Synthesis and Characterization of Ferrocene Derivatives Containing Hydroquinone Unit Exhibiting Mesomorphism

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ABSTRACT

Hydroquinone containing ferrocene derivatives (10a-10d) were synthesized characterized and have been evaluated for their liquid crystalline property by polarizing optical microscopy and differential scanning calorimetry. Compound 10c was found to be mesomorphic while compounds 10a, 10b and 10d were nonmesomorphic.

Keywords: Ferrocene, Hydroquinone, Liquid Crystal, Ferrocenomesogens, Polarizing Optical Microscopy (POM).

INTRODUCTION

Liquid crystals are the materials which are known to exhibit intermediate phases between solid and liquid. These materials have the ability to show the collective properties of both crystalline and liquid state [1]. During last two decades liquid crystalline materials have given an access to the large number of applications to scientific and industrial research [2], which includes liquid crystal displays [3-5], temperature measurement [3-7], advanced materials [8], biological membranes [9,10]. The most common applications of liquid crystal materials is in display devices such as laptops, watches, computer screens, car, aircraft and ship in instruments and word processors etc. [11].

Metallomesogens are mesogenic molecules that contain metal atom in its moiety [12], if such molecules contain ferrocene they are termed as ferrocenomesogens [13]. Metallomesogens bring additional properties to the liquid crystalline materials such as color, optical, electric, and magnetic, as compared to their organic counterpart [14, 15].

Due to remarkable thermal stability and aromaticity, ferrocene based liquid crystalline materials are very interesting. Due to easy solubility in common organic solvents makes their characterization is easy. Large number of ferrocene derivatives can be easily synthesized due to its three dimensional structure [13, 16]. Ferrocene based liquid crystalline compounds can be used in various applications such as information storage and ferroelectric devices [17, 18], switchable anisotropic materials [19], ferrocene based sensors.
Heterocyclic based ferrocenomesogens can exhibit strong fluorescence along with light emitting properties [22]. Due to switchable oxidation-reduction properties of ferrocene switchable ferrocenomesogens can be easily prepared [23, 24]. Due to the wide range of applications it is of interest to prepare newer derivatives of ferrocenomesogens having specific electrophysical and magnetophysical properties [25-28].

**MATERIALS AND METHODS**

All reactions were carried out in oven-dried glassware under argon atmosphere unless otherwise stated. $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded on Bruker AVANCE spectrometer (Bruker BioSpin AG, Fällanden, Switzerland; 300 MHz) using CDCl$_3$ ($\delta$ 7.26 for $^1$H) and ($\delta$ 77.5/77.4 for $^{13}$C) as solvent and TMS as an internal standard. The peak multiplicities are given as follows: s = singlet; d = doublet; dd = doublet of doublet; t = triplet; m = multiplet. Chemical shifts ($\delta$) are given in ppm relative to TMS, coupling constants ($J$) in Hz. UV spectra were scanned on Shimadzu 240 PC and Shimadzu 2450, Japan, Spectrophotometer. HRMS spectra were recorded on positive ion electrospray ionisation (ESI) mode. FT-Infrared spectra were recorded on a Perkin Elmer (Model-Frontier) spectrometer (Waltham, MA, USA). Mesomorphic nature was investigated by DSC analysis (Mettler-Toledo AG Analytical, Schwerzenbach, Switzerland) under a nitrogen atmosphere, with samples measured in closed-lid aluminum pans and POM using Mettler Toledo FP90 heating stage containing temperature control unit in conjunction with a Carl Zeiss polarizing optical microscope (Carl Zeiss MicroImaging GmbH, Koenigsallee, Goettingen, Germany). Silica gel of commercial source (60-120 mesh) was used in column chromatography. Unless otherwise stated, materials obtained from commercial suppliers were used without further purification. Dichloromethane (DCM) was dried using calcium hydride. All reactions involving N, N’-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were performed under dry atmosphere.

**Synthesis of compounds:**

Compound 2 has been synthesized as per literature procedure [35].

**Synthesis of compound 3:** 4-Ferrocenylphenol (2) (5.00 g, 17.98 mmol) and p-nitro chlorobenzene (2.82 g, 17.98 mmol), potassium carbonate (6.21 g, 44.96 mmol) and dimethylformamide (50 mL) were charged in a round bottom flask under stirring, the reaction mass was then refluxed at 153°C for 5h. The progress of the reaction was monitored by TLC, after completion of the reaction, the reaction mass was then quenched in (100 mL) deionized water. The solid obtained was thus isolated by filtration. This solid was then purified by column chromatography using silica gel adsorbent. Elution with mixture of benzene (2.82 g) and chloroform (80:20) followed by distillation for recovery of solvent gave a red crystalline solid of 1-nitro-4-(4-ferrocenylphenoxy)-benzene (3) (4.74g, yield: 71.5 %), m.p. 114-116°C.

**Synthesis of compound 4:** In a round bottom flask 1-nitro-4-(4-ferrocenylphenoxy)-benzene (3) (4.00 g, 10.02 mmol) and (40 mL) of 95% ethanol was placed, and then the reaction mixture was warm at 50°C on steam bath. 0.1 g of 10% Pd/C (as a catalyst previously moistened with alcohol) was added, after that about 5 mL of hydrazine hydrate was added by using dropping funnel over a period of 30 min. at this point an additional 0.05 g. of catalyst (previously moistened with alcohol) was added and reaction mixture was refluxed for 3h. The catalyst was removed by filtration with gentle suction through a thin layer of celite. The catalyst and celite was washed several times by hot ethanol. Combined filtrate was concentrated under reduced pressure, and then 150 mL of water was added and reaction mixture was extracted with ethyl acetate (3X50 mL), the ethyl acetate extract was then dried over anhydrous sodium sulphate and then concentrate under reduced pressure to afforded red crystals of 4-(4-ferrocenylphenoxy) aniline (4) (3.55g, yield: 95.0 %), m.p. 158-160°C.

**Synthesis of compound 7a-7d (General Procedure):** Hydroquinone (5) (29.2 mmol), n-alkyl bromides (6a-6d) (29.2 mmol) and KHCO$_3$ (29.2 mmol) were stirred in DMF (100 mL) for 3h under reflux. The

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mixture was then cooled to 0°C and poured into an aqueous solution of hydrochloric acid (6N, 100 mL). The mixture was extracted with dichloromethane (3X50 ml) and then the combined organic layers were concentrated in vacuo and purified by column chromatography using silica gel adsorbent. Elution with mixture of petroleum ether (60-80°) and chloroform (80:20) followed by distillation for recovery of solvent to give a white solid of 4-(n-alkoxy) phenols (7a-7d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R=CₙH₂ₙ₊₁ Where n=</th>
<th>Yield (%)</th>
<th>m. p.(°C) [Ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>12</td>
<td>45</td>
<td>77-79°C [31]</td>
</tr>
<tr>
<td>7b</td>
<td>14</td>
<td>47</td>
<td>76-78°C [31]</td>
</tr>
<tr>
<td>7c</td>
<td>16</td>
<td>49</td>
<td>86-87°C [33]</td>
</tr>
<tr>
<td>7d</td>
<td>18</td>
<td>50</td>
<td>91-92°C [33]</td>
</tr>
</tbody>
</table>

Synthesis of compound 9a-9d (General Procedure): 4-(n-alkoxy) phenols (7a-7d) (7.18 mmol) and 4-formylbenzoic acid (8) (7.18 mmol) and a catalytic amount of DMAP, was taken in 100 mL anhydrous CH₂Cl₂, and to this solution (8.62 mmol) DCC dissolved in 20 mL anhydrous CH₂Cl₂ was added. The reaction mixture was stirred at room temperature for 24 h. After the completion of reaction, dicyclohexylurea was filtered off and the solution was concentrated i in vacuo at 30°C. The white residue thus obtained was purified by column chromatography using silica gel adsorbent. Elution with mixture of petroleum ether (60-80°) and chloroform (80:20) followed by distillation for recovery of solvent gave an white solid of 4-(alkoxy)phenyl 4-formylbenzoates (9a-9d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R=CₙH₂ₙ₊₁ Where n=</th>
<th>Yield (%)</th>
<th>m. p.(°C) [Ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>12</td>
<td>80.0</td>
<td>106-107°C [31]</td>
</tr>
<tr>
<td>9b</td>
<td>14</td>
<td>81.0</td>
<td>111-113°C [31]</td>
</tr>
<tr>
<td>9c</td>
<td>16</td>
<td>80.2</td>
<td>98-100°C</td>
</tr>
<tr>
<td>9d</td>
<td>18</td>
<td>80.0</td>
<td>110-112°C</td>
</tr>
</tbody>
</table>

Synthesis of compound 10a-10d (General Procedure): 4-(4-ferrocenylphenoxy)aniline (4) (2.70 mmol) and 4-(alkoxy)phenyl 4-formylbenzoxoates (9a-9d) (2.70 mmol) was taken in a round bottom flask containing 100mL of methanol. To this solution, a few drops of glacial acetic acid were added. The solution was refluxed with stirring for 6h, after the completion of reaction the mixture was filtered while hot and the solid was washed on filter with hot methanol for several times. The resulting solid was recrystallized from methanol, to obtained an pale yellow solid of 4-(alkoxy)phenyl 4-(4-ferrocenylphenoxy)phenyl(imino)methylbenzoates (10a-10d).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R=CₙH₂ₙ₊₁ Where n=</th>
<th>Yield (%)</th>
<th>m. p.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>12</td>
<td>74.3</td>
<td>168-170°C</td>
</tr>
<tr>
<td>10b</td>
<td>14</td>
<td>75.0</td>
<td>156-158°C</td>
</tr>
<tr>
<td>10c</td>
<td>16</td>
<td>75.6</td>
<td>137-139°C</td>
</tr>
<tr>
<td>10d</td>
<td>18</td>
<td>75.0</td>
<td>134-136°C</td>
</tr>
</tbody>
</table>

Spectral data for products
1-Nitro-4-(4-ferrocenylphenoxy)-benzene (3): UV (CHCl₃) λmax (logε): 286.0(4.37), 242.8(4.37), IR(neat, cm⁻¹): 3076.92 (v C-H), 1606.29 (v C=C), 1487.68 (v C=C of ferrocene), 1519.22 and 1341.79 (v C-NO₂ aromatic), 843.47 (v of 1, 4 disubstituted benzene), 495.75 (v Fe-cyclopentadiene stretching of ferrocene), ¹H-NMR (CDCl₃): 8.234 (d, J = 9.0 Hz, 2H, Ar-H), 7.548 (d, J = 8.1 Hz, 2H, Ar-H), 7.062 (d, J = 8.7 Hz, 7.748 (d, J = 8.9 Hz, 2H, Ar-H), 7.062 (d, J = 8.7 Hz,
2H, Ar-H), 7.040 (d, J = 7.8 Hz, 2H, Ar-H), 4.656 (s, 2H, C₃H₅ of ferrocene), 4.364 (s, 2H, C₃H₅ of ferrocene), 4.095 (s, 5H, C₃H₅ of ferrocene), ¹³C-NMR (CDCl₃):163.4, 152.7, 142.6, 136.8, 127.7, 125.9, 120.4, 117.0 (8C aromatic), 88.6, 69.7, 69.2, 66.6 (-C₃H₅ and -C₃H₅ of ferrocene).

4-(4-Ferrocenylphenoxy) aniline (4): UV (CHCl₃) λₘₐₓ(logε):284.8(4.24), 246.4(4.34), IR(neat, cm⁻¹):3351.40 (v -NH₂), 3076.92 (v C-H), 1595.34 (v C=C of ferrocene), 1451.64 (v C=C of ferrocene), 851.10 (v of 1, 4 disubstituted benzene), 500.95 (v Fe-cyclopentadiene stretching of ferrocene), ¹¹H-NMR (CDCl₃):7.436 (d, J = 7.2 Hz, 2H, Ar-H), 6.922 (bs, 2H, Ar-H), 6.723 (bs, 4H, Ar-H), 4.604 (s, 2H, C₃H₅ of ferrocene), 4.307 (s, 2H, C₃H₅ of ferrocene), 4.076 (s, 5H, C₃H₅ of ferrocene), 3.712 (s, 2H, -NH₂ proton), ¹³C-NMR (CDCl₃):157.1, 149.1, 142.0, 133.0, 127.2, 120.8, 117.3, 116.6 (8C aromatic), 85.5, 69.5, 68.6, 66.3 (-C₃H₅ and -C₃H₅ of ferrocene).

4-(Hexadecyloxy)phenyl 4-formylbenzoate (9c): UV (CHCl₃) λₘₐₓ(logε):253.4(3.81), IR(neat, cm⁻¹):2916.49 (v C-H), 1742.93 (v C=O of ester), 1693.46 (v C=O of aldehyde), 1608.37 (v C=C), 1276.07 (v C-O alkyl chain), 1162.84 (v C-O ester), 843.34 (v of 1, 4 disubstituted benzene). ¹¹H-NMR (CDCl₃): 10.148 (s, 1H, CH of aldehyde), 8.376 (t, J = 6.9 Hz, 2H, Ar-H), 8.037-8.009 (m, 2H, Ar-H), 7.153-7.122 (m, 2H, Ar-H), 6.962-6.931 (m, 2H, Ar-H), 3.992 (t, J = 6.6 Hz, 2H, -OCH₂), 1.824-1.272 (m, 28H, -CH₂ of aliphatic chain), 0.910 (t, J = 6.6 Hz, 3H, -CH₃).

4-(Dodecyl oxy)phenyl 4-(4-(4-ferrocenylphen oxy)phenyl)imino)methyl)benzoate (10a): UV (CHCl₃) λₘₐₓ(logε):350.5(4.17), 283.6(4.45), 251.2(4.37), IR(neat, cm⁻¹):3104.06 (v C-H aromatic), 2926.18 (v C-H, 1727.09 (v C=O of ester), 1627.30 (v C=N, Schiff’s base), 1594.69 (v C=C), 1494.59 (v C=C of ferrocene), 1283.13 (v C-O alkyl chain), 1187.33 (v C-O ester), 851.57 (v of 1, 4 disubstituted benzene), 480.29 (v Fe-cyclopentadiene stretching of ferrocene), HRMS: m/z cal. mass for C₅₀Hₙ₂FeNO₄ [M+H]⁺ = 762.3238, obs. mass [M+H]⁺ = 762.3241, ¹¹H-NMR (CDCl₃):8.318 (s, 1H, CH of Schiff’s base), 8.061 (d, J = 8.4 Hz, 2H, Ar-H), 7.491 (d, J = 8.4 Hz, 2H, Ar-H), 7.334 (d, J = 8.7 Hz, 2H, Ar-H), 7.168 (d, J = 2.1 Hz, 2H, Ar-H), 7.138 (d, J = 3.3 Hz, 2H, Ar-H), 7.117 (d, J = 8.7 Hz, 2H, Ar-H), 7.008 (d, J = 8.7 Hz, 2H, Ar-H), 6.970 (d, J = 9.3 Hz, 2H, Ar-H), 4.626 (t, J = 1.8 Hz, 2H, C₃H₅ of ferrocene), 4.325 (t, J = 1.8 Hz, 2H, C₃H₅ of ferrocene), 4.077 (s, 5H, C₃H₅ of ferrocene), 4.000 (t, J = 6.6 Hz, 2H, -OCH₂), 1.832-1.313 (m, 20H, -CH₂ of aliphatic chain), 0.932 (t, J = 6.3 Hz, 3H, -CH₃), ¹³C-NMR (CDCl₃):165.0 (>C=O of ester), 157.0, 156.4, 155.3, 146.4, 144.1, 140.5, 134.5, 131.7, 130.5, 128.6, 127.4, 122.5, 123.1, 119.3, 118.9, 115.1 (16C aromatic), 85.1 (-OCH₂), 69.5, 68.8, 68.4, 66.3 (-C₃H₅, -C₃H₅ of ferrocene), 31.8, 29.3, 29.2, 29.2, 26.0, 22.6 (-CH₂ aliphatic chain), 14.1 (-CH₃).

4-(Tetradecyloxy)phenyl-4-((4-(4-ferrocenylphenoxy)phenyl)imino)methyl)benzoate (10b): UV (CHCl₃) λₘₐₓ(logε):350.5(4.30), 278.8(4.58), 249.8 (4.50), IR(neat, cm⁻¹):3104.06 (v C-H aromatic), 2920.13 (v C-H), 1730.27 (v C=O of ester), 1626.23 (v C=N, Schiff’s base), 1592.86 (v C=C), 1494.70 (v C=C of ferrocene), 1243.93 (v C-O alkyl chain), 1167.04 (v C-O ester), 850.03 (v of 1, 4 disubstituted benzene), 438.32 (v Fe-cyclopentadiene stretching of ferrocene), HRMS: m/z cal. mass for C₅₀Hₙ₄FeNO₄ [M+H]⁺ = 790.3553, obs. mass [M+H]⁺ = 790.3554, ¹¹H-NMR (CDCl₃):8.595 (s, 1H, CH of Schiff’s base), 8.318 (d, J = 8.4 Hz, 2H, Ar-H), 8.061 (d, J = 8.4 Hz, 2H, Ar-H), 7.491 (d, J = 8.7 Hz, 2H, Ar-H), 7.334 (d, J = 8.7 Hz, 2H, Ar-H), 7.168 (d, J = 9.0 Hz, 2H, Ar-H), 7.117 (d, J = 8.7 Hz, 2H, Ar-H), 7.008 (d, J = 8.4 Hz, 2H, Ar-H), 6.969 (d, J = 9.0 Hz, 2H, Ar-H), 4.625 (t, J = 1.5 Hz, 2H, C₃H₅ of ferrocene), 4.324 (t, J = 1.5 Hz, 2H, C₃H₅ of ferrocene), 4.077 (s, 5H, C₃H₅ of ferrocene), 3.999 (t, J = 6.6 Hz, 2H, -OCH₂), 1.830-1.282
(m, 24H, -CH2 of aliphatic chain), 0.898 (t, J = 6.3 Hz, 3H, -CH3), 13C-NMR (CDCl3):165.0 (>C=O of ester), 157.7 (−C=CH=), 157.0, 156.3, 155.3, 146.4, 144.1, 140.5, 134.5, 131.7, 130.5, 128.6, 127.4, 122.5, 122.3, 119.3, 118.9, 115.1 (16C aromatic), 85.1 (−OCH3), 69.5, 68.8, 68.4, 66.3 (−C6H4, -C5H5 of ferrocene), 31.9, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.6, (−CH2 aliphatic chain), 14.1 (−CH3).

4-(Hexadecyloxy)phenyl-4-((4-(4-ferrocenylphenoxy)phenylimino)methyl)benzoate (10c): UV (CHCl3) λmax (logε): 332.7 (4.29), 284.8 (4.61), 246.4 (4.32), IR(neat, cm⁻¹): 3104.06 (ν C=H aromatic), 2918.96 (ν C-H), 1730.43 (ν C=O of ester), 1625.17 (ν C=N, Schiff’s base), 1592.86 (ν C=C), 1509.34 (ν C=C of ferrocene), 1249.54 (ν C=O alkyl chain), 1167.04 (ν C-O ester), 856.09 (ν (of 1, 4 disubstituted benzene), 438.32 (ν Fe-cyclopentadiene stretching of ferrocene), HRMS: m/z cal. mass for C54H40FeNO4 [M+H]+ = 818.3856, obs. mass [M+H]+ = 818.3867, 1H-NMR (CDCl3): 8.594 (s, 1H, CH of Schiff’s base), 8.316 (d, J = 8.4 Hz, 2H, Ar-H), 8.061 (d, J = 8.1 Hz, 2H, Ar-H), 7.489 (d, J = 8.7 Hz, 2H, Ar-H), 7.333 (d, J = 8.7 Hz, 2H, Ar-H), 7.166 (d, J = 9.0 Hz, 2H, Ar-H), 7.115 (d, J = 8.7 Hz, 2H, Ar-H), 7.008 (d, J = 8.7 Hz, 2H, Ar-H), 6.966 (d, J = 9.0 Hz, 2H, Ar-H), 4.624 (t, J = 1.5 Hz, 2H, C2H4 of ferrocene), 4.324 (t, J = 1.5 Hz, 2H, C2H4 of ferrocene), 4.076 (s, 5H, C5H5 of ferrocene), 3.998 (t, J = 6.3 Hz, 2H, -OCH2), 1.827-1.276 (m, 28H, -CH2 of aliphatic chain), 0.915 (t, J = 6.6 Hz, 3H, -CH3), 13C-NMR (CDCl3): 165.0 (>C=O of ester), 157.7 (−CH=CH2), 157.0, 156.4, 155.3, 146.4, 144.1, 140.5, 134.6, 131.7, 130.5, 128.6, 127.4, 122.4, 122.3, 119.3, 118.8, 115.1 (16C aromatic), 81.3 (−OCH2), 69.8, 69.0, 68.4, 66.6 (−C6H4, -C5H5 of ferrocene), 31.9, 29.6, 29.5, 29.3, 29.2, 26.0, 22.6, (−CH2 aliphatic chain), 14.1 (−CH3).

4-(Octadecyloxy)phenyl-1-4-((4-(4-ferrocenylphenoxy)phenylimino)methyl)benzoate (10d): UV (CHCl3) λmax (logε): 348.2 (4.17), 281.2 (4.50), 254.8 (4.50), IR(neat, cm⁻¹): 3104.06 (ν C=H aromatic), 2917.29 (ν C-H), 1734.06 (ν C=O of ester), 1624.44 (ν C=N, Schiff’s base), 1589.23 (ν C=C), 1494.82 (ν C=C of ferrocene), 1247.95 (ν C-O alkyl chain), 1168.05 (ν C-O ester), 855.17 (ν (of 1, 4 disubstituted benzene), 434.55 (ν Fe-cyclopentadiene stretching of ferrocene), HRMS: m/z cal. mass for C56H42FeNO4 [M+H]+ = 846.4185, obs. mass [M+H]+ = 846.4181, 1H-NMR (CDCl3): 8.594 (s, 1H, CH of Schiff’s base), 8.317 (d, J = 8.1 Hz, 2H, Ar-H), 8.060 (d, J = 7.8 Hz, 2H, Ar-H), 7.491 (d, J = 8.4 Hz, 2H, Ar-H), 7.334 (d, J = 8.7 Hz, 2H, Ar-H), 7.168 (d, J = 9.0 Hz, 2H, Ar-H), 7.117 (d, J = 8.7 Hz, 2H, Ar-H), 7.008 (d, J = 8.7 Hz, 2H, Ar-H), 6.968 (d, J = 8.7 Hz, 2H, Ar-H), 4.620 (s, 2H, C2H4 of ferrocene), 4.319 (s, 2H, C2H4 of ferrocene), 4.077 (s, 5H, C5H5 of ferrocene), 3.998 (t, J = 6.6 Hz, 2H, -OCH2), 1.827-1.276 (m, 32H, -CH2 of aliphatic chain), 0.917 (t, J = 6.0 Hz, 3H, -CH3), 13C-NMR (CDCl3): 165.0 (>C=O of ester), 157.7 (−CH=CH2), 157.0, 156.4, 155.3, 146.4, 144.1, 140.5, 134.6, 131.7, 130.5, 128.6, 127.4, 122.5, 122.3, 119.3, 118.9, 115.1 (16C aromatic), 85.1 (−OCH2), 69.5, 68.8, 68.4, 66.3 (−C6H4, -C5H5 of ferrocene), 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 22.6. (−CH2 aliphatic chain), 14.1 (−CH3).

RESULTS AND DISCUSSION

Recently we have reported the synthesis of novel low temperature ferrocnomesogens [29, 30] exhibiting low temperature mesomorphism. In view of the above observations from the literature and our interest in the synthesis of ferrocnomesogens as a latent candidate for liquid crystal applications, we now report herein the synthesis of compounds (10a-10d) in three stages as delineated in Scheme having hydroquinone unit, as many hydroquinone derivatives are known to exhibit liquid crystalline behavior [31-33].

All the newly synthesized ferrocene derivatives (10a-10d) were examined for their liquid crystalline behavior with the help of Differential Scanning Calorimetry (DSC) and Polarizing Optical Microscopy (POM). Both DSC(Fig.-1) and POM(Fig.-2) study confirmed that compound 10c exhibits monotropic liquid crystalline behavior while other members of the series (10a, 10b, and 10d) are known to exhibit nonmesomorphic behavior.

DSC analysis showed two endothermic peaks at 109°C and 138°C for compound 10c during first heating cycle (Fig.-1), while POM study confirmed the melting temperature at 138°C. This is due to the crystal to
crystal transition behavior for compound 10c during heating cycle [34]. The compound 10c exhibited nematic phase during cooling cycle as shown in Fig.-2.

Scheme:

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>12</td>
</tr>
<tr>
<td>10b</td>
<td>14</td>
</tr>
<tr>
<td>10c</td>
<td>16</td>
</tr>
<tr>
<td>10d</td>
<td>18</td>
</tr>
</tbody>
</table>
The detailed thermal behavior of the compounds 10a-10d along with entropy change (expressed as $\Delta S/R$) for compound 10c are summarized in Table-1.

Table-1: Transition temperature data of the Compounds 10a-10d.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition Temperature/$^0C$</th>
<th>$\Delta H$ (J g$^{-1}$)</th>
<th>$\Delta S/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>Cr $\rightarrow$ 169$^0C$ $\rightarrow$ 121$^0C$ I</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10b</td>
<td>Cr $\rightarrow$ 139$^0C$ $\rightarrow$ 102$^0C$ $\rightarrow$ 157$^0C$ $\rightarrow$ 122$^0C$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10c</td>
<td>Cr $\rightarrow$ 109$^0C$ $\rightarrow$ 123$^0C$ $\rightarrow$ 138$^0C$</td>
<td>4.30 56.80 1.10 13.59</td>
<td>38.35 14.85 9.52 3.66</td>
</tr>
<tr>
<td>10d</td>
<td>Cr $\rightarrow$ 135$^0C$ $\rightarrow$ 124$^0C$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Where Cr, Cr1, Cr2= Crystal, N= Nematic, I= Isotropic, $\Delta H$ is the enthalpy change associated with phase transition, $\Delta S/R$ is the entropy change associated with phase transition.
Mesomorphic behavior as a function of the number of carbon atoms (n=12, 14, 16, 18) in the terminal alkoxy chain are shown in fig.-3.

![Figure-3 Mesomorphic behavior as a function of the number of carbon atoms (n) in the terminal alkoxy chain for compounds 10a-10d.](image)

**APPLICATIONS**

- The method used for the synthesis of final compounds in the manuscript is very useful. The final molecules are very big. Synthesis of bigger compounds generally required multistep synthesis which normally ended with lower yield and synthetic chemistry problem. During synthesis of above molecules we have first synthesized different intermediate first and in the last step we used intermediates for synthesis of final compound (Single step reaction), which results in higher yield.
- All the starting materials are readily available and inexpensive.
- Product formed with good yield.

This approach is good for synthesis of ferrocenomesogens comparing with reported methods used for synthesis of ferrocenomesogens

**CONCLUSIONS**

Novel monosubstituted ferrocenomesogens containing hydroquinone unit have been synthesized by using readily available and inexpensive chemicals in a good yield. Compound 10e exhibited monotropic nematic liquid crystalline behavior while other members 10a, 10b, and 10d exhibited nonmesomorphism.

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