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## Liquid Crystals

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## Synthesis and smectogenic properties of novel phloroglucinol-based star-shaped liquid crystals containing three peripheral alkyloxylated Schiff base arms

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A series of symmetrical trimeric liquid crystalline compounds of which the molecular structure with a central core of 1,3,5-benzene attached by three rod-like mesogenic Schiff base moieties via the propylene spacers and ether linkages has successfully been synthesised and characterised by infra red and nuclear magnetic resonance spectroscopic techniques. All the star-shaped compounds in this series exhibit predominantly SmC phase except the analogue possessing terminal C<sub>8</sub>H<sub>17</sub> group. It is apparent that the members with even parity from C<sub>10</sub>H<sub>21</sub> to C<sub>16</sub>H<sub>33</sub> show enantiotropic SmC phase while the member with longest terminal chain of C<sub>18</sub>H<sub>37</sub> is inclined to monotropic smectogen. The X-ray diffraction measurements reveal that the tilted smectic layer structures of the SmC phase are confirmed to have an obvious sharp peak at small angles of  $2\theta \sim 1.03^\circ\text{--}1.48^\circ$  with *d*-spacing values of 4.01–4.58 nm, which are corresponding to tilt angles of  $\sim 48^\circ$  in the SmC phase.

**Keywords:** phloroglucinol; Schiff bases; star-shaped liquid crystals; smectic C; XRD

### 1. Introduction

The development in science and technology has led to the growing interest in the synthesis and investigation of unconventional liquid crystals. Apart from the typical classes of conventional liquid crystals composed of rod-like (calamitic) and disc-like (discotic) molecules, the liquid crystals such as multi-arm mesogens [1–4], oligomers [5–10], bent-core mesogen [11–15] as well as supramolecular mesogens including the metallomesogens [16–22] and hydrogen-bonded mesogens [23–26] have also been widely studied. These compounds can be used as the fundamental prerequisite for the formation of unconventional thermotropic liquid crystals because their anisotropic properties play a vital role in this interesting state of soft material. Unconventional star-shaped liquid crystals consisting of a small central core connected with a few extended semi-rigid mesogenic units as the peripheral arm has attracted increasing attention and research interest [27–35]. Following the pioneering work by Attard et al. [36], the simplest star-shaped liquid crystals composed of a small aromatic core unit surrounded by three mesogenic units had become the most commonly studied liquid crystalline materials even though more sophisticated star-shaped liquid crystals consisting up to three mesogenic arms had been reported [1–4]. In general, the molecular design of star-shaped or disc-like liquid crystals have based on benzene core and 1,3,5-triazine

core bearing long, flexible alkyl or alkoxy chains at the periphery.

Phloroglucinol or 1,3,5-trihydroxybenzene is a simple six-membered ring with three hydroxyl groups attached to 1, 3 and 5 positions in aromatic ring. It is an important class of organic compound which has commonly been used in cosmetics, pesticides, paints and dyeing [37] as well as in the synthesis of pharmaceuticals, explosives and polymeric substances. In addition, researchers has once isolated phloroglucinol from natural sources such as the coastal woodfern *Dryopteris arguta* [38] and subsequently some of its derivatives were found naturally in certain plant species [39–42].

On the other hand, phloroglucinol had also been employed in the synthesis of star-shaped and discotic liquid crystals [27–30] as well as hydrogen-bonded phloroglucinol-based system [23–25]. The incorporation of different mesogenic side chain has conveniently led to the molecular rearrangement which entailed the crossing from rod-like to disc-like domains. Moreover, the mesogenic unit thus introduced could enhance the mesomorphic properties. Hence, star-shaped liquid crystals are considered as one of the important aspects for the theoretical understanding of the liquid crystalline phenomenon.

The earlier study showed that the direct esterification of  $\omega$ -[4-(*p*-alkoxybenzoxo)phenoxy]carbonyl

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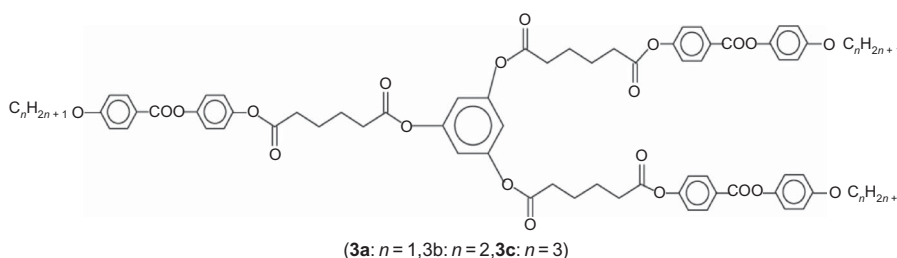


Figure 1. Molecular structures of the star-shaped liquid crystals *tri*[( $\omega$ -4-(*p*-alkoxybenzoyloxy)phenoxy)carbonyl] valeric acid phloroglucinol ester, **3a–3c**, prepared by Zhang et al. [28]

valeric acid (Figure 1) as mesogenic arms would result in a typical nematic phase. Besides, the documented liquid crystals did not undergo crystallisation upon cooling but vitrify into a glassy state. This observation had received a considerable attention because the glass-forming liquid crystalline materials possess interesting optical, mechanical as well as thermal stable properties [43–46] which may be useful as soft materials for fabrication of thermo-electro-optical storage and different optical components [1,28]. In relation to this study, the star-shaped liquid crystals incorporating cholesterol unit as the chiral component had also been given great attention [29].

We have recently reported a series of three-armed star-shaped analogues containing (4-benzylidene-substituted-aniline-4'-oxy)-6-bromohexane as peripheral arm in which the 4-position at one end consisting different terminal substituent  $X$  ( $X = \text{F, Cl, Br, I}$  and  $\text{C}_2\text{H}_5$ ) [47]. They were found to exhibit calamitic mesophase. Consequently, the question on how to modify the substitution of the peripheral arm of 1,3,5-trisubstituted-benzene central core in order to exhibit highly ordered smectic phases has driven us to investigate further. Therefore, as the continuation of our effort to further investigate the properties of star-shaped compounds, we report in this article another new series of the homologous three-armed star-shaped liquid crystals wherein the three rod-like (*p*-alkyloxybenzylidene) anilines with different length of even parity alkyl chain ranging from 8 to 18 are attached to a disc-shaped benzene ring via a propylene spacer and ether linkages. Since the liquid crystalline properties of the star-shaped liquid crystals bearing three Schiff base fragments comprising different polarity and molecular size of terminal substituent has been explored, our present objective is to investigate the mesomorphic properties of the star-shaped liquid crystals consisting of three Schiff base moieties with different length of terminal alkyl chain.

## 2. Experimental

### 2.1 Chemicals and reagents

Phloroglucinol anhydrous, *p*-aminophenol and *p*-hydroxybenzaldehyde were purchased from Acros Organics (Geel, Belgium). Bromooctane, bromodecane, bromododecane, bromotetradecane, bromohexadecane, bromooctadecane and 1,3-dibromopropane were obtained from Merck (Darmstadt, Germany). While potassium carbonate was purchased from System (Kielce, Poland), potassium iodide was obtained from Fischer Scientific (Waltham, MA, USA). All the chemicals as well as solvents were purchased commercially and used directly from the bottles without further purification.

### 2.2 Methods and characterisation

Structural elucidation of intermediary and title compounds was carried out by elemental analyses, Fourier transform infrared (FTIR) and NMR spectroscopies. The carbon, hydrogen and nitrogen (CHN) microanalyses were conducted via Perkin-Elmer 2400 LS series CHN analyser. The IR spectra were recorded and measured on a Perkin-Elmer 2000 FTIR spectrophotometer where the samples were prepared in the form of KBr pellet and the spectra were recorded within a frequency range of  $400\text{--}4000\text{ cm}^{-1}$ . NMR spectra were recorded by using Bruker Avance 300 MHz and 500 MHz Ultrashield FT-NMR spectrometers in which the deuterated chloroform ( $\text{CDCl}_3$ ) and  $\text{DMSO-d}_6$  with tetramethylsilane as internal standard were used as the solvents. Complete  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments of the representative compounds were obtained and substantiated by means of the two-dimensional spectroscopic measurement such as  $^1\text{H}\text{--}^1\text{H}$  correlation spectroscopy,  $^1\text{H}\text{--}^{13}\text{C}$  heteronuclear multiple quantum correlation and  $^1\text{H}\text{--}^{13}\text{C}$  heteronuclear multiple bond correlation.

Phase-transition temperatures and enthalpy changes were measured using Differential Scanning

Calorimeter Mettler Toledo DSC823<sup>e</sup> with the heating and cooling rates of +2°C/min and -2°C/min, respectively. Carl Zeiss polarizing optical microscope (POM) equipped with Linkam heating stage in the School of Chemical Sciences, USM (Penang, Malaysia), was used for temperature-dependent studies and texture observation. Samples were prepared as thin films sandwiched between a glass slide and a coverslip.

Synchrotron powder X-ray diffraction (XRD) measurements were performed at beamline BL17A of the National Synchrotron Radiation Research Center, Taiwan, where the wavelength of X-ray was 1.33366 Å. The powder samples were packed into capillary tubes and heated by a heat gun, whose temperature controller was programmable by a computer with a proportional, integral and differential feedback system. The scattering angle  $\theta$  was calibrated by a mixture of silver behenate and silicon.

### 2.3 Synthesis

Scheme 1 illustrates the structures and the synthetic pathway towards the formation of intermediates **1a–1f**, **2a–2f**, **3a–3f** and the symmetric star-shaped compounds **4a–4f**. The peripheral mesogenic units were prepared by alkylation of various bromoalkane with *p*-hydroxybenzaldehyde and then condensation of *p*-alkoxybenzaldehyde with *p*-aminophenol to afford the Schiff bases **2a–2f**. The flexible spacers were subsequently introduced by alkylation of compounds **2a–2f** with the excess of 1,3-dibromopropane in the presence of potassium carbonate as a base to yield compounds **3a–3f**. Excess of compounds **3a–3f** was further reacted with phloroglucinol anhydrous (1,3,5-trihydroxybenzene) by Williamson etherification to produce the desired star-shaped molecule 2,4,6-tri{[ $\omega$ -4-(alkoxybenzylidene)aniline-4'-oxy]propoxy}benzene, **4a–4f**. The codes for compounds **3a–3f** and **4a–4f** were shown in Table 1.

#### 2.3.1 Synthesis of compound 2

In a round-bottom flask containing an equimolar of compound **1** and *p*-aminophenol in 50 mL absolute ethanol, three drops of acetic acid were added. The reaction mixture was then heated at reflux for 3 h before it was cooled down to room temperature. The precipitate thus isolated was then recrystallised from ethanol to yield the desired intermediate **2**. The analytical data for compounds **2a–2f** are summarised as follows:

**2a**: Yield: 78%. Beige. Elemental analysis: found, C 77.72, H 8.40, N 4.33; calculated (C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>), C 77.50, H 8.36, N 4.30. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3392 (OH phenolic), 2954, 2920, 2851 (C–H aliphatic), 1609–1627 (C=N azomethine), 1262 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 3H, CH<sub>3</sub>), 1.29–1.49 (*m*, 10H, CH<sub>2</sub>), 1.77–1.86 (*m*, 2H, CH<sub>2</sub>), 4.05 (*t*, 2H, OCH<sub>2</sub>), 5.01 (*s*, 1H, OH), 6.86 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.17 (*d*, 2H, Ar), 7.84 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**2b**: Yield: 81%. Beige. Elemental analysis: found, C 78.48, H 8.81, N 4.09; calculated (C<sub>23</sub>H<sub>31</sub>NO<sub>2</sub>), C 78.15, H 8.84, N 3.96. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3392 (OH phenolic), 2955, 2917, 2851 (C–H aliphatic), 1609–1625 (C=N azomethine), 1254 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.92 (*t*, 3H, CH<sub>3</sub>), 1.29–1.50 (*m*, 14H, CH<sub>2</sub>), 1.77–1.85 (*m*, 2H, CH<sub>2</sub>), 4.05 (*t*, 2H, OCH<sub>2</sub>), 4.97 (*s*, 1H, OH), 6.87 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.15 (*d*, 2H, Ar), 7.84 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**2c**: Yield: 83%. Beige. Elemental analysis: found, C 78.88, H 9.30, N 3.73; calculated (C<sub>25</sub>H<sub>35</sub>NO<sub>2</sub>), C 78.70, H 9.25, N 3.67. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3392 (OH phenolic), 2854, 2918, 2850 (C–H aliphatic), 1609–1625 (C=N azomethine), 1254 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.92 (*t*, 3H, CH<sub>3</sub>), 1.29–1.50 (*m*, 18H, CH<sub>2</sub>), 1.77–1.86 (*m*, 2H, CH<sub>2</sub>), 4.04 (*t*, 2H, OCH<sub>2</sub>), 4.99 (*s*, 1H, OH), 6.87 (*d*, 2H, Ar), 7.00 (*d*, 2H, Ar), 7.18 (*d*, 2H, Ar), 7.86 (*d*, 2H, Ar), 8.40 (*s*, 1H, CH=N).

**2d**: Yield: 84%. Beige. Elemental analysis: found, C 79.45, H 9.80, N 3.56; calculated (C<sub>27</sub>H<sub>39</sub>NO<sub>2</sub>), C 79.17, H 9.60, N 3.42. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3397 (OH phenolic), 2955, 2918, 2851 (C–H aliphatic), 1610–1625 (C=N azomethine), 1255 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 3H, CH<sub>3</sub>), 1.28–1.48 (*m*, 22H, CH<sub>2</sub>), 1.75–1.85 (*m*, 2H, CH<sub>2</sub>), 4.04 (*t*, 2H, OCH<sub>2</sub>), 5.07 (*s*, 1H, OH), 6.89 (*d*, 2H, Ar), 7.00 (*d*, 2H, Ar), 7.19 (*d*, 2H, Ar), 7.85 (*d*, 2H, Ar), 8.40 (*s*, 1H, CH=N).

**2e**: Yield: 89%. Beige. Elemental analysis: found, C 79.77, H 9.94, N 3.21; calculated (C<sub>29</sub>H<sub>43</sub>NO<sub>2</sub>), C 79.59, H 9.90, N 3.20. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3399 (OH phenolic), 2954, 2917, 2849 (C–H aliphatic), 1610–1625 (C=N azomethine), 1255 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 3H, CH<sub>3</sub>), 1.27–1.50 (*m*, 26H, CH<sub>2</sub>), 1.75–1.85 (*m*, 2H, CH<sub>2</sub>), 4.03 (*t*, 2H, OCH<sub>2</sub>), 5.05 (*s*, 1H, OH), 6.86 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.17 (*d*, 2H, Ar), 7.83 (*d*, 2H, Ar), 8.40 (*s*, 1H, CH=N).

**2f**: Yield: 88%. Beige. Elemental analysis: found, C 80.15, H 10.15, N 3.14; calculated (C<sub>31</sub>H<sub>47</sub>NO<sub>2</sub>), C 79.95, H 10.17, N 3.01. IR (KBr)  $\nu/\text{cm}^{-1}$ : 3399

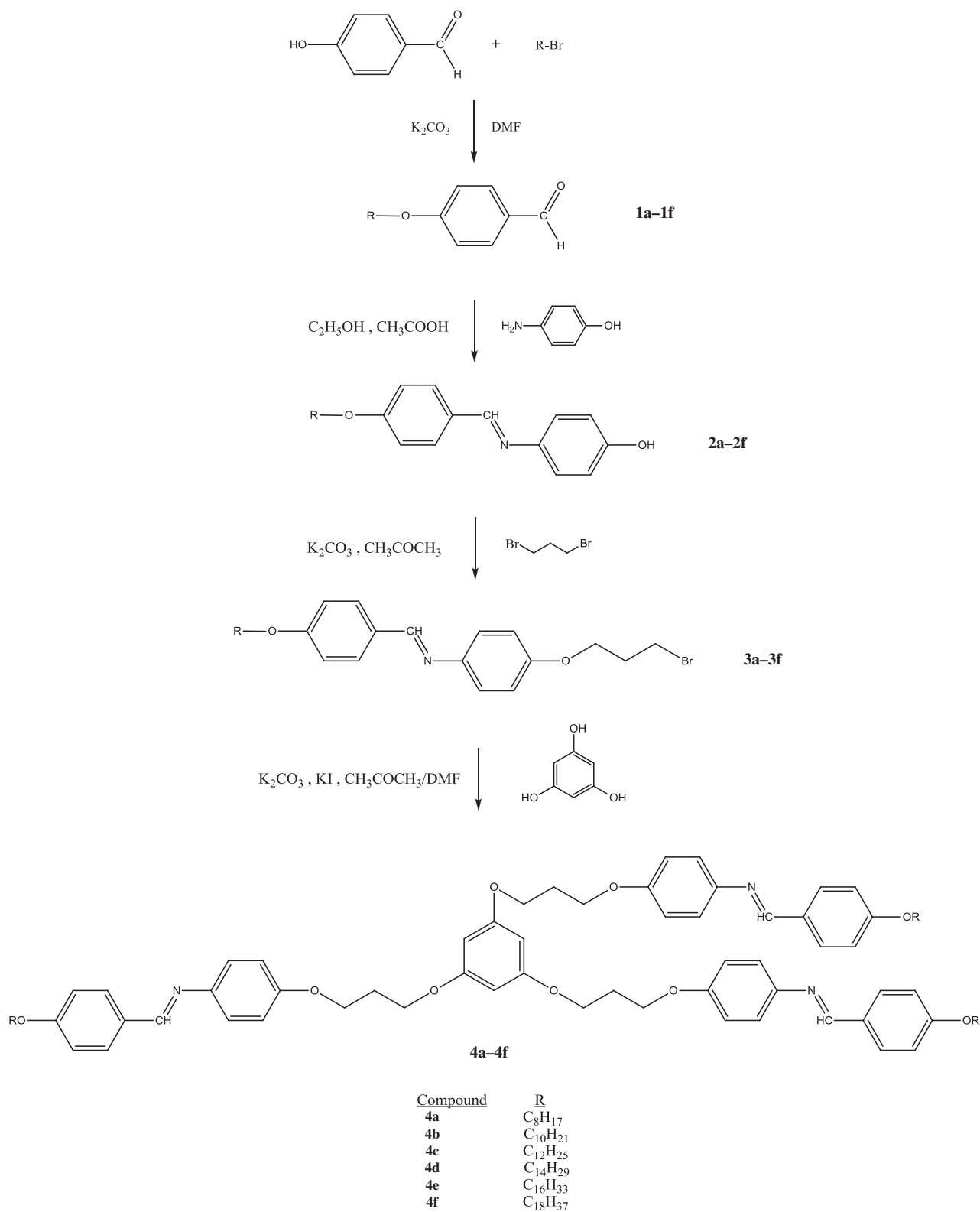
Scheme 1. Synthetic pathway towards the formation of intermediates and star-shaped compounds **4a–4f**.

Table 1. The Schiff base intermediates **3a–3f** and the title star-shaped compounds **4a–4f**.

R	Intermediate	Compound
C <sub>8</sub> H <sub>17</sub>	<b>3a</b>	<b>4a</b>
C <sub>10</sub> H <sub>21</sub>	<b>3b</b>	<b>4b</b>
C <sub>12</sub> H <sub>25</sub>	<b>3c</b>	<b>4c</b>
C <sub>14</sub> H <sub>29</sub>	<b>3d</b>	<b>4d</b>
C <sub>16</sub> H <sub>33</sub>	<b>3e</b>	<b>4e</b>
C <sub>18</sub> H <sub>37</sub>	<b>3f</b>	<b>4f</b>

(OH phenolic), 2954, 2918, 2849 (C-H aliphatic), 1609–1625 (C=N azomethine), 1255 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.90 (*t*, 3H, CH<sub>3</sub>), 1.28–1.51 (*m*, 30H, CH<sub>2</sub>), 1.77–1.85 (*m*, 2H, CH<sub>2</sub>), 4.03 (*t*, 2H, OCH<sub>2</sub>), 5.07 (*s*, 1H, OH), 6.87 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.18 (*d*, 2H, Ar), 7.85 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

### 2.3.2 Synthesis of compound **3**

A mixture of compound **2** (0.015 mol) and excess of 1,3-dibromopropane (0.06 mol, 12.1 g) were dissolved in 50 mL acetone followed by the addition of anhydrous potassium carbonate (0.045 mol, 6.2 g). The reaction mixture was refluxed for 8 h before it was left at room temperature to allow complete evaporation of the solvent. Fifty millilitre of distilled water was added and the resulting precipitate was filtered and rinsed with hexane to remove the excess dibromoalkane. The crude product was recrystallised from acetone to yield the pure compound **3**. Summary of the analytical data for **3a–3f** is shown below:

**3a**: Yield: 67%. White. Elemental analysis: found, C 64.72, H 7.29, N 3.20; calculated (C<sub>24</sub>H<sub>32</sub>NO<sub>2</sub>Br), C 64.57, H 7.23, N 3.14. IR (KBr)  $\nu$ /cm<sup>-1</sup>: 2955, 2922, 2854 (C-H aliphatic), 1606–1620 (C=N azomethine), 1249 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.90 (*t*, 3H, CH<sub>3</sub>), 1.29–1.49 (*m*, 10H, CH<sub>2</sub>), 1.77–1.87 (*m*, 2H, CH<sub>2</sub>), 2.31–2.40 (*m*, 2H, CH<sub>2</sub>), 3.64 (*t*, 2H, BrCH<sub>2</sub>), 4.05 (*t*, 2H, OCH<sub>2</sub>), 4.14 (*t*, 2H, OCH<sub>2</sub>), 6.95 (*d*, 2H, Ar), 7.00 (*d*, 2H, Ar), 7.24 (*d*, 2H, Ar), 7.86 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**3b**: Yield: 71%. White. Elemental analysis: found, C 65.90, H 7.67, N 3.03; calculated (C<sub>26</sub>H<sub>36</sub>NO<sub>2</sub>Br), C 65.82, H 7.65, N 2.95. IR (KBr)  $\nu$ /cm<sup>-1</sup>: 2954, 2918, 2849 (C-H aliphatic), 1607–1622 (C=N azomethine), 1251 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.90 (*t*, 3H, CH<sub>3</sub>), 1.30–1.52 (*m*, 14H, CH<sub>2</sub>), 1.78–1.85 (*m*, 2H, CH<sub>2</sub>), 2.31–2.38 (*m*, 2H, CH<sub>2</sub>), 3.64 (*t*, 2H, BrCH<sub>2</sub>), 4.04 (*t*, 2H, OCH<sub>2</sub>), 4.15 (*t*, 2H, OCH<sub>2</sub>), 6.94 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.22 (*d*, 2H, Ar), 7.84 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**3c**: Yield: 70%. White. Elemental analysis: found, C 67.04, H 8.14, N 2.83; calculated (C<sub>28</sub>H<sub>40</sub>NO<sub>2</sub>Br), C 66.92, H 8.02, N 2.79. IR (KBr)  $\nu$ /cm<sup>-1</sup>: 2954, 2919, 2848 (C-H aliphatic), 1608–1623 (C=N azomethine), 1255 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.90 (*t*, 3H, CH<sub>3</sub>), 1.29–1.52 (*m*, 18H, CH<sub>2</sub>), 1.78–1.86 (*m*, 2H, CH<sub>2</sub>), 2.31–2.39 (*m*, 2H, CH<sub>2</sub>), 3.64 (*t*, 2H, BrCH<sub>2</sub>), 4.04 (*t*, 2H, OCH<sub>2</sub>), 4.15 (*t*, 2H, OCH<sub>2</sub>), 6.95 (*d*, 2H, Ar), 7.00 (*d*, 2H, Ar), 7.24 (*d*, 2H, Ar), 7.86 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**3d**: Yield: 72%. White. Elemental analysis: found, C 68.00, H 8.39, N 2.62; calculated (C<sub>30</sub>H<sub>44</sub>NO<sub>2</sub>Br), C 67.91, H 8.36, N 2.64. IR (KBr)  $\nu$ /cm<sup>-1</sup>: 2954, 2918, 2850 (C-H aliphatic), 1608–1623 (C=N azomethine), 1252 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.90 (*t*, 3H, CH<sub>3</sub>), 1.28–1.51 (*m*, 22H, CH<sub>2</sub>), 1.78–1.87 (*m*, 2H, CH<sub>2</sub>), 2.31–2.39 (*m*, 2H, CH<sub>2</sub>), 3.64 (*t*, 2H, BrCH<sub>2</sub>), 4.04 (*t*, 2H, OCH<sub>2</sub>), 4.14 (*t*, 2H, OCH<sub>2</sub>), 6.95 (*d*, 2H, Ar), 6.99 (*d*, 2H, Ar), 7.24 (*d*, 2H, Ar), 7.86 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**3e**: Yield: 75%. White. Elemental analysis: found, C 68.94, H 8.70, N 2.55; calculated (C<sub>32</sub>H<sub>48</sub>NO<sub>2</sub>Br), C 68.80, H 8.66, N 2.51. IR (KBr)  $\nu$ /cm<sup>-1</sup>: 2955, 2918, 2850 (C-H aliphatic), 1608–1622 (C=N azomethine), 1251 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.90 (*t*, 3H, CH<sub>3</sub>), 1.28–1.51 (*m*, 26H, CH<sub>2</sub>), 1.78–1.87 (*m*, 2H, CH<sub>2</sub>), 2.30–2.39 (*m*, 2H, CH<sub>2</sub>), 3.64 (*t*, 2H, BrCH<sub>2</sub>), 4.03 (*t*, 2H, OCH<sub>2</sub>), 4.14 (*t*, 2H, OCH<sub>2</sub>), 6.94 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.21 (*d*, 2H, Ar), 7.83 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

**3f**: Yield: 72%. White. Elemental analysis: found, C 70.01, H 8.92, N 2.40; calculated (C<sub>34</sub>H<sub>52</sub>NO<sub>2</sub>Br), C 69.61, H 8.93, N 2.39. IR (KBr)  $\nu$ /cm<sup>-1</sup>: 2954, 2917, 2849 (C-H aliphatic), 1607–1622 (C=N azomethine), 1252 (C-O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ/ppm: 0.89 (*t*, 3H, CH<sub>3</sub>), 1.28–1.52 (*m*, 26H, CH<sub>2</sub>), 1.78–1.87 (*m*, 2H, CH<sub>2</sub>), 2.31–2.39 (*m*, 2H, CH<sub>2</sub>), 3.64 (*t*, 2H, BrCH<sub>2</sub>), 4.03 (*t*, 2H, OCH<sub>2</sub>), 4.14 (*t*, 2H, OCH<sub>2</sub>), 6.94 (*d*, 2H, Ar), 6.98 (*d*, 2H, Ar), 7.22 (*d*, 2H, Ar), 7.83 (*d*, 2H, Ar), 8.41 (*s*, 1H, CH=N).

### 2.3.3 Synthesis of compound **4**

Although the same reaction has previously been reported by Yoon et al. [48], the present compounds **4a–4f** are obtained by using the method which has been modified as follows.

In a round bottom flask, phloroglucinol anhydrous was dissolved in 10 mL dimethylformamide (DMF) followed by the addition of potassium carbonate anhydrous. The mixture was stirred at 80°C for an hour and then compounds **3a–3f**, which were dissolved in DMF, were added into the reaction mixture with a catalytic amount of potassium iodide. The reaction mixture was heated at 80°C for 48 h. When the reaction mixture

was cooled to room temperature, 500 mL of cold water was added. The crude precipitate was collected by filtration and then recrystallised twice by using DMF to afford the desired star-shaped compounds **4a–4f**.

**4a:** Yield: 24%. Beige. Elemental analysis: found, C 76.69, H 8.20, N 3.48; calculated (C<sub>78</sub>H<sub>99</sub>N<sub>3</sub>O<sub>9</sub>), C 76.62, H 8.16, N 3.44. IR (KBr)  $\nu/\text{cm}^{-1}$ : 2956, 2922, 2854 (C–H aliphatic), 1621 (C=N azomethine), 1249 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.91 (*t*, 9H, CH<sub>3</sub>), 1.31–1.53 (*m*, 30H, CH<sub>2</sub>), 1.80–1.85 (*m*, 6H, CH<sub>2</sub>), 2.25–2.30 (*m*, 6H, CH<sub>2</sub>), 4.02 (*t*, 6H, OCH<sub>2</sub>), 4.13–4.19 (*m*, 12H, OCH<sub>2</sub>), 6.15 (*s*, 3H, Ar), 6.95 (*d*, 6H, Ar), 6.98 (*d*, 6H, Ar), 7.20 (*d*, 6H, Ar), 7.83 (*d*, 6H, Ar), 8.40 (*s*, 3H, CH=N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 158.04 (CH=N), 161.64, 160.77, 157.22, 145.37, 130.25, 129.22, 122.08, 115.00, 114.66, 94.15 (C<sub>aromatic</sub>), 68.20, 64.70, 64.56 (OCH<sub>2</sub>), 22.71–31.93 (C<sub>aliphatic</sub>), 14.13 (CH<sub>3</sub>).

**4b:** Yield: 24%. Beige. Elemental analysis: found, C 77.41, H 8.65, N 3.16; calculated (C<sub>84</sub>H<sub>111</sub>N<sub>3</sub>O<sub>9</sub>), C 77.20, H 8.56, N 3.22. IR (KBr)  $\nu/\text{cm}^{-1}$ : 2955, 2920, 2851 (C–H aliphatic), 1622 (C=N azomethine), 1251 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.91 (*t*, 9H, CH<sub>3</sub>), 1.31–1.52 (*m*, 42H, CH<sub>2</sub>), 1.80–1.85 (*m*, 6H, CH<sub>2</sub>), 2.25–2.30 (*m*, 6H, CH<sub>2</sub>), 4.03 (*t*, 6H, OCH<sub>2</sub>), 4.14–4.19 (*m*, 12H, OCH<sub>2</sub>), 6.16 (*s*, 3H, Ar), 6.95 (*d*, 6H, Ar), 6.98 (*d*, 6H, Ar), 7.21 (*d*, 6H, Ar), 7.83 (*d*, 6H, Ar), 8.41 (*s*, 3H, CH=N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 158.05 (CH=N), 161.64, 160.76, 157.21, 145.37, 130.25, 129.22, 122.08, 114.99, 114.66, 94.14 (C<sub>aromatic</sub>), 68.19, 64.69, 64.55 (OCH<sub>2</sub>), 22.70–31.92 (C<sub>aliphatic</sub>), 14.14 (CH<sub>3</sub>).

**4c:** Yield: 23%. Beige. Elemental analysis: found, C 77.92, H 8.95, N 3.04; calculated (C<sub>90</sub>H<sub>123</sub>N<sub>3</sub>O<sub>9</sub>), C 77.71, H 8.91, N 3.02. IR (KBr)  $\nu/\text{cm}^{-1}$ : 2954, 2919, 2851 (C–H aliphatic), 1622 (C=N azomethine), 1250 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 9H, CH<sub>3</sub>), 1.30–1.53 (*m*, 54H, CH<sub>2</sub>), 1.80–1.86 (*m*, 6H, CH<sub>2</sub>), 2.25–2.30 (*m*, 6H, CH<sub>2</sub>), 4.03 (*t*, 6H, OCH<sub>2</sub>), 4.14–4.19 (*m*, 12H, OCH<sub>2</sub>), 6.16 (*s*, 3H, Ar), 6.95 (*d*, 6H, Ar), 6.98 (*d*, 6H, Ar), 7.21 (*d*, 6H, Ar), 7.83 (*d*, 6H, Ar), 8.40 (*s*, 3H, CH=N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 158.02 (CH=N), 161.64, 160.76, 157.21, 145.37, 130.25, 129.22, 122.08, 114.99, 114.65, 94.16 (C<sub>aromatic</sub>), 68.19, 64.69, 64.55 (OCH<sub>2</sub>), 22.70–31.92 (C<sub>aliphatic</sub>), 14.13 (CH<sub>3</sub>).

**4d:** Yield: 30%. Beige. Elemental analysis: found, C 78.09, H 9.25, N 2.81; calculated (C<sub>96</sub>H<sub>135</sub>N<sub>3</sub>O<sub>9</sub>), C 78.17, H 9.22, N 2.85. IR (KBr)  $\nu/\text{cm}^{-1}$ : 2954, 2918, 2850 (C–H aliphatic), 1622 (C=N azomethine), 1252 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 9H, CH<sub>3</sub>), 1.29–1.51 (*m*, 66H, CH<sub>2</sub>), 1.80–1.85 (*m*, 6H, CH<sub>2</sub>), 2.23–2.28 (*m*, 6H, CH<sub>2</sub>), 4.02 (*t*, 6H, OCH<sub>2</sub>), 4.13–4.19 (*m*, 12H, OCH<sub>2</sub>), 6.15 (*s*, 3H,

Ar), 6.94 (*d*, 6H, Ar), 6.98 (*d*, 6H, Ar), 7.20 (*d*, 6H, Ar), 7.83 (*d*, 6H, Ar), 8.40 (*s*, 3H, CH=N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 158.02 (CH=N), 161.64, 160.77, 157.22, 145.38, 130.25, 129.25, 122.08, 115.00, 114.67, 94.17 (C<sub>aromatic</sub>), 68.20, 64.70, 64.56 (OCH<sub>2</sub>), 22.72–31.95 (C<sub>aliphatic</sub>), 14.15 (CH<sub>3</sub>).

**4e:** Yield: 28%. Beige. Elemental analysis: found, C 78.66, H 9.61, N 2.72; calculated (C<sub>102</sub>H<sub>147</sub>N<sub>3</sub>O<sub>9</sub>), C 78.57, H 9.50, N 2.69. IR (KBr)  $\nu/\text{cm}^{-1}$ : 2954, 2918, 2850 (C–H aliphatic), 1622 (C=N azomethine), 1251 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 9H, CH<sub>3</sub>), 1.29–1.51 (*m*, 78H, CH<sub>2</sub>), 1.80–1.85 (*m*, 6H, CH<sub>2</sub>), 2.23–2.38 (*m*, 6H, CH<sub>2</sub>), 4.02 (*t*, 6H, OCH<sub>2</sub>), 4.13–4.20 (*m*, 12H, OCH<sub>2</sub>), 6.15 (*s*, 3H, Ar), 6.95 (*d*, 6H, Ar), 6.98 (*d*, 6H, Ar), 7.20 (*d*, 6H, Ar), 7.83 (*d*, 6H, Ar), 8.41 (*s*, 3H, CH=N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 158.02 (CH=N), 161.64, 160.77, 157.22, 145.38, 130.25, 129.24, 122.08, 115.00, 114.66, 94.17 (C<sub>aromatic</sub>), 68.20, 64.70, 64.56 (OCH<sub>2</sub>), 22.71–31.95 (C<sub>aliphatic</sub>), 14.14 (CH<sub>3</sub>).

**4f:** Yield: 33%. Beige. Elemental analysis: found, C 79.05, H 9.80, N 2.58; calculated (C<sub>108</sub>H<sub>159</sub>N<sub>3</sub>O<sub>9</sub>), C 78.93, H 9.75, N 2.56. IR (KBr)  $\nu/\text{cm}^{-1}$ : 2954, 2917, 2849 (C–H aliphatic), 1621 (C=N azomethine), 1250 (C–O ether). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 0.90 (*t*, 9H, CH<sub>3</sub>), 1.29–1.51 (*m*, 90H, CH<sub>2</sub>), 1.80–1.85 (*m*, 6H, CH<sub>2</sub>), 2.23–2.28 (*m*, 6H, CH<sub>2</sub>), 4.02 (*t*, 6H, OCH<sub>2</sub>), 4.14–4.20 (*m*, 12H, OCH<sub>2</sub>), 6.15 (*s*, 3H, Ar), 6.95 (*d*, 6H, Ar), 6.99 (*d*, 6H, Ar), 7.20 (*d*, 6H, Ar), 7.83 (*d*, 6H, Ar), 8.41 (*s*, 3H, CH=N). <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta/\text{ppm}$ : 158.04 (CH=N), 161.65, 160.77, 157.23, 145.38, 130.25, 129.25, 122.08, 114.99, 114.67, 94.15 (C<sub>aromatic</sub>), 68.21, 64.71, 64.56 (OCH<sub>2</sub>), 22.72–31.95 (C<sub>aliphatic</sub>), 14.15 (CH<sub>3</sub>).

### 3. Results and discussion

The thermal stability and mesomorphic properties of the peripheral mesogenic units **3a–3f** have earlier been reported [49]. While the phase-transition temperatures, associated enthalpy and entropy changes for the SmC-I transition obtained from differential scanning calorimetry (DSC) analysis on heating and cooling for compounds **4a–4f** are listed in Table 2, the DSC traces for a representative compound **4d** on heating and cooling are depicted in Figure 2.

#### 3.1 Thermal stability and mesomorphic properties

All the star-shaped compounds except for member possessing octyl terminal chain (compound **4a**) exhibit liquid crystalline properties as revealed by DSC and POM. From the results thus obtained, compounds **4c**, **4d** and **4e** are found to display enantiotropic liquid crystals behaviour with the appearance of SmC

Table 2. Phase transition temperature and the corresponding enthalpy changes for compounds **4a–4f** during heating and cooling scan.

Compound	Phase transition temperature, °C (enthalpy change, kJ mol <sup>-1</sup> )	$\Delta S_{\text{SmC-I}}/R$
<b>4a</b> ( $R = \text{C}_8\text{H}_{17}$ )	Cr 136.7 (93.3) I	–
	<i>I 132.4 (23.8) Cr<sub>1</sub> 111.3 (51.2) Cr<sub>2</sub></i>	–
<b>4b</b> ( $R = \text{C}_{10}\text{H}_{21}$ )	Cr 129.6 (58.9) SmC 134.8 (40.0) I	11.8
	<i>I 130.9 (23.4) SmC 111.4 (70.4) Cr</i>	7.0
<b>4c</b> ( $R = \text{C}_{12}\text{H}_{25}$ )	Cr 124.2 (86.1) SmC 137.5 (31.7) I	9.3
	<i>I 136.0 (19.1) SmC 100.7 (70.0) Cr</i>	5.6
<b>4d</b> ( $R = \text{C}_{14}\text{H}_{29}$ )	Cr 127.7 (102.2) SmC 144.6 (29.8) I	8.6
	<i>I 141.4 (30.4) SmC 103.7 (105.7) Cr</i>	8.8
<b>4e</b> ( $R = \text{C}_{16}\text{H}_{33}$ )	Cr 119.2 (123.7) SmC 141.0 (29.5) I	8.6
	<i>I 139.8 (29.8) SmC 106.4 (118.7) Cr</i>	8.7
<b>4f</b> ( $R = \text{C}_{18}\text{H}_{37}$ )	Cr 142.9 (238.3) I	–
	<i>I 140.8 (29.1) SmC 131.9 (230.1) Cr</i>	8.4

Notes: Cr, crystal; SmC, smectic C; I, isotropic. Data in italic font denote the cooling cycle.

phase characterised by Schlieran texture (Figure 3) on both heating and cooling cycles. The SmC phase of compound **4b** showed a broken fan-shaped texture (Figure 4) instead of Schlieren texture. One of the notable observations is the presence of both broken fan-shaped and Schlieren textures in SmC phase (Figure 5).

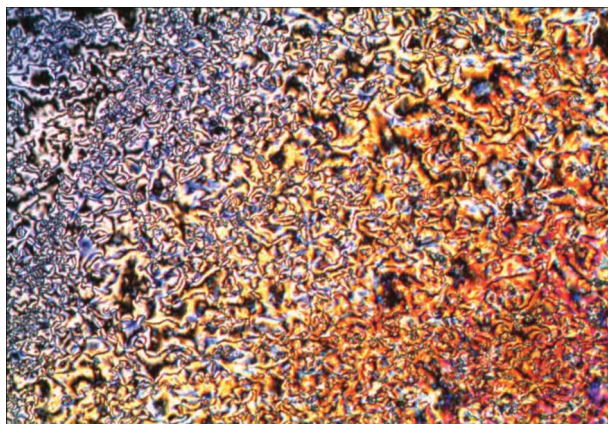


Figure 3. Optical photomicrograph of compound **4d** ( $R = \text{C}_{14}\text{H}_{29}$ ) showing the Schlieran texture of SmC phase during cooling cycle.

A correlation between the transition temperatures and number of carbon atom in the alkyloxy terminal chain is shown in Figure 6. It can be inferred from Figure 6 that the SmC phase range apparently increases as the length of the terminal alkyl chain is increased. However, the SmC phase range descends as the chain length reaches the maximum ( $R = \text{C}_{18}\text{H}_{37}$ ). Larger SmC phase range is exhibited by the members possessing medium chain length. In short, on cooling, compound **4f** exhibits the narrowest mesogenic region (8.9°C), while compound **4d** displays the widest mesophase temperature range of 37.7°C. An interesting feature in relation to the liquid crystalline properties for these star-shaped mesogens is that the SmC phase is less stable in the homologues

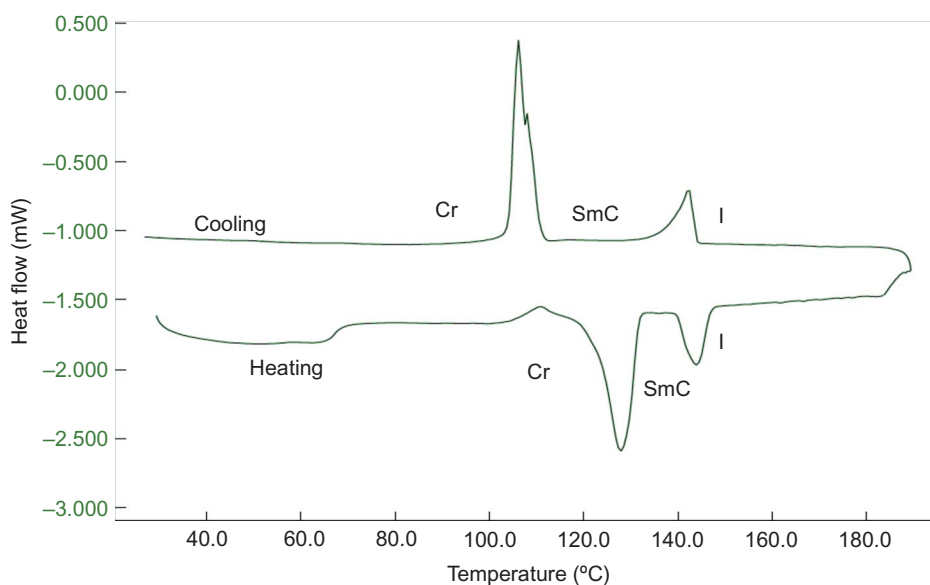


Figure 2. DSC trace for compound **4d** ( $R = \text{C}_{14}\text{H}_{29}$ ) on heating and cooling cycles at the rate of  $\pm 2^\circ\text{C min}^{-1}$ .



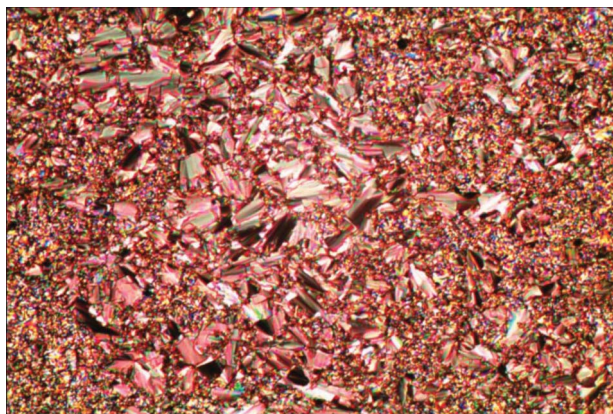


Figure 4. Optical photomicrograph of compound **4b** ( $R=C_{10}H_{21}$ ) showing the broken fan-shaped texture of SmC phase during cooling cycle.

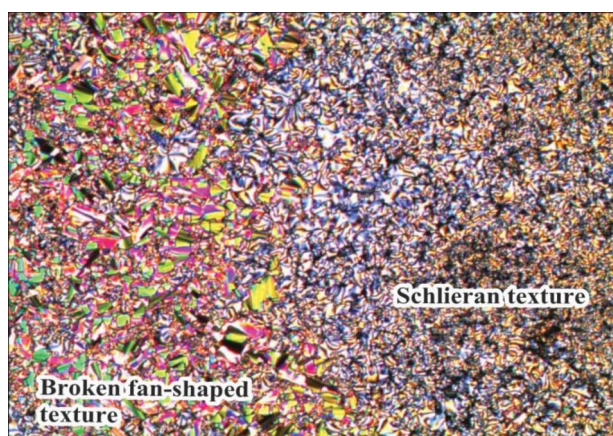


Figure 5. Optical photomicrograph of compound **4f** ( $R=C_{18}H_{37}$ ) whereby simultaneous occurrence of Schlieran texture and broken fan-shaped texture of SmC phase at the same time.

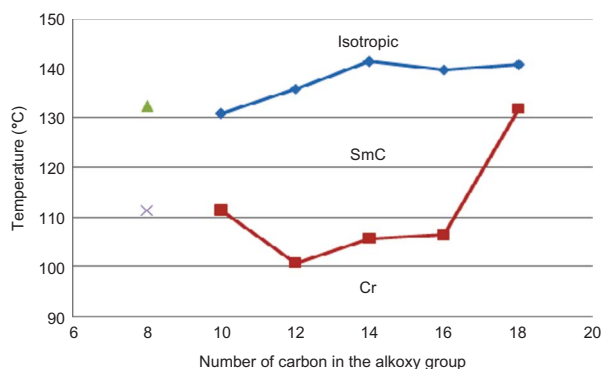


Figure 6. Plot of transition temperature against the number of carbon in the alkoxy chain during the cooling cycle.

possessing shortest and longest terminal chain length. This observation has earlier been reported for cyclic trimers derived from benzene-1,3,5-tricarboxylic acid

[36]. Although the present star-shaped molecule is derived from 1,3,5-trihydrobenzene, it also comprise of an aromatic benzene unit as the central core. Hence, it can be suggested that the terminal polarity group played an important factor in this phenomenon as it maintains the molecular orientation through the acting forces of molecular induction and polarisation [28].

When the length of the terminal alkoxy chain reaches  $R=C_{14}H_{29}$  (compound **4d**), the attraction between the long alkyl chain leading to intertwining which is essential to facilitates the molecular packing. As a result, it increases the structural anisotropy that gives widest mesogenic region detected in compound **4d**.

However, compounds **4a** and **4f** exhibit an endotherm corresponding to the direct melting from crystal to isotropic liquid upon heating run. The subsequent cooling on compound **4a** demonstrates an exotherm characteristic of the Iso-Cr and Cr-Cr transitions, which is indicative of the non-mesogenic properties. In contrary to compound **4a**, compound **4f** exhibits monotropic behaviour in which the SmC phase is observed upon cooling cycle while the mesophase is absent upon heating.

It is worthwhile to mention that on cooling the present trimeric star-shaped mesogens exhibit I-SmC transition with the enthalpy changes ranging from 19.1 to 30.4 kJ mol<sup>-1</sup>. These values can be considered high and comparable to those found in earlier reported unconventional trimeric analogues (27.1–43.1 kJ mol<sup>-1</sup>) [50]. The high enthalpy of I-SmC reveals a change of the star-shaped mesogens from high molecular order of the tilted arrangement to the diffuse isotropic state. In addition, the entropy changes associated with SmC-I transition of the star-shaped mesogens have also been determined and expressed in dimensionless quantity,  $\Delta S_{\text{SmC-I}}/R$  in which  $R$  is the universal gas constant. The overall  $\Delta S_{\text{SmC-I}}/R$  values of **4b–4f** fall in the range 5.6–11.8. These values are similar to the earlier reported cyclic trimers homologues [36], even though the latter exhibited I-SmA instead of I-SmC transition. The entropy change is seemed to be on the high side and this observation could be due to the higher order of the smectic phase, which has resulted from the specific interactions between the neighbouring molecules [36].

It can also be inferred from Table 2 that the entropy change with respect to I-SmC transition on cooling is dependence on the chain length of the methylene unit. A drastic change of  $\Delta S_{\text{SmC-I}}/R$  from 7.0 to 5.6 can be observed when the alkoxy chain length increases from **4b** to **4c**. However, on ascending alkoxy chain from compounds **4d–4f**, only small

reduction of entropy values towards elongation of terminal chain length is observed. The differences of entropy values among **4d–4f** are relatively small, which lie in the range of  $\pm 0.4$  only. This can probably be ascribed to the conformational degrees of freedom of the terminal alkyloxy chain which affects the transition.

### 3.2 XRD analysis

In addition to two-phase transition peaks revealed by DSC, all liquid crystalline compounds (**4b–4f**) characterised as birefringent liquids by POM in their mesophase were also further investigated by powder XRD measurements. Figures 7–10 demonstrate typical XRD patterns of 1- and 2-dimensional (1-D and 2-D) images of **4c** and **4d**, respectively, in the SmC

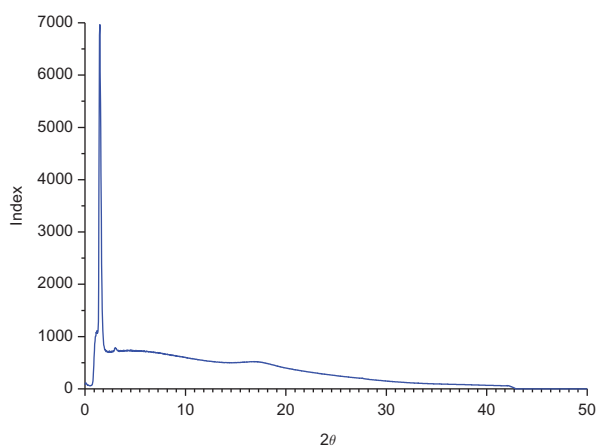


Figure 7. XRD data of compound **4c** at 120°C during the cooling process.

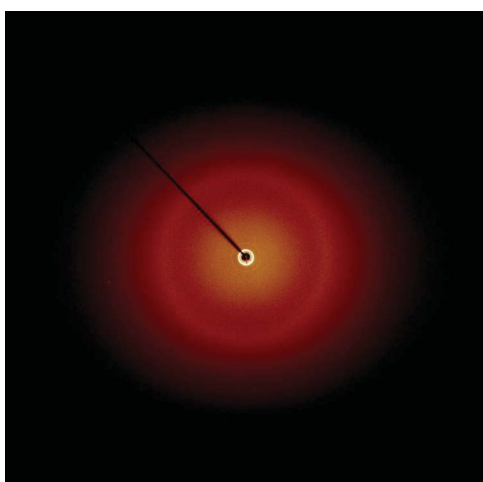


Figure 8. XRD data of compound **4c** at 120°C during the cooling process (2-D image).

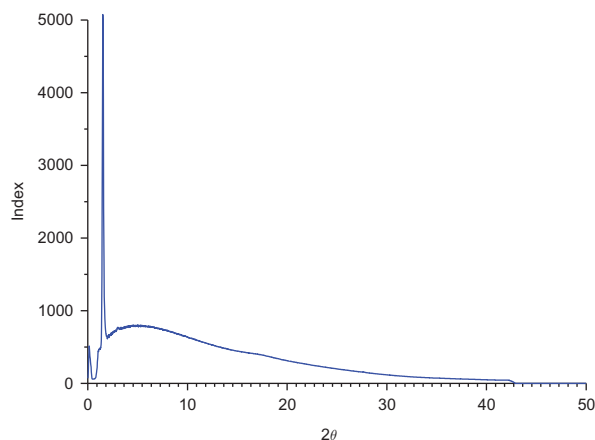


Figure 9. XRD data of compound **4d** at 120°C during the cooling process.

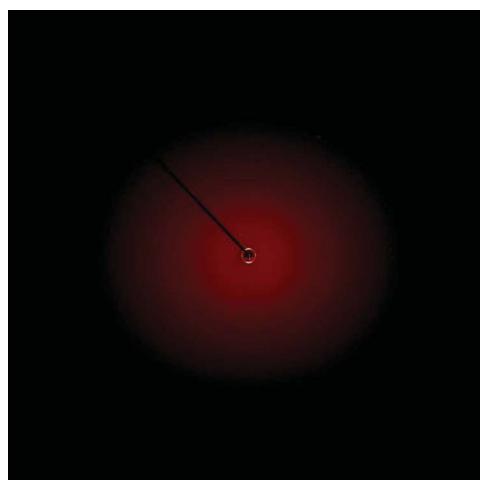


Figure 10. XRD data of compound **4d** at 120°C during the cooling process (2-D image).

Table 3. XRD data ( $2\theta$  and  $d$ -spacing values) of all liquid crystalline samples.

Compound	Temperature	$2\theta$ (°)		$d$ -Spacing (nm)	
<b>4b</b>	160°C (cooling)	1.03	16.3	4.58	0.36
<b>4c</b>	120°C (cooling)	1.48	17.4	4.01	0.34
<b>4d</b>	120°C (cooling)	1.48	—	4.01	—
<b>4e</b>	120°C (cooling)	1.39	—	4.26	—
<b>4f</b>	160°C (cooling)	1.36	16.4	4.35	0.36

phase with layered structures obtained during the cooling process. XRD data of all liquid crystalline compounds **4b–4f** are illustrated in Table 3. All compounds **4b–4f** show an obvious sharp peak at small angles of  $2\theta \sim 1.03^\circ\text{--}1.48^\circ$  (with  $d$ -spacing values of 4.01–4.58 nm, which are correspondent to tilt angles of  $\sim 48^\circ$  with respect to a fully extended molecular chain length of 5.8 nm), which could verify the tilted smectic

layered structures of the SmC phase in compounds **4b–4f**. The broad peaks at the wide angles of  $2\theta \sim 16.3^\circ\text{--}17.4^\circ$  (with  $d$ -spacing values of 0.34–0.36 nm) are correspondent to the average distances between rigid rods of the SmC phase, which should be irrelevant to their molecular chain lengths. Interestingly, as shown in Figure 10, we found that the 2-D image with two arcs of XRD data for compound **4d** at 120 °C during the cooling process had a special aligned orientation, which was not observed in the 2-D images of the other compounds. Further XRD investigations for compound **4d** will be needed to realise this particular aligned phenomenon.

The formation of smectic phase by the star-shaped mesogens **4b–4f** is presumably due to a side-by-side organisation of the Schiff base peripheral units which lie parallel to each other. The conformation adopted by the trimeric compounds also explains why only smectic phase is present instead of a discotic phase because the propyl spacer linking the linearly aromatic peripherals and the benzene core is flexible enough to allow the peripherals to rotate freely. Consequently, they favour the side-by-side interaction between neighbouring molecules. In short, the symmetric star-shaped molecule is capable of folding an anisotropic shape to give rise to the appearance of smectic liquid crystalline order. The molecular structures of rod-like Schiff base ether fragment as well as the non-polar terminal aliphatic chain are contributing factors towards the thermal stability as well as the structure of mesophase thus formed, that is, the smectic layers should be formed by the rod-like units and the benzene core acts only as a linking unit interconnecting the rods.

In the present series, a much easier conformational change is resulted when benzene core and peripheral Schiff base ether are linked by a flexible spacer. As a result, the rod-like fragments can easily align parallel to give a smectic layer structure. This kind of possible self-assembly by mesogens **4b–4f** in the smectic phase is similar to the earlier statement used to rationalise the behaviour of other three-armed star-shaped homologues series which show smectic phases in their liquid crystalline state [25,36,51].

#### 4. Conclusions

A novel series of trimeric star-shaped liquid crystals **4a–4f** in which the phloroglucinol core incorporated with peripheral (*p*-alkyloxybenzylidene) anilines possessing different terminal alkyloxy chains is reported in the current article. The trimeric star-shaped compounds are found to be smectogenic exhibiting predominantly the SmC phase. The homologue member with the shortest terminal alkyl chain was found

to be non-mesogenic, while member with terminal octadecyl chain exhibited the monotropic SmC phase. Initially, the Schlieran texture associated with compound **4d** suggests the existence of nematic phase, but the ambiguity was then resolved by using XRD as the analysis confirms that SmC phase is the only mesophase present during cooling cycles for compounds **4b–4f**. In addition, the appearance of broken fan-shaped texture observed on compound **4b** has further ascertained the SmC phase. The study also revealed that the length of the terminal alkyl chain exerts a significant effect upon the mesomorphic properties, whereby larger smectic phase range was observed for medium-chain derivatives ( $R=\text{C}_{12}\text{H}_{25}$ ,  $\text{C}_{14}\text{H}_{29}$  and  $\text{C}_{16}\text{H}_{33}$ ). In addition, the generation of calamitic SmC phase by the star-shaped mesogens was accomplished by the assembly of the rod-shaped mesogenic Schiff base ether peripheral mesogenic units.

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