

## *Supporting Information*

### **Monolayer to Interdigitated Partial Bilayer Smectic C Transition in Thiophene based Spacer Mesogens: X-ray Diffraction and $^{13}\text{C}$ Nuclear Magnetic Resonance Studies**

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## **EXPERIMENTAL SECTION**

### **Materials**

1,12-dodecane diol, 1,10-decane diol, 1, 8-octane diol, 1, 6-hexane diol, 4-chlorobutyl acetate, n-bromoalkanes ( $\text{C}_2$  to  $\text{C}_{12}$  even carbons), 4-hydroxy benzaldehyde, 2, 5-thiophene dicarboxylic acid, dicyclohexylcarbodiimide, 4-dimethylamino pyridine and 4-acetamido phenol were purchased from Aldrich (USA) and used without further purification. Thionyl chloride ( $\text{SOCl}_2$ ), triethylamine (TEA), N, N'-dimethylformamide (DMF), tetrahydrofuran (THF), ethanol and methanol (SD Fine, Mumbai) were used as received. 4-hydroxy methyl benzoate, Ethyl acetate, diethyl ether, n-hexane, pet ether, n-heptane, acetone, toluene, glacial acetic acid, ethyl methyl ketone (EMK), anhydrous sodium sulphate, sodium chloride, potassium hydroxide, anhydrous potassium carbonate, calcium chloride, sodium hydroxide, hydrochloric acid, hydrobromic acid and silica gel (100-200 mesh) were obtained from Merck (India) and used as received. 1-bromo hexanol, 1-bromo octanol, 1-bromo decanol and 1-bromo dodecanol and also 4-ethoxy benzoic acid, 4-butoxy benzoic acid, 4-hexyloxy

benzoic acid, 4-octyloxy benzoic acid, 4-decyloxy benzoic acid and 4-dodecyloxy benzoic acid were synthesized in laboratory.

*Synthetic details and spectral data of all the intermediates and target mesogens is furnished below.*

### **Bromination of diols**

#### **Synthesis of 6-bromohexan-1-ol (1a)**

1, 6- hexane diol (24.2 g, 0.205 mol), HBr (27 ml, 0.24 mol) were placed in a 1000 ml single necked round bottomed flask fitted with a double wall reflux condenser and toluene (600 ml) was added to the flask.<sup>1</sup> The reaction mixture was refluxed for 75hours and the progress of the reaction is monitored with TLC. Then the reaction mixture was cooled to room temperature, transferred to separating funnel (500 ml) and extracted with diethyl ether. The organic layer collected was washed with 1M NaOH solution (2×100 ml) and water (3×100 ml) respectively and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The toluene was removed under reduced pressure and the brown color liquid obtained was chromatographed on silica gel and eluted with hexane. The removal of solvent from elute gave a colorless liquid.

Similar procedure was used for other compounds namely 8-bromooctan-1-ol (1b), 10-bromodecan-1-ol (1c) and 12-bromododecan-1-ol (1d).

#### **6-bromohexan-1-ol (1a)**

Yield: 73.5%, FT-IR (KBr, cm<sup>-1</sup>): 3429 (-OH), 2929, 2859 (C-H<sub>str</sub>), 1459, 1399 (C-H<sub>ben</sub>); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ3.54 (t, 2H), 3.30 (t, 2H), 2.71 (s, OH), 1.71 (m, 2H), 1.69 (m, 2H), 1.24 (m, 4H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ34.01, 31.72, 30.94, 29.21, 28.11 and 24.31.

### **8-bromooctan-1-ol (1b)**

Yield: 76.2%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3407 (-OH), 2928, 2857 ( $\text{C-H}_{\text{str}}$ ), 1457, 1250 ( $\text{C-H}_{\text{ben}}$ );  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 3.51 (t, 2H), 3.32 (t, 2H), 2.75 (s, -OH), 1.77 (m, 2H), 1.46 (m, 2H), 1.35 (m, 2H), 1.24 (m, 6H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 34.06, 32.83, 32.64, 29.28, 28.76, 28.13 and 25.71.

### **10-bromodecan-1-ol (1c)**

Yield: 73.7%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3321 (-OH), 2927, 2855 ( $\text{C-H}_{\text{str}}$ ), 1441, 1254 ( $\text{C-H}_{\text{ben}}$ );  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 3.55 (m, 2H), 3.33 (m, 2H), 1.79 (m, 2H), 1.52 (m, 2H), 1.35 (m, 2H), 1.27 (m, 10H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 62.73, 34.13, 32.86, 32.44, 29.56, 29.45, 28.82, 28.21 and 25.29.

### **12-bromododecan-1-ol (1d)**

Yield: 74.4%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3337 (-OH), 2926, 2854 ( $\text{C-H}_{\text{str}}$ ), 1461, 1361 ( $\text{C-H}_{\text{ben}}$ );  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 3.58 (m, 2H), 3.37 (m, 2H), 2.07 (s, -OH), 1.81 (m, 2H), 1.52 (s, 2H), 1.38 (m, 2H), 1.38 (m, 2H), 1.24 (m, 12H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 63.01, 34.17, 32.90, 32.81, 34.17, 32.90, 32.81, 29.67, 29.61, 29.59, 28.84 and 25.83.

### **Synthesis of 4-(4-hydroxybutoxy) benzaldehyde (2, 3a)**

#### **Step 1: Synthesis of 4-(4-formylphenoxy) butyl acetate (2)**

In a representative experiment, 4-hydroxy benzaldehyde (7 g, 0.057 mol) was placed in a 500 ml three necked round bottom flask equipped with stirrer and thermometer. DMF (200 ml) and potassium carbonate (9 g, 0.065 mol) were added to the flask. The resulting mixture was stirred while maintaining the temperature at  $90^\circ\text{C}$ , then 4-chlorobutyl acetate (7.9

ml, 0.057 mol) was added through a pressure equalizing dropping funnel over a period of 45 minutes and the stirring was continued for 4 hours.<sup>2</sup> Then the reaction mixture was allowed to cool to room temperature, poured into a two liter beaker. The contents were diluted with water (250 ml) and then transferred into a 500 ml separating funnel and extracted with diethyl ether. The ether layer collected was washed with 10% potassium hydroxide solution (2×100 ml) followed by distilled water (3×100 ml). Then the ether layer was dried with anhydrous sodium sulphate and upon evaporation of solvent, 4-(4-formylphenoxy) butyl acetate was obtained as a liquid.

#### Step 2: Hydrolysis of 4-(4-formylphenoxy) butyl acetate (**3a**)

4-(4-formylphenoxy) butyl acetate was placed in a 500 ml single necked round bottom flask equipped with double wall water condenser. Ethanol (200 ml) and potassium hydroxide solution (6 g, 200 ml) in equal volume were added to the flask. The reaction mixture was refluxed for two hours and allowed to cool to room temperature. It was then neutralized with 10% hydrochloric acid and extracted with diethyl ether. The organic layer collected was washed twice with distilled water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Liquid was obtained on evaporation of ether which was purified by column chromatography on silica gel using a mixture of 40% ethyl acetate in hexane as an eluent.

#### 4-(4-formylphenoxy) butylacetate (**2**)

Yield: 66.7%, FT-IR (KBr, cm<sup>-1</sup>): 2854, 2856 (C-H<sub>str</sub>), 1736 (C=O<sub>str</sub>), 1691 (-HC=O), 1601, 1511 (C=C<sub>str</sub> aromatic), 1429, 1368 (C-H<sub>ben</sub>), 1249, 1161 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ 9.79 (s, 1H), 7.75 (d, 2H), 6.92 (d, 2H), 4.08 (t, 2H), 4.00 (t, 2H), 1.97 (s, 3H), 1.77 (m, 4H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ 190.86, 171.17, 164.03, 132.03, 129.91, 114.77, 67.73, 63.99, 25.72, 25.33 and 20.98.

#### 4-(4-hydroxybutoxy) benzaldehyde (3a)

Yield: 64.2%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3402 (-OH), 2945, 2876 ( $\text{C-H}_{\text{str}}$ ), 2745 ( $\text{CHO-C-H}_{\text{str}}$ ), 1685 ( $-\text{HC}=\text{O}$ ), 1601, 1511 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1471, 1396 ( $\text{C-H}_{\text{ben}}$ ), 1162, 1110 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$  9.76 (s, 1H), 7.74 (d, 2H), 6.91 (d, 2H), 4.01 (t, 2H), 3.65 (t, 2H), 2.83 (s, -OH), 1.84 (m, 2H), 1.68 (m, 2H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$  191.19, 164.22, 132.13, 129.73, 114.83, 68.23, 62.19, 29.16 and 25.64.

#### Synthesis of 4-(6-hydroxyhexyloxy) benzaldehyde (3b-e)

In this experiment, 4-hydroxybenzaldehyde (5 g, 0.04 mol) was placed in a 500 ml three necked round bottom flask equipped with stirrer and thermometer. To this, DMF (175 ml) and potassium carbonate (7 g, 0.05 mol) were added. The resulting mixture was stirred while maintaining the temperature at  $90^\circ\text{C}$ . 6-bromohexan-1-ol (7.24 g, 0.04 mol) was added through a pressure equalizing dropping funnel for 45 minutes and the stirring was continued for 5 hours<sup>2</sup> and then reaction mixture was allowed to cool to room temperature, poured into a two liter beaker. The contents were diluted with water (500 ml) and then transferred into a 500 ml separating funnel and extracted with diethyl ether. The ether layer collected was washed using 10% potassium hydroxide solution ( $2 \times 100$  ml) and distilled water ( $3 \times 100$  ml). Then the organic layer was dried over anhydrous sodium sulphate. Upon evaporation of ether, resulted 4-(12-hydroxydodecyloxy) benzaldehyde as a brown solid and was purified by column chromatography on silica gel using a mixture of 30% ethyl acetate in pet ether as an eluent. Removal of solvent resulted in solid compound.

Similarly the synthesis of 4-(8-hydroxyoctyloxy) benzaldehyde (**3c**), 4-(10-hydroxydecyloxy) benzaldehyde (**3d**) and 4-(12-hydroxydodecyloxy) benzaldehyde (**3e**) were carried out.

#### 4-(6-hydroxyhexyloxy) benzaldehyde (3b)

Yield: 64.9%, FT-IR(KBr,  $\text{cm}^{-1}$ ): 3408 (-OH), 2936, 2863 ( $\text{C-H}_{\text{str}}$ ), 2742 ( $\text{CHO-C-H}_{\text{str}}$ ), 1687 ( $-\text{HC}=\text{O}$ ), 1600, 1511 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1467, 1395 ( $\text{C-H}_{\text{ben}}$ ), 1259, 1161, 1110 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 9.71 (s, 1H), 7.69 (d, 2H), 6.85 (d, 2H), 3.90 (t, 2H), 3.52 (t, 2H), 3.11 (s, -OH), 1.68 (m, 2H), 1.48 (m, 2H), 1.34 (m, 4H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 191.09, 164.30, 132.06, 129.62, 114.78, 68.32, 62.40, 32.56, 29.01, 25.80 and 25.57.

#### 4-(8-hydroxyoctyloxy) benzaldehyde (3c)

Yield: 66%, m.p-48°C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3444 (-OH), 3075 (aromatic  $\text{C-H}_{\text{str}}$ ), 2929, 2854 ( $\text{C-H}_{\text{str}}$ ), 2752 ( $\text{CHO-C-H}_{\text{str}}$ ), 1678 ( $-\text{HC}=\text{O}$ ), 1599, 1510 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1469, 1394 ( $\text{C-H}_{\text{ben}}$ ), 1259, 1165 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 9.79 (s, 1H), 7.76 (d, 2H), 6.92 (d, 2H), 3.96 (t, 2H), 3.56 (t, 2H), 2.34 (s, -OH), 1.73 (m, 2H), 1.51 (m, 2H), 1.40 (m, 2H), 1.29 (m, 6H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 191.03, 164.34, 132.08, 129.72, 114.81, 68.44, 62.80, 32.74, 29.37, 29.34, 29.07, 25.94 and 25.76.

#### 4-(10-hydroxydecyloxy) benzaldehyde (3d)

Yield: 64.3%, m.p-61.2°C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3448 (-OH), 3074 (aromatic  $\text{C-H}_{\text{str}}$ ), 2923, 2852 ( $\text{C-H}_{\text{str}}$ ), 2752 ( $\text{CHO-C-H}_{\text{str}}$ ), 1679 ( $-\text{HC}=\text{O}$ ), 1599, 1510 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1469, 1396 ( $\text{C-H}_{\text{ben}}$ ), 1258, 1165 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 9.81 (s, 1H), 7.78 (d, 2H), 6.95 (d, 2H), 3.98 (t, 2H), 3.58 (t, 2H), 2.23 (s, -OH), 1.76 (m, 2H), 1.52 (m, 2H), 1.42 (m, 2H), 1.38 (m, 10H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 191.01, 164.36, 132.08, 129.75, 114.83, 68.48, 62.93, 32.80, 29.57, 29.52, 29.47, 29.36, 29.09, 26.00 and 25.82.

#### **4-(12-hydroxydodecyloxy) benzaldehyde (3e)**

Yield: 61% m.p-70.2 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3445 (-OH), 2920, 2850 ( $\text{C-H}_{\text{str}}$ ), 2752 ( $\text{CHO-C-H}_{\text{str}}$ ), 1679 ( $-\text{HC}=\text{O}$ ), 1599, 1511 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1469, 1395 ( $\text{C-H}_{\text{ben}}$ ), 1258, 1166, 1111 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$  9.78 (s, 1H), 7.79 (d, 2H), 6.93 (d, 2H), 3.97 (t, 2H), 3.55 (t, 2H), 1.90 (s, -OH), 1.78 (m, 2H), 1.55 (m, 2H), 1.40 (m, 2H), 1.37 (m, 14H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$  191.01, 164.37, 132.10, 129.74, 114.82, 68.49, 63.00, 32.84, 29.66, 29.62, 29.60, 29.51, 29.39, 26.11, 26.01 and 25.84.

#### **Preparation of 2,5-thiophene dicarbonyl chloride (4)**

2,5-thiophene dicarboxylic acid (2.8 g, 0.016 mol) was placed in a 100 ml single necked round bottomed flask fitted with a double wall reflux condenser and a calcium chloride guard tube and  $\text{SOCl}_2$  (4.5 ml, 0.064 mol) and a few drops of DMF were added to the flask. The reaction mixture was refluxed for one hour and the excess  $\text{SOCl}_2$  was removed by vacuum pump then 2,5-thiophene- di- carbonyl chloride was resulted as a liquid.

#### **Synthesis of bis (4-(4-formylphenoxy) dodecyl) thiophene-2, 5-dicarboxylate (5)**

It was synthesised by two step process. In this experiment, 4-(4-hydroxybutoxy) benzaldehyde (6.22 g , 0.032 mol) was placed in a 500 ml two necked round bottomed flask equipped with stirrer. Triethyl amine (5.6 ml, 0.04 mol) dissolved in ethyl methyl ketone was added to the flask which was kept in an ice bath. To this, thiophene-2,5-dicarbonyl dichloride (as synthesised above (4)) dissolved in EMK (50 ml) was slowly added through a pressure equalizing dropping funnel for a period of 45 minutes while stirring the contents. The triethyl amine salt precipitated was filtered and the solvent was removed under reduced pressure. The

semi-solid obtained was purified by column chromatography on silica gel using a mixture of 40% ethyl acetate in pet ether. Upon evaporation of solvent white solid was obtained.

Same procedure was followed for other compounds namely bis (4-(4-formylphenoxy) hexyl) thiophene-2, 5-dicarboxylate (**5b**), bis (4-(4-formylphenoxy) octyl) thiophene-2, 5-dicarboxylate (**5c**), (bis (4-(4-formylphenoxy) decyl) thiophene-2, 5-dicarboxylate (**5d**), bis (4-(4-formylphenoxy) dodecyl) thiophene-2, 5-dicarboxylate (**5e**).

**Bis (4-(4-formylphenoxy) butyl) thiophene-2, 5-dicarboxylate (5a)**

Yield: 58.7%, m.p-81 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3108 (aromatic C-H<sub>str</sub>), 2957, 2832, 2746 (C-H<sub>str</sub>), 1709 (C=O<sub>str</sub>), 1601, 1512 (C=C<sub>str</sub> aromatic), 1453, 1393 (C-H<sub>ben</sub>), 1260, 1158 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$ 9.81 (s, 1H), 7.77 (d, 2H), 7.66 (s, 1H), 6.95 (d, 2H), 4.36 (t, 2H), 4.07 (t, 2H), 1.93 (m, 4H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$ 190.83, 163.96, 161.55, 139.01, 133.13, 132.04, 129.98, 114.80, 67.68, 65.31, 25.79 and 25.44.

**Bis (6-(4-formylphenoxy) hexyl) thiophene-2, 5-dicarboxylate (5b)**

Yield: 63.1%, m.p-79 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2939, 2856, 2744 (C-H<sub>str</sub>), 1695 (-HC=O<sub>str</sub>), 1603, 1577, 1512 (C=C<sub>str</sub> aromatic)1464, 1394 (C-H<sub>ben</sub>), 1259, 1159 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):  $\delta$ 9.81 (s, 1H), 7.76 (d, 2H), 7.66 (s, 1H), 6.93 (d, 2H), 4.27 (t, 2H), 3.99 (t, 2H), 1.77 (m, 4H), 1.48 (m, 4H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):  $\delta$ 190.84, 164.20, 161.66, 139.13, 133.01, 132.03, 129.83, 114.79, 68.20, 65.66, 28.97, 28.56, 25.73 and 25.71.

**Bis (8-(4-formylphenoxy) octyl) thiophene-2, 5-dicarboxylate (5c)**

Yield: 60.7%, m.p-67°C, FT-IR (KBr, cm<sup>-1</sup>): 2933, 2861, 2746 (C-H<sub>str</sub>), 1707 (C=O<sub>str</sub>), 1601, 1513 (C=C<sub>str</sub> aromatic), 1469, 1392 (C-H<sub>ben</sub>), 1219, 1158 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ9.82 (s, 1H), 7.77 (d, 2H), 7.67 (s, 1H), 6.94 (d, 2H), 4.26 (t, 2H), 3.98 (t, 2H), 1.75 (m, 4H), 1.37 (m, 8H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ190.87, 164.27, 161.72, 139.19, 132.98, 132.04, 129.78, 114.80, 68.39, 65.83, 29.24, 29.16, 29.07, 28.62, 25.94 and 25.89.

**Bis (10-(4-formylphenoxy) decyl) thiophene-2, 5-dicarboxylate (5d)**

Yield: 61.2%, m.p-65°C, FT-IR (KBr, cm<sup>-1</sup>): 2926, 2851, 2738 (C-H<sub>str</sub>), 1703 (C=O<sub>str</sub>), 1601, 1573, 1512 (C=C<sub>str</sub> aromatic), 1468, 1396 (C-H<sub>ben</sub>), 1258, 1159 (C-O-C<sub>asym&symstr</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ9.82 (s, 1H), 7.79 (d, 2H), 7.68 (s, 1H), 6.95 (d, 2H), 4.26 (t, 2H), 3.97 (t, 2H), 1.76 (m, 4H), 1.39 (m, 12H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ190.91, 164.31, 161.76, 139.20, 132.97, 132.07, 129.76, 114.80, 68.45, 65.89, 29.50, 29.47, 29.37, 29.25, 29.11, 28.65, 26.02 and 25.96.

**Bis (12-(4-formylphenoxy) dodecyl) thiophene-2, 5-dicarboxylate (5e)**

Yield: 59.3%, m.p-63°C, FT-IR (KBr, cm<sup>-1</sup>): 2925, 2850, 2737 (C-H<sub>str</sub>), 1706 (C=O<sub>str</sub>), 1602, 1574, 1512 (C=C<sub>str</sub> aromatic), 1468, 1395 (C-H<sub>ben</sub>), 1260, 1160 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ9.82 (s, 1H), 7.76 (d, 2H), 7.67 (s, 1H), 6.94 (d, 2H), 4.25 (t, 2H), 3.97 (t, 2H), 1.74 (m, 4H), 1.38 (m, 16H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ190.86, 164.30, 161.74, 139.20, 132.95, 132.04, 129.75, 114.79, 68.46, 65.89, 29.60, 29.56, 29.48, 29.41, 29.28, 29.12, 28.65, 26.03 and 25.97.

## Synthesis of 4-ethoxybenzoic acid (6, 7)

### Step1: Preparation of 4-ethoxy methyl benzoate (6)

In a representative experiment, 4-hydroxy methylbenzoate (5 g, 0.032 mol) was placed in a 250 ml three necked round bottom flask equipped with stirrer, thermometer and double walled condenser with cold water circulation. To that, DMF (100 ml) and potassium carbonate (8.83 g, 0.064 mol) were added. The resulting mixture was stirred while maintaining the temperature at 90 °C, then n-bromoethane (2.38 ml, 0.032 mol) was added through a pressure equalizing dropping funnel over a period of 30 minutes and the stirring was continued for about 5 hours and then the reaction mixture was allowed to cool to room temperature, poured into a two litre beaker.<sup>3-5</sup> The contents were diluted with water (100 ml) and then transferred to 250 ml separating funnel and diethyl ether was added. The ether layer collected was washed twice using 10% potassium hydroxide solution and followed by distilled water. Then the organic layer was dried over anhydrous sodium sulphate and upon evaporation of ether resulted in liquid 4-ethoxy methyl benzoate.

### Step 2: Hydrolysis of 4- ethoxy methyl benzoate (7)

4-Ethoxy methyl benzoate (4g, 0.02 mol) was placed in 500 ml single necked round bottom flask equipped with double wall water condenser. Ethanol (125 ml) and potassium hydroxide (2.69 g, 0.048 mol) dissolved in distilled water (125 ml) were added to the flask. The solution was refluxed for two hours and allowed to cool to room temperature and neutralized with 10% hydrochloric acid to get a white precipitate.<sup>3-5</sup> The compound was purified by recrystallizing from methanol.

The above procedure was used for synthesizing other compounds namely 4-butoxy benzoic acid, 4-hexyloxy benzoic acid, 4-octyloxy benzoic acid, 4-decyloxy benzoic acid and 4-dodecyloxy benzoic acid.

#### **4-ethoxy benzoic acid (7a)**

Yield: 64.4%, m.p-195.2 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2976, 2894 ( $\text{C-H}_{\text{str}}$ ), 2552 ( $\text{O-H}_{\text{str}}$  of carboxylic acid), 1677 ( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1608, 1526 ( $\text{C=C}_{\text{str}}$  aromatic), 1477, 1435 ( $\text{C-H}_{\text{ben}}$ ) 1299, 1266, 1157 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 8.05 (d, 2H), 6.91 (d, 2H), 4.06 (m, 2H), 0.99 (t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 172.24, 163.81, 132.55, 121.27, 114.36, 68.07 and 13.94.

#### **4-butoxy benzoic acid (7b)**

Yield: 80.7%, m.p-152 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2956, 2872 ( $\text{C-H}_{\text{str}}$ ), 2557 ( $\text{O-H}_{\text{str}}$  of carboxylic acid), 1680 ( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1604, 1513 ( $\text{C=C}_{\text{str}}$  aromatic), 1464, 1425 ( $\text{C-H}_{\text{ben}}$ ) 1297, 1255, 1169 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 8.06 (d, 2H), 6.93 (d, 2H), 4.03 (t, 2H), 1.79 (m, 2H), 1.49 (m, 2H), 0.98(t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 172.22, 163.79, 132.43, 121.49, 114.26, 68.05, 31.20, 19.27 and 13.90.

#### **4-hexyloxy benzoic acid (7c)**

Yield: 84.7%, m.p-112 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2941, 2867 ( $\text{C-H}_{\text{str}}$ ), 2549 ( $\text{O-H}_{\text{str}}$  of carboxylic acid), 1683 ( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1604, 1511 ( $\text{C=C}_{\text{str}}$  aromatic), 1467, 1426 ( $\text{C-H}_{\text{ben}}$ ) 1297, 1253, 1166, 1121, ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 8.06 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.78 (m, 2H), 1.46 (m, 2H), 1.33 (m, 4H), 0.90 (t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 172.38, 163.79, 132.43, 121.48, 114.26, 68.37, 31.64, 29.15, 25.76, 22.69 and 14.13.

#### 4-octyloxy benzoic acid (7d)

Yield: 79.4% m.p-104°C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2929, 2849, 2671( $\text{C-H}_{\text{str}}$ ), 2557 ( $\text{O-H}_{\text{str}}$ .of carboxylic acid), 1689 ( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1607, 1513 ( $\text{C=C}_{\text{str}}$  aromatic), 1463, 1426, 1389, 1318 ( $\text{C-H}_{\text{ben}}$ ), 1294, 1253, 1168 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 8.06 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.31 (m, 8H), 0.88 (t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 172.21, 163.78, 132.43, 121.48, 114.26, 68.38, 31.89, 29.42, 29.32, 29.17, 26.07, 22.75 and 14.20.

#### 4-decyloxy benzoic acid (7e)

Yield: 81.3 % m.p-98 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2922, 2852, 2664(aromatic  $\text{C-H}_{\text{str}}$ ), 2559( $\text{O-H}_{\text{str}}$ .of carboxylic acid) 1678( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1605, 1512( $\text{C=C}_{\text{str}}$  aromatic), 1467, 1427( $\text{C-H}_{\text{ben}}$ ), 1305, 1255, 1167( $\text{C-O-C}_{\text{asym\&symstr}}$  of ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ )  $\delta$ 8.05(d, 2H), 6.93(d, 2H), 4.01(t, 2H), 1.80(m, 2H), 1.45(m, 2H), 1.33(m, 12H), 0.87(t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ )  $\delta$ 171.97, 163.78, 132.42, 121.47, 114.27, 68.38, 31.98, 29.63, 29.44, 29.39, 29.17, 26.05, 22.76 and 14.19.

#### 4-dodecyloxy benzoic acid (7f)

Yield: 80%, m.p-96.5°C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2921, 2851 ( $\text{C-H}_{\text{str}}$ ), 2558 ( $\text{O-H}_{\text{str}}$ .of carboxylic acid), 1681 ( $\text{C=O}_{\text{str}}$  of carboxylic acid), 1605, 1512 ( $\text{C=C}_{\text{str}}$  aromatic), 1467, 1427 ( $\text{C-H}_{\text{ben}}$ ), 1255, 1167 ( $\text{C-O-C}_{\text{asym\&symstr}}$  ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 8.05 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.34 (m, 16H), 0.87 (t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 171.91, 163.86, 132.42, 120.91, 114.27, 68.38, 32.02, 29.76, 29.73, 29.69, 29.65, 29.45, 29.17, 26.06, 22.79 and 14.23.

## Synthesis of 4-aminophenyl 4-ethoxybenzoate (**8**, **9**)

### Step.1: Synthesis of 4-[(tert-butoxycarbonyl) amino] phenyl 4-ethoxybenzoate (**8a**)

In this experiment, 4-ethoxy benzoic acid (3.32 g, 0.02 mol) and N-BOC-4-amino phenol (4.18 g, 0.02 mol) were placed in a 250 ml conical flask. To this, dichloromethane (150 ml) was added and the solution was stirred at room temperature with magnetic stirrer. 4-dimethylamino pyridine (0.24 g, 0.002 mol) was added as a catalyst to the solution. After 10 minutes, dicyclohexylcarbodiimide (5.15 g, 0.025 mol) dissolved in dichloromethane was added to the flask<sup>6</sup> and the solution was allowed to stir for 15 hours. The precipitated N, N'-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into separating funnel and then washed with 5% KOH solution (2×100 ml), 10% HCl solution (2×100 ml) and followed by distilled water (3×100 ml). The organic layer collected was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Upon evaporation of solvent, the white solid resulted was purified by recrystallization from isopropyl alcohol.

Similar protocol was followed for other compounds namely 4-[(tert-butoxycarbonyl) amino] phenyl 4-butoxybenzoate (**8b**), 4-[(tert-butoxycarbonyl) amino] phenyl 4-hexyloxybenzoate (**8c**), 4-[(tert-butoxycarbonyl) amino] phenyl 4-octyloxybenzoate (**8d**), 4-[(tert-butoxycarbonyl) amino] phenyl 4-decyloxybenzoate (**8e**) and 4-[(tert-butoxycarbonyl) amino] phenyl 4-dodecyloxybenzoate (**8f**)

### Step.2: Deblocking of 4-[(tert-butoxycarbonyl) amino] phenyl 4-ethoxybenzoate (**9a**)

In a typical experiment, 4-[(tert-butoxycarbonyl) amino] phenyl 4-ethoxybenzoate (3.46 g, 0.0097 mol) was placed in a 250 ml two necked round bottom flask which was kept in an ice bath. Dichloromethane (150 ml) was added to the flask while maintaining 0°C. Then trifluoroacetic acid (13.7 ml, 0.185 mol) was added and the reaction mixture was stirred for

two hours.<sup>7</sup> Later it was taken out from the ice bath; saturated sodium bicarbonate solution (50 ml) was added and stirred for 20 minutes. The contents were transferred to a 500 ml separating funnel and dichloromethane was added. The organic layer was washed twice with 1% potassium hydroxide and distilled water respectively. Upon evaporation of dichloromethane, solid (4-aminophenyl 4-ethoxybenzoate) was resulted. It was purified by recrystallisation from heptane.

Similar protocol was followed for other compounds namely 4-aminophenyl 4-butoxybenzoate (**9b**), 4-aminophenyl 4-hexyloxybenzoate (**9c**), 4-aminophenyl 4-octyloxybenzoate (**9d**), 4-aminophenyl 4-decyloxybenzoate (**9e**), 4-aminophenyl 4-dodecyloxybenzoate (**9f**).

#### **4-[(*tert*-butoxycarbonyl) amino] phenyl 4-ethoxybenzoate (8a)**

Yield: 68%, m.p-194 °C, FT-IR (KBr, cm<sup>-1</sup>): 3358 (N-H<sub>str</sub>), 2984, 2931 (C-H<sub>str</sub>), 1718 (C=O<sub>str</sub>), 1605, 1531 (C=C<sub>str</sub> aromatic), 1475, 1366 (C-H<sub>ben</sub>), 1259, 1194, 1160 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.13 (d, 2H), 7.39 (d, 2H), 7.11 (d, 2H), 6.95 (d, 2H), 6.63 (s, 1H), 4.09 (t, 2H), 1.51 (m, 9H), 1.43 (m, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.25, 163.38, 152.90, 146.43, 136.07, 132.35, 122.24, 121.69, 119.54, 114.33, 80.65, 63.88, 28.43 and 14.76.

#### **4-[(*tert*-butoxycarbonyl) amino] phenyl 4-butoxybenzoate (8b)**

Yield: 74.7%, m.p-195 °C, FT-IR (KBr, cm<sup>-1</sup>): 3374 (N-H<sub>str</sub>), 2964, 2939, 2874 (C-H<sub>str</sub>), 1726, 1703 (C=O<sub>str</sub>), 1607, 1521 (C=C<sub>str</sub>aromatic), 1467, 1370 (C-H<sub>ben</sub>), 1264, 1165 (C-O-C<sub>asym&symstr</sub>of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.12 (d, 2H), 7.38 (d, 2H), 7.11 (d, 2H), 6.95 (d, 2H), 6.55 (s, 1H), 4.03 (t, 2H), 1.79 (m, 2H), 1.49 (m, 11H), 0.88 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.26, 163.59, 152.87, 146.45, 136.01, 132.34, 122.28, 121.60, 119.50, 114.34, 68.07, 31.21, 28.43, 19.28 and 13.93.

#### **4-[(*tert*-butoxycarbonyl) amino] phenyl 4-hexyloxybenzoate (8c)**

Yield: 63.5%, m.p-180 °C, FT-IR (KBr, cm<sup>-1</sup>):3353(N-H<sub>str</sub>), 2949, 2866(aromatic C-H<sub>str</sub>), 1721(C=O<sub>str</sub>), 1606, 1525(C=C<sub>str</sub> aromatic), 1466, 1403, 1367(C-H<sub>ben</sub>), 1266, 1162(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>) δ8.12(d, 2H), 7.39(d, 2H), 7.12(d, 2H), 6.96(d, 2H), 6.59(s, 1H), 4.02(t, 2H), 1.82(m, 2H), 1.45(m, 11H), 1.34(m, 4H), 0.90(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>) δ165.28, 163.58, 152.88, 146.42, 136.03, 132.34, 122.27, 121.58, 119.50, 114.33, 80.68, 68.39, 31.65, 29.15, 28.43, 25.76, 22.69 and 14.15.

#### **4-[(*tert*-butoxycarbonyl) amino] phenyl 4-octyloxybenzoate (8d)**

Yield:70.8 %, m.p-147 °C, FT-IR (KBr, cm<sup>-1</sup>):3370(N-H<sub>str</sub>), 2941, 2861(C-H<sub>str</sub>), 1727, 1703(C=O<sub>str</sub>), 1608, 1525(C=C<sub>str</sub> aromatic), 1467, 1412, 1367, 1313(C-H<sub>ben</sub>), 1269, 1241, 1193, 1162(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>) δ8.12(d, 2H), 7.39(d, 2H), 7.09(d, 2H), 6.94(d, 2H), 6.66(s, 1H), 4.02(t, 2H), 1.80(m, 2H), 1.46(m, 19H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>) δ165.91, 165.30, 163.59, 152.91, 146.40, 136.07, 132.35, 122.25, 121.58, 119.51, 114.34, 80.65, 68.39, 31.90, 29.43, 29.33, 29.18, 28.43, 26.08, 22.76 and 14.23.

#### **4-[(*tert*-butoxycarbonyl) amino] phenyl 4-decyloxybenzoate (8e)**

Yield:67.8%, m.p-138 °C, FT-IR (KBr, cm<sup>-1</sup>):3363(N-H<sub>str</sub>), 2926, 2856(C-H<sub>str</sub>), 1720(C=O<sub>str</sub>), 1608, 1526(C=C<sub>str</sub> aromatic), 1464, 1408, 1366(C-H<sub>ben</sub>), 1273, 1232, 1165(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>) δ8.11(d, 2H), 7.39(d, 2H), 7.11(d, 2H), 6.95(d, 2H), 6.70(s,1H), 4.02(t, 2H), 1.80(m, 2H), 1.46(m, 23H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>) δ165.31, 163.59, 152.93, 146.39, 136.10, 132.35, 122.24, 121.58, 119.53, 114.34, 68.39, 32.00, 29.66, 29.47, 29.43, 29.19, 28.43, 26.08, 22.79 and 14.25.

#### **4-[(*tert*-butoxycarbonyl) amino] phenyl 4-dodecyloxybenzoate (8f)**

Yield:70%, m.p-125 °C, FT-IR (KBr, cm<sup>-1</sup>):3370(N-H<sub>str</sub>), 2927, 2856(C-H<sub>str</sub>), 1729(C=O<sub>str</sub>), 1703, 1608, 1525(C=C<sub>str</sub> aromatic), 1468, 1411, 1367, 1312(C-H<sub>ben</sub>), 1269,

1164(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>) δ8.12(d, 2H), 7.39(d, 2H), 7.10(d, 2H), 6.95(d, 2H), 6.64(s, 1H), 4.02(t, 2H), 1.80(m, 2H), 1.51(m, 8H), 1.35(m, 19H), 0.87(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>) δ165.28, 163.59, 152.90, 146.42, 136.05, 132.34, 122.26, 121.58, 119.51, 114.34, 68.39, 32.02, 29.76, 29.75, 29.70, 29.66, 29.46, 29.18, 28.43, 26.07, 22.80 and 14.25.

#### **4-aminophenyl 4-ethoxybenzoate (9a)**

Yield: 65.3%, m.p-154 °C, FT-IR (KBr, cm<sup>-1</sup>): 3492, 3394 (NH<sub>2str</sub>), 2980, 2932, 2882 (C-H<sub>str</sub>), 1716 (C=O<sub>str</sub>), 1608 and 1511 (C=C<sub>str</sub> aromatic), 1469, 1394 (C-H<sub>ben</sub>), 1261, 1195, 1163 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>) δ8.16 (d, 2H), 6.94 (m, 4H), 6.69 (d, 2H), 4.09 (t, 2H), 3.62 (s, 2H), 1.44 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>) δ165.65, 163.25, 144.29, 143.20, 132.30, 122.46, 121.96, 115.78, 114.28, 63.87, and 14.80.

#### **4-aminophenyl 4-butoxybenzoate (9b)**

Yield: 67.4%, m.p-113 °C, FT-IR (KBr, cm<sup>-1</sup>): 3453, 3365 (NH<sub>2str</sub>), 2938, 2873 (C-H<sub>str</sub>), 1711 (C=O<sub>str</sub>), 1606 and 1511 (C=C<sub>str</sub> aromatic), 1471, 1423 (C-H<sub>ben</sub>), 1270, 1172 and 1125 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.14 (d, 2H), 6.95 (m, 4H), 6.68 (d, 2H), 4.01 (t, 2H), 3.58 (s, 2H), 1.81 (m, 2H), 1.52 (m, 2H), 0.99 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.68, 163.47, 144.33, 143.19, 132.28, 122.46, 121.89, 115.78, 114.32, 68.06, 31.24, 19.31 and 13.97.

#### **4-aminophenyl 4-hexyloxybenzoate (9c)**

Yield: 74.9%, m.p-91 °C, FT-IR (KBr, cm<sup>-1</sup>):3407, 3329(NH<sub>2str</sub>), 3212 (aromatic C-H<sub>str</sub>), 2934, 2861 (C-H<sub>str</sub>), 1721 (C=O<sub>str</sub>), 1607 and 1512 (C=C<sub>str</sub> aromatic), 1467, 1420, 1395 and 1315 (C-H<sub>ben</sub>), 1261, 1196 and 1166 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.13 (d, 2H), 6.96(m, 4H), 6.69 (d, 2H), 4.03 (t, 2H), 3.54(s, 2H), 1.81(m, 2H),

1.47 (m, 2H), 1.35 (m, 4H), 0.92 (t, 3H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ ): $\delta$ 165.68, 163.47, 144.31, 143.21, 132.28, 122.46, 121.88, 115.80, 114.31, 68.38, 31.66, 29.17, 25.77, 22.72 and 14.18.

#### **4-aminophenyl 4-octyloxybenzoate (9d)**

Yield: 72.3%, m.p-98 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ):3468, 3373( $\text{NH}_{2\text{str}}$ ), 2919, 2852(aromatic  $\text{C-H}_{\text{str}}$ ), 1712( $\text{C=O}_{\text{str}}$ ), 1606, 1512, ( $\text{C=C}_{\text{str}}$  aromatic), 1466, 1423, 1392( $\text{C-H}_{\text{ben}}$ ), 1280, 1257, 1195,1173( $\text{C-O-C}_{\text{asym\&symstr}}$  of ester and ether);  $^1\text{H}$ -NMR ppm ( $\text{CDCl}_3$ )  $\delta$ 8.14(d, 2H), 6.97(m, 4H), 6.69(d, 2H), 4.01(t, 2H), 3.57(s, 2H), 1.81(m, 2H), 1.45(m, 2H), 1.31(m, 8H), 0.90(t, 3H); $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ )  $\delta$ 165.68, 163.47, 144.33, 143.20, 132.28, 122.46, 121.89, 115.78, 114.32, 68.38, 31.93, 29.46, 29.36, 29.22, 26.11, 22.79 and 14.26.

#### **4-aminophenyl 4-decyloxybenzoate (9e)**

Yield: 68.1%, m.p-99 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ):3407, 3329( $\text{NH}_{2\text{str}}$ ), 2924, 2853(aromatic  $\text{C-H}_{\text{str}}$ ), 1722( $\text{C=O}_{\text{str}}$ ), 1606, 1512, ( $\text{C=C}_{\text{str}}$  aromatic), 1468, 1398, 1316( $\text{C-H}_{\text{ben}}$ ), 1262, 1197, 1167( $\text{C-O-C}_{\text{asym\&symstr}}$  of ester and ether);  $^1\text{H}$ -NMR ppm ( $\text{CDCl}_3$ )  $\delta$ 8.13(d, 2H), 6.96(m, 4H), 6.70(d, 2H), 4.02(t, 2H), 3.46(s, 2H), 1.81(m, 2H), 1.46(m, 2H), 1.34(m, 12H), 0.89(t, 3H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ )  $\delta$ 165.66, 163.46, 144.24, 143.24, 132.27, 122.47, 121.88, 115.20, 114.30, 68.38, 32.02, 29.68, 29.49, 29.44, 29.21, 26.10, 22.81 and 14.26.

#### **4-aminophenyl 4-dodecyloxybenzoate (9f)**

Yield:71.5%, m.p-96 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ):3460, 3406( $\text{NH}_{2\text{str}}$ ), 2954, 2919, 2850(aromatic  $\text{C-H}_{\text{str}}$ ), 1715( $\text{C=O}_{\text{str}}$ ), 1629( $\text{NH}_{\text{ben}}$ ), 1605, 1579, 1513( $\text{C=C}_{\text{str}}$  aromatic), 1471, 1420, 1394, 1315( $\text{C-H}_{\text{ben}}$ ), 1258, 1191, 1167, 1120( $\text{C-O-C}_{\text{asym\&symstr}}$  of ester and ether);  $^1\text{H}$ -NMR ppm ( $\text{CDCl}_3$ )  $\delta$ 8.13(d, 2H), 6.98(m, 4H), 6.70(d, 2H), 4.02(t, 2H), 3.65(s, 2H), 1.81(m, 2H), 1.46(m, 2H), 1.34(m, 12H), 0.89(t, 3H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ )  $\delta$ 165.66, 163.46,

144.26, 143.23, 132.27, 122.47, 121.88, 115.78, 114.30, 68.38, 32.01, 29.67, 29.48, 29.44, 29.21, 26.09, 22.81, 14.26.

**Synthesis of bis(4-(4-((E)-((4-(4-(ethoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy) butyl) thiophene-2,5-dicarboxylate (S<sub>4</sub>-C<sub>2</sub>) (10)**

In an experiment, 4-aminophenyl 4-ethoxybenzoate (0.98 g, 0.0038 mol) and bis (4-(4-formylphenoxy) butyl) thiophene-2, 5-dicarboxylate (1 g, 0.0019 mol) were placed in a 50 ml single necked round bottom flask equipped with a double wall reflux condenser. 20 ml of ethanol and a few drops of acetic acid were added to the flask and refluxed for four hours. Then it was allowed to cool to room temperature, filtered and the solid was washed thrice with methanol, dried and the solid obtained was recrystallized twice from toluene and EMK respectively.

The above experimental procedure was used to synthesise other mesogens (S<sub>4</sub>-C<sub>4</sub>, S<sub>4</sub>-C<sub>6</sub>, S<sub>4</sub>-C<sub>8</sub>, S<sub>4</sub>-C<sub>10</sub> and S<sub>4</sub>-C<sub>12</sub> respectively).

Yield: 73%, m.p-141.9 °C, FT-IR (KBr, cm<sup>-1</sup>):2978, 2935(C-H<sub>str</sub>),1729,1702(C=O<sub>str</sub>), 1605, 1571, 1510, 1528(C=C<sub>str</sub> aromatic), 1473, 1454, 1423, 1393(C-H<sub>ben</sub>), 1255, 1201, 1167,1187,1167(C-O-C<sub>asym&symstr</sub> of ester and ether);<sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.15(d, 2H), 7.84(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.40(t, 2H), 4.13(t, 2H), 4.09(t, 2H), 1.97(m, 4H), 1.45(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.15, 163.42, 161.67, 161.65, 159.83, 149.95, 148.99, 139.05, 133.15, 132.38, 130.65, 129.31, 122.45, 121.85, 121.74, 114.76, 114.36, 67.46, 65.43, 63.89, 25.93, 25.52 and 14.77.

**Bis(4-(4-((E)-((4-(4-(butoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy) butyl) thiophene-2,5-dicarboxylate (S<sub>4</sub>-C<sub>4</sub>) (10)**

Yield: 68.7%, m.p-138.5 °C, FT-IR (KBr, cm<sup>-1</sup>):2955, 2872(C-H<sub>str</sub>),1725, 1707(C=O<sub>str</sub>), 1605, 1572, 1511(C=C<sub>str</sub> aromatic), 1422, 1387(C-H<sub>ben</sub>), , 1255, 1196, 1167(C-

O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38(s, 1H), 8.14(d, 2H), 7.84(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.41(t, 2H), 4.09(t, 2H), 4.03(t, 2H), 1.97(m, 4H), 1.80(m, 2H), 1.50(m, 2H), 0.99(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.16, 163.63, 161.67, 161.53, 159.81, 149.94, 149.0, 139.06, 133.14, 132.36, 130.65, 129.32, 122.45, 121.84, 121.64, 114.76, 114.38, 68.09, 67.47, 65.42, 31.22, 25.93, 25.53, 19.28 and 13.92.

**Bis(4-(4-((E)-((4-((4-(hexyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy) butyl) thiophene-2,5-dicarboxylate (S<sub>4</sub>-C<sub>6</sub>) (10)**

Yield: 70.1%, m.p-146.8 °C, FT-IR (KBr, cm<sup>-1</sup>): 2935, 2867(C-H<sub>str</sub>), 1725, 1705(C=O<sub>str</sub>), 1605, 1571, 1510(C=C<sub>str</sub> aromatic), 1469, 1422, 1389(C-H<sub>ben</sub>), , 1262, 1195, 1165(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38(s, 1H), 8.14(d, 2H), 7.84(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.40(t, 2H), 4.09(t, 2H), 4.02(t, 2H), 1.97(m, 4H), 1.83(m, 2H), 1.49(m, 2H), 1.35(m, 4H), 0.91(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.16, 163.63, 161.67, 161.59, 159.81, 149.94, 149.0, 139.06, 133.14, 132.36, 130.65, 129.32, 122.45, 121.84, 121.63, 114.76, 114.39, 68.41, 67.47, 65.42, 31.64, 29.15, 25.93, 25.75, 25.53, 22.68 and 14.23.

**Bis(4-(4-((E)-((4-((4-(octyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy) butyl) thiophene-2,5-dicarboxylate (S<sub>4</sub>-C<sub>8</sub>) (10)**

Yield: 67.1%, m.p-144.5 °C, FT-IR (KBr, cm<sup>-1</sup>): 2924, 2856(C-H<sub>str</sub>), 1734, 1710(C=O<sub>str</sub>), 1606, 1511, (C=C<sub>str</sub> aromatic), 1466, 1349(C-H<sub>ben</sub>), 1252, 1168(C-O-C<sub>asym&symstr</sub> of ester and ether ); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38(s, 1H), 8.14(d, 2H), 7.84(d, 2H), 7.71(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.40(t, 2H), 4.08(t, 2H), 4.02(t, 2H), 1.97(m, 4H), 1.81(m, 2H), 1.45(m, 2H), 1.33(m, 8H), 0.89(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.15, 163.63, 161.67, 161.64, 159.79, 149.93, 149.01, 139.06, 133.14, 132.36, 130.65, 129.32,

122.46, 121.85, 121.63, 114.76, 114.39, 68.42, 67.47, 65.43, 31.90, 29.43, 29.33, 29.20, 26.08, 25.93, 25.53, 22.75 and 14.22.

**Bis(4-(4-((E)-((4-(4-(decyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy) butyl) thiophene-2,5-dicarboxylate (S<sub>4</sub>-C<sub>10</sub>) (10)**

Yield: 64.1%, m.p-140 °C, FT-IR (KBr, cm<sup>-1</sup>): 2921, 2852 (C-H<sub>str</sub>), 1727 (C=O<sub>str</sub>), 1628(-C=N<sub>str</sub>), 1605, 1573, 1512 (C=C<sub>str</sub> aromatic), 1473, 1425, 1421, 1391 (C-H<sub>ben</sub>), 1288, 1258, 1203, 1190, 1168 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38(s, 1H), 8.15(d, 2H), 7.84(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.40(t, 2H), 4.09(t, 2H), 4.03(t, 2H), 1.98(m, 4H), 1.83(m, 2H), 1.48(m, 2H), 1.34(m, 12H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.18, 163.63, 163.42, 161.66, 159.84, 149.93, 148.99, 139.05, 133.16, 132.37, 130.66, 129.29, 122.47, 121.86, 121.60, 114.75, 114.38, 68.41, 67.46, 65.43, 32.00, 29.66, 29.47, 29.42, 29.19, 26.08, 25.93, 25.52, 22.79 and 14.25.

**Bis(4-(4-((E)-((4-(4-(dodecyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy) butyl) thiophene-2,5-dicarboxylate (S<sub>4</sub>-C<sub>12</sub>) (10)**

Yield: 66%, m.p-134.7 °C, FT-IR (KBr, cm<sup>-1</sup>): 2921, 2853 (C-H<sub>str</sub>), 1722, 1699 (C=O<sub>str</sub>), 1605, 1571, 1511 (C=C<sub>str</sub> aromatic), 1474 (C-H<sub>ben</sub>), 1257, 1167 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38 (s, 1H), 8.14 (d, 2H), 7.83 (d, 2H), 7.72 (s, 1H), 7.23 (m, 4H), 6.95 (m, 4H), 4.41 (t, 2H), 4.09 (t, 2H), 4.02 (t, 2H), 1.97 (m, 4H), 1.82 (m, 2H), 1.48 (m, 2H), 1.35 (m, 17H), 0.87 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.19, 163.63, 163.41, 161.67, 159.86, 149.93, 148.99, 139.05, 133.15, 132.36, 130.66, 129.29, 122.45, 121.84, 121.60, 114.76, 114.38, 68.41, 67.46, 65.43, 32.01, 29.73, 29.68, 29.44, 29.19, 26.07, 25.92, 25.52, 22.79 and 14.22.

**Synthesis of bis(6-(4-((E)-((4-((4-(ethoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy)hexyl) thiophene-2,5-dicarboxylate (S<sub>6</sub>-C<sub>2</sub>) (10)**

In a typical experiment, bis (6-(4-formylphenoxy) hexyl) thiophene-2, 5-dicarboxylate (0.75 g, 0.0013 mol) and 4-aminophenyl 4-ethoxybenzoate (0.66 g, 0.0026 mol) were placed in a 50 ml single necked round bottom flask equipped with a double wall reflux condenser. 25 ml of ethanol and a few drops of acetic acid were added to the flask and refluxed for four hours. Then it was allowed to cool to room temperature, filtered and the solid was washed thrice with methanol, dried and the solid obtained was recrystallized twice from toluene and EMK respectively.

The above procedure was followed for making other mesogens (S<sub>6</sub>-C<sub>4</sub>, S<sub>6</sub>-C<sub>6</sub>, S<sub>6</sub>-C<sub>8</sub>, S<sub>6</sub>-C<sub>10</sub> and S<sub>6</sub>-C<sub>12</sub> respectively).

Yield: 68%, m.p-130.4 °C, FT-IR (KBr, cm<sup>-1</sup>):2936, 2864 (C-H<sub>str</sub>),1728, 1713(C=O<sub>str</sub>), 1605, 1511, (C=C<sub>str</sub> aromatic),1394(C-H<sub>ben</sub>), 1254, 1196, 1165(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.81(d, 2H), 7.72(s, 1H), 7.21(m, 4H), 6.94(m, 4H), 4.32(t, 2H), 4.11(t, 2H), 4.01(t, 2H), 1.82(m, 4H), 1.53(m, 4H), 1.44(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.14, 163.42, 161.90, 161.75, 159.89, 149.97, 148.97, 139.17, 133.05, 132.38, 130.64, 129.13, 122.45, 121.86, 121.69, 114.76, 114.36, 68.01, 65.74, 63.90, 29.14, 28.63, 25.82 and 14.78.

**Bis(6-(4-((E)-((4-((4-(butoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy)hexyl) thiophene-2,5-dicarboxylate (S<sub>6</sub>-C<sub>4</sub>) (10)**

Yield: 72.7%, m.p-114.1 °C, FT-IR (KBr, cm<sup>-1</sup>):2939, 2869(C-H<sub>str</sub>),1722(C=O<sub>str</sub>), 1607, 1511, (C=C<sub>str</sub> aromatic), 1466, 1394, 1349(C-H<sub>ben</sub>),1288, 1248, 1207, 1172(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.13(d, 2H), 7.82(d, 2H), 7.72(s, 1H), 7.22(m, 4H), 6.95(m, 4H), 4.33(t, 2H), 4.04(m, 4H), 1.81(m, 6H), 1.52(m, 6H),

0.99(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.17, 163.63, 161.90, 161.77, 159.91, 149.98, 148.97, 139.17, 133.05, 132.36, 130.63, 129.13, 122.45, 121.85, 121.63, 114.76, 114.38, 68.09, 68.01, 65.73, 31.22, 29.14, 28.63, 25.82, 19.29 and 13.93.

**Bis(6-(4-((E)-((4-((4-(hexyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)hexyl)thiophene-2,5-dicarboxylate (S<sub>6</sub>-C<sub>6</sub>) (10)**

Yield: 65.1%, m.p-116.9 °C, FT-IR (KBr, cm<sup>-1</sup>): 2938, 2863(C-H<sub>str</sub>),1725, 1712(C=O<sub>str</sub>), 1605, 1572, 1510, (C=C<sub>str</sub> aromatic), 1469, 1421, 1388(C-H<sub>ben</sub>), 1253, 1196, 1165(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.96(m, 4H), 4.33(t, 2H), 4.02(m, 4H), 1.84(m, 6H), 1.51(m, 6H), 1.35(m, 4H), 0.91(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.18, 163.63, 161.90, 161.77, 159.91, 149.98, 148.97, 139.17, 133.06, 132.36, 130.63, 129.13, 122.45, 121.85, 121.62, 114.76, 114.38, 68.41, 68.01, 65.73, 31.64, 29.15, 28.63, 25.82, 22.76, 22.69 and 14.14.

**Bis(6-(4-((E)-((4-((4-(octyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)hexyl)thiophene-2,5-dicarboxylate (S<sub>6</sub>-C<sub>8</sub>) (10)**

Yield: 69%, m.p-124.3 °C, FT-IR (KBr, cm<sup>-1</sup>):2928, 2857(C-H<sub>str</sub>),1726, 1711(C=O<sub>str</sub>), 1605, 1569,1510(C=C<sub>str</sub> aromatic), 1468, 1421, 1388(C-H<sub>ben</sub>), 1252, 1196, 1165(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.96(m, 4H), 4.33(t, 2H), 4.02(m, 4H), 1.82(m, 6H), 1.51(m, 6H), 1.31(m, 8H), 0.89(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.17, 163.63, 161.90, 161.76, 159.88, 149.98, 148.97, 139.17, 133.05, 132.36, 130.63, 129.13, 122.45, 121.84, 121.63, 114.76, 114.38, 68.41, 68.01, 65.73, 31.90, 29.42, 29.32, 29.19, 29.14, 28.63, 26.08, 25.82, 22.75 and 14.21.

**Bis(6-(4-((E)-((4-((4-(decyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy) hexyl) thiophene-2,5-dicarboxylate (S<sub>6</sub>-C<sub>10</sub>) (10)**

Yield: 64.2%, m.p-112.4 °C, FT-IR (KBr, cm<sup>-1</sup>):2925, 2856(C-H<sub>str</sub>),1722(C=O<sub>str</sub>), 1606, 1511(C=C<sub>str</sub> aromatic), 1469, 1394(C-H<sub>ben</sub>), 1253, 1167(C-O-C<sub>asym&symstr</sub> of ester and ether);<sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.81(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.96(m, 4H), 4.33(t, 2H), 4.02(m, 4H), 1.81(m, 6H), 1.51(m, 6H), 1.34(m, 12H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.03, 163.52, 161.79, 161.62, 159.73, 149.87, 148.89, 139.07, 132.90, 132.23, 130.51, 129.05, 122.31, 121.71, 121.54, 114.66, 114.28, 68.41, 68.01, 65.73, 32.00, 29.65, 29.47, 29.41, 29.19, 29.14, 28.63, 26.08, 25.82, 22.78 and 14.23.

**Bis(6-(4-((E)-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy) hexyl) thiophene-2,5-dicarboxylate (S<sub>6</sub>-C<sub>12</sub>) (10)**

Yield: 61.5%, m.p-115.9 °C, FT-IR (KBr, cm<sup>-1</sup>): 2924, 2855 (C-H<sub>str</sub>),1720, 1708 (C=O<sub>str</sub>), 1606, 1512 (C=C<sub>str</sub> aromatic), 1468, 1391 (C-H<sub>ben</sub>), 1256, 1167 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38 (s, 1H), 8.15 (d, 2H), 7.83 (d, 2H), 7.72 (s, 1H), 7.23 (m, 4H), 6.96 (m, 4H), 4.33 (t, 2H), 4.02 (m, 4H), 1.97 (m, 4H), 1.82 (m, 6H), 1.51 (m, 6H), 1.34 (m, 16H), 0.88 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.19, 163.63, 161.89, 161.77, 159.92, 149.98, 148.96, 139.16, 133.06, 132.37, 130.64, 129.11, 122.46, 121.86, 121.60, 114.75, 114.38, 68.41, 68.0, 65.74, 32.02, 29.76, 29.75, 29.70, 29.67, 29.46, 29.19, 29.14, 28.63, 26.08, 25.83, 22.80 and 14.25.

**Synthesis of bis(8-(4-((E)-((4-((4-(ethoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy)octyl) thiophene-2,5-dicarboxylate (S<sub>8</sub>-C<sub>2</sub>) (10)**

In a typical experiment, a mixture of 4-aminophenyl 4-ethoxybenzoate (0.65 g, 0.0025 mol) and bis (8-(4-formylphenoxy) octyl) thiophene-2, 5-dicarboxylate (0.8 g, 0.0012 mol) was placed in a 50 ml single necked round bottom flask equipped with a double wall

reflux condenser. 25 ml of ethanol and a few drops of acetic acid were added to the flask and refluxed for four hours. Then it was allowed to cool to room temperature, filtered and the solid was washed thrice with methanol, dried and the solid obtained was recrystallized twice from toluene and EMK respectively.

The above experimental procedure was used to synthesise other mesogens ( $S_8-C_4$ ,  $S_8-C_6$ ,  $S_8-C_8$ ,  $S_8-C_{10}$  and  $S_8-C_{12}$  respectively).

Yield: 69.8%, m.p-127 °C, FT-IR (KBr,  $cm^{-1}$ ):2978, 2935, 2854( $C-H_{str}$ ), 1725( $C=O_{str}$ ), 1625( $-C=N_{str}$ ), 1607, 1575, 1530, 1511( $C=C_{str}$  aromatic), 1475, 1422, 1394, 1313( $C-H_{ben}$ ), 1274, 1251, 1205( $C-O-C_{asym\&symstr}$  of ester and ether);  $^1H-NMR$  ppm ( $CDCl_3$ ): $\delta$ 8.38(s, 1H), 8.14(d, 2H), 7.82(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.96(m, 4H), 4.30(t, 2H), 4.11(t, 2H), 4.0(t, 2H), 1.76(m, 4H), 1.45(m, 11H), 0.99(t, 3H);  $^{13}C-NMR$  ppm ( $CDCl_3$ ): $\delta$ 165.16, 163.41, 161.98, 161.79, 159.94, 149.99, 148.96, 139.22, 133.01, 132.38, 130.63, 129.05, 122.45, 121.85, 121.69, 114.78, 114.36, 68.19, 65.89, 63.89, 29.33, 29.22, 28.67, 26.03, 25.94 and 14.78.

**Bis(8-(4-((E)-((4-((4-(butoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy)octyl)thiophene-2,5-dicarboxylate ( $S_8-C_4$ ) (10)**

Yield: 71%, m.p-120.8 °C, FT-IR (KBr,  $cm^{-1}$ ):2956, 2935, 2871, 2853( $C-H_{str}$ ), 1716( $C=O_{str}$ ), 1624( $-C=N_{str}$ ), 1607, 1575, 1531, 1512( $C=C_{str}$  aromatic), 1467, 1421, 1395, 1350( $C-H_{ben}$ ), 1258, 1250, 1208, 1189, 1170( $C-O-C_{asym\&symstr}$  of ester and ether);  $^1H-NMR$  ppm ( $CDCl_3$ ): $\delta$ 8.38(s, 1H), 8.13(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.22(m, 4H), 6.97(m, 4H), 4.31(t, 2H), 4.02(m, 4H), 1.80(m, 6H), 1.48(m, 10H), 0.99(t, 3H);  $^{13}C-NMR$  ppm ( $CDCl_3$ ): $\delta$ 165.17, 163.63, 161.98, 161.79, 159.92, 149.99, 148.96, 139.23, 133.01, 132.36, 130.63, 129.06, 122.45, 121.85, 121.62, 114.78, 114.38, 68.19, 68.09, 65.89, 31.22, 29.33, 29.23, 28.67, 26.03, 25.94, 19.29 and 13.94.

**Bis(8-(4-((E)-((4-((4-(hexyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)octyl)thiophene-2,5-dicarboxylate (S<sub>8</sub>-C<sub>6</sub>) (10)**

Yield: 75%, m.p-118.3 °C, FT-IR (KBr, cm<sup>-1</sup>):2936, 2854(C-H<sub>str</sub>), 1724, 1701(C=O<sub>str</sub>), 1625(-C=N<sub>str</sub>), 1606, 1575, 1530, 1510(C=C<sub>str</sub> aromatic), 1474, 1421, 1394, 1313(C-H<sub>ben</sub>), 1275, 1251, 1205, 1190, 1170(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.81(d, 2H), 7.72(s, 1H), 7.21(m, 4H), 6.96(m, 4H), 4.32(t, 2H), 4.00(m, 4H), 1.80(m, 6H), 1.36(m, 14H), 0.91(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.15, 163.63, 161.98, 161.77, 159.90, 149.97, 148.97, 139.23, 133.01, 132.36, 130.64, 129.07, 122.45, 121.86, 121.62, 114.78, 114.39, 68.40, 68.18, 65.89, 31.65, 29.33, 29.23, 29.16, 28.68, 26.03, 26.03, 25.95, 25.77, 22.70 and 14.16.

**Bis(8-(4-((E)-((4-((4-(octyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)octyl)thiophene-2,5-dicarboxylate (S<sub>8</sub>-C<sub>8</sub>) (10)**

Yield: 73.9%, m.p-120.4 °C, FT-IR (KBr, cm<sup>-1</sup>):2934, 2854(C-H<sub>str</sub>), 1725(C=O<sub>str</sub>), 1625(-C=N<sub>str</sub>), 1606, 1576, 1530, 1511(C=C<sub>str</sub> aromatic), 1475, 1422, 1394(C-H<sub>ben</sub>), 1275, 1252, 1205, 1190, 1169(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.82(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.97(m, 4H), 4.31(t, 2H), 4.01(m, 4H), 1.80(m, 6H), 1.39(m, 19H), 0.89(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.18, 163.63, 161.98, 161.80, 159.94, 149.98, 148.96, 139.22, 133.01, 132.36, 130.63, 129.06, 122.45, 121.85, 121.61, 114.78, 114.38, 68.41, 68.19, 65.89, 31.90, 29.43, 29.33, 29.23, 29.20, 28.67, 26.08, 26.03, 25.94, 22.76 and 14.22.

**Bis(8-(4-((E)-((4-((4-(decyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)octyl)thiophene-2,5-dicarboxylate (S<sub>8</sub>-C<sub>10</sub>) (10)**

Yield: 65.1%, m.p-119.5 °C, FT-IR (KBr, cm<sup>-1</sup>):2922, 2853(C-H<sub>str</sub>), 1723(C=O<sub>str</sub>), 1625(-C=N<sub>str</sub>), 1606, 1575, 1530, 1510(C=C<sub>str</sub> aromatic), 1474, 1421, 1394(C-H<sub>ben</sub>), 1275,

1252, 1206, 1190, 1170(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.15(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.96(m, 4H), 4.31(t, 2H), 4.01(m, 4H), 1.79(m, 6H), 1.43(m, 22H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.17, 163.63, 161.98, 161.79, 159.91, 149.99, 148.96, 139.23, 133.00, 132.36, 130.63, 129.07, 122.45, 121.85, 121.62, 114.77, 114.38, 68.41, 68.19, 65.89, 32.00, 29.66, 29.47, 29.42, 29.33, 29.23, 28.67, 26.08, 26.03, 25.94, 22.78 and 14.24.

**Bis(8-(4-((E)-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)octyl) thiophene-2,5-dicarboxylate (S<sub>8</sub>-C<sub>12</sub>) (10)**

Yield: 67%, m.p-118 °C, FT-IR (KBr, cm<sup>-1</sup>): 2922, 2852 (C-H<sub>str</sub>), 1723 (C=O<sub>str</sub>), 1624 (C=N<sub>str</sub>), 1606, 1530, 1511 (C=C<sub>str</sub> aromatic), 1473, 1394 (C-H<sub>ben</sub>), 1275, 1189, 1169 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38 (s, 1H), 8.16 (d, 2H), 7.82 (d, 2H), 7.72 (s, 1H), 7.23 (m, 4H), 6.95 (m, 4H), 4.32 (t, 2H), 4.01 (m, 4H), 1.79 (m, 6H), 1.43 (m, 27H), 0.88 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.17, 163.63, 161.89, 161.79, 159.91, 149.99, 148.96, 139.23, 133.0, 132.36, 130.63, 129.07, 122.44, 121.85, 121.62, 114.77, 114.38, 68.41, 68.19, 65.88, 32.02, 29.74, 29.70, 29.66, 29.46, 29.33, 29.23, 29.20, 28.67, 26.08, 26.03, 25.94, 22.79 and 14.24.

**Synthesis of bis(10-(4-((E)-((4-((4-(ethoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy) decyl) thiophene-2,5-dicarboxylate (S<sub>10</sub>-C<sub>2</sub>) (10)**

In an experiment, to a 50 ml single necked round bottom flask equipped with a double wall reflux condenser, bis (10-(4-formylphenoxy) decyl) thiophene-2, 5-dicarboxylate (1 g, 0.0014 mol) and 4-aminophenyl 4-ethoxybenzoate (0.74 g, 0.0029 mol) were added and then 25 ml of ethanol and a few drops of acetic acid were added to the flask and refluxed for four hours. Then it was cooled to room temperature, filtered and the solid was washed thrice with

methanol, dried and the solid obtained was recrystallized thrice from EMK and toluene respectively.

The above procedure was used to make other mesogens (S<sub>10</sub>-C<sub>4</sub>, S<sub>10</sub>-C<sub>6</sub>, S<sub>10</sub>-C<sub>8</sub>, S<sub>10</sub>-C<sub>10</sub> and S<sub>10</sub>-C<sub>12</sub> respectively).

Yield: 72.2%, m.p-124.5 °C, FT-IR (KBr, cm<sup>-1</sup>):2977, 2932, 2952(C-H<sub>str</sub>), 1725, 1700(C=O<sub>str</sub>), 1624(-C=N<sub>str</sub>), 1606, 1576, 1529, 1511(C=C<sub>str</sub> aromatic), 1474, 1422, 1393, 1313(C-H<sub>ben</sub>), 1277, 1248, 1205, 1190, 1170(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.13(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.22(m, 4H), 6.95(m, 4H), 4.29(t, 2H), 4.04(m, 4H), 1.74(m, 6H), 1.50(m, 14H), 0.99(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.15, 163.41, 162.0, 161.80, 159.93, 149.99, 148.96, 139.24, 132.99, 132.38, 130.63, 129.04, 122.45, 121.86, 121.69, 114.78, 114.36, 68.26, 65.93, 63.89, 29.55, 29.52, 29.44, 29.29, 29.27, 26.09, 25.99 and 14.78.

**Bis(10-(4-((E)-((4-((4-(butoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy)decyl)thiophene-2,5-dicarboxylate (S<sub>10</sub>-C<sub>4</sub>) (10)**

Yield: 65.8%, m.p-122 °C, FT-IR (KBr, cm<sup>-1</sup>):2956, 2934, 2917, 2849, 2872(C-H<sub>str</sub>), 1717(C=O<sub>str</sub>), 1607, 1575, 1533, 1510(C=C<sub>str</sub> aromatic), 1467, 1420, 1396, 1350(C-H<sub>ben</sub>), 1291, 1148, 1209, 1188, 1171(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.82(d, 2H), 7.72(s, 1H), 7.24(m, 4H), 6.96(m, 4H), 4.30(t, 2H), 4.03(m, 4H), 1.78(m, 6H), 1.48(m, 15H), 0.99(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.15, 163.63, 162.0, 161.80, 159.93, 149.99, 148.96, 139.24, 132.98, 132.36, 130.63, 129.04, 122.45, 121.85, 121.63, 114.78, 114.38, 68.26, 68.09, 65.93, 31.22, 29.54, 29.51, 29.44, 29.29, 28.68, 26.09, 25.99, 19.29 and 13.94.

**Bis(10-(4-((E)-((4-((4-(hexyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)decyl)thiophene-2,5-dicarboxylate (S<sub>10</sub>-C<sub>6</sub>) (10)**

Yield: 76%, m.p-117 °C, FT-IR (KBr, cm<sup>-1</sup>):2934, 2918, 2851(aromatic C-H<sub>str</sub>), 1718(C=O<sub>str</sub>), 1624(-C=N<sub>str</sub>), 1607, 1575, 1510, 1531(C=C<sub>str</sub> aromatic), 1468, 1421, 1395, 1349, 1310(C-H<sub>ben</sub>), 1249, 1207, 1189, 1170(C-O-C<sub>asym&symstr</sub> of ester and ether respectively); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.16(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.29(t, 2H), 4.03(m, 4H), 1.80(m, 6H), 1.35(m, 18H), 0.91(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.16, 163.63, 162.0, 161.80, 159.91, 149.99, 148.97, 139.25, 132.97, 132.36, 130.62, 129.06, 122.44, 121.84, 121.64, 114.78, 114.39, 68.41, 68.26, 65.92, 31.64, 29.54, 29.50, 29.43, 29.28, 29.15, 28.68, 26.09, 25.99, 25.75, 22.68 and 14.13.

**Bis(10-(4-((E)-((4-((4-(octyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)decyl)thiophene-2,5-dicarboxylate (S<sub>10</sub>-C<sub>8</sub>) (10)**

Yield: 71.9%, m.p-118.3 °C, FT-IR (KBr, cm<sup>-1</sup>):2925, 2855(C-H<sub>str</sub>), 1723(C=O<sub>str</sub>), 1607, 1511(C=C<sub>str</sub> aromatic), 1468, 1420, 1394, 1348(C-H<sub>ben</sub>), 1250, 1169(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.13(d, v 2H), 7.82(d, 2H), 7.72(s, 1H), 7.24(m, 4H), 6.97(m, 4H), 4.30(t, 2H), 4.02(m, 4H), 1.79(m, 6H), 1.45(m, 23H), 0.89(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.15, 163.63, 162.0, 161.79, 159.91, 149.99, 148.97, 139.25, 132.97, 132.35, 130.62, 129.06, 122.43, 121.84, 121.64, 114.78, 114.39, 68.41, 68.26, 65.92, 31.90, 29.54, 29.50, 29.43, 29.32, 29.28, 29.19, 28.68, 26.08, 25.99, 22.77 and 14.21.

**Bis(10-(4-((E)-((4-((4-(decyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)decyl)thiophene-2,5-dicarboxylate (S<sub>10</sub>-C<sub>10</sub>) (10)**

Yield: 77%, m.p-115.1 °C, FT-IR (KBr, cm<sup>-1</sup>):2922, 2852(C-H<sub>str</sub>), 1724, 1701(C=O<sub>str</sub>), 1625(-C=N<sub>str</sub>), 1606, 1576, 1529, 1511(C=C<sub>str</sub> aromatic), 1471, 1421, 1394, 1311(C-H<sub>ben</sub>), , 1279, 1250, 1205, 1190, 1170(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.22(m, 4H), 6.95(m, 4H),

4.30(t, 2H), 4.01(m, 4H), 1.78(m, 6H), 1.44(m, 27H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.16, 163.63, 162.0, 161.79, 159.91, 149.99, 148.97, 139.25, 132.96, 132.35, 130.62, 129.06, 122.43, 121.84, 121.64, 114.78, 114.39, 68.41, 68.26, 65.92, 31.99, 29.65, 29.54, 29.50, 29.46, 29.41, 29.28, 29.19, 28.68, 26.08, 25.99, 22.77 and 14.22.

**Bis(10-(4-((E)-((4-(dodecyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)decyl thiophene-2,5-dicarboxylate (S<sub>10</sub>-C<sub>12</sub>) (10)**

Yield: 71.7%, m.p-116.7 °C, FT-IR (KBr, cm<sup>-1</sup>): 3065 (aromatic C-H<sub>str</sub>), 2921, 2853 (C-H<sub>str</sub>), 1723 (C=O<sub>str</sub>), 1607, 1511 (C=C<sub>str</sub> aromatic), 1467, 1393 (C-H<sub>ben</sub>), 1250, 1169 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38 (s, 1H), 8.14 (d, 2H), 7.83 (d, 2H), 7.72 (s, 1H), 7.23 (m, 4H), 6.96 (m, 4H), 4.30 (t, 2H), 4.02 (m, 4H), 1.79 (m, 6H), 1.45 (m, 30H), 0.87 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ165.21, 163.62, 161.83, 161.67, 160.0, 149.99, 148.95, 139.22, 133.0, 132.37, 130.63, 129.0, 122.46, 121.86, 121.58, 114.77, 114.37, 68.41, 68.25, 65.95, 32.02, 29.76, 29.70, 29.67, 29.56, 29.52, 29.47, 29.30, 29.26, 28.68, 26.09, 26.00, 22.80 and 14.25.

**Synthesis of bis(12-(4-((E)-((4-(ethoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy) dodecyl thiophene-2,5-dicarboxylate (S<sub>12</sub>-C<sub>2</sub>) (10)**

In a representative experiment, 4-aminophenyl 4-ethoxybenzoate (1g, 0.0039 mol) and bis (12-(4-formylphenoxy) dodecyl) thiophene-2, 5-dicarboxylate (1.46 g, 0.00195 mol) were placed in a 50 ml single necked round bottom flask equipped with a double wall reflux condenser. 25 ml of ethanol and a few drops of acetic acid were added to the flask and refluxed for four hours. Then it was allowed to cool to room temperature, filtered and the solid was washed thrice with methanol, dried and the solid obtained was recrystallized thrice from EMK and toluene respectively.

The above procedure was used for synthesising other mesogens ( $S_{12}-C_4$ ,  $S_{12}-C_6$ ,  $S_{12}-C_8$ ,  $S_{12}-C_{10}$  and  $S_{12}-C_{12}$  respectively).

Yield: 63%, m.p-125.4 °C, FT-IR (KBr,  $cm^{-1}$ ):2926, 2853(C-H<sub>str</sub>), 1725(C=O<sub>str</sub>), 1605, 1574, 1511(C=C<sub>str</sub> aromatic), 1468, 1392(C-H<sub>ben</sub>), 1251, 1193, 1165(C-O-C<sub>asym&symstr</sub> of ester and ether ); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.14(d, 2H), 7.81(d, 2H), 7.71(s, 1H), 7.24(m, 4H), 6.95(m, 4H), 4.29(t, 2H), 4.10(t, 2H), 4.0(t, 2H), 1.74(m, 4H), 1.44(m, 19H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.18, 163.41, 162.01, 161.83, 160.0, 149.99, 148.94, 139.23, 132.98, 132.39, 130.63, 128.99, 122.45, 121.86, 121.68, 114.78, 114.35, 68.28, 68.28, 65.96, 63.89, 29.64, 29.59, 29.49, 29.32, 29.27, 26.10, 26.0 and 13.78.

**Bis(12-(4-((E)-((4-((4-(butoxybenzoyl)oxy)phenyl)imino)methyl)phenoxy)dodecyl)thiophene-2,5-dicarboxylate ( $S_{12}-C_4$ ) (10)**

Yield: 65.5%, m.p-126.3 °C, FT-IR (KBr,  $cm^{-1}$ ):2918, 2851(C-H<sub>str</sub>), 1721(C=O<sub>str</sub>), 1607, 1511(C=C<sub>str</sub> aromatic), 1468, ), 1395, 1349(C-H<sub>ben</sub>), 1289, 1248, 1209, 1173(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.15(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.96(m, 4H), 4.29(t, 2H), 4.02(m, 4H), 1.80(m, 6H), 1.50(m, 19H), 0.99(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>):δ165.20, 163.62, 162.01, 161.83, 160.0, 149.99, 148.95, 139.23, 132.98, 132.37, 130.63, 129.0, 122.45, 121.86, 121.61, 114.78, 114.37, 68.28, 68.08, 65.95, 31.22, 29.64, 29.58, 29.48, 29.32, 28.68, 26.10, 26.0, 19.29 and 13.94.

**Bis(12-(4-((E)-((4-((4-(hexyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)dodecyl)thiophene-2,5-dicarboxylate ( $S_{12}-C_6$ ) (10)**

Yield: 58.4%, m.p-118.8 °C, FT-IR (KBr,  $cm^{-1}$ ):2926, 2855(C-H<sub>str</sub>), 1725(C=O<sub>str</sub>), 1607, 1575, 1511(C=C<sub>str</sub> aromatic), 1468, 1422, 1391(C-H<sub>ben</sub>), 1254, 1199, 1167(C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>):δ8.38(s, 1H), 8.15(d, 2H), 7.81(d, 2H), 7.71(s, 1H), 7.21(m, 4H), 6.97(m, 4H), 4.30(t, 2H), 4.01(m, 4H), 1.78(m, 6H), 1.41(m, 24H),

0.89(t, 3H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ ): $\delta$ 165.16, 163.63, 162.01, 161.80, 159.91, 149.99, 148.97, 139.25, 132.95, 132.35, 130.62, 129.05, 122.43, 121.84, 121.64, 114.79, 114.39, 68.41, 68.29, 65.93, 31.89, 29.63, 29.57, 29.48, 29.42, 29.32, 29.27, 29.19, 28.69, 26.0, 22.74 and 14.20.

**Bis(12-(4-((E)-((4-((4-(octyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)dodecyl)thiophene-2,5-dicarboxylate (S<sub>12</sub>-C<sub>8</sub>) (10)**

Yield: 61%, m.p-119.7 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ):2920, 2853(C-H<sub>str</sub>), 1722(C=O<sub>str</sub>), 1608, 1511(C=C<sub>str</sub> aromatic), 1468, 1394, 1349(C-H<sub>ben</sub>), 1250, 1206, 1172(C-O-C<sub>asym&symstr</sub> of ester and ether);  $^1\text{H}$ -NMR ppm ( $\text{CDCl}_3$ ): $\delta$ 8.38(s, 1H), 8.14(d, 2H), 7.83(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.95(m, 4H), 4.30(t, 2H), 4.01(m, 4H), 1.79(m, 6H), 1.46(m, 28H), 0.89(t, 3H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ ): $\delta$ 165.20, 163.62, 162.01, 161.82, 159.98, 149.99, 148.96, 139.23, 132.98, 132.37, 130.63, 129.00, 122.46, 121.86, 121.60, 114.77, 114.37, 68.41, 68.28, 65.95, 31.91, 29.65, 29.59, 29.49, 29.44, 29.33, 29.27, 29.19, 28.69, 26.09, 26.01, 22.76, 14.23.

**Bis(12-(4-((E)-((4-((4-(decyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)dodecyl)thiophene-2,5-dicarboxylate (S<sub>12</sub>-C<sub>10</sub>) (10)**

Yield: 71.4%, m.p-118.9 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 2920, 2851 (C-H<sub>str</sub>), 1717 (C=O<sub>str</sub>), 1608, 1576, 1510 (C=C<sub>str</sub> aromatic), 1470, 1418, 1392, 1352(C-H<sub>ben</sub>), 1288, 1248, 1208, 1164 (C-O-C<sub>asym&symstr</sub> of ester and ether);  $^1\text{H}$ -NMR ppm ( $\text{CDCl}_3$ ): $\delta$ 8.38(s, 1H), 8.14(d, 2H), 7.82(d, 2H), 7.72(s, 1H), 7.23(m, 4H), 6.97(m, 4H), 4.30(t, 2H), 4.03(m, 4H), 1.78(m, 6H), 1.41(m, 31H), 0.88(t, 3H);  $^{13}\text{C}$ -NMR ppm ( $\text{CDCl}_3$ ): $\delta$ 165.19, 163.62, 162.01, 161.82, 159.97, 150.00, 148.95, 139.23, 132.97, 132.36, 130.63, 129.02, 122.45, 121.85, 121.61, 114.78, 114.38, 68.41, 68.28, 65.96, 31.99, 29.64, 29.58, 29.47, 29.41, 29.31, 29.27, 29.19, 28.68, 26.08, 26.0, 22.78 and 14.22.

**Bis(12-(4-((E)-((4-((4-(dodecyloxy)benzoyl)oxy)phenyl)imino)methyl)phenoxy)dodecyl)thiophene-2,5-dicarboxylate (S<sub>12</sub>-C<sub>12</sub>) (10)**

Yield: 69%, m.p-118.3 °C, FT-IR (KBr, cm<sup>-1</sup>): 2918, 2850 (C-H<sub>str</sub>), 1718 (C=O<sub>str</sub>), 1607, 1575, 1511 (C=C<sub>str</sub> aromatic), 1468, 1395 (C-H<sub>ben</sub>), 1292, 1170 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.38 (s, 1H), 8.13 (d, 2H), 7.82 (d, 2H), 7.72 (s, 1H), 7.22 (m, 4H), 6.95 (m, 4H), 4.30 (t, 2H), 4.02 (m, 4H), 1.78 (m, 6H), 1.43 (m, 35H), 0.87 (t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ164.97, 163.52, 161.92, 161.64, 159.67, 149.91, 148.90, 139.17, 132.78, 132.21, 130.48, 129.02, 122.28, 121.68, 121.61, 114.69, 114.29, 68.37, 68.24, 65.84, 31.94, 29.67, 29.65, 29.60, 29.55, 29.50, 29.39, 29.36, 29.23, 29.14, 28.64, 26.04, 26.01, 25.93, 22.70 and 14.11. MS (HRMS) : m/z calculated for C<sub>94</sub>H<sub>126</sub>N<sub>2</sub>O<sub>12</sub>S [M+H]<sup>+</sup> - 1507.40: found 1507.3694.

**Synthesis of 4-dodecyloxyaniline (11, 12)**

Step: 1 Synthesis of 4-dodecyloxy acetanilide (11)

In a representative experiment, 4-acetamido phenol (4g, 0.025 mol) was placed in a 250 ml three necked round bottom flask equipped with stirrer and thermometer. DMF (75 ml) and potassium carbonate (4.8 g, 0.035 mol) were added to the flask. The resulting mixture was stirred while maintaining the temperature at 90 °C. Then, 12-bromododecane (6.35 ml, 0.025 mol) was added through a pressure equalizing dropping funnel for 45 minutes and the stirring was continued for 4 hours and then the reaction mixture was allowed to cool to room temperature, poured into a one liter beaker.<sup>8</sup> It was diluted with water (150 ml) and 4-dodecyloxy acetanilide formed was filtered using a Buchner funnel. The solid was washed twice with 10% KOH solution followed by water. The solid after drying in vacuum was purified by recrystallizing twice from heptane.

## Step: 2 Preparation of 4-dodecyloxyaniline (**12**)

4-dodecyloxy acetanilide (6.5 g, 0.021mol) (as synthesized above) was placed in a 250 ml two necked round bottom flask equipped with double wall water condenser. Ethanol was added to the flask and the solution was refluxed. While refluxing, conc HCl was added drop wise through a pressure equalizing dropping funnel over a period of 20 minutes and the refluxion was continued for two more hours. Then it was allowed to cool to room temperature, poured into ice water in one liter beaker, neutralized with 10% NaOH solution. The solid obtained was filtered, dried and purified by recrystallization from heptane.

To synthesize 4-hexyloxy aniline the above procedure was used.

### **4-dodecyloxyaniline (12a)**

Yield: 72.4%, m.p-58 °C, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3378, 3311( $\text{NH}_{2\text{str}}$ ), 2951, 2920, 2853( $\text{C-H}_{\text{str}}$ ), 1610( $\text{NH}_{\text{ben}}$ ), 1516 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1468, 1392 ( $\text{C-H}_{\text{ben}}$ ) 1297, 1249, 1168, 1124 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ester and ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 6.72(d, 2H), 6.64(d, 2H), 3.86(t, 2H), 2.85(s, 2H), 1.72(m, 2H), 1.42(m, 2H), 1.29(m, 16H), 0.87(t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):152.41, 140.01, 116.65, 115.91, 68.74, 31.94, 29.58, 29.55, 29.54, 29.51, 29.40, 29.34, 26.21, 22.80 and 14.26.

### **4-hexyloxyaniline (12b)**

Yield: 70.4%, FT-IR (KBr,  $\text{cm}^{-1}$ ): 3399, 3318( $\text{NH}_{2\text{str}}$ ), 3018(aromatic  $\text{C-H}_{\text{str}}$ ), 2928, 2856( $\text{C-H}_{\text{str}}$ ), 1633( $\text{NH}_{\text{ben}}$ ), 1592, 1511 ( $\text{C}=\text{C}_{\text{str}}$  aromatic), 1470 ( $\text{C-H}_{\text{ben}}$ ), 1231, 1177, 1129 ( $\text{C-O-C}_{\text{asym\&symstr}}$  of ester and ether);  $^1\text{H-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 6.76(d, 2H), 6.63(d, 2H), 3.89(t, 2H), 3.34(s, 2H), 1.75(m, 2H), 1.45(m, 2H), 1.34(m, 4H), 0.92(t, 3H);  $^{13}\text{C-NMR}$  ppm ( $\text{CDCl}_3$ ):  $\delta$ 152.36, 140.0, 116.51, 115.71, 68.76, 31.77, 29.54, 25.89, 22.76 and 14.21.

**Synthesis of bis (4- (4-((E)-4-(dodecyloxy) phenylimino) methyl) phenoxy) butyl) thiophene-2, 5-dicarboxylate (S<sub>4</sub>-C<sub>12</sub>) (13)**

In a representative experiment, a mixture of dodecyloxy aniline (0.52 g, 0.0019 mol) and bis (4-(4-formylphenoxy) butyl) thiophene-2, 5-dicarboxylate (0.5 g, 0.00095 mol) was kept in a 100 ml conical flask. A few drops of ethanol were added and made as pasty and the flask was kept in a microwave oven (power: 40 W) for about 15 minutes.<sup>9</sup> Then it was cooled to room temperature, washed twice with methanol and the solid was recrystallized thrice from EMK.

The above procedure was followed to synthesise other compounds namely (S<sub>6</sub>-C<sub>6</sub> and S<sub>6</sub>-C<sub>12</sub>)

**Bis (4- (4-((E)-4-(dodecyloxy) phenylimino) methyl) phenoxy) butyl) thiophene-2, 5-dicarboxylate (S<sub>4</sub>-C<sub>12</sub>) (13a)**

Yield: 74.3%, m.p-145 °C, FT-IR (KBr, cm<sup>-1</sup>): 2919, 2851 (C-H<sub>str</sub>), 1711 (C=O<sub>str</sub>), 1615 (-C=N<sub>str</sub>), 1573, 1511 (C=C<sub>str</sub> aromatic), 1466, 1391 (C-H<sub>ben</sub>), 1245, 1168, 1102 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.40(s, 1H), 7.82(d, 2H), 7.73(s, 1H), 7.20(m, 2H), 6.97(d, 2H), 6.92(d, 2H), 4.41(t, 2H), 4.09(t, 2H), 3.96(t, 2H), 1.98(m, 4H), 1.79(m, 2H) 1.46(m, 2H), 1.27(m, 16H), 0.88(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ161.75, 161.51, 157.74, 157.58, 144.97, 139.29, 133.09, 130.25, 129.54, 122.06, 114.95, 114.62, 68.29, 67.68, 65.35, 31.94, 29.69, 29.65, 29.61, 29.39, 29.35, 29.24, 28.10, 26.08, 25.85, 25.45, 22.71 and 14.15.

**Synthesis of bis (6-((E)-4-(hexyloxy) phenylimino) methyl) phenoxy) hexyl) thiophene-2, 5-dicarboxylate (S<sub>6</sub>-C<sub>6</sub>) (13b)**

Yield: 76% m.p-142.2 °C, FT-IR (KBr, cm<sup>-1</sup>): 2936, 2865 (C-H<sub>str</sub>), 1712 (C=O<sub>str</sub>), 1614 (CH=N), 1573, 1510 (C=C<sub>str</sub> aromatic), 1466, 1394 (C-H<sub>ben</sub>), 1244, 1168 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.40(s, 1H), 7.82(d, 2H), 7.73(s, 1H), 7.20(m, 2H), 6.97(d, 2H), 6.92(d, 2H), 4.33(t, 2H), 4.02(t, 2H), 3.96(t, 2H), 1.80(m, 6H) 1.53(m, 6H), 1.34(m, 4H), 0.91(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ161.71, 161.47, 157.81, 157.55, 145.07, 139.09, 132.98, 130.23, 129.37, 122.05, 114.95, 114.63, 68.29, 67.89, 65.67, 31.63, 29.32, 29.08, 28.55, 25.77, 25.74, 22.65 and 14.08.

**Synthesis of bis (6-((E)-(4-(dodecyloxy) phenylimino) methyl) phenoxy) hexyl) thiophene-2, 5-dicarboxylate (S<sub>6</sub>-C<sub>12</sub>) (13c)**

Yield: 68%, m.p-139 °C, FT-IR (KBr, cm<sup>-1</sup>): 2922, 2854 (C-H<sub>str</sub>), 1711 (C=O<sub>str</sub>), 1615 (CH=N), 1573, 1511 (C=C<sub>str</sub> aromatic), 1468, 1395 (C-H<sub>ben</sub>), 1246, 1170 (C-O-C<sub>asym&symstr</sub> of ester and ether); <sup>1</sup>H-NMR ppm (CDCl<sub>3</sub>): δ8.39(s, 1H), 7.80(d, 2H), 7.73(s, 1H), 7.18(m, 2H), 6.96(d, 2H), 6.90(d, 2H), 4.33(t, 2H), 4.02(t, 2H), 3.96(t, 2H), 1.80(m, 6H), 1.54(m, 2H) 1.48(m, 2H), 1.27(m, 18H), 0.90(t, 3H); <sup>13</sup>C-NMR ppm (CDCl<sub>3</sub>): δ161.72, 161.47, 157.81, 157.55, 145.08, 139.07, 132.98, 130.23, 129.38, 122.05, 114.95, 114.62, 68.29, 67.90, 65.67, 31.95, 29.69, 29.67, 29.63, 29.61, 29.45, 29.38, 29.35, 29.08, 28.55, 26.09, 25.74, 22.72 and 14.16.

**Polarisation measurements**

The electro-optical switching studies were performed on planarly aligned samples using commercial liquid crystal cells (Instec Inc.) with cell gap 5 μm and electrode area 5x5 mm<sup>2</sup>. The temperature of the sample was monitored by a temperature controller coupled with a hotstage (Instec Inc). The polarization state of the layers in the smectic phase was determined by measuring the current response of the sample under the application of a triangular wave voltage. The current response was determined by measuring the voltage drop

across a resistor (1 k $\Omega$ ) connected in series with the sample using an oscilloscope (Agilent MSO6012A). The triangular wave voltage was applied using an arbitrary waveform generator (Agilent 33220A) and a high voltage amplifier (Trek 601-2).

### **Solid state NMR measurements for S<sub>6</sub>-C<sub>10</sub> mesogen**

Solid-state NMR experiments were carried out in the smectic C and the nematic mesophases for S<sub>6</sub>-C<sub>10</sub> mesogen using a Bruker Avance-III HD 400 WB NMR spectrometer. The proton and carbon resonance frequencies were 400.07 and 100.61 MHz respectively. The experiments in the liquid crystalline phases of the sample were performed using a static double resonance probe equipped with a 5 mm horizontal solenoid coil. <sup>13</sup>C NMR spectra were acquired by using standard Hartmann-Hahn cross-polarization pulse sequence with a contact time of 3 ms. Typical 90° proton pulse width for all the experiments was 5  $\mu$ s. During carbon signal acquisition SPINAL-64<sup>10</sup> decoupling was employed using a proton decoupling power of 30 kHz. A recycle delay of 8 s was used to avoid sample heating. Each spectrum was obtained typically with 256 scans. The 2D SAMPI-4 spectra under static condition at two different temperatures were obtained and the experimental parameters were chosen as follow: contact time ( $\tau$ ): 3 ms, number of data t<sub>1</sub> points: 148, number of data t<sub>2</sub> points: 512 and 1024 at temperature 140 °C and 160 °C respectively, number of scans: 32, recycle delay: 15 s. The 2D data matrix is double Fourier transformed with 2k and 512 points in the F<sub>2</sub> and F<sub>1</sub> dimensions respectively. A shifted sine bell window function was applied to the time domain data and the spectrum was processed in the phase sensitive mode.

### **Thermo Gravimetric Analysis (TGA)**

Thermo Gravimetric Analysis (TGA) of mesogens were carried out in nitrogen atmosphere with a heating rate of 10 °C/min using TA instruments (Q10).

**Table S1: DSC transition temperatures and enthalpy values of S<sub>4</sub>, S<sub>6</sub>, S<sub>8</sub>, S<sub>10</sub> and S<sub>12</sub> Series (on heating)**

S.No	Code	Cr-S <sub>C</sub> (°C)	Cr-N (°C)	S <sub>C</sub> -N (°C)	N-I (°C)	ΔT (S <sub>C</sub> -N) (°C)	ΔT (N-I) (°C)	ΔH (Cr-S <sub>C</sub> ) (k.cal/mole)	ΔH (Cr- N) (k.cal/mole)	ΔH (S <sub>C</sub> -N) (k.cal/mole)	ΔH (N-I) (k.cal/mole)
1	S <sub>4</sub> -C <sub>2</sub>	-	141.9	-	289.7	-	147.8	-	6.42	-	0.42
2	C <sub>4</sub>	-	138.6	-	264.2	-	125.6	-	11.33	-	0.65
3	C <sub>6</sub>	-	146.9	-	245.9	-	99.0	-	14.06	-	0.54
4	C <sub>8</sub>	-	144.6	-	231.5	-	86.9	-	13.03	-	0.58
5	C <sub>10</sub>	140.1	-	172.1	219.9	32.0	47.8	11.05	-	1.92	0.69
6	C <sub>12</sub>	134.7	-	172.0	206.5	37.3	34.5	7.59	-	1.41	0.50
7	S <sub>6</sub> -C <sub>2</sub>	-	130.5	-	275.3	-	144.8	-	5.31	-	0.64
8	C <sub>4</sub>	-	114.2	-	253.8	-	139.6	-	14.09	-	0.82
9	C <sub>6</sub>	-	116.9	-	236.0	-	119.1	-	11.45	-	0.59
10	C <sub>8</sub>	124.4	-	135.2	223.8	10.8	88.6	11.86	-	0.28	0.56
11	C <sub>10</sub>	112.5	-	154.1	212.1	41.6	58.0	16.19	-	1.62	0.75
12	C <sub>12</sub>	115.9	-	172.7	203.1	56.8	30.4	28.69	-	3.01	1.02
13	S <sub>8</sub> -C <sub>2</sub>	-	127.1	-	257.1	-	130.0	-	22.51	-	0.77
14	C <sub>4</sub>	-	120.9	-	240.9	-	120.0	-	20.70	-	0.65
15	C <sub>6</sub>	-	118.4	-	222.8	-	104.4	-	20.12	-	0.69
16	C <sub>8</sub>	120.5	-	144.6	215.6	24.1	71.0	19.68	-	0.25	0.69
17	C <sub>10</sub>	119.6	-	156.1	205.4	36.5	49.3	17.88	-	0.28	0.66
18	C <sub>12</sub>	118.1	-	163.1	197.8	45.0	34.7	23.45	-	1.02	0.60
19	S <sub>10</sub> -C <sub>2</sub>	-	124.5	-	246.1	-	121.6	-	24.46	-	0.67
20	C <sub>4</sub>	-	122.0	-	228.5	-	106.5	-	23.75	-	0.77
21	C <sub>6</sub>	117.1	-	130.9	216.1	13.8	85.2	21.26	-	0.14	0.75
22	C <sub>8</sub>	118.4	-	149.9	207.0	31.5	57.1	22.33	-	0.22	0.71
23	C <sub>10</sub>	117.9	-	159.7	198.7	41.8	39.0	19.25	-	0.36	0.71
24	C <sub>12</sub>	116.8	-	163.7	190.8	46.9	27.1	27.75	-	0.49	0.79
25	S <sub>12</sub> -C <sub>2</sub>	-	125.5	-	231.6	-	106.1	-	23.84	-	0.80
26	C <sub>4</sub>	-	126.4	-	216.5	-	90.1	-	27.40	-	0.85
27	C <sub>6</sub>	118.9	-	136.7	205.9	17.8	69.2	25.64	-	0.14	0.87
28	C <sub>8</sub>	119.7	-	151.4	197.9	31.7	46.5	25.0	-	0.23	0.80
29	C <sub>10</sub>	118.9	-	160.5	191.5	41.1	31.5	24.67	-	0.38	0.99
30	C <sub>12</sub>	118.3	-	163.5	184.5	45.2	21.0	20.37	-	0.72	0.98

**Table S2: DSC transition temperatures of synthesized mesogens (cooling)**

S.No	Code	I-N (°C)	N-S <sub>C</sub> (°C)	S <sub>C</sub> -Cr (°C)	N-Cr (°C)
1	S <sub>4</sub> -C <sub>2</sub>	287.3	-	-	108.5
2	C <sub>4</sub>	262.3	-	-	115.6
3	C <sub>6</sub>	245.7	-	-	132.1
4	C <sub>8</sub>	231.1	[142.5]	132.6	-
5	C <sub>10</sub>	219.6	171.5	127.0	-
6	C <sub>12</sub>	206.3	175.9	124.6	-
7	S <sub>6</sub> -C <sub>2</sub>	273.8	-	-	101.2
8	C <sub>4</sub>	253.2	-	-	69.1
9	C <sub>6</sub>	235.3	[106.5]	96.1	-
10	C <sub>8</sub>	222.6	133.6	105.6	-
11	C <sub>10</sub>	211.7	153.7	97.3	-
12	C <sub>12</sub>	202.5	172.1	92.7	-
13	S <sub>8</sub> -C <sub>2</sub>	249.8	-	-	76.6
14	C <sub>4</sub>	240.6	[90.9]	57.3	-
15	C <sub>6</sub>	223.1	[113.8]	82.2	-
16	C <sub>8</sub>	214.9	143.8	81.6	-
17	C <sub>10</sub>	204.9	155.1	87.7	-
18	C <sub>12</sub>	197.5	162.8	90.1	-
19	S <sub>10</sub> -C <sub>2</sub>	245.3	-	-	80.9
20	C <sub>4</sub>	227.7	[108.4]	72.5	-
21	C <sub>6</sub>	215.6	130.0	72.5	-
22	C <sub>8</sub>	206.3	149.1	85.6	-
23	C <sub>10</sub>	197.7	158.6	97.2	-
24	C <sub>12</sub>	190.5	163.2	87.7	-
25	S <sub>12</sub> -C <sub>2</sub>	231.0	[104.1]	90.2	-
26	C <sub>4</sub>	215.4	[118.9]	90.1	-
27	C <sub>6</sub>	205.6	136.2	86.8	-
28	C <sub>8</sub>	197.7	151.2	88.0	-
29	C <sub>10</sub>	190.8	161.0	88.9	-
30	C <sub>12</sub>	184.1	163.0	91.2	-

- Square bracket indicates monotropic mesophase

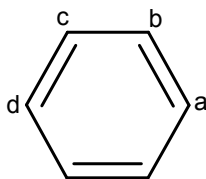
**Table S3: Powder X-ray diffraction data of mesogens at different temperatures**

Code	T(°C)	d <sub>1</sub> (Å)	d <sub>2</sub> (Å)	d <sub>3</sub> (Å)	d <sub>4</sub> (Å)	d/L	Code	T(°C)	d <sub>1</sub> (Å)	d <sub>2</sub> (Å)	d <sub>3</sub> (Å)	d/L
S <sub>4</sub> -C <sub>10</sub>	170	57.05	29.15	19.41	4.50	1.33	S <sub>10</sub> -C <sub>6</sub>	130	35.04	-	4.44	0.76
	165	57.07	29.0	19.01	4.48			125	34.68	-	4.45	
	155	56.11	28.48	18.90	4.50			120	34.67	-	4.48	
	150	56.11	28.50	18.89	4.47			115	34.34	-	4.43	
	140	55.16	28.77	18.69	4.49			105	34.01	-	4.43	
S <sub>4</sub> -C <sub>12</sub>	175	61.23	30.59	-	4.58	1.35	S <sub>10</sub> -C <sub>8</sub>	140	35.41	-	4.46	0.75
	165	60.13	31.13	-	4.54			130	35.05	-	4.44	
	155	60.09	30.58	-	4.53			120	34.70	-	4.45	
	145	61.22	30.30	-	4.49			110	34.67	-	4.44	
S <sub>6</sub> -C <sub>8</sub>	125	30.87	-	-	4.44	0.73	S <sub>10</sub> -C <sub>10</sub>	155	37.38	-	4.52	0.73
	120	30.59	-	-	4.40			145	36.61	-	4.50	
S <sub>6</sub> -C <sub>10</sub>	150	62.33	31.13	20.76	4.47	1.37		135	36.18	-	4.51	
	140	61.22	30.58	20.38	4.44			125	36.17	-	4.47	
	130	60.13	30.31	20.13	4.46			115	35.79	-	4.46	
	120	60.14	30.03	20.02	4.44			105	35.79	-	4.47	
S <sub>6</sub> -C <sub>12</sub>	170	66.01	33.02	22.06	4.51	1.39	S <sub>10</sub> -C <sub>12</sub>	150	37.62	-	4.52	0.72
	165	64.77	32.98	21.95	4.48			140	37.31	-	4.48	
	160	64.80	32.67	21.71	4.49			130	37.31	-	4.43	
	150	63.53	32.33	21.43	4.53			120	36.57	-	4.44	
	145	63.55	32.35	21.64	4.53			110	36.57	-	4.45	
	135	63.52	32.33	21.29	4.51			S <sub>12</sub> -C <sub>6</sub>	135	38.68	-	4.50
	125	63.57	32.35	21.53	4.49				125	37.80	-	4.48
	115	63.43	32.33	21.40	4.48			120	37.80	-	4.47	
S <sub>8</sub> -C <sub>8</sub>	140	33.31	-	-	4.49	0.74		115	37.40	-	4.45	0.81
	130	32.99	-	-	4.46			S <sub>12</sub> -C <sub>8</sub>	150	39.59	-	
	125	32.35	-	-	4.44				140	38.68	-	4.51
	115	32.04	-	-	4.45				130	38.24	-	4.47
	105	31.74	-	-	4.44				120	37.81	-	4.49
S <sub>8</sub> -C <sub>10</sub>	150	34.68	-	-	4.51	0.73		110	37.78	-	4.48	0.74
	140	33.99	-	-	4.47			105	37.39	-	4.47	
	130	33.32	-	-	4.48		S <sub>12</sub> -C <sub>10</sub>	160	41.56	-	4.55	
	120	66.02	32.98	21.84	4.48	1.42		150	39.98	-	4.52	
	110	66.05	32.67	21.70	4.46				140	39.13	-	
	100	66.03	32.66	21.71	4.45				130	38.68	-	4.51
S <sub>8</sub> -C <sub>12</sub>	160	71.70	35.80	-	4.48	1.42		120	38.68	-	4.49	0.74
	155	70.19	35.50	-	4.50			110	38.27	-	4.47	
	150	70.08	35.02	23.02	4.50			100	38.22	-	4.48	
	145	70.08	34.66	23.03	4.49			S <sub>12</sub> -C <sub>12</sub>	160	40.55	-	
	135	68.04	34.31	22.87	4.49				150	40.06	-	4.53
	125	68.63	34.31	22.72	4.49				140	40.06	-	4.52
	115	68.65	34.31	22.79	4.48				130	39.59	19.66	4.55
	110	68.65	34.31	22.79	4.48				120	39.59	19.84	4.49
	105	68.72	34.31	22.87	4.49				110	39.59	19.75	4.50

**Table S4:  $^{13}\text{C}$  NMR data of  $\text{S}_6\text{-C}_{10}$  mesogen in solution, smectic C and nematic phases**

C. N	Solution (ppm)	Smectic C 140 °C			Nematic 160 °C		
		CS (ppm)	AIS (ppm)	DC (kHz)	CS (ppm)	AIS (ppm)	DC (kHz)
1	161.8	229.4	67.6	1.54	223.0	61.2	1.44
2	114.3	141.9	27.6	2.88	139.7	25.4	2.64
3	132.2	161.8	29.6	2.97	158.8	26.6	2.72
4	121.5	190.7	69.2	1.56	184.5	63.0	1.44
5	165.0	215.9	50.9	0.62	210.1	45.1	0.54
6	148.9	226.9	78.0	1.60	219.7	70.8	1.50
7	121.7	147.6	25.9	3.07	145.1	23.4	2.80
8	122.3	153.1	30.8	2.84	150.3	28.0	2.61
9	149.9	219.3	69.4	1.59	213.2	63.3	1.52
10	159.7	201.8	42.1	4.92	197.4	37.7	4.55
11	129.0	201.8	72.8	2.02	194.6	65.6	1.92
12	130.5	165.1	34.6	2.66	162.1	31.6	2.45
13	114.7	141.9	27.2	2.88	139.7	25.0	2.64
14	161.6	229.4	67.8	1.54	223.0	61.4	1.44
15	163.5	215.9	52.4	0.62	210.1	46.6	0.54
16	139.1	190.7	51.6	0.66	187.4	48.3	0.54
17	132.9	157.7	24.8	2.40	157.2	24.3	2.10

**Table S5: Orientational order parameter values for phenyl rings<sup>a</sup> (S<sub>6</sub>-C<sub>10</sub> mesogen)**



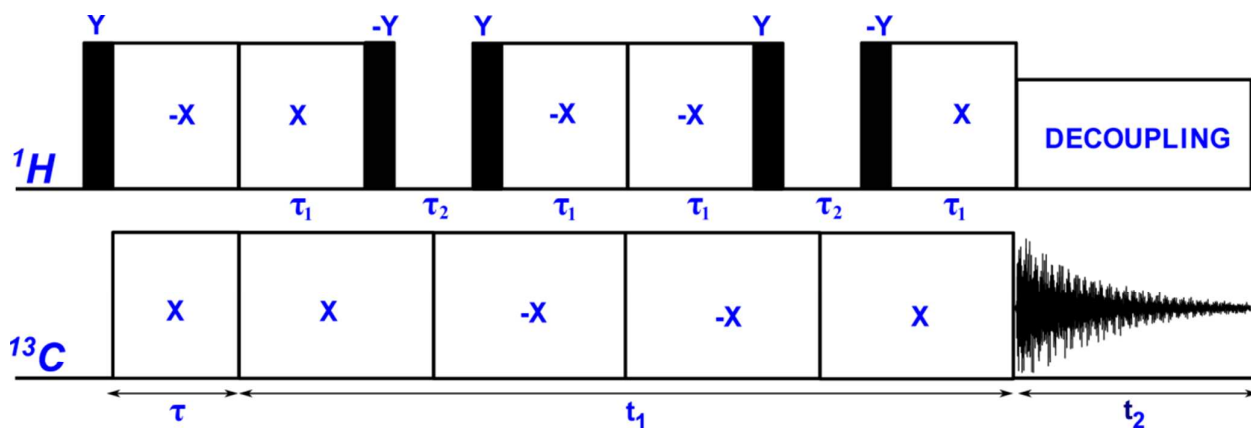
T (°C)	Ring	Angle		$S'_{zz}$	$S'_{xx}-S'_{yy}$	Calculated Dipolar Oscillation Frequencies (kHz)			
		$\theta_b$	$\theta_c$			b	c	a <sup>b</sup>	d
140	I	119.9	119.6	0.67	0.068	2.89	2.98	1.54	1.53
	II	119.6	120.3	0.69	0.072	3.08	2.86	1.58	1.60
	III	120.5	119.9	0.66	0.068	2.67	2.85	2.08	1.52
160	I	119.9	119.7	0.62	0.062	2.66	2.72	1.43	1.42
	II	119.8	120.5	0.64	0.066	2.79	2.59	1.47	1.49
	III	120.6	119.9	0.62	0.060	2.45	2.65	1.95	1.42

<sup>a</sup> In the figure above the table, *b* and *c* are methine carbons, *a* and *d* are quaternary carbons respectively for ring-I, II and III.

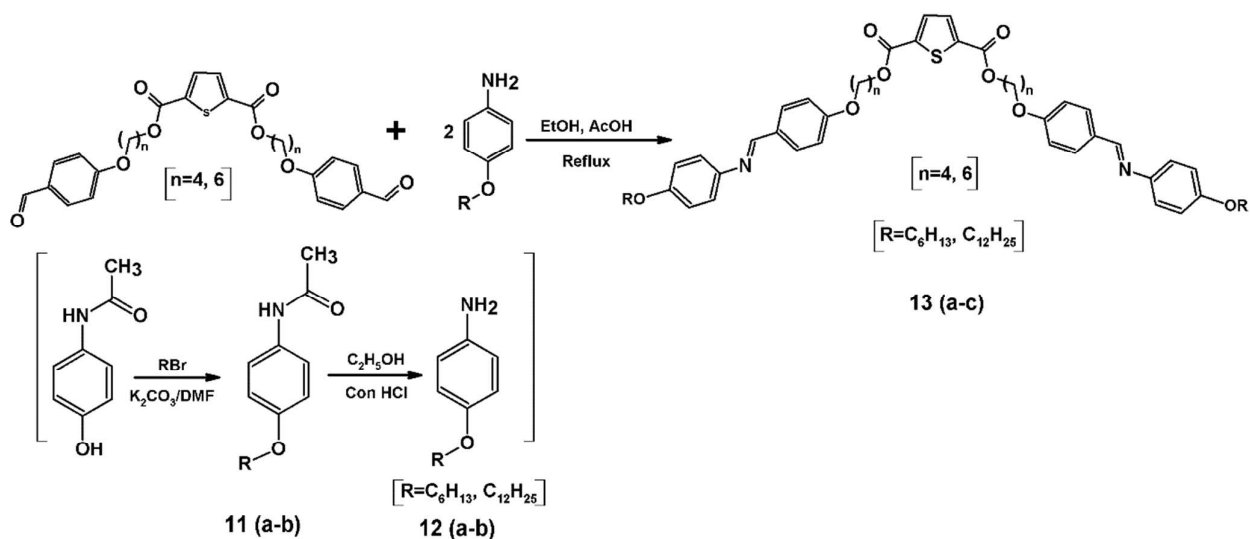
<sup>b</sup> For carbon *a* in ring-III, the contribution of the azomethine proton has also been taken into account.

**Table S6: Thiophene Orientational Order Parameter Values (S<sub>6</sub>-C<sub>10</sub> mesogen)**

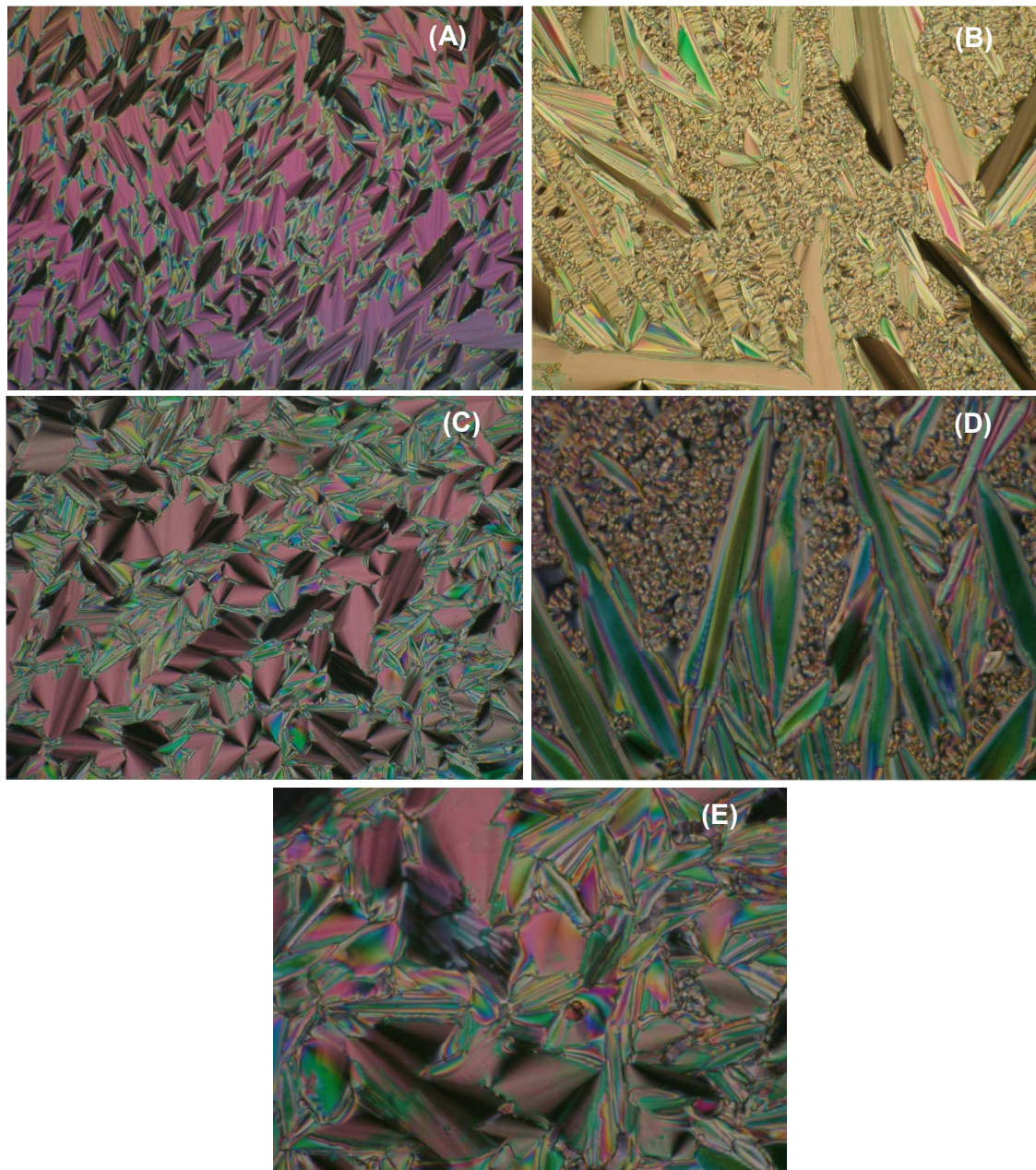
T (°C)	Tilt Angle $\theta$	$S'_{zz}$	$S'_{xx}-S'_{yy}$	Calculated Dipolar Oscillation Frequencies (kHz)	
				C17	C16
140	10.3	0.23	0.042	2.40	0.66
160	9.5	0.19	0.008	2.10	0.55



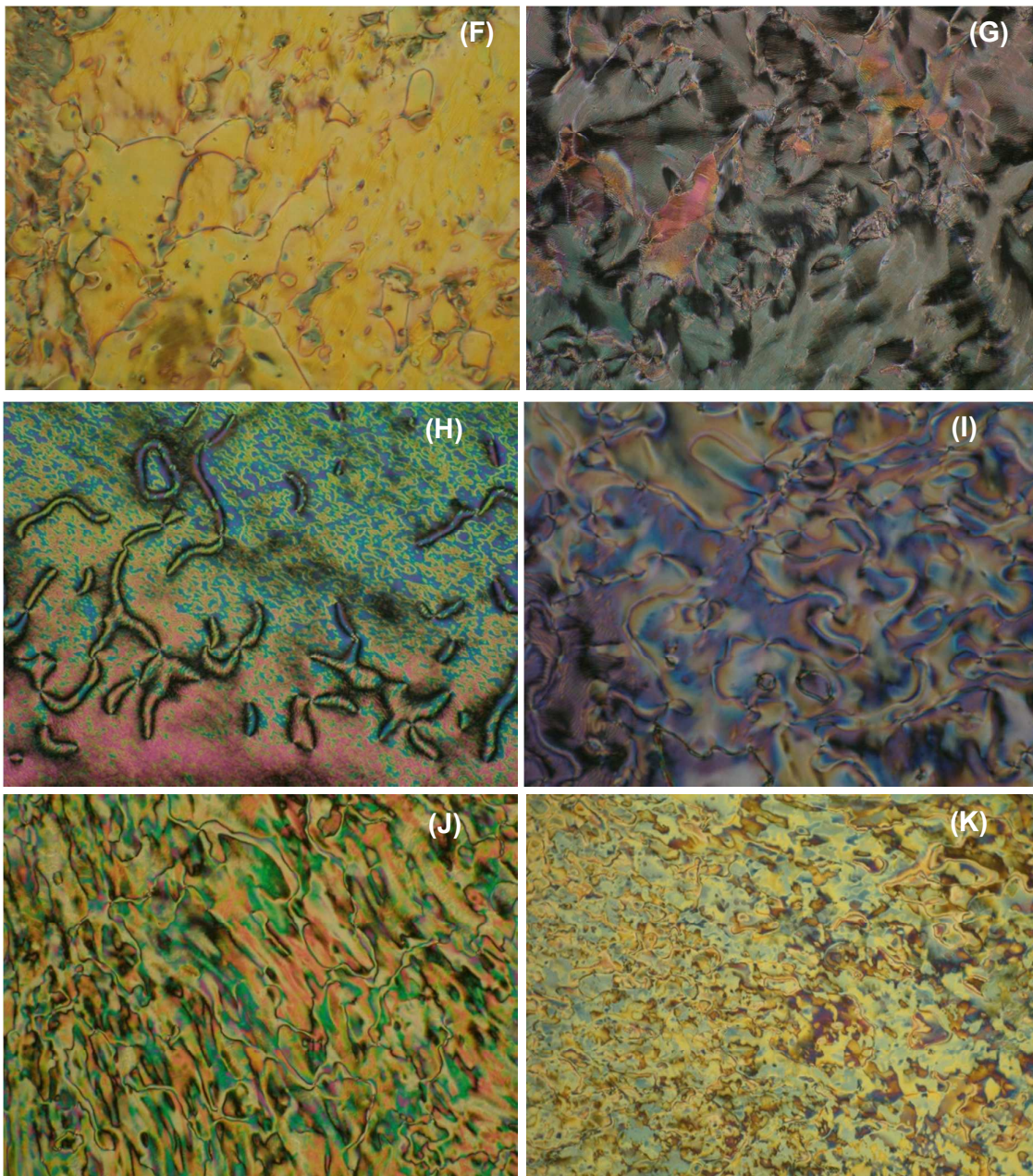
**Scheme S1:** SAMPI-4<sup>11</sup> pulse sequence used for obtaining the 2D-SLF spectrum in the mesophase. Here  $\tau$  is CP contact time and the darker boxes represent  $90^\circ$  pulses.



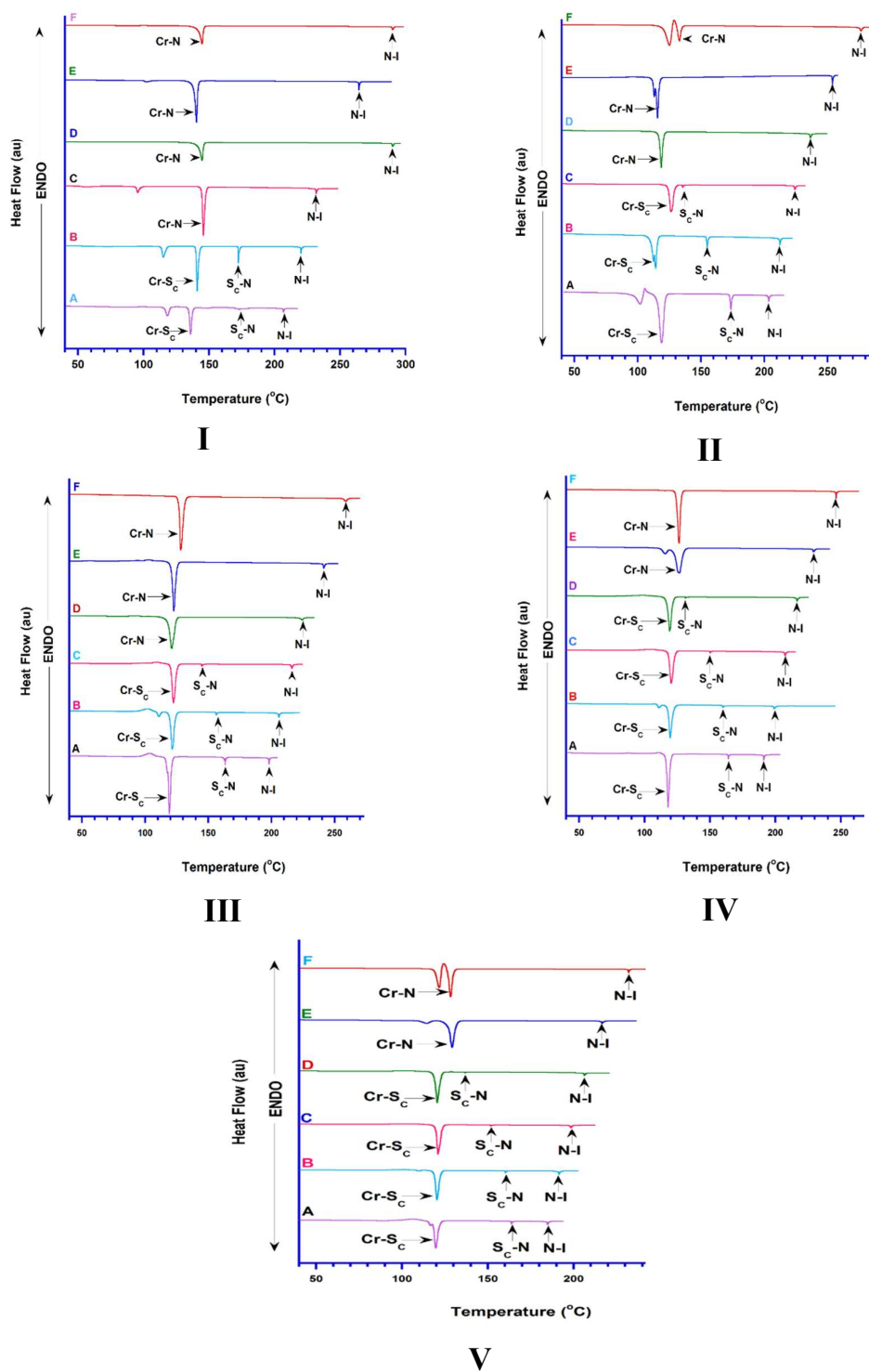
**Scheme S2:** Synthetic strategy for the target mesogens.



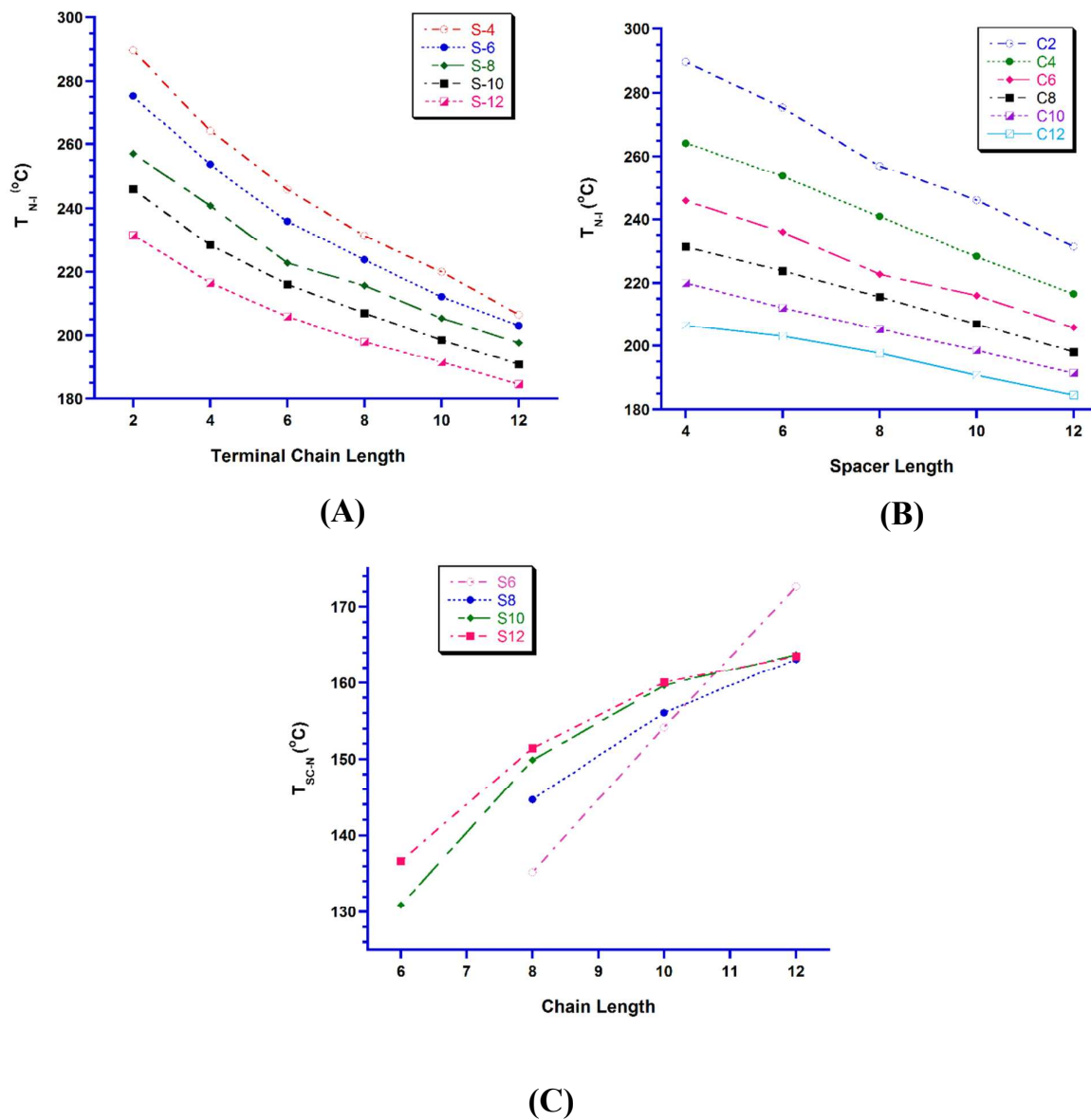
**Figure S1:** HOPM photographs of mesogens while cooling from isotropic phase-(S<sub>4</sub>-C<sub>12</sub>)-  
 (A): 144.2 °C, S<sub>4</sub>-C<sub>10</sub>-(B): 166.5 °C, S<sub>6</sub>-C<sub>10</sub>-(C): 151.4 °C, S<sub>6</sub>-C<sub>12</sub>-(D): 165.4 °C, S<sub>6</sub>-C<sub>10</sub>-  
 (E):148.1 °C (interdigitated partial bilayer smectic C phases)



**Figure S2:** HOPM photographs of mesogens while cooling from isotropic phase-(S<sub>8</sub>-C<sub>10</sub>)-(F): 145.2 °C (monolayer smectic C phase), (G): 116.7 °C (interdigitated partial bilayer smectic C phase), (S<sub>8</sub>-C<sub>4</sub>)-(H):180.8 °C (nematic phase), (S<sub>8</sub>-C<sub>6</sub>)-(I):102.6 °C (monolayer smectic C phase); (S<sub>8</sub>-C<sub>2</sub>)-(J):239.6 °C (nematic phase); (S<sub>10</sub>-C<sub>12</sub>)-(K):153.5 °C (monolayer smectic C phase)



**Figure S3:** DSC heating cycle scans of: (A) C<sub>12</sub>, (B) C<sub>10</sub>, (C) C<sub>8</sub>, (D) C<sub>6</sub>, (E) C<sub>4</sub> and (F) C<sub>2</sub> of (I)-S<sub>4</sub> series, (II)- S<sub>6</sub> series, (III)- S<sub>8</sub> series, (IV)-S<sub>10</sub> series and (V)-S<sub>12</sub> series.



**Figure S4:** (A)  $T_{N-I}$  versus Terminal chain length (S<sub>4</sub>-C<sub>2</sub> to S<sub>12</sub>-C<sub>12</sub>), (B)  $T_{N-I}$  versus Spacer length (S<sub>4</sub>-C<sub>2</sub> to S<sub>12</sub>-C<sub>12</sub>) and (C)  $T_{SC-N}$  versus Terminal chain length (S<sub>6</sub>-C<sub>8</sub> to S<sub>6</sub>-S<sub>12</sub>; S<sub>8</sub>-C<sub>8</sub> to S<sub>8</sub>-C<sub>12</sub>; S<sub>10</sub>-C<sub>6</sub> to S<sub>10</sub>-C<sub>12</sub> and S<sub>12</sub>-C<sub>6</sub> to S<sub>12</sub>-C<sub>12</sub>).

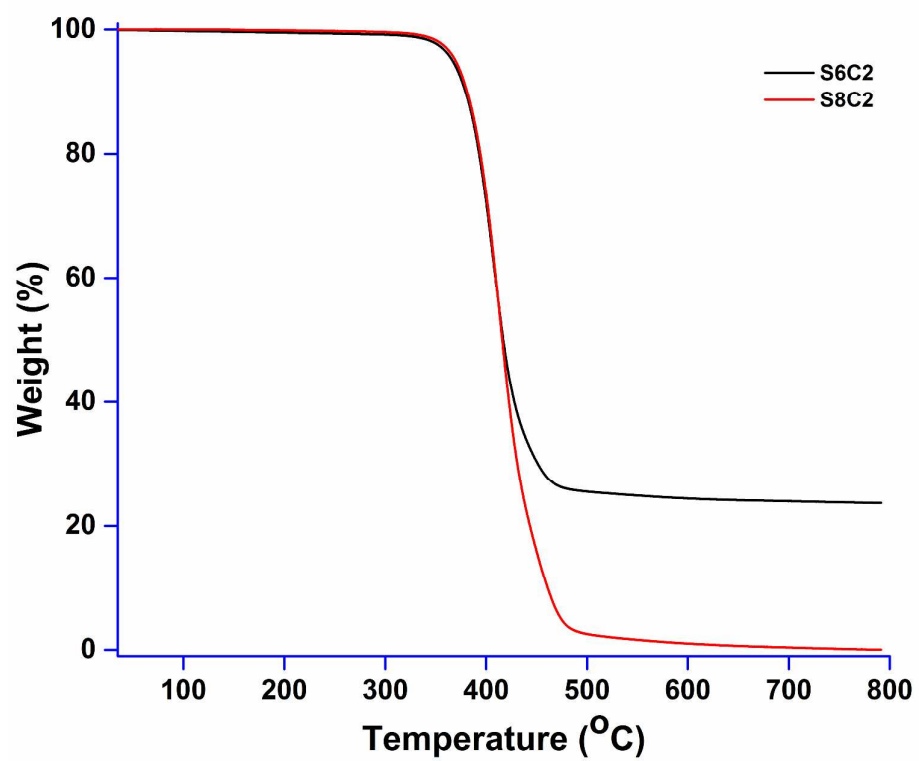
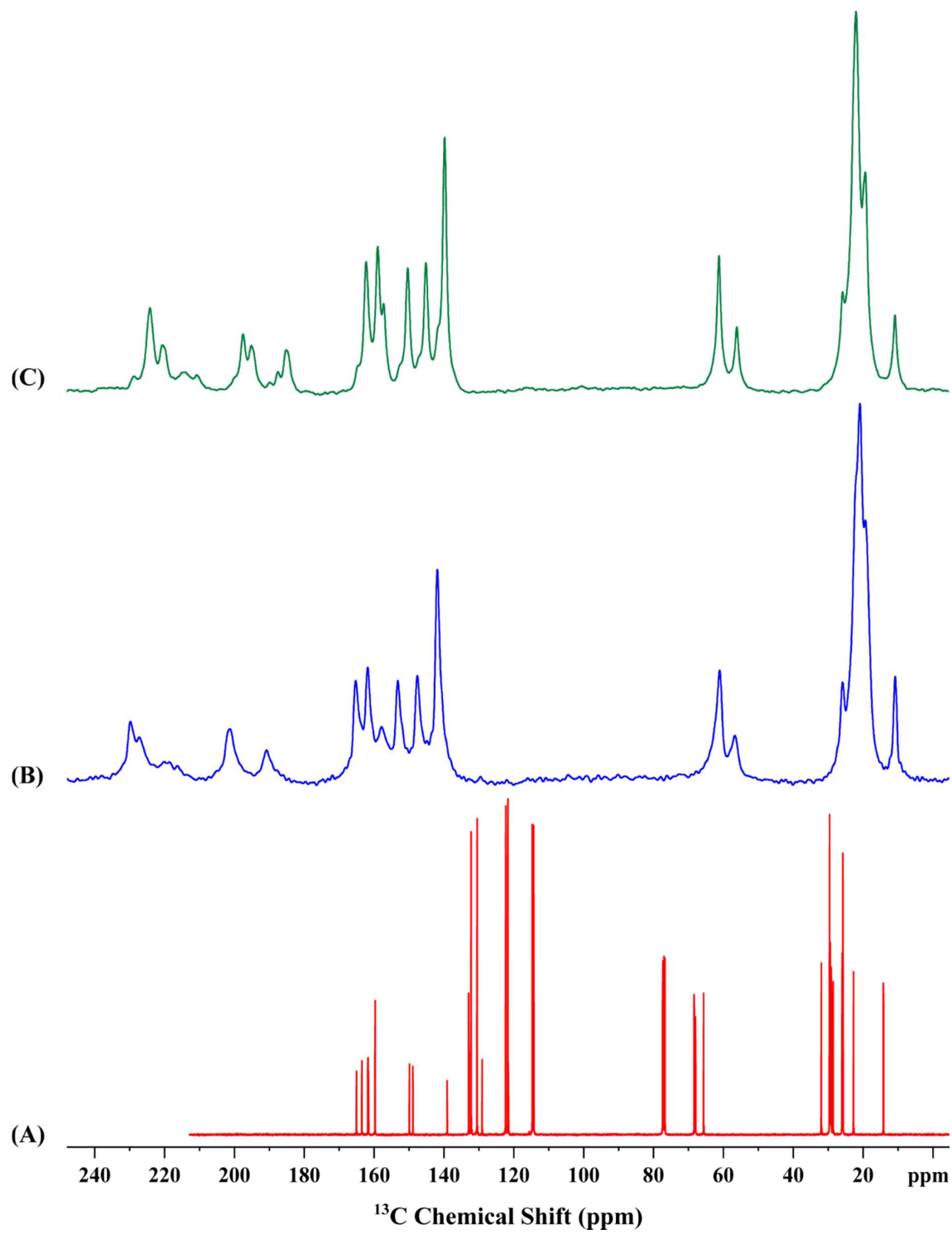
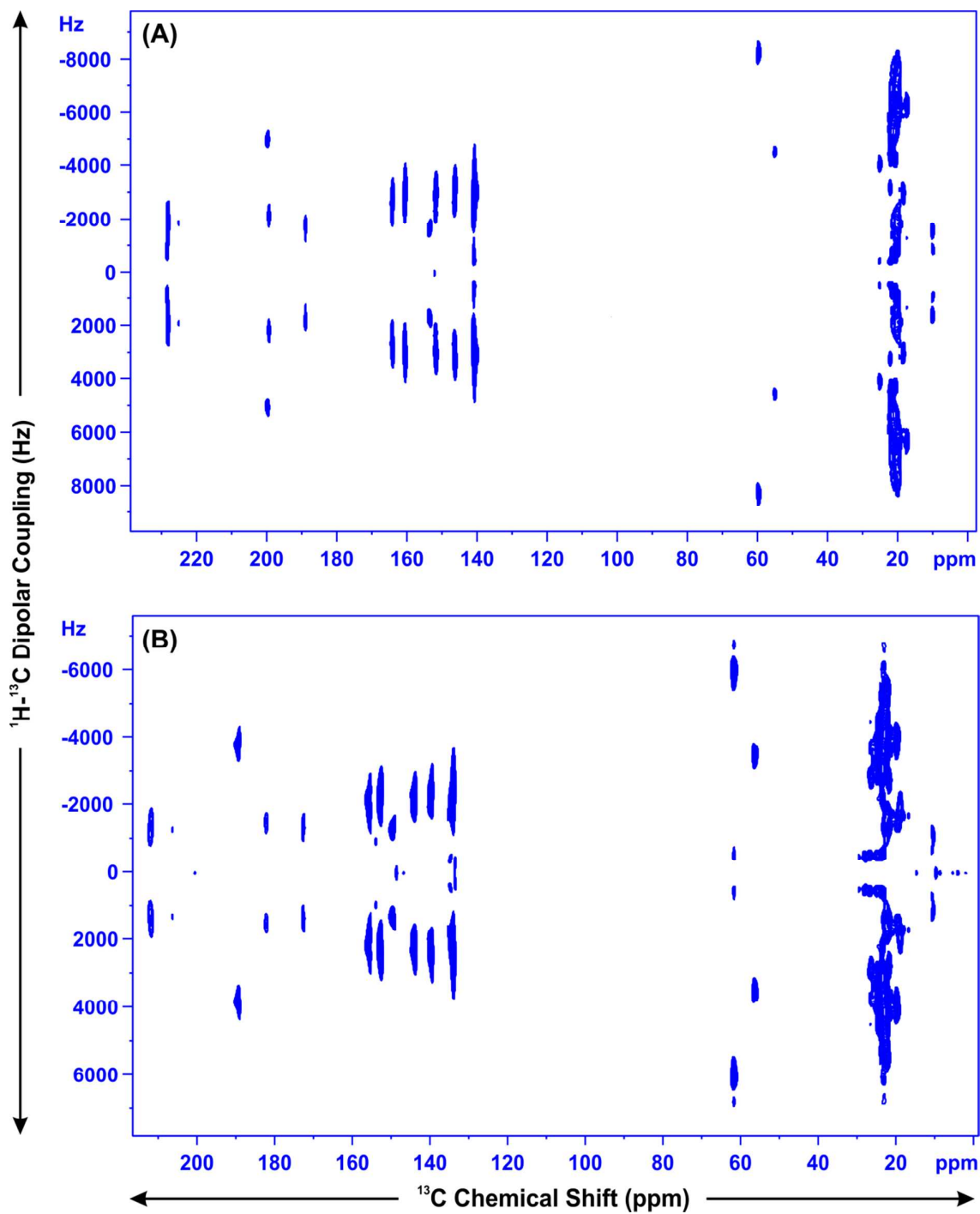


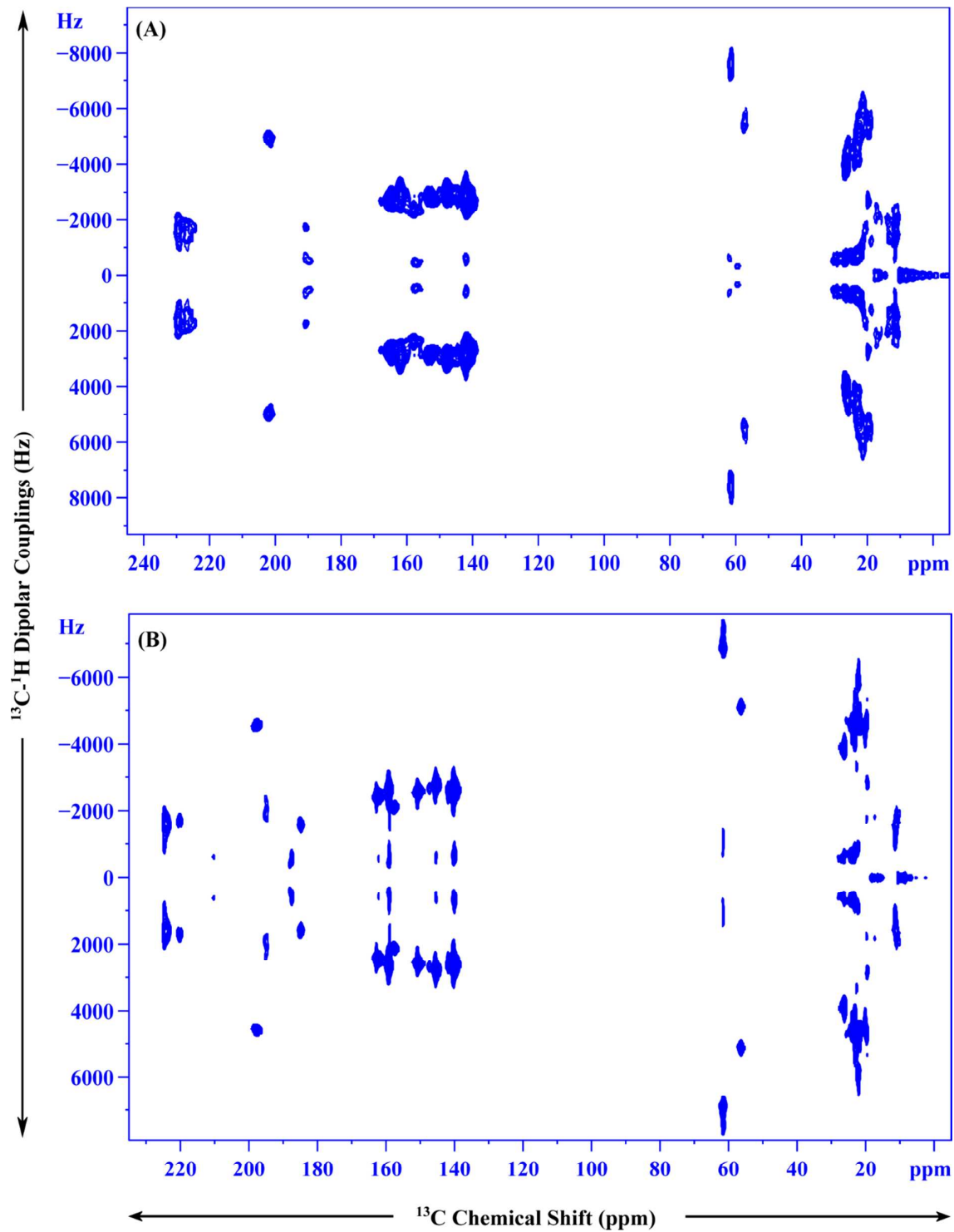
Figure S5: TGA curves of S<sub>6</sub>-C<sub>2</sub> and S<sub>8</sub>-C<sub>2</sub> mesogens.



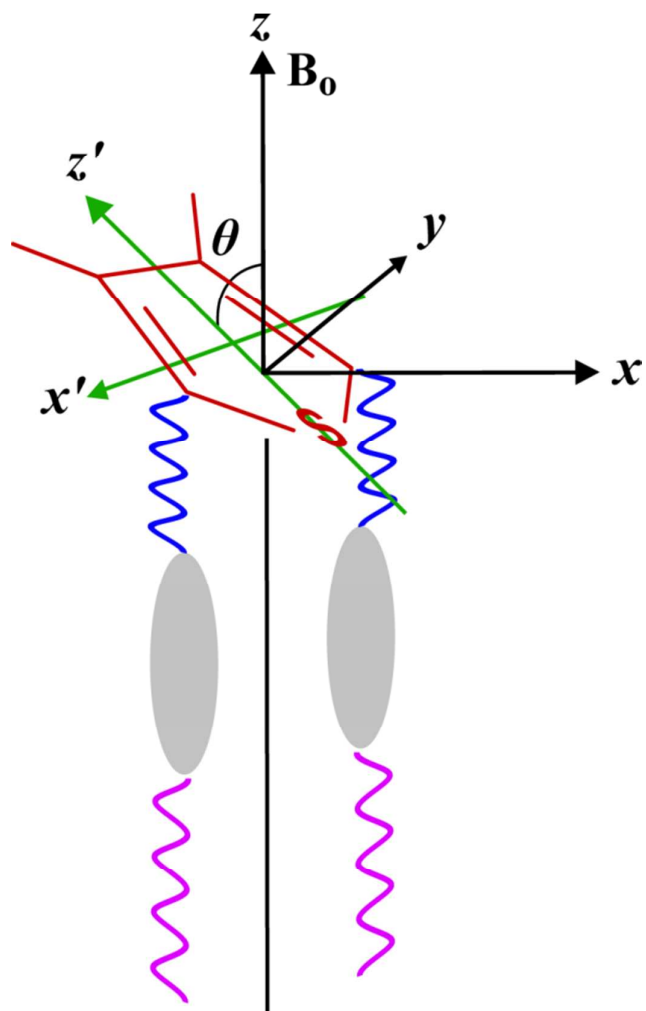
**Figure S6:**  $^{13}\text{C}$  NMR spectra of  $\text{S}_6\text{-C}_{10}$  mesogen in (A) solution, (B) smectic C phase ( $140^\circ\text{C}$ ) and (C) nematic phase ( $160^\circ\text{C}$ ).



**Figure S7:** 2D full region SAMPI-4 spectra of  $\text{S}_{12}\text{-C}_{12}$  in (A) smectic C phase at 140 °C and (B) nematic phase at 175 °C



**Figure S8:** 2D full region SAMPI-4 spectra of  $S_6-C_{10}$  mesogen in (A) smectic C phase at 140 °C and (B) nematic phase at 160 °C.



**Figure S9:** Proposed model for the determination of orientational order parameter of thiophene ring

## REFERENCES

- (1) Chong, J. M.; Heuft, M. A.; Rabbat, P. Solvent Effects on the Monobromination of  $\alpha,\omega$ -Diols: A Convenient Preparation of  $\omega$ -Bromoalkanols. *J. Org. Chem.* **2000**, *65*, 5837- 5838.
- (2) Neubert, M. E.; Laskos, Jr. S. J.; Maurer, L. J.; Carlino, L. T.; Ferrato, J. P. Preparation of Liquid Crystal Intermediates: 4-Substituted Alkoxybenzenes. *Mol. Cryst. Liq. Cryst.* **1978**, *44*, 197-210.
- (3) Jensen, J.; Grundy, S.C.; Bretz, S. L.; Hartley, C. S. Synthesis and Characterization of Self-Assembled Liquid Crystals: p-alkoxybenzoic acids. *J. Chem. Educ.* **2011**, *88*, 1133-1136.
- (4) Kesava Reddy, M.; Subramanyam Reddy, K.; Prakash, M.; Narasimhaswamy, T. Synthesis and Characterization of Two Phenyl Ring Core-Based Thiophene Mesogens. *Mol. Cryst. Liq. Cryst.*, **2013**, *582*, 1-14.
- (5) Kesava Reddy, M.; Subramanyam Reddy, K.; Phani Kumar, B. V. N.; Narasimhaswamy, T. Synthesis, Structural and Mesophase Characterization of Three Ring Based Thiophene Liquid Crystals. *Mol. Cryst. Liq. Cryst.*, **2014**, *593*, 1-24.
- (6) Neises, B.; Steglich, W. Simple Method for the Esterification of Carboxylic Acids. *Angew. Chem. Int. Ed.* **1978**, *17*, 522-524.
- (7) Shendage, D.M., Fröhlich, R.; Haufe, G. Highly Efficient Stereoconservative Amidation and Deamidation of  $\alpha$ -amino acids. *Org. Lett.* **2004**, *6*, 3675-3678.
- (8) Sudhakar, S.; Narasimhaswamy, T.; Srinivasan, K. S. V. Synthesis, Characterization and Thermal Properties of 4, 4'-bis (4-n-alkoxybenzoyloxy) benzylideneanilines and bis (4-benzylidene-4'-n-alkoxyaniline) terephthalates. *Liq. Cryst.* **2000**, *27*, 1525-1532.

- (9) Kesava Reddy, M.; Subramanyam Reddy, K.; Narasimhaswamy, T.; Das, B. B.; Lobo, N. P.; Ramanathan, K. V.  $^{13}\text{C}$ - $^1\text{H}$  Dipolar Couplings for Probing Rod-Like Hydrogen Bonded Mesogens. *New J. Chem.* **2013**, *37*, 3195-3206.
- (10) Fung, B. M.; Khitritin, A. K.; Ermolaev, K. An Improved Broad Band Decoupling Sequence for Liquid Crystals and Solids. *J. Magn. Reson.* **2000**, *142*, 97-101.
- (11) Nevzorov, A. A.; Opella, S. J. Selective Averaging for High Resolution Solid-State NMR Spectroscopy of Aligned Samples. *J. Magn. Reson.* **2007**, *185*, 59-70.