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Synthesis and characterization of cholesterol-based nonsymmetric dimers terminated with ferrocenyl core

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ABSTRACT

The molecular design, synthesis, and thermal behavior of cholesterol-based nonsymmetric dimers, which can also be regarded as metallomesogens, consisting of either two- or three-ring aromatic cores terminated with ferrocenyl unit are reported. The spacer length connecting the cholesterol and aromatic cores is held constant while the length of the spacer connecting ferrocene and aromatic cores has been varied. The occurrence of the enantiotropic mesomorphism in these compounds has been adjudged by optical, calorimetric, and X-ray diffraction studies. In particular these systems exhibit liquid crystal phases such as chiral nematic, twist grain boundary, and smectic A phases. Of these, the chiral nematic phase commonly occurs in all the synthesized compounds.

1. Introduction

Liquid crystalline compounds containing a metallic atom in their structure combine properties of the metal with those of the mesogens, leading to processable material with interesting magnetic, electronic, optical, and anisotropic properties. Ferrocene-based metallomesogens have emerged as important liquid crystalline materials over last 10–20 years due to their novel thermal, optical, and magnetic properties.[1,2] Ferrocene, because of its aromatic character, facilitates several substitutions whereby a range of low molecular mass calamitic (rod-like) systems can be prepared by mono-substitution, or 1,1-, 1,2-, 1,3-, di-substitution or 1,1,3-tri-substitution of the ferrocene nucleus.[3–12] However, there are few reports on mono-substituted ferrocene-based metallomesogen in recent years.[13,14] This may be partly attributed to their unfavorable molecular shape (L-shaped geometry) and to the repulsive steric effects of the ferrocene unit reducing the ability of the molecules to be arranged in layers thus favoring mostly the formation of nematic phase.

Chiral liquid crystalline dimers composed of either identical (symmetrical) or non-identical (unsymmetrical) mesogenic segments, connected through a flexible paraffinic central spacer, are attracting a great deal of attention. This is because the symmetric dimers are regarded as model compounds for polymeric liquid crystals[15–18] while the unsymmetrical dimers exhibit smectic phases.[19–31] Moreover, chiral unsymmetrical dimers, in particular compound possessing a cholesteryl ester unit as the chiral entity joined to different aromatic mesogens through an alkyl spacer, show interesting thermal properties. Recently we have synthesized such unsymmetrical dimers exhibiting smectic A (SmA), twist grain boundary (TGB), and cholesteric (N*) phase.[14] Due to wide spread applicability of both cholesterol-based liquid crystalline materials and ferrocene-based metallomesogens, we are interested in the design of ferrocene-based metallomesogens with interesting structure, in which the ferrocenyl unit is connected as a terminal group onto a rod-like molecule composed of cholesteryl unit.

2. Synthesis and characterization

The methodology for the synthesis of the required intermediate for the preparation of the aforesaid ferrocene-based metallomesogens is depicted in Scheme 1.

Ferrocene was first converted to either 6-bromohexyloyl ferrocene (**2a**) or 11-bromodecyloyl ferrocene (**2b**) by treatment with respective acid chlorides in dry chloroform in the presence of anhydrous aluminum chloride. Compound **2a** or **2b** on treatment with zinc amalgam in the presence of concentrated hydrochloric acid in benzene–water under refluxing conditions afforded compound **3a** or **3b**. Compound **3a** or **3b** in turn was alkylated with *p*-hydroxybenzaldehyde in refluxing acetone in

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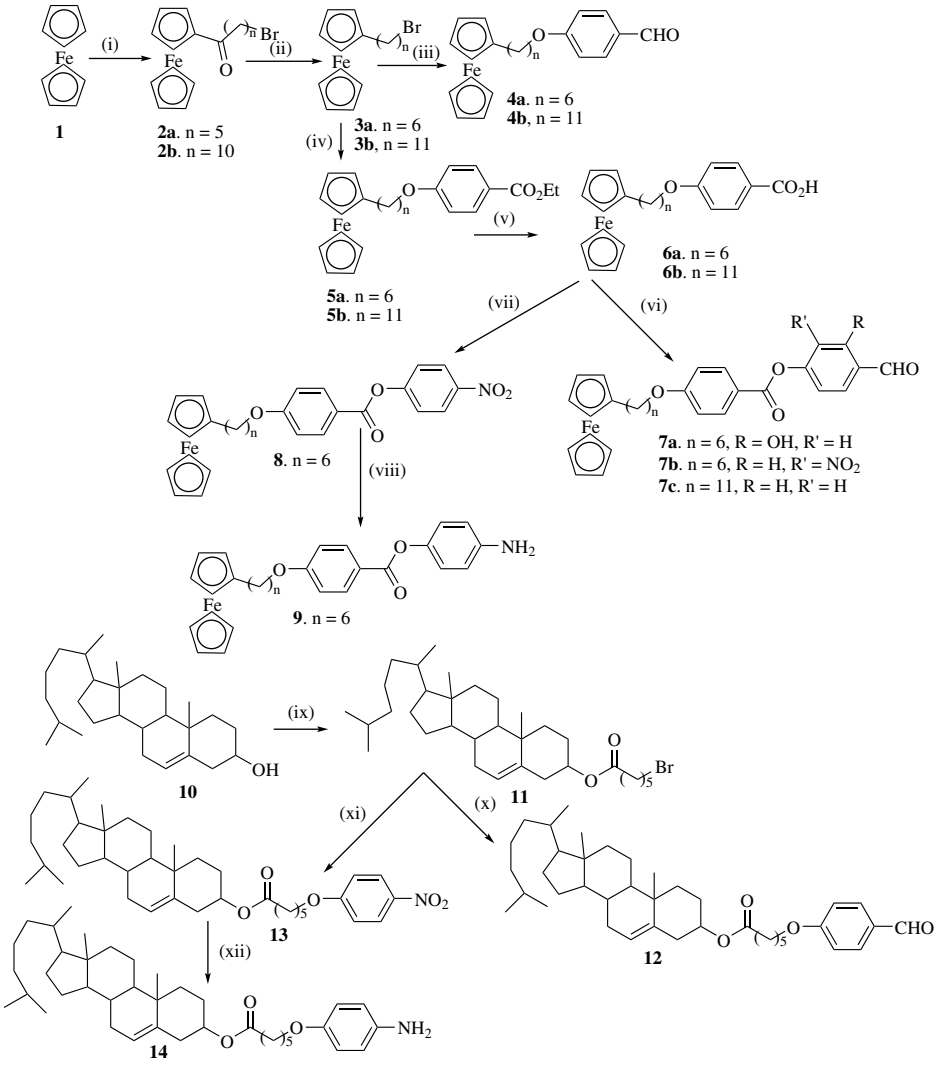
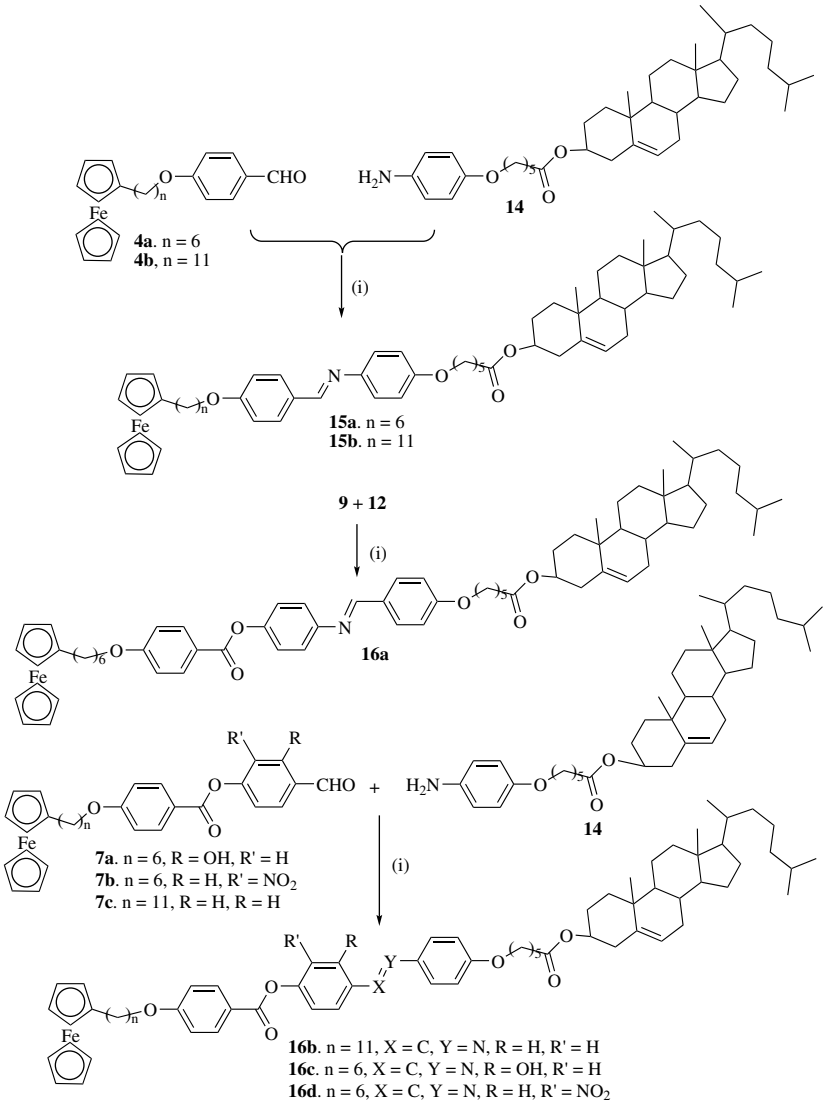


Scheme 1. Reagents and conditions: (i) 6-bromohexanoyl chloride/11-bromodecanoyl chloride, $AlCl_3$, $CHCl_3$, rt, 2h; (ii) Zn–Hg, concd HCl, benzene–water, reflux, 36–48 h; (iii) *p*-hydroxybenzaldehyde, acetone, K_2CO_3, reflux, 12 h; (iv) *p*-hydroxyethylbenzoate, acetone, K_2CO_3, reflux, 12 h; (v) C_2H_5OH, KOH, reflux, 2 h; (vi) *p*-hydroxybenzaldehyde/2,4-dihydroxybenzaldehyde/3-nitro-4-hydroxybenzaldehyde, DCC, DMAP, $CHCl_3$, rt, 2 h; (vii) *p*-nitrophenol, DCC, DMAP, $CHCl_3$, rt, 2 h; (viii) Pd–C, H_2, ethyl acetate, rt, 4 h; (ix) 6-bromohexanoyl chloride, THF, pyridine, rt, 12 h; (x) *p*-hydroxybenzaldehyde, acetone, K_2CO_3, reflux, 12 h; (xi) *p*-nitrophenol, acetone, K_2CO_3, reflux, 12 h, (xii) Pd–C, H_2, ethyl acetate, rt, 8 h.

the presence of anhydrous potassium carbonate to give the product **4a** or **4b**. On the other hand, compound **3a** or **3b** upon reaction with *p*-hydroxyethylbenzoate and anhyd potassium carbonate in refluxing acetone and subsequent hydrolysis of the resulting ester with ethanolic potassium hydroxide afforded the acid derivatives **6a** or **6b**. The acid derivatives on esterification with either *p*-nitrophenol or different hydroxybenzaldehydes give corresponding nitro derivative **8** or aldehyde derivatives **7a–c**. The nitro derivatives on reduction with hydrogen in the presence of palladised charcoal in ethyl acetate afforded corresponding amine derivative **9**. Reaction between cholesterol and 6-bromohexanoyl chloride in THF at room temperature gave the corresponding ester derivative **11**. The ester derivatives were then subjected to alkylation with *p*-hydroxybenzaldehyde and *p*-nitrophenol, respectively, in refluxing dry acetone in the presence of anhyd K_2CO_3 to afford the corresponding aldehyde **12** and nitro derivative **13** (Scheme 1). The nitro derivative on hydrogenation gave the corresponding amine derivative **14**. The aldehyde **12** and amine **14** derivatives on condensation with different amines and aldehydes afforded a series of compounds **15a**,**b** and **16a–d** (Scheme 2).

3. Results and discussion

All the intermediate compounds containing ferrocenyl moiety are non-mesomorphic in nature (**2–9**). Intermediate **11** is also non-mesomorphic. Compound **13** exhibits only the N* phase. The intermediate compounds **12** and **14** on slow cooling from the isotropic phase exhibit characteristic textures on N* phase, on further cooling homeotropic textures appears and it exists till room temperature for both the compounds. But on standing both the compounds solidify. The transition temperatures and associated enthalpy of all the final compounds obtained from their DSC thermogram (Figs. 1 and 2) are summarized in Table 1. Compound **15a** with two aromatic ring and a hexa-methylene spacer between phenyl ring and ferrocenyl unit exhibits two transitions in heating cycles and only one transition in cooling cycles in DSC experiment. On cooling the isotropic phase of compound **15a**, elliptical shape droplet is found to appear, which coalesces to form fan-like texture of cholesteric phase (in accordance with the reported texture for cholesteric phase). On very slow cooling of the sample it solidifies at about 75 °C in POM study. Compound **15a** on heating also exhibited typical oily-streak texture of N* phase. When hexa-methylene spacer of **15a** was replaced by



Scheme 2. Reagents and conditions: (i) C_2H_5OH, Cat. AcOH, reflux.

undeca-methylene spacer we observed another two transitions in heating as well as in cooling cycle. The first transition corresponds to crystal–crystal transition. On slow heating of compound **15b**, the filament texture of the TGB phase shown in Figure 3, grows slowly in the homeotropic regions of the SmA phase and ends up into a cholesteric phase with a fan-shaped texture (Fig. 4). Oily streaks are seen upon subjecting the preparation to mechanical stress. Compound **15b** when placed in thin cell with a cell gap of d=5±0.2 μm with homogenous planar boundary condition, texture for the cholesteric, TGB, and smectic phase (typical focal conic texture of SmA phase, Fig. 5) were observed.

The influence of orientation of the ester linkage, which diverts the electron delocalization and the coplanarity of the two aromatic rings of benzylideneaniline probably enhances the polarizability of the rigid core due to extended conjugation. This in turn enhances the preponderance of smectic phases and creates favorable packing condition. Furthermore, the presence of a long flexible spacer between phenyl ring and ferrocenyl unit in **15b** is primarily responsible for the formation of ordered phase, in the absence of a long flexible spacer only N* phase was observed. Introduction of another aromatic ring to the structure **15a** increases not only the melting and clearing temperatures but also increases the stability of N* phase over a wider temperature ranges. We then turn our attention to alternate the structure of **16a** by lateral introduction of groups like hydroxyl (**16c**) and nitro (**16d**) groups. Seemingly the salicyalaldimines and Schiff's base compounds virtually possess same transitional behavior with obvious exception that transition temperatures are higher for the former case due to the presence of intramolecular H-bonding compared to the latter. On the other hand introduction of nitro group to the lateral position decreases the melting and clearing temperatures dramatically compared to **16a**, and also reduces the thermal stability of the compound. Compound **16d** decomposes above the isotropic temperature. Both **16c** and **16d** possess only the N* phase over a wide temperature ranges (Figs. 6 and 7). However, introduction of an additional aromatic ring in structure **15b** suppresses the appearance of TGB phase but increases the stability of N* phase over a wide range of temperature. It also shows the textures of SmA phase underneath of N* phase (Fig. 8).

The diffraction diagram exhibits a sharp peak in the small angle region with 2θ=2.42 (d=36.38 Å) and a broad diffuse peak in the wide angle region centered at d-spacing of 5.19 Å. We also observed a diffuse peak in the low angle region in between 2θ=5–7.5 due to fluctuation of the holder, which was confirmed by taking the X-ray at same temperature in the absence of any samples. The sharp Bragg's reflection in the small angle region is due to one-dimensional

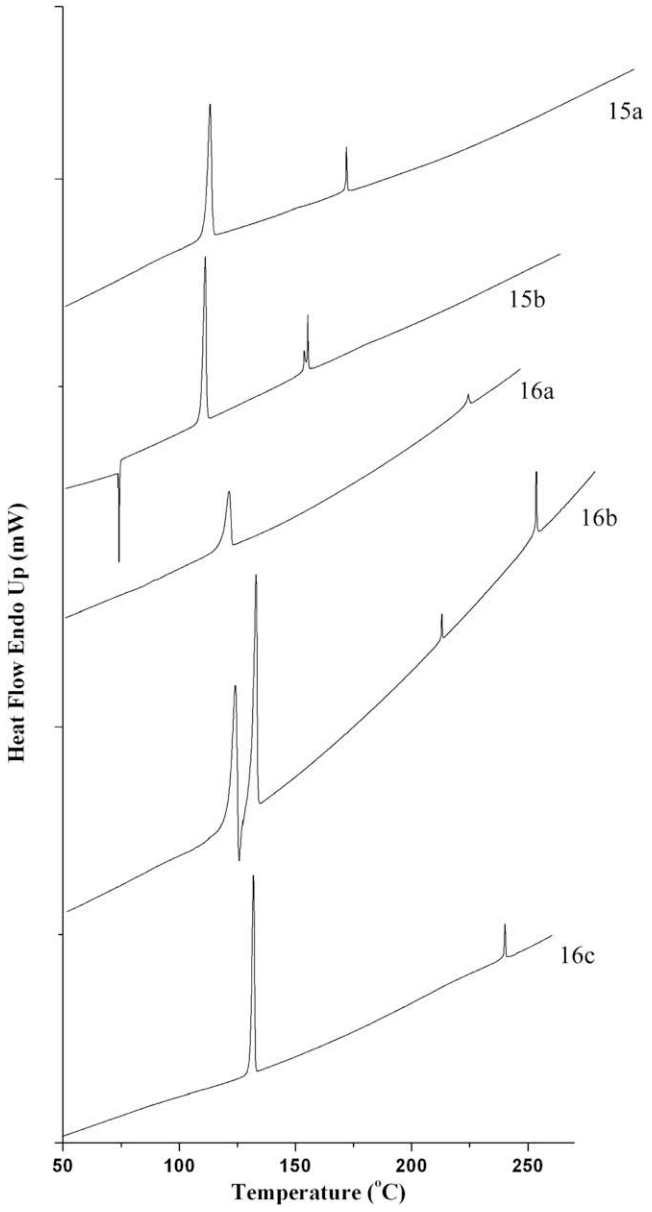


Figure 1. DSC thermogram in heating cycles.

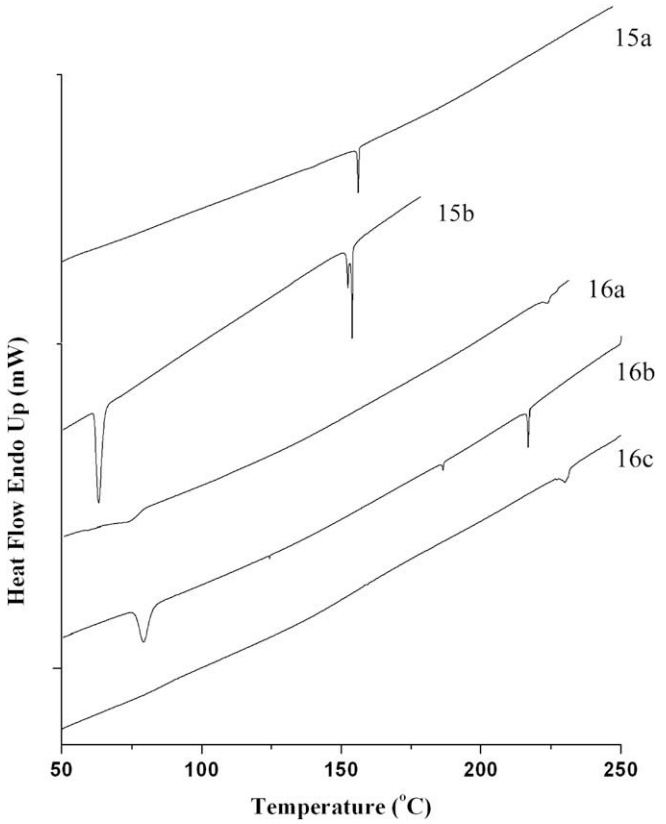


Figure 2. DSC thermogram in cooling cycles.

layering in the condensed SmA phase and a diffuse peak in the wide angle region is due to liquid-like correlation of the molecules. The calculated molecular length from molecular modeling is about 53.3 Å. Therefore, we expect a intercalated SmA phase. A schematic diagram of packing of molecules in smectic phase deduced from X-ray diffraction study is presented in Figure 9.

Compound **16b** however causes a severe damage to the holder after taking the X-ray at different temperatures; this may be due to the partial decomposition of the sample. So, it is not possible for us to know the layer arrangement of the SmA phase of the compound **15b**. Imrie and Loubser[6] synthesized a series of mono-substituted ferrocene derivatives with ester linkages. They observed that the size and shape of the aromatic core of the substituent on ferrocene play an important role in determining the thermal properties of these compounds. According to them minimum of three rings in the substituent core are necessary for stabilizing the nematic phase, but that four rings vastly enhance the nematic behavior. Seshadri and Haupt[8] reported a mono-substituted ferrocene-based metallomesogen with a chiral Schiff's base with long chiral smectic C (SmC*) phase domain, a TGBA phase in between SmA and N*, and a blue phase just before the clearing point, in spite of a bulky pendant ferrocene unit on the other side and a relatively small terminal group appended to the chiral center on the other side. Recently[32] they synthesized several mono-mesogens of ferrocene derivatives bearing *N*-benozyl-*N*′-arylthiourea (BATU) bidentate ligand, and a nonsymmetric dimesogen in which two structurally different mesogenic groups, namely the BATU and cholesteryl moieties, interlinked by a flexible spacer. The achiral mono-mesogens exhibit enantiotropic smectic C and nematic phases, while the chiral mono-mesogens show a cholesteric phase. The dimesogen, on the other hand, exhibits an enantiotropic cholesteric phase with selective reflection in the visible region with iridescent colors. We have also synthesized[14] cholesterol-based chiral dimer with mono-substituted ferrocene unit but unfortunately we did not observe any mesophase behavior. In conclusion we have synthesized a series of Schiff's base dimer with either varying the number of aromatic rings, the spacer between phenyl ring and ferrocenyl unit, introducing lateral substitution. Most of the dimers exhibit only an N* phase over a wide temperature ranges. One of the dimers shows interesting phase sequence of N*-TGB-SmA. Introduction of one aromatic ring to that dimer suppresses the formation of TGB phase. Appearance of TGB phase in the Schiff's base dimer with two aromatic rings is interesting. To the best of our knowledge there is no report for the appearances of such phase in mono-substituted ferrocene containing materials with two aromatic rings.

4. Experimental

4.1. General

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd or Spectrochem, India. Silica gel (60–120 mesh)

Table 1
Transition temperature (°C) and associated enthalpy (kJ/mol) calculated from DSC thermogram

15a* :

Cr $\xrightarrow[(36.8)]{113.6}$ N* $\xrightarrow[(3.0)]{157.5}$ I $\xrightarrow[(3.3)]{156.1}$ N*

15b :

Cr $\xrightarrow[(7.9)]{73.2}$ Cr_1 $\xrightarrow[(54.3)]{110.4}$ SmA $\xrightarrow[(....)]{152.2}$ TGB $\xrightarrow[(1.61)]{153.1}$ N* $\xrightarrow[(3.7)]{154.6}$ I $\xrightarrow[(4.0)]{153.8}$ N*

N* $\xrightarrow[(....)]{152.6}$ TGB $\xrightarrow[(1.4)]{152.2}$ SmA $\xrightarrow[(22.8)]{53.0}$ Cr'

16a :

Cr $\xrightarrow[(26.7)]{122.3}$ N* $\xrightarrow[(2.4)]{227.7}$ I $\xrightarrow[(1.0)]{223.4}$ N* $\xrightarrow[(6.4)]{73.7}$ Cr'

16b :

Cr $\xrightarrow[(30.4)]{124.2}$ Cr_1 $\xrightarrow[(35.9)]{130.6}$ SmA $\xrightarrow[(0.68)]{188.8}$ N* $\xrightarrow[(2.7)]{218.5}$ I $\xrightarrow[(2.7)]{216.8}$ N*

N* $\xrightarrow[(0.5)]{186.3}$ SmA $\xrightarrow[(13.6)]{124.2}$ Cr_1 $\xrightarrow[(18.7)]{79.1}$ Cr'

16c* :

Cr $\xrightarrow[(39.7)]{131.9}$ N* $\xrightarrow[(2.9)]{240.2}$ I $\xrightarrow[(2.5)]{229.8}$ N*

16d :**

Cr $\xrightarrow[(18.9)]{90.2}$ N* $\xrightarrow[(2.5)]{191.9}$ I

For both the compounds we did not observe N–Cr transitions in the cooling cycles of DSC experiments.
Compound **16d decomposes after isotropization both in POM and DSC, so we did not observe any transition in cooling cycles of DSC experiment.

was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60 °C and 80 °C. IR spectra were recorded on a Perkin–Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. ^1H NMR (400 MHz) spectra were recorded on a Bruker DPX-400 spectrometer or DPX-300 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. CHN was recorded on 2400 series II CHN analyzer Perkin Elmer from the Chemistry Department of Kalyani University. The liquid crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL attached with Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302 and the phase transitions were confirmed by differential scanning calorimetry (Perkin–Elmer Diamond DSC Pyris1 system)).

Powder X-ray diffraction was carried out on a Philips powder diffractometer, equipped with a temperature controller permitting low as well as high temperature operation as needed (with Cu Kα radiation of λ=1.5418 nm).

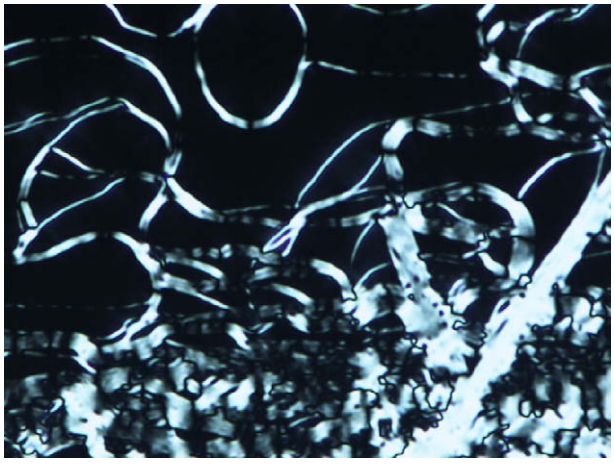


Figure 3. TGB phase of **15b** at 152.5 °C observed in thin cell with a cell gap of d=5±0.2.

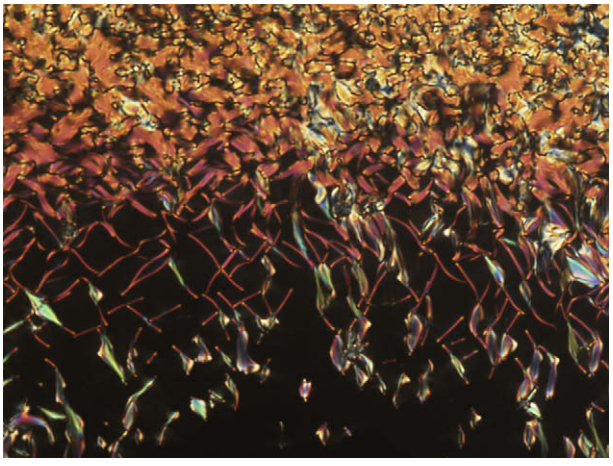


Figure 4. POM textures of **15b** at 152.2 °C.

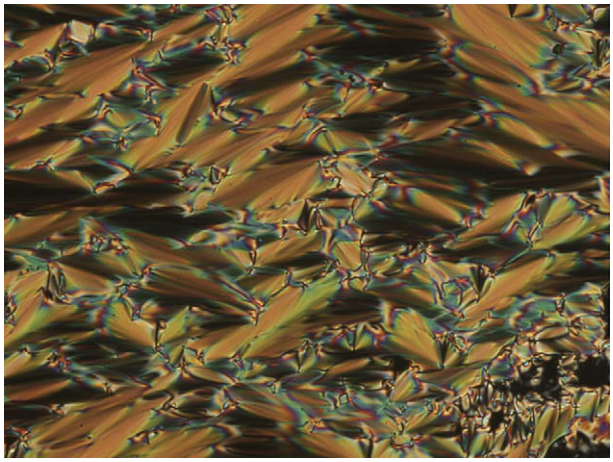


Figure 5. SmA of 15b at 150.4 °C observe in thin cell with a cell gap of $d=5\pm0.2$.

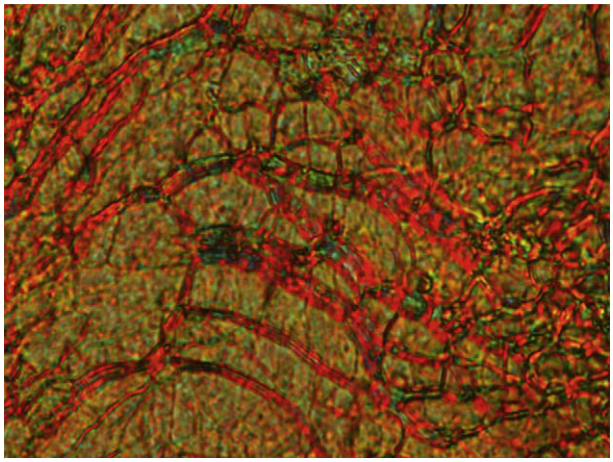


Figure 6. Oily-streak texture of **16c** at 225.2 °C.

4.2. Procedure for the preparation of intermediates 2a and 2b

To a mixture of 6-bromohexanoyl chloride (5.0 g, 23.41 mmol) and $AlCl_3$ (3.1 g, 23.41 mmol) in 50 ml $CHCl_3$ a solution of ferrocene (4.3 g, 23.41 mmol) in 50 ml $CHCl_3$ was added dropwise. After stirring for 2 h at room temperature, the reaction mixture was quenched with ice water (50 ml). The organic layer was separated, washed with dilute aqueous $NaHCO_3$ solution (2×25 ml), and dried over Na_2SO_4. The residue obtained after removing the solvent was

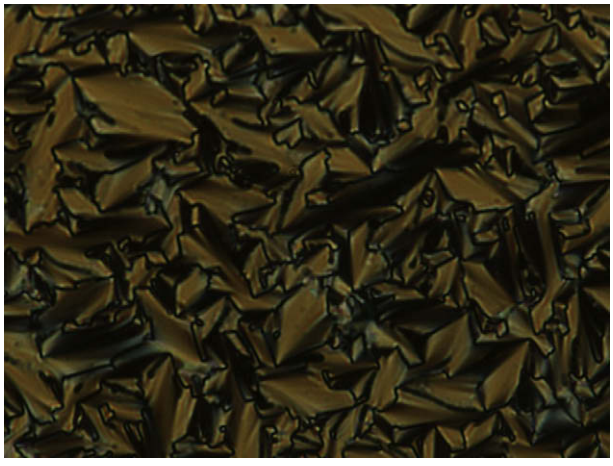


Figure 7. N* phase of **16d** at 152 °C.

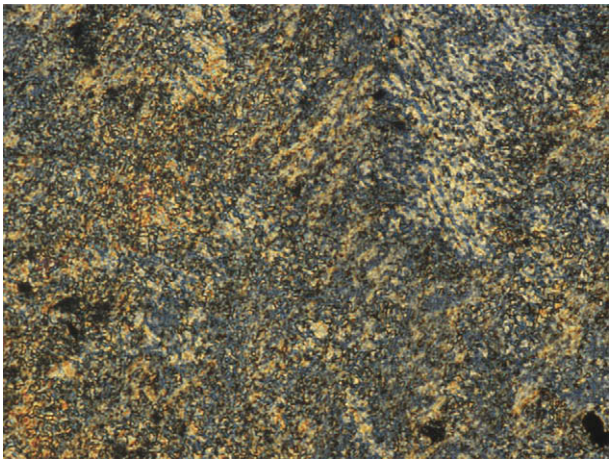


Figure 8. POM texture of **16b** at 175 °C.

subjected to column chromatography over silica gel using petroleum ether/ethyl acetate (99:1) as eluent to afford the product **2a**. The procedure for the preparation of compound **2b** was already reported.[32]

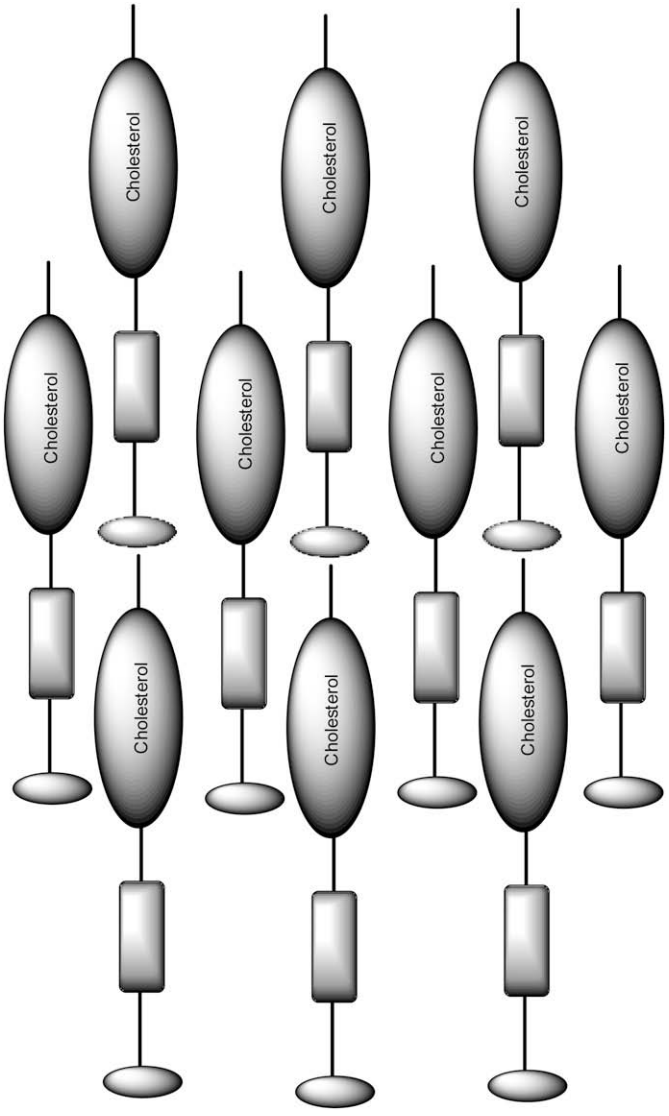


Figure 9. A schematic diagram of packing of molecules in smectic phase deduced from X-ray diffraction study.

*4.2.1. Compound **2a**.* Deep red liquid, yield 75%, R_f=0.7 (1% EtOAc/pet. ether), IR (KBr) ν_{max}: 3096, 2936, 1667, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 4.78 (2H, s, Ferrocenyl **H**), 4.50 (2H, s, Ferrocenyl **H**), 4.19 (5H, s, Ferrocenyl **H**), 3.44 (2H, t, *J* 7.1 Hz, C**H**$_2$Br), 2.72 (2H, t, *J* 7.8 Hz, C**H**$_2$), 1.92 (2H, quin, *J* 7.2 Hz, –CH_2–C**H**$_2$–CH_2), 1.50–1.73 (4H, m, aliphatic **H**); Anal. Calcd for $C_{16}H_{19}BrFeO$: C, 52.93; H, 5.27. Found: C, 53.20; H, 5.37%.

*4.2.2. Compound **2b**.* Ref. 32.

4.3. Procedure for preparation of intermediates 3a and 3b

A mixture of Zn (10.3 g, 16.51 mmol), $HgCl_2$ (0.8 g, 2.9 mmol), acetyl derivative **2a** (4 g, 11.01 mmol), and concentrated HCl (15 ml) in benzene/water mixture (20 ml each) was heated under reflux for 48 h. Then the mixture was filtered through filter paper and the filtrate was washed with water (2×10 ml). The residue obtained after removing the solvent was subjected to column chromatography over silica gel using petroleum ether/ethyl acetate (99:1) as eluent to afford the product **3a**. The procedure for the preparation of compound **3b** was already reported.[32]

*4.3.1. Compound **3a**.* Deep red liquid, yield 80%, R_f=0.75 (1% EtOAc/pet. ether), IR (KBr) ν_{max}: 3092, 2929, 2854, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 4.07 (5H, S, Ferrocenyl **H**), 4.02 (4H, S, Ferrocenyl **H**), 3.76 (2H, t, *J* 7.0 Hz, C**H**$_2$Br), 2.29 (2H, t, *J* 7.9 Hz, C**H**$_2$), 1.79–1.83 (2H, quin, *J* 7.2 Hz, –CH_2–C**H**$_2$–CH_2), 1.32–1.53 (6H, m, aliphatic **H**); Anal. Calcd for $C_{16}H_{21}BrFe$: C, 55.05; H, 6.06. Found: C, 55.20; H, 6.17%.

*4.3.2. Compound **3b**.* Ref. 32.

4.4. Procedure for preparation of intermediates 4a and 4b

A mixture of **3a** (1 g, 2.9 mmol), 4-hydroxybenzaldehyde (0.4 g, 3.3 mmol), K_2CO_3 (3.0 g) in 50 ml acetone was heated under reflux for 12 h. After removal of the solvent 25 ml water was added to the residue and the mixture was extracted with chloroform. The organic phase was washed with water (2×15 ml) and dried over Na_2SO_4. The residue obtained after removing the solvent was subjected to column chromatography over silica gel using petroleum ether/ethyl acetate (19:1) as eluent to afford the product **4a**. The other intermediate **4b** also prepared similarly.

*4.4.1. Compound **4a**.* Yellow solid, mp 80–82 °C; R_f=0.65 (5% EtOAc/pet. ether), ^1H NMR ($CDCl_3$, 300 MHz) 9.87 (1H, s, C**H**O), 7.80 (2H, d, *J* 8.4 Hz, Ar**H**), 6.97 (2H, d, *J* 8.4 Hz, Ar**H**), 4.08 (5H, s, Ferrocenyl **H**), 4.01–4.03 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 2.31 (2H, t, *J* 7.8 Hz, –C**H**$_2$), 1.76–1.83 (2H, quint, *J* 6.3 Hz, –CH_2–C**H**$_2$–CH_2), 1.39–1.63 (6H, m, aliphatic **H**); Anal. Calcd for $C_{23}H_{26}FeO_2$: C, 70.78; H, 6.71. Found: C, 70.90; H, 6.51%.

*4.4.2. Compound **4b**.* Yellow solid, mp 54–56 °C, R_f=0.7 (5% EtOAc/pet. ether), IR (KBr) ν_{max}: 3094, 2919, 2849, 1685, 1603 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 9.87 (1H, s, C**H**O), 7.81 (2H, d, *J* 7.5 Hz, Ar**H**), 6.97 (2H, d, *J* 7.5 Hz, Ar**H**), 4.08 (5H, s, Ferrocenyl **H**), 4.01–4.03 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 2.30 (2H, t, *J* 7.8 Hz, –C**H**$_2$), 1.29–1.81 (18H, m, aliphatic **H**); ^{13}C NMR ($CDCl_3$, 100 MHz) 190.8, 164.3, 132.0, 129.7, 114.7, 68.6, 68.4, 68.2, 68.1, 31.1, 29.7, 29.6, 29.5, 29.3, 29.0, 25.9; Anal. Calcd for $C_{28}H_{36}FeO_2$: C, 73.04; H, 7.88. Found: C, 73.24; H, 7.96%.

4.5. Procedure for preparation of intermediates 5a and 5b

A mixture of **3a** (1 g, 2.9 mmol), ethyl 4-hydroxyethylbenzoate (0.5 g, 3.2 mmol), K_2CO_3 (3.0 g) in 50 ml acetone was heated under reflux for 12 h. After removal of the solvent 25 ml water was added to the residue and the mixture was extracted with chloroform. The organic phase was washed with water (2×15 ml) and dried over Na_2SO_4. The residue obtained after removing the solvent was subjected to column chromatography over silica gel using petroleum ether/ethyl acetate (19:1) as eluent to afford the product **5a**. The procedure for the preparation of compound **5b** was already reported.[32]

*4.5.1. Compound **5a**.* Deep red liquid, yield 90%, R_f=0.7 (5% EtOAc/pet. ether), IR (KBr) ν_{max}: 3090, 2933, 1710, 1606, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 7.96 (2H, d, *J* 8.6 Hz, Ar**H**), 6.87 (2H, d, *J* 8.6 Hz, Ar**H**), 4.30 (q, 2H, *J* 7.1 Hz, –C**H**$_2$$CH_3$), 4.08 (5H, S, Ferrocenyl **H**), 3.97–4.03 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 2.30 (2H, t, *J* 7.8 Hz, –C**H**$_2$), 1.77–1.81 (2H, quin, *J* 7.4 Hz, –CH_2–C**H**$_2$–CH_2), 1.35–1.57 (9H, m, aliphatic **H**+–C**H**$_3$); Anal. Calcd for $C_{25}H_{30}FeO_3$: C, 69.13; H, 6.96. Found: C, 69.09; H, 7.06%.

*4.5.2. Compound **5b**.* Ref. 32.

4.6. Procedure for preparation of intermediates 6a and 6b

In a mixture of **5a** (0.9 g, 2.07 mmol) in 50 ml of alcohol, KOH (1 g) in 2 ml of water was added and the mixture was heated under reflux for 2 h. Dilute HCl was added gradually to the mixture in cold condition. The product **6a** is precipitated as yellow solid, which was filtered out from the mixture. The pure product was obtained after recrystallization from ethanol. The procedure for the preparation of compound **6b** was already reported.[32]

*4.6.1. Compound **6a**.* Yellow solid, mp 146–148 °C, yield 86%, IR (KBr) ν_{max}: 3075, 2942, 1680, 1605, 1577 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 8.02 (2H, d, *J* 8.5 Hz, Ar**H**), 6.90 (2H, d, 8.5 Hz, Ar**H**), 4.07 (5H, S, Ferrocenyl **H**), 3.99–4.03 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 2.31 (2H, t, *J* 7.8 Hz, –C**H**$_2$), 1.76–1.83 (2H, quin, *J* 6.7 Hz, –CH_2–C**H**$_2$–CH_2), 1.38–1.56 (6H, m, aliphatic **H**); Anal. Calcd for $C_{23}H_{26}FeO_3$: C, 67.99; H, 6.45. Found: C, 68.19; H, 6.60%.

*4.6.2. Compound **6b**.* Ref. 32.

4.7. Procedure for preparation of intermediates 8 and 7a–c

A mixture of acid **6a** (0.4 g, 0.9 mmol), 4-nitrophenol (0.16 g, 1.18 mmol) or 2,4-dihydroxybenzaldehyde (0.2 g, 1.47 mmol) or 3-nitro-4-hydroxybenzaldehyde (0.197 g, 1.17 mmol), DCC (0.3, 1.47 mmol) and catalytic amount of DMAP in 50 ml dry DCM was stirred at room temperature for 2 h. The residue left after removal of the solvent was subjected to column chromatography over silica gel using petroleum ether/ethyl acetate (9:1) as eluent to afford either the product **8** or **7a** or **7b**. The procedure for the preparation of compound **7c** was already reported.[32]

*4.7.1. Compound **8**.* Yellow solid, mp 94–96 °C, yield 84%, R_f=0.55 (10% EtOAc/pet. ether), IR (KBr) ν_{max}: 3083, 2936, 1739, 1605, 1589, 1489, 1343 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 8.29 (2H, d, *J* 8.9 Hz, Ar**H**), 8.11 (2H, d, *J* 8.6 Hz, Ar**H**), 7.38 (2H, d, *J* 8.9 Hz, Ar**H**), 6.96 (2H, d, 8.6 Hz, Ar**H**), 4.08 (5H, S, Ferrocenyl **H**), 4.03–4.06 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 2.31 (2H, t, *J* 7.8 Hz, –C**H**$_2$), 1.80–1.84 (2H, quin, *J* 7.3 Hz, –CH_2–C**H**$_2$–CH_2), 1.39–1.55 (6H, m, aliphatic **H**); ^{13}C NMR ($CDCl_3$, 100 MHz) 164.0, 163.9, 155.9, 145.2, 132.5, 125.2, 122.7, 120.4, 114.5, 69.3, 68.7, 68.4, 67.7, 31.0, 29.5, 29.3, 29.0, 25.9; Anal. Calcd for $C_{29}H_{29}FeNO_5$: C, 66.04; H, 5.54; N, 2.66. Found: C, 66.29; H, 5.60; N, 2.49%.

*4.7.2. Compound **7a**.* Yellow solid, mp 88–90 °C, R_f=0.65 (10% EtOAc/pet. ether), IR (KBr) ν_{max}: 3327, 2927, 2851, 1738, 1658,

1604 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 9.88 (1H, s, C**H**O), 8.10 (2H, d, *J* 8.1 Hz, Ar**H**), 7.59 (1H, d, *J* 8.1 Hz, Ar**H**), 6.87–6.98 (5H, m, Ar**H**+O**H**), 4.09 (5H, s, Ferrocenyl **H**), 4.01–4.04 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 2.32 (2H, t, *J* 7.2 Hz, –C**H**$_2$), 1.17–1.94 (8H, m, aliphatic **H**); yield 80%, ^{13}C NMR ($CDCl_3$, 100 MHz) 195.5, 163.9, 163.2, 157.9, 134.9, 132.5, 120.7, 118.6, 114.4, 114.2, 110.9, 68.6, 68.4, 68.3, 69.0, 67.8, 67.7, 67.0, 33.9, 31.2, 31.0, 29.5, 29.3, 29.0, 25.9, 25.6, 24.9; Anal. Calcd for $C_{30}H_{30}FeO_5$: C, 68.45; H, 5.74. Found: C, 68.13; H, 5.84%.

4.7.3. Compound ***7b***. Gummy mass, yield 75%, R_f=0.7 (10% EtOAc/pet. ether), IR (KBr) ν_{max}: 3083, 2929, 1744, 1704, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 10.54 (1H, S, –C**H**O), 8.57 (1H, S, Ar**H**), 8.11–8.19 (3H, m, Ar**H**), 7.57 (1H, d, *J* 7.8 Hz, Ar**H**), 6.97 (2H, d, *J* 7.8 Hz, Ar**H**), 4.08 (5H, S, Ferrocenyl **H**), 4.03–4.04 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 1.08–2.34 (10H, m, aliphatic **H**); Anal. Calcd for $C_{30}H_{29}FeNO_6$: C, 64.88; H, 5.26; N, 2.52. Found: C, 64.99; H, 5.29; N, 2.57%.

4.7.4. Compound ***7c***. Ref. 32.

4.8. Procedure for preparation of intermediate 9

The nitro derivative **8** (0.3 g, 0.6 mmol) was dissolved in 25 ml ethyl acetate and 15 mg of 10% Pd/C was added and stirred under hydrogen atmosphere for 4 h and filtered through Celite to remove the catalyst. The residue left after removal of the solvent was subjected to column chromatography over silica gel using petroleum ether/ethyl acetate (5:1) as eluent to afford either the product **9**.

4.8.1. Compound ***9***. Yellow solids, mp 96–98 °C, yield 95%, R_f=0.5 (20% EtOAc/pet. ether), IR (KBr) ν_{max}: 3380, 3309, 2921, 1717, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 8.09 (2H, d, *J* 8.7 Hz, Ar**H**), 6.95 (2H, d, *J* 8.6 Hz, Ar**H**), 6.93 (2H, d, *J* 8.7 Hz, Ar**H**), 6.68 (2H, d, 8.6 Hz, Ar**H**), 4.08 (5H, S, Ferrocenyl **H**), 4.00–4.04 (6H, m, Ferrocenyl **H**+–OC**H**$_2$), 3.63 (2H, broad s, N**H**$_2$) 2.31 (2H, t, *J* 7.8 Hz, –C**H**$_2$), 1.79–1.82 (2H, quin, *J* 7.3 Hz, –CH$_2$–C**H**$_2$–CH$_2$), 1.39–1.55 (6H, m, aliphatic **H**); ^{13}C NMR ($CDCl_3$, 100 MHz) 165.6, 163.3, 144.2, 143.2, 132.2, 122.4, 121.9, 115.7, 114.3, 68.5, 68.2, 68.1, 67.0, 31.1, 29.6, 29.3, 29.1, 25.9; Anal. Calcd for $C_{29}H_{31}FeNO_3$: C, 70.03; H, 6.28; N, 2.82. Found: C, 70.23; H, 6.24; N, 2.90%.

4.9. Procedure for preparation of intermediates 11–14

Procedure for preparation of all the compounds and respective data were already reported.[14]

4.10. General procedure for the Schiff's base formation 15a,b and 16a–d

4.10.1. Compound ***15a***. A mixture of **4a** (0.10 g, 0.25 mmol) and **14** (0.15 g, 0.25 mmol) was refluxed in absolute ethanol (10 ml) in the presence of a catalytic amount of glacial acetic acid for 3 h. The Schiff's base **15a** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, and dried in vacuum.

Yellow solids, yield 96%, $[\alpha_D]^{\lambda=589nm}$=−4.90 at *C*=1% solution in $CHCl_3$ at 26.8 °C, IR (KBr) ν_{max}: 2923, 2851, 1730, 1621, 1609 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 8.38 (1H, s, C**H**=N), 7.79 (2H, d, *J* 8.7 Hz, Ar**H**), 7.16 (2H, d, *J* 8.8 Hz, Ar**H**), 6.93 (2H, d, *J* 8.7 Hz, Ar**H**), 6.87 (2H, d, *J* 8.8 Hz, Ar**H**), 5.36 (1H, d, *J* 4.0 Hz, =C**H**), 4.59–4.62 (1H, m, OC**H**), 4.11 (3H, s, Ferrocenyl **H**), 3.98–4.08 (6H, m, Ferrocenyl **H**), 3.94 (2H, t, *J* 6.4 Hz, OC**H**$_2$), 0.66–2.34 (63H, m, aliphatic and cholesteric protons are overlapped); ^{13}C NMR ($CDCl_3$, 100 MHz) 173.0, 161.6, 157.8, 157.4, 145.0, 139.7, 130.3, 129.1, 122.6, 122.0, 114.9, 114.7, 73.8, 68.6, 68.2, 68.1, 67.9, 67.1, 56.7, 56.1, 50.0, 42.3, 39.74, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.8, 31.0, 29.5, 29.3, 29.1, 29.0, 28.2, 28.0, 27.8, 25.9, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9; Anal. Calcd for $C_{62}H_{85}FeNO_4$: C, 77.23; H, 8.89; N, 1.45. Found: C, 77.50; H, 8.99; N, 1.30%.

4.10.2. Compound ***15b***. A mixture of **4b** (0.10 g, 0.22 mmol) and **14** (0.13 g, 0.22 mmol) was refluxed in absolute ethanol (10 ml) in the presence of a catalytic amount of glacial acetic acid for 3 h. The Schiff's base **15b** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, and dried in vacuum.

Yellow solids, yield 90%, $[\alpha_D]^{\lambda=589nm}$=−4.86 at *C*=1% solution in $CHCl_3$ at 26.8 °C, IR (KBr) ν_{max}: 2921, 2853, 1729, 1620, 1608 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 8.39 (1H, s, C**H**=N), 7.80 (2H, d, *J* 8.7 Hz, Ar**H**), 7.17 (2H, d, *J* 8.8 Hz, Ar**H**), 6.94 (2H, d, *J* 8.7 Hz, Ar**H**), 6.88 (2H, d, *J* 8.8 Hz, Ar**H**), 5.36 (1H, d, *J* 4.7 Hz, =C**H**), 4.58–4.65 (1H, m, OC**H**), 4.08 (3H, s, Ferrocenyl **H**), 3.99–4.04 (6H, m, Ferrocenyl **H**), 3.96 (2H, t, *J* 6.4 Hz, OC**H**$_2$), 0.67–2.33 (73H, m, aliphatic and cholesteric protons are overlapped); ^{13}C NMR ($CDCl_3$, 100 MHz) 173.0, 161.6, 157.8, 157.4, 145.0, 139.7, 130.3, 129.2, 122.6, 122.0, 114.9, 114.6, 73.8, 68.6, 68.2, 68.1, 67.9, 67.1, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.8, 31.1, 29.7, 29.6, 29.4, 29.2, 29.0, 28.2, 28.0, 27.8, 26.0, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9; Anal. Calcd for $C_{67}H_{95}FeNO_4$: C, 77.80; H, 9.26; N, 1.35. Found: C, 77.98; H, 9.50; N, 1.45%.

4.10.3. Compound ***16a***. A mixture of **9** (0.10 g, 0.26 mmol) and **12** (0.16 g, 0.26 mmol) was refluxed in absolute ethanol (10 ml) in the presence of a catalytic amount of glacial acetic acid for 3 h. The Schiff's base **16a** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, and dried in vacuum.

Yellow solids yield 92%, $[\alpha_D]^{\lambda=589nm}$=−10.14 at *C*=1% solution in $CHCl_3$ at 26.6 °C, IR (KBr) ν_{max}: 2933, 2865, 1727, 1620, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) 8.48 (1H, s, C**H**=N), 8.12 (2H, d, *J* 8.8 Hz, Ar**H**), 7.92 (2H, d, *J* 8.6 Hz, Ar**H**), 7.29 (2H, d, *J* 8.6 Hz, Ar**H**), 7.20 (2H, d, *J* 8.8 Hz, Ar**H**), 6.95 (2H, d, *J* 8.9 Hz, Ar**H**), 6.89 (2H, d, *J* 8.8 Hz, Ar**H**), 5.35 (1H, d, *J* 3.8 Hz, =C**H**), 4.61–4.62 (1H, m, OC**H**), 4.02–4.07 (9H, m, Ferrocenyl **H**), 3.95 (2H, t, *J* 6.4 Hz, OC**H**$_2$), 0.66–2.33 (63H, m, aliphatic and cholesteric protons are overlapped); ^{13}C NMR ($CDCl_3$, 100 MHz) 173.0, 165.0, 163.5, 159.9, 148.9, 139.6, 132.3, 132.1, 132.0, 130.7, 122.6, 122.4, 121.8, 121.5, 114.7, 114.3, 114.2, 78.8, 69.5, 68.9, 68.3, 68.0, 67.9, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.5, 31.9, 31.8, 31.0, 29.5, 29.3, 29.0, 28.9, 28.7, 28.2, 28.0, 27.8, 25.9, 25.6, 24.7, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.9; Anal. Calcd for $C_{69}H_{89}FeNO_6$: C, 76.43; H, 8.27; N, 1.29. Found: C, 76.70; H, 8.48; N, 1.40%.

4.10.4. Compound ***16b***. A mixture of **7c** (0.10 g, 0.17 mmol) and **14** (0.1 g, 0.17 mmol) was refluxed in absolute ethanol (10 ml) in the presence of a catalytic amount of glacial acetic acid for 3 h. The Schiff's base **16b** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, and dried in vacuum.

Pale yellow solids yield 92%, $[\alpha_D]^{\lambda=589nm}$=−10.60 at *C*=1% solution in $CHCl_3$ at 26.6 °C, IR (KBr) ν_{max}: 2934, 2863, 1728, 1622, 1604 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 8.48 (1H, s, C**H**=N), 8.13 (2H, d, *J* 8.9 Hz, Ar**H**), 7.94 (2H, d, *J* 8.6 Hz, Ar**H**), 7.30 (2H, d, *J* 8.6 Hz, Ar**H**), 7.21 (2H, d, *J* 8.8 Hz, Ar**H**), 6.96 (2H, d, *J* 8.9 Hz, Ar**H**), 6.90 (2H, d, *J* 8.8 Hz, Ar**H**), 5.36 (1H, d, *J* 4.7 Hz, =C**H**), 4.59–4.63 (1H, m, OC**H**), 4.08 (3H, s, Ferrocenyl **H**), 4.02–4.06 (6H, m, Ferrocenyl **H**), 3.97 (2H, t, *J* 6.4 Hz, OC**H**$_2$), 0.67–2.33 (73H, m, aliphatic and cholesteric protons are overlapped); ^{13}C NMR ($CDCl_3$, 100 MHz) 173.3, 164.3, 163.7, 157.9, 157.0, 153.2, 144.5, 139.7, 134.0, 132.3, 129.7,

122.60, 122.2, 121.2, 115.0, 114.3, 73.7, 68.5, 68.3, 68.2, 68.1, 67.0, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.7, 31.9, 31.8, 31.1, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.2, 28.0, 27.8, 26.0, 25.9, 25.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9; Anal. Calcd for $C_{74}H_{99}FeNO_6$: C, 76.99; H, 8.64; N, 1.21. Found: C, 77.22; H, 8.48; N, 1.43%.

4.10.5. Compound ***16c****.* A mixture of **7a** (0.10 g, 0.19 mmol) and **14** (0.11 g, 0.19 mmol) was refluxed in absolute ethanol (10 ml) in the presence of a catalytic amount of glacial acetic acid for 3 h. The Schiff's base **16c** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, and dried in vacuum.

Yellow solids yield 92%, $[\alpha_D]^{\lambda=589nm}=-7.12$ at $C=1\%$ solution in $CHCl_3$ at 26.0 °C, IR (KBr) ν_{max}: 2936, 2862, 1729, 1622, 1607 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 13.80 (1H, s, O**H**), 8.60 (1H, s, C**H**=N), 8.11 (2H, d, *J* 7.0 Hz, Ar**H**), 7.38 (1H, d, *J* 8.5 Hz, Ar**H**), 7.24 (1H, d, *J* 8.7 Hz, Ar**H**), 6.91–6.97 (5H, m, Ar**H**), 6.85 (1H, d, *J* 2.2 Hz, Ar**H**), 6.78 (1H, dd, *J* 8.5, 2.2 Hz, Ar**H**), 5.36 (1H, d, *J* 4.7 Hz, =C**H**), 4.59–4.63 (1H, m, OC**H**), 4.07 (3H, s, Ferrocenyl **H**), 4.02–4.05 (6H, m, Ferrocenyl **H**), 3.96 (2H, t, *J* 6.4 Hz, OC$\mathbf{H}_2$), 0.66–2.35 (63H, m, aliphatic and cholesteric protons are overlapped); ^{13}C NMR ($CDCl_3$, 100 MHz) 173.0, 164.4, 163.6, 159.4, 158.4, 153.7, 145.8, 143.3, 140.8, 139.6, 132.8, 132.4, 125.7, 122.6, 122.3, 121.3, 115.2, 114.3, 113.0, 73.8, 69.6, 68.3, 67.9, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.8, 30.9, 29.5, 29.3, 29.0, 28.9, 28.2, 28.0, 27.8, 25.9, 26.6, 24.8, 24.3, 23.8, 22.5, 21.0, 19.3, 18.7, 11.8; Anal. Calcd for $C_{69}H_{89}FeNO_7$: C, 75.32; H, 8.15; N, 1.27. Found: C, 75.62; H, 8.40; N, 1.42%.

4.10.6. Compound ***16d****.* A mixture of **7b** (0.10 g, 0.23 mmol) and **14** (0.13 g, 0.23 mmol) was refluxed in absolute ethanol (10 ml) in the presence of a catalytic amount of glacial acetic acid for 3 h. The Schiff's base **16d** was precipitated out from reaction mixture. It was collected, washed repeatedly with hot ethanol, and dried in vacuum.

Brown solids, yield 94%, $[\alpha_D]^{\lambda=589nm}=-7.82$ at $C=1\%$ solution in $CHCl_3$ at 26.7 °C, IR (KBr) ν_{max}: 2936, 2864, 1725, 1625, 1604 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): 8.59 (1H, d, *J* 2.0 Hz), 8.52 (1H s), 8.11 (1H, dd, *J* 8.5, 2.0 Hz), 8.12 (2H, d, *J* 8.8 Hz), 7.46 (1H, d, *J* 8.4 Hz), 7.26 (1H, d, *J* 8.9 Hz), 6.96 (2H, d, *J* 8.8 Hz), 6.91 (2H, d, *J* 8.9 Hz), 5.35 (1H, d, *J* 4.5 Hz), 4.57–4.65 (1H, m), 4.07 (3H, s), 4.03–4.06 (6H, m), 3.97 (2H, t, *J* 6.4 Hz), 0.66–2.36 (63H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) 173.0, 164.1, 163.8, 158.5, 153.7, 145.9, 143.4, 142.42, 139.7, 135.2, 133.4, 132.8, 125.8, 125.5, 122.65, 122.5, 120.1, 115.0, 114.6, 73.8, 68.3, 67.9, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.6, 31.9, 31.8, 31.0, 29.5, 29.2, 29.0, 28.9, 28.2, 28.0, 27.8, 25.9, 25.6, 24.8, 24.3, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8; Anal. Calcd for $C_{69}H_{88}FeN_2O_8$: C, 73.39; H, 7.85; N, 2.48. Found: C, 73.63; H, 8.03; N, 2.63%.

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