 1597.06, 1492.9, 1463.97, 1375.24, 1278.8, 1195.86, 1122.57, 1122.57, 1008.77, 927.76, 864.11, 771.52, 736.81, 696.3, 545.85. ^{1}H NMR δ_H ($CDCl_3$): 8.20 (d, 2H, aromatic), 7.99 (d, 2H, aromatic), 7.94 (d, 2H, aromatic), 7.33 (t, 2H, aromatic), 7.23 (m, 5H, aromatic), 5.45 (d, 1H, –C═CH–), 4.91 (m, 1H, COO–CH–), 2.79 (t, 2H, –CH_2–), 2.64 (t, 2H, –CH_2–), 2.51 (d, 2H, cholesteryl), 2.14 (qv, 2H, C–CH_2–C), 2.06–0.88 (41H, aliphatic protons), 0.72 (s, 3H, cholesteryl). ^{13}C NMR: 171.59, 165.45, 155.01, 153,30, 150.0, 141.13, 139.66, 132.68, 130.64, 128.59, 126.25, 124.46, 122.96, 122.66, 122.37, 75.07, 56.80, 56.26, 50.16, 42.43, 39.84, 39.62, 38.32, 37.13, 36.76, 36.29, 35.90, 35.14, 33.76, 32.04, 31.99, 29.79, 28.33, 28.11, 28.00, 26.46, 24.39, 23.95, 22.92, 22.66, 21.17, 19.48, 18.83, 11.97. m/z: 757 $[M]^+$.

CONCLUSIONS

1. A series of ferrocene liquid crystals bearing a cholesteryl unit has been synthesized and characterized. The influence of each structural unit (ferrocene, cholesterol, azo aromatic core and flexible chain length) has been studied by comparing analogous compounds possessing a similar structure, but without the cholesteryl element.
2. All the liquid-crystalline compounds contain ferrocene or phenyl units flexibly connected to the mesogenic unit. In this case, it seems that mesophase stability was not affected and both phenyl analogues and ferrocene derivatives possess liquid-crystalline properties, with similar high clearing points, but above the stability of azo groups. Surprisingly, the three-dimensional bulky unit of ferrocene does not cause a decrease in mesophase stability through steric repulsions with neighboring molecules.
3. The introduction of a bend in the molecular structure, determined by substitution in the third position of the benzene nucleus (samples Fc_1M_2 and Fc_2M_2) affects the organization in liquid-crystalline structures negatively, the liquid-crystalline phase being completely suppressed.
4. The slight increase in flexible chain length from 2.54 to 2.97 ´Å for samples with similar dipole moments (Fc_2M_1 and Fc_4M_1) leads to a decrease in the melting point; but, in the case of samples with very different values of the dipole moment (Fc_1M_1 and Fc_2M_1), the highest value induces strong interactions in the solid state and increases the melting points.

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