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# 1. Introduction

Thermotropic liquid crystals based on a rod-like core are continuing to lure the attention of investigators because of their structural simplicity and well-known structure–property correlation.<sup>1–4</sup> The recent past has witnessed increasing interest in  $\pi$ -conjugated mesogens in which the core is often rod-like in shape.<sup>5–8</sup> These molecules are generally synthesized by directly linking the carbocyclic or heterocyclic aromatic rings with suitable terminal chains.<sup>9–11</sup> Because of the direct link of the rings of the core, the  $\pi$ -conjugated mesogens conceivably exhibit interesting optoelectronic and opto-photonic properties.<sup>12–14</sup> Even though a direct link between the rings of the core favors excellent  $\pi$ -conjugation,

<sup>b</sup> Inorganic & Physical Chemistry, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India

# Effect of alkyl chain and linking units on mesophase transitions and molecular order of rod-like thiophene mesogens: <sup>13</sup>C NMR investigation<sup>†</sup>

Y. Santhosh Kumar Reddy,<sup>a</sup> Nitin P. Lobo<sup>b</sup> and T. Narasimhaswamy 🝺 \*<sup>a</sup>

Thermotropic liquid crystals with  $\pi$ -conjugated cores are increasingly witnessed due to their promising optoelectronic and optophotonic properties. As  $\pi$ -conjugated mesogens are often realized by direct linking of the rings of the core, the mesophase transitions are usually modulated by inserting the required alkyl/alkoxy chains either at a terminal or lateral location. In this work, five mesogens in which thiophene and two phenyl rings are common in the core unit with terminal alkyl/alkoxy chains are investigated to probe the influence of (a) a terminal alkyl chain on the mesophase characteristics, (b) the linking units on the mesophase range and (c) the disparity of thiophene orientational constraints. The mesophase properties reveal that whenever the alkyl chain is located at one end of the molecule, polymesomorphism is observed. The XRD studies reveal layer ordering typical of smectic mesophases with lower temperature and higher order phases, namely SmB and CrE phases. A detailed <sup>13</sup>C NMR study of the mesogens in the liquid crystalline phase indicates that the order parameters are governed by the nature of the substitution of thiophene and its linkage with two phenyl rings. Importantly, the <sup>13</sup>C NMR data of the terminal chains in the liquid crystalline phase are compared with the recently reported thiophene mesogen in which the *n*-hexyl chain is located at the lateral position and completely different orientation characteristics were found for the terminal *versus* lateral chains.

due to inherent rigidity of the core unit, the melting and clearing transitions are generally found to be high.<sup>15-17</sup> To modulate the mesophase transitions of such mesogens, either normal or branched alkyl chains are introduced at different locations of the molecules.18-24 For instance, in the case of thiophene-based  $\pi$ -conjugated systems, the alkyl chains are often inserted at the 3-position of the thiophene ring so that the molecules show solubility in common solvents at room temperature.<sup>25,26</sup> In low molar mass and oligometric  $\pi$ -conjugated mesogens, the alkyl chains are placed at the terminal position not only to achieve solubility without disrupting the  $\pi$ -conjugation but also to enhance the aspect ratio of the molecule.27,28 Recent research results also emphasized the role of alkyl chains in influencing the property characteristics as well as the morphology of materials.<sup>29,30</sup> In other words, depending on the position of the alkyl chain, *i.e.*, the terminal versus lateral location, the mesophase properties dramatically differ.<sup>23,31</sup> For instance, placing the alkyl chain at the terminal location of mesogens may favor layer ordering while its location at the lateral position would disrupt the layer ordering.<sup>32,33</sup> It is generally noticed that mesogens with two terminal chains which can be independently varied in length can exhibit tilted phases if the lengths are similar.<sup>19-22</sup> On the other hand, orthogonal phases such as



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<sup>&</sup>lt;sup>a</sup> Polymer Science & Technology, CSIR-Central Leather Research Institute, Adyar, Chennai 600020. India. E-mail: tnswamv99@hotmail.com

<sup>†</sup> Electronic supplementary information (ESI) available: It contains synthetic details, HRMS data, figure of SAMPI-4 pulse sequence, solution 1D and 2D NMR spectra of mesogens, plots of SAMPI-4 1D dipolar slices, thiophene models for orientational order parameter computation, figure of PELF pulse sequence, PELF experimentsl details, data and spectra for aliphatic region of mesogens. See DOI: 10.1039/c7nj03525j

SmB, crystal B and crystal E are found if the shorter chains are at the terminal location.<sup>19–22</sup> In order to understand the influence of alkyl chains on the mesophase properties as well as orientational constraints of thiophene mesogens, hot-stage optical polarizing microscopy (HOPM), differential scanning calorimetry (DSC) and 2D solid state <sup>13</sup>C NMR investigations are carried out respectively.

In recent years, solid state <sup>13</sup>C NMR studies of liquid crystals have been increasingly witnessed owing to the accessibility of anisotropic information in the form of alignment-induced chemical shifts, as well as <sup>13</sup>C-<sup>1</sup>H dipolar couplings that can be extracted from 1D and 2D experiments in the mesophase.<sup>34-37</sup> Furthermore, the extracted anisotropic information of the different moieties of the mesogens, i.e. the constituent units of the core as well as the terminal/lateral chains, provide order parameter values which are a direct consequence of the dynamics of the corresponding moieties.<sup>38,39</sup> By comparing the orientational order of the constituent rings of the core unit, the molecular shape or topology can be extracted. As a result, a wide range of topologically different mesogens have been subjected to <sup>13</sup>C NMR investigation in the mesophase to map the orientational constraints. It is also noticed that on the replacement of the phenyl ring with a thiophene ring in the core, profound changes in molecular shape or topology results which is well reflected through the order parameter values.<sup>40,41</sup> Hence, in the present work, <sup>13</sup>C NMR is employed for understanding the orientational constraints of phenyl as well as thiophene rings of rod-like mesogens with terminal alkyl/alkoxy chains. Furthermore, the orientational constraints of terminal alkyl chains determined from <sup>13</sup>C NMR data are compared with the recently reported mesogen in which the alkyl chain is located on the thiophene at the 3-position *i.e.* at a lateral location.<sup>23</sup> In other words, the influence of orientational constraints on terminal versus lateral location of the alkyl chain is evaluated. For better comprehension, for all the mesogens examined, the core is designed to have two phenyl rings with an additional thiophene ring as part of the mesogenic core. The main focus of the study is to address (i) the influence of the terminal alkyl chain on the mesophase characteristics, (ii) the effect of the linking unit on the mesophase range and (iii) the variation of thiophene orientational constraints with respect to the molecular structure. Towards this goal, the synthesized mesogens are investigated by HOPM, DSC and powder X-ray diffraction (XRD) for phase assignment as well as transition temperatures and by <sup>13</sup>C NMR to find the orientational constraints.

# 2. Experimental section

#### Materials

5-Hexylthiophene-2-carbaldehyde, 2-hexyl thiophene, 5-bromothiophene-2-carboxaldehyde, 4-(dodecyloxy) phenol, 4-hydroxybenzaldehyde, thiophene 2-boronic acid, potassium carbonate, dichloromethane, tetrakis(triphenylphosphine) palladium (0), tetrahydrofuran, dicyclohexyl carbodiimide, 4-dimethylamino pyridine, phosphorous oxychloride, 4'-bromobiphenyl-4-ol, and 1-bromododecane were purchased from Sigma-Aldrich, USA and used without further purification. Dimethyl formamide, chloroform, potassium hydroxide, sodium chlorite, sodium dihydrogen orthophosphate dihydrate, anhydrous sodium sulfate, acetonitrile, dichloromethane, hexane, ethyl acetate and silica gel (100–200 mesh) were obtained from Merck, India, and 5-octyl thiophene-2carbaldehyde was obtained from Avra Synthesis, India, and used as received.

#### Instrumental details

Both <sup>1</sup>H and <sup>13</sup>C NMR spectra were run on a 400 MHz Bruker Avance-III HD spectrometer at room temperature using CDCl<sub>3</sub> as a solvent and tetramethylsilane (TMS) as an internal reference. The resonance frequencies of <sup>1</sup>H and <sup>13</sup>C were 400.23 and 100.64 MHz respectively. The optical polarizing micrographs were taken using a Carl Zeiss axiocam MRC5 Polarizing microscope equipped with a Linkam THMS heating stage with a TMS 94 temperature programmer. The samples were placed between 12 mm glass coverslips and transferred to the heating stage and heated at a programmed heating rate. The photomicrographs were taken using an imager A2M digital camera. The differential scanning calorimetry traces were recorded using a DSC Q 200 instrument at a heating rate of 10 °C per minute in a nitrogen atmosphere. The samples were subjected to two heating and two cooling cycles. The data obtained from the second heating and cooling cycle were considered for discussion. High-Resolution Mass Spectra (HRMS) of the mesogens were recorded using a MICROMASS-O-TOF mass spectrometer (Fig. S1-S3, ESI<sup>+</sup>).

The synthetic details of the intermediates and final mesogens are given in the ESI.†

#### Solid state NMR measurements

All the solid-state NMR experiments were conducted under static conditions on a Bruker Avance III HD 400 WB NMR spectrometer (9.4 T) at a frequency of 400.07 MHz for <sup>1</sup>H and 100.61 MHz for <sup>13</sup>C. A 5 mm double resonance Bruker VTN probe with a horizontal solenoid coil was used for the measurements. At room temperature, the powdered samples were packed in a 4 mm Zirconia rotor with a Zirconia cap and placed inside a 5 mm glass tube. In order to achieve the sample alignment, all the samples were gradually heated to their corresponding isotropic phase and later slowly cooled to the respective mesophases for the measurement. The cross-polarization  $(CP)^{42}$ sequence along with a linear ramp from 100-50% (<sup>1</sup>H channel) was employed to get 1D static 13C NMR spectra of the mesogens in their respective mesophases. Typically, a contact time  $\tau$  of 3 ms, number of scans 128, recycle delay of 8 s and 62.5 kHz of radio frequency (RF) field strength on both the <sup>1</sup>H and <sup>13</sup>C channels during the period  $\tau$  were used. High-resolution 2D separated local field (SLF)43,44 spectra were obtained by using the SAMPI-4 pulse scheme<sup>45</sup> (Fig. S4, ESI<sup>†</sup>) and its utility for topologically different mesogens was highlighted in our earlier works.<sup>23,31,32,36-40,46</sup> The SAMPI-4 experimental parameters for the five mesogens were as follows KTC/HTC/OTC/OTPC/BTC: CP contact time  $\tau = 3$  ms,  $t_1$ increments = 128, number of scans = 24/28/20/42/28, <sup>1</sup>H 90° pulse length = 5  $\mu$ s and recycle delay = 13 s/15 s/14 s/16 s/13 s

(to avoid RF heating effects). The 2D data sets were zero-filled in both the  $t_1$  and  $t_2$  dimensions to form a 256 × 4096 data matrix. Phase-shifted sine bell multiplication was applied in both dimensions prior to Fourier transformation. For all the experiments, 30 kHz SPINAL-64<sup>47</sup> proton decoupling was employed during carbon acquisition. The Bruker BVTB-3500 temperature control unit was used for temperature regulation and the <sup>13</sup>C chemical shifts were referenced externally to adamantane methine resonance at 29.5 ppm.

#### **Computational details**

The gas phase molecular geometries of the representative mesogens were optimized using the density functional theory (DFT)<sup>48</sup> based Becke's three-parameter hybrid exchange functional



A = NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, THF, H<sub>2</sub>O, R.T, 12h; B = DCC, DMAP, DCM,0°C, 24h; C = NaClO<sub>2</sub>, NaH<sub>2</sub>PO<sub>4</sub>, THF, H<sub>2</sub>O, 12h;

D = DCC, DMAP, DCM, 0°C, 24h; E = Pd(PPh<sub>3</sub>)<sub>4</sub>, THF, H<sub>2</sub>O, K<sub>2</sub>CO<sub>3</sub>, 70°C, 16h;



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Scheme 1 Synthetic strategy for mesogens. (a) KTC, HTC, OTC, BTC and (b) OTPC mesogens.

and Lee–Yang–Parr correlation functional (B3LYP) method employing the 6-31G(d) basis set using the Gaussian 09W suite of programs.<sup>49</sup>

#### Powder X-ray measurements

The powder XRD studies of the un-oriented samples in a Lindemann capillary with a diameter of 1 mm (Hampton Research, Aliso Viejo, CA, USA) were carried out using a PANalytical instrument (DY 1042-Empyrean) operating with a line focused Ni-filtered Cu-K $\alpha$  ( $\lambda$  = 1.54 Å) beam and a linear detector (PIXcel 3D). The sample temperature was controlled with a precision of 0.1 °C using a heater and a temperature controller (Linkam).<sup>50</sup>

# 3. Results and discussion

Five mesogens in which thiophene is at one end of the core unit and a dodecyloxy chain at the other end are synthesized as per the strategy outlined in Schemes 1a and b and in the ESI.† The two phenyl ring based thiophene containing mesogens are synthesized from 5-substituted thiophene-2-carboxaldehyde. In the case of the mesogen with the bithiophene unit (BTC), the second thiophene is introduced by Suzuki coupling<sup>51-54</sup> of the corresponding bromo mesogen with thiophene-2-boronic acid. For the case of OTPC, where no connecting units are present in the core, synthesis was conducted by direct arylation<sup>31,55,56</sup> of 2-hexyl thiophene using 4-bromo-4'-(dodecyloxy)-1,1'-biphenyl employing palladium acetate as a catalyst. The main focus of the investigation is to find the influence of terminal chains on the mesophase transition temperatures as well as on the molecular order. Furthermore, the <sup>13</sup>C NMR data of terminal chains in the liquid crystalline phase are compared with the recently reported thiophene mesogen in which the *n*-hexyl chain is located at the lateral position. It is anticipated that by comparing the ordering of the terminal chain on thiophene versus the chain at the lateral location of the reported mesogen, the utility of <sup>13</sup>C NMR for understating the dynamics and orientation of the chains in mesogens can be correlated with the molecular structure (Fig. 1). Among the five mesogens *i.e.* KTC, HTC, OTC, OTPC and BTC, KTC with no substituent on the terminal thiophene serves as a benchmark mesogen for comparing the mesophase properties. The synthesized mesogens are initially characterized by solution 1D <sup>1</sup>H and <sup>13</sup>C NMR, and later 2D NMR experiments are performed to establish the structural integrity (Fig. S5-S50, ESI<sup>+</sup>).

#### Mesophase identification by HOPM and DSC

The mesophase assignment of the synthesized molecules is carried out by HOPM, where the formation of texture upon cooling the sample from the isotropic phase is observed (Fig. 2 and 3). In KTC, on cooling from the isotropic phase, birefringent threads (Fig. 2a) are observed at 118 °C. On further cooling, the threaded nematic texture<sup>57,58</sup> characteristic of the nematic phase is noticed. The sample experienced crystallization at 85.8 °C. For HTC, the formation of birefringent droplets is seen at 116.8 °C.

followed by a threaded nematic texture. At 73 °C transition bars (Fig. 2b) are noticed succeeded by a broken fan texture<sup>57,58</sup> indicating the phase transition to the SmC phase. The crystallization of the sample, on the other hand, is noticed at 62.6 °C. For OTC also birefringent threads are witnessed at 125.4 °C on cooling the isotropic phase. Similar to HTC, the phase change at 102 °C is noticed where transition bars<sup>59</sup> are observed (Fig. 2c). The appearance of a schlieren texture<sup>57,58</sup> at 102.9  $^{\circ}$ C indicates the SmC phase. On further cooling, the sample crystallizes at 70.8 °C. For BTC, the appearance of the nematic phase is confirmed by noticing birefringent threads (Fig. 2d) at 188.6 °C and crystallization is noted at 109 °C. In the case of OTPC, upon cooling from the isotropic liquid, formation of broken fans characteristic of the SmC phase (Fig. 3a) is observed and on further cooling OTPC shows the SmB and CrE phases (Fig. 3b and c). The crystallization of OTPC is observed at 60 °C.

The HOPM assignments are further confirmed by DSC investigations where multiple peaks associated with the corresponding phase transitions are clearly noted (Fig. 4 and Tables 1 and 2). On cooling, the transition enthalpy values of the isotropic to nematic phase for the mesogens are in the range of 0.12 to 0.13 kcal  $mol^{-1}$ , while that of isotropic to SmC phase is found to be 3.40 kcal mol<sup>-1</sup>. For OTC the nematic to SmC transition (98.5 °C) showed an enthalpy value of 0.27 kcal mol<sup>-1</sup>. For OTPC the SmC-SmB transition is observed at 165.6 °C showed an enthalpy value of 0.81 kcal  $mol^{-1}$ . For all the mesogens, the enthalpy values of mesophase to crystallization varied in the range of 2-10 kcal mol<sup>-1</sup>. In the case of KTC only nematic phase is noticed (Fig. 4a). Furthermore, for HTC and OTC (cooling cycle) multiple peaks are noticed with characteristic transition enthalpies (Fig. 4b and c). For OTPC, the SmB to CrE transition which is further confirmed by X-ray diffraction exhibited an enthalpy of 0.75 kcal mol<sup>-1</sup>. XRD is also used for confirming the SmC-SmB transition. The HOPM and DSC investigations provide data which can be correlated with the molecular structure. The common feature of all the mesogens is the presence of two phenyl rings along with either one or two thiophene rings in the core. Since the alkyl chain is located at one end of the molecule for HTC, OTC and OTPC, polymesomorphism is observed. Furthermore, the presence of smectic phases in HTC, OTC, and OTPC could be attributed to a high aspect ratio of the molecule due to the presence of the alkoxy and alkyl chains at both ends of the molecule.<sup>19–22</sup> As a result, the segregation of aliphatic chains from the rigid core units leads to nano segregation resulting in layer order.<sup>39,60-62</sup>

#### Powder XRD studies

The existence of smectic mesophases for OTC and OTPC is ascertained using the powder XRD technique. Fig. 5a shows the XRD scan of OTC in the smectic C phase in the temperature range of 85–95 °C. The XRD profile measured at 95 °C shows an intense sharp reflection at  $2\theta = 2.8^{\circ}$  with a layer spacing (*d*) of 31.51 Å and a diffuse and broad peak in the wide angle region (4.54 Å). The intense peak in the small angle region is a characteristic of layer ordering commonly observed in smectic mesophases.<sup>63</sup> The wide angle broad diffuse reflection, on the







Fig. 2 HOPM textures of mesogens on cooling from the isotropic phase. (a) Nematic phase at 118 °C for KTC, (b) SmC phase at 73 °C for HTC, (c) SmC phase at 102 °C for OTC and (d) nematic phase of BTC at 188.6 °C.

Fig. 3 HOPM textures of OTPC on cooling from the isotropic phase. (a) SmC phase at 169  $^\circ$ C, (b) SmB phase at 164  $^\circ$ C, and (c) CrE phase at 160  $^\circ$ C.

other hand, indicates the liquid-like nature of molecules within the layers.<sup>58</sup> These observations further indicate the fluid

nature of the smectic mesophase. To estimate the tilt angle of the molecules in the fluid smectic phase, the d/L ratio is

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Fig. 4 DSC scans of mesogens in heating and cooling cycles. (a) KTC, (b) HTC, (c) OTC, (d) BTC and (e) OTPC.

calculated where L is the energy optimized molecular structure of OTC in the fully extended conformation. The molecular length of OTC is found to be L = 42.90 Å (Fig. 1c) and accordingly, the d/L ratio is 0.72 which suggests that the molecules are tilted in the layers. The estimated tilt angle based on the expression  $d = L \cos \theta$  is 43°, which is the value usually

Table 1Transition temperatures and enthalpy values of the synthesizedmesogens from the second heating cycle

Code	Phase transition temperatures and enthalpy values ( $\Delta H$ kcal mol <sup>-1</sup> )									
КТС	Cr-N 96.6 °C (4.41)	N–I 118.9 °C (0.12)								
HTC	Cr–N 83.7 °C (7.13)	N–I 117.4 °C (0.20)								
OTC	Cr–SmC 91.7 °C (6.94)	SmC–N 99.4 °C (0.15)	N–I 122.5 °C (0.23)							
OTPC	Cr–SmB 162.3 °C (0.71)	SmB–SmC 165.6 °C (0.81)	SmC–I 170.5 °C (3.49)							
BTC	Cr–N 126.3 °C (12.81)	N−I 1́89.7 °C (0.20)	· · ·							
Cr: crys	tallization; N: nemati	c; I: isotropic; SmC: smo	ectic C.							

found for mesogens that show a nematic to smectic C phase.<sup>39,64</sup> Thus, the XRD data are in agreement with the HOPM and DSC observations where the appearance of a smectic C phase is noted. Furthermore, the *d* spacing shows a decreasing trend in OTC with lowering of the temperature suggesting an increase in tilt angle in the SmC phase. The XRD patterns of OTPC measured in different smectic mesophases in the temperature range of 160-175 °C are shown in Fig. 5b. The XRD profile measured at 175 °C shows a sharp and intense signal in the small angle region with  $2\theta = 2.70^{\circ}$  corresponding to a layer spacing (d) of 32.68 Å and a diffuse peak in the wide angle region at 4.58 Å. At 168 °C, the XRD pattern shows changes both in the small angle and wide angle regions. The position of the small angle reflection changed from  $(2\theta)$  2.70 to 2.51 while the wide angle peak split into two peaks. At 160 °C, in the wide angle region, multiple peaks are noted while the reflection in the small-angle region is unchanged ( $2\theta = 2.51^{\circ}$ ). Accordingly, the phases have been identified as SmC, SmB and CrE<sup>31,58,65</sup> respectively. The tilt angle in the SmC phase is 33.13° and is determined from  $d = L\cos\theta$  where L is the length of the molecule (39.03 Å) calculated from the energy optimized structure from DFT calculations (Fig. 1e). Thus, the smectic polymesopmorphism in OTPC is clearly established by XRD studies.

### Solid state <sup>13</sup>C NMR investigations of the mesogens

The synthesized mesogens are characterized by <sup>13</sup>C NMR in the liquid crystalline phase to determine the orientational order parameters. The common structural feature of the mesogens is

the presence of two phenyl rings in the core unit and also the location of thiophene at one end of the molecule. Thus, the determination of the order parameters of the synthesized mesogens would yield information that can be correlated with the individual molecular structure. Furthermore, the presence of flexible hexyl/octyl chains at one end of the mesogen significantly influences the mesophase sequence as well as the ordering of the thiophene rings. Hence, all the mesogens are examined by 1D and 2D <sup>13</sup>C experiments in the mesophase to find the alignment-induced chemical shifts ( $\delta_{LC}$ - $\delta_{iso}$ ) as well as the <sup>13</sup>C-<sup>1</sup>H dipolar couplings. For all the molecules, the solution <sup>13</sup>C NMR is run in CDCl<sub>3</sub> at room temperature and then the static 1D <sup>13</sup>C NMR experiments in the liquid crystalline phase. Furthermore, 2D SAMPI-4 experiments were also performed to get the <sup>13</sup>C-<sup>1</sup>H dipolar couplings and using them the orientational order parameters are computed.

The solution <sup>13</sup>C NMR spectra of the mesogens are shown in Fig. 6a-e. For KTC, HTC and OTC, the solution <sup>13</sup>C NMR spectra show 14 lines for the core unit which include phenyl rings, ester carbonyls and a thiophene ring. The chemical shift assignment of the core unit carbons is attempted by comparing the spectra generated from chemsketch and also comparing the literature <sup>13</sup>C NMR data.<sup>23,31,32,36-40</sup> Table 3 lists the chemical shift values of 14 carbons of the core unit of KTC, HTC and OTC. A close look at the chemical shift values indicates that the chemical shifts of C1-C10 are similar for the three mesogens while for C<sub>11</sub>-C<sub>14</sub>, a slight change is noticed. Furthermore, the change in the values is attributed to the presence of a hexyl/ octyl chain in the HTC and OTC cases as opposed to KTC. For these two mesogens, however, the C11-C14 values are similar since the hexyl/octyl chain is part of the thiophene ring. For BTC and OTPC, not only the number of lines but also the chemical shifts of the core unit carbons are different. This is comprehensible since ester linking units are part of the core for BTC while in OTPC, the rings are connected directly without any linking units. Accordingly, BTC shows 18 lines while OTPC exhibited 12 lines for the core unit carbons. For all the mesogens the chemical shift range for the core unit carbons is from 114.0 to 165.0 ppm.

In the liquid crystalline phase, static 1D <sup>13</sup>C NMR experiments are carried out to find the alignment-induced chemical shifts of all the mesogens (Fig. 6f–j). For assigning the chemical shifts of the core unit carbons of the mesogens, the literature

Table 2 Trai	nsition temperatures and enthalp	y values of the synthesized mesogens	from the second cooling cycle	
Code	Phase transition temper	atures and enthalpy values ( $\Delta H$ kcal i	$mol^{-1}$ )	
KTC	I–N 116.1 °C (0.12)	N–Cr 85.8 °C (1.57)		
HTC	I–N 116.3 °C (0.24)	N–[SmC] 71.2 °C (0.24)	[SmC]–Cr 65.6 °C (9.40)	
OTC	I–N 121.8 °C (0.30)	N–SmC 98.5 °C (0.27)	SmC–Cr 72.5 °C (7.20)	
OTPC	I–SmC 169.2 °C (3.40)	SmC–SmB 165.1 °C (0.81)	[SmB]–CrE 161.6 °C (0.75)	[CrE]–Cr 68.7 °C (0.67)
BTC	Ì−N Í88.6 °C (0.16)	N–Cr 110.1 °C (2.16)		、 <i>)</i>

[] indicates monotropic transition. Cr: crystallization; N: nematic; I: isotropic; SmC: smectic C. SmB: smectic B; CrE: crystal E.

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Fig. 5 Powder X-ray diffraction profile of the mesogens. (a) OTC in the SmC phase at 95 °C and (b) OTPC at 160 °C, 166 °C, and 175 °C.

data of structurally related mesogens are considered. 23,31,32,36-40,66 For instance, <sup>13</sup>C NMR data from our earlier work on thiophenebased mesogens as well as the data of 4-hexyloxy benzoic acid are utilized for assigning the core unit carbons.23,31,32,36,37,67,68 Further, 2D SAMPI 4 experiments that provide <sup>13</sup>C-<sup>1</sup>H dipolar couplings are also employed for assigning the thiophene ring carbons. It is clear from Table 3 that the mesophase <sup>13</sup>C NMR data of KTC, HTC and OTC mesogens are dissimilar from their respective solution NMR chemical shifts. For example, in solution, the chemical shift values of C<sub>1</sub>-C<sub>10</sub> are exactly the same, while for C<sub>11</sub>-C<sub>14</sub>, minor variation is noticed. In the mesophase, on the other hand, the differences in the <sup>13</sup>C chemical shifts between the core units of KTC, HTC and OTC are due to the fact that the mesophase transition temperatures are not similar. Furthermore, OTC exhibits the SmC phase as opposed to KTC and HTC which show the nematic phase. The calculated alignment induced chemical shift values of the mesogens are listed in Table 3.

The 2D SAMPI-4 experiments for all the mesogens are performed in the liquid crystalline phase to find the <sup>13</sup>C<sup>-1</sup>H dipolar couplings (Fig. 7). The 1D dipolar slices for aromatic resonances for each mesogen are shown in Fig. S51–S55, ESI.† From the structure point of view, the thiophene ring in KTC is

mono substituted. For other cases i.e. HTC, OTC, BTC and OTPC, the thiophene ring is 2,5-disubstituted. This variation in thiophene substitution is clearly reflected in the <sup>13</sup>C NMR data in the mesophase. In particular, the <sup>13</sup>C-<sup>1</sup>H dipolar couplings of the thiophene ring show a characteristic trend. In HTC, due to the presence of three CH carbons in thiophene, the CH contours in 2D are clearly separated from the rest of the phenyl ring CH contours owing to the variation in the orientation of the phenyl rings from the thiophene ring with reference to the long axis. For other rings, owing to the 2,5-disubstitution nature of thiophene, only two CH carbons are noticed. The 2D spectra of these mesogens show <sup>13</sup>C-<sup>1</sup>H dipolar couplings which are almost comparable in magnitude with the phenyl ring methine carbons. This particular feature, *i.e.*, a large variation in the <sup>13</sup>C-<sup>1</sup>H dipolar couplings from monosubstituted thiophene to 2,5-disubstituted thiophene is due to the change in thiophene ring orientation with respect to the location of the long axis.<sup>23,31</sup> As a result, the <sup>13</sup>C-<sup>1</sup>H dipolar couplings of KTC versus other mesogens dramatically vary as noticed in 2D SAMPI-4. BTC, by virtue of the presence of two thiophene rings, is different from the other mesogens. In the 2D spectrum, five CH contours of the bithiophene unit are expected as seen in the spectrum (Fig. 7). As stated earlier, for OTPC, the linking units such as ester groups are absent and all the rings are directly connected.

Generally, in SAMPI-4 experiment when carbons are coupled to more than one proton, the dipolar coupling information needs to be extracted from the experimental dipolar oscillation frequency.<sup>69,70</sup> Considering the established procedure,<sup>23,31,32,36–40,46,66–68,71</sup> the relationship between the main orientational order parameters and dipolar couplings for the phenyl or thiophene ring will be expressed by the following equation.<sup>72,73</sup>

$$D_{\text{CH}} = K[S_{zz}(3\cos^2\theta_z - 1)/2 + (S_{xx} - S_{yy})(\cos^2\theta_x - \cos^2\theta_y)/2 + S_{xz}(\cos\theta_x \cos\theta_z)]$$
(1)

where  $K = -h\gamma_{\rm H}\gamma_{\rm C}/4\pi^2 r_{\rm CH}^3$ , where h is the Planck constant,  $\gamma_{\rm H}$  and  $\gamma_{\rm C}$  are the gyromagnetic ratios of <sup>1</sup>H and <sup>13</sup>C nuclei respectively and  $r_{CH}$  is the C–H bond,  $\theta$  s are the angles formed by  $r_{\rm CH}$  with the respective coordinate axes of the molecular fragment (phenyl or thiophene ring) under consideration. For a 1-4 disubstituted phenyl ring having  $D_2$  symmetry, the z axis is taken along the para axis and the remaining perpendicular x and y axes are respectively, in and out of the ring plane. During fitting, the standard bond distances  $r_{CH}$  = 1.1 Å for the C–H bond and  $r_{\rm CC}$  = 1.4 Å for the C–C bond are employed. The CCH bond angles are varied  $\sim 120^{\circ}$  to arrive at the best fit.<sup>74</sup> On the other hand, the thiophene ring possessing irregular pentagonal geometry requires three order parameters, namely,  $S_{22}$ ,  $(S_{xx} - S_{yy})$ , and  $S_{xz}$  for an arbitrary choice of the axis system.<sup>75,76</sup> The procedure and model adopted for computing the order parameters for the thiophene moiety which are connected by a linking unit or directly linked to the phenyl ring are described in our previous work in detail.<sup>23,31,32,36,40,76</sup> Initially, the z-axis is chosen along the C10-C11 bond for the KTC, HTC, OTC and BTC mesogens, the C8-C9 bond for the OTPC mesogen and the C14-C15 bond for the lateral thiophene of the BTC mesogen

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**Fig. 6**  ${}^{13}$ C NMR spectra of mesogens in different phases. Left column: solution  ${}^{13}$ C NMR spectra of (a) KTC, (b) HTC, (c) OTC, (d) OTPC and (e) BTC. Right column: mesophase  ${}^{13}$ C NMR spectra of (f) KTC in the nematic phase (98 °C), (g) HTC in the SmC phase (85 °C), (h) OTC in the SmC phase (96 °C), (i) OTPC in the SmC phase (166 °C) and (j) BTC in the nematic phase (130 °C).

(Fig. S56, ESI<sup>†</sup>). Later this *z*-axis is slightly varied by an angle  $\beta$  in order to improve the quality of the fit. This fit is further improved by the marginal variation in CCH bond angles. Apparently, the addition of the third order parameter  $S_{xz}$ , did not improve the fit significantly and hence, only two order parameters were retained, namely,  $S_{zz}$  and  $(S_{xx} - S_{yy})$ . The order

parameters of the phenyl as well as thiophene rings are listed in Table 4. In all the cases, two order parameters for two phenyl rings and one order parameter for thiophene are determined except for BTC where two thiophene rings are present in the core unit. For KTC, the order parameter values for both the phenyl rings are 0.55 and for the thiophene ring, the value is 0.51.

Table 3 <sup>13</sup>C NMR data for the core unit of the five mesogens in solution and mesophases<sup>a</sup>

		KTC				HTC				OTC			BTC				OTPC			
		98 °C (nematic)				85 °C (smectic C)			96 °C (smectic C)			130 °C (nematic)				166 °C (smec		tic C)		
C. N.	Soln (ppm)	LC (ppm)	AIS (ppm)	DOF <sup>b</sup> (kHz)	Soln (ppm)	LC (ppm)	AIS (ppm)	DOF <sup>b</sup> (kHz)	Soln (ppm)	LC (ppm)	AIS (ppm)	DOF <sup>b</sup> (kHz)	Soln (ppm)	LC (ppm)	AIS (ppm)	DOF <sup>b</sup> (kHz)	Soln (ppm)	LC (ppm)	AIS (ppm)	DOF <sup>b</sup> (kHz)
1	156.9	217.3	60.4	1.29	156.2	229.6	73.4	1.51	156.9	234.0	77.1	1.71	156.9	223.9	67.0	1.41	158.8	229.1	70.3	1.75
2	115.1	137.5	22.4	2.40	115.1	142.3	27.2	2.83	115.1	143.9	28.8	3.15	115.1	139.9	24.8	2.59	114.9	143.1	28.2	3.33
3	122.3	146.5	24.2	2.13	122.3	151.8	29.5	2.54	122.3	153.9	31.6	2.85	122.3	148.9	26.6	2.36	127.7	154.0	26.3	3.65
4	144.1	202.7	58.6	1.25	144.2	211.3	67.1	1.42	144.2	214.3	70.1	1.61	144.1	208.3	64.2	1.38	132.9	208.2	75.3	1.63
5	164.7	201.5	36.8	0.47	164.8	210.3	45.5	0.70	164.8	214.3	49.5	1.17	164.7	206.2	41.5	0.53	141.4	217.3	75.9	1.71
6	127.3	186.5	59.2	1.26	127.2	197.4	70.2	1.52	127.1	201.6	74.5	1.75	127.3	192.2	64.9	1.42	125.7	150.3	24.6	3.54
7	131.8	158.9	27.1	2.20	131.7	164.6	32.9	2.65	131.7	166.7	35.0	2.95	131.8	161.4	29.6	2.47	126.9	152.8	25.9	3.63
8	121.8	146.5	24.7	2.13	121.9	152.1	30.2	2.58	121.9	153.9	32.0	2.85	121.8	148.9	27.1	2.36	133.1	214.2	81.1	1.70
9	154.6	208.7	54.1	1.27	156.9	219.0	62.1	1.53	154.8	222.6	67.8	1.74	154.6	213.5	58.9	1.40	139.4	208.6	69.2	1.25
10	159.9	201.5	41.6	0.47	159.9	210.3	50.4	0.70	159.9	214.3	54.4	1.17	159.7	206.2	46.5	0.53	122.5	157.7	35.2	5.69
11	132.3	166.4	34.1	0.71	129.1	173.2	44.1	1.10	129.1	176.4	47.3	1.28	129.7	177.3	47.6	0.76	124.9	178.1	53.2	4.25
12	135.1	171.2	36.1	5.29	135.4	168.1	32.7	2.45	135.4	169.8	34.4	2.47	136.0	172.4	36.4	3.73	145.6	192.6	47.0	1.19
13	128.1	163.9	35.8	4.38	125.6	177.4	51.8	2.80	125.6	180.9	55.3	2.74	124.3	152.7	28.4	3.00				
14	134.0	182.5	48.5	7.20	154.8	214.3	59.5	1.51	156.2	218.4	62.2	1.61	136.1	172.4	36.3	0.98				
15													146.0	197.2	51.2	0.93				
16													125.6	177.3	51.7	2.10				
17													128.1	159.2	31.1	1.85				
18													126.6	177.3	50.7	8.90				

 $^{a}$  Soln: solution chemical shift, LC: mesophase chemical shift; AIS: alignment induced shift; DOF: dipolar oscillation frequencies.  $^{b}$  The errors on the values of DOF are about  $\pm 0.040$  and 0.055 kHz respectively, for protonated and non protonated carbons.

In the case of HTC, the phenyl ring order parameter values are 0.638 (ring I) and 0.65 (ring II) and 0.753 for the thiophene ring. In the case of OTC, the values are 0.729 and 0.743 for the phenyl rings and for thiophene, the value is 0.83. A large variation in the order parameter values of the phenyl as well as thiophene for these mesogens is understandable if the phase transition temperatures as well as the nature of the mesophase are taken into consideration. For instance in KTC and HTC, the experiments are done in the nematic phase whereas for OTC, the measurement is carried out in the smectic phase. Furthermore, the mesophase transition temperatures of KTC and HTC are slightly different even though experiments are performed in the nematic phase. For BTC and OTPC, the phenyl ring order parameters are 0.601 and 0.607 and for thiophene rings they are 0.55 and 0.471 whereas in OTPC the phenyl ring order parameters are 0.748 (ring 1), 0.757 (ring 2) and 0.809 for the thiophene ring. Here again, the mesophase transitions of both the mesogens largely differ. Also for BTC, the experiments are carried out in the nematic phase while for OTPC the experiments are done in the SmC phase. A close inspection of Table 4 pertaining to the order parameters indicates some noticeable trend. For the mesogens in which the alkyl chain is present in the terminal thiophene ring, the order parameters of the thiophene ring are higher than those corresponding to the phenyl rings of the core unit. However, if an alkyl chain is not present (KTC) or if thiophene is connected to other thiophene rings (BTC) directly, the thiophene order parameter is lower than those corresponding to the phenyl rings of the core unit. Thus, the presence of an alkyl chain in thiophene, *i.e.*, when thiophene is 2,5-disubstituted, the order parameter of the ring is higher than that of the corresponding phenyl rings of the mesogen. If KTC is considered a benchmark molecule, for HTC, OTC and OTPC in which thiophene is 2,5-disubstituted, the thiophene ring order parameters are high. This suggests that

the location of the long axis depends on the second substituent on the thiophene ring. In other words, for 2,5-disubstituted thiophene, the long axis is more or less collinear to the  $C_{12}$ - $C_{13}$  bond (HTC, OTC) and  $C_{10}$ - $C_{11}$  bond (OTPC). For the case of KTC where thiophene is mono substituted, the long axis is not collinear to the  $C_{12}$ - $C_{13}$  bond. These subtle changes are clearly reflected in the <sup>13</sup>C NMR data in the mesophase where the chemical shifts as well as <sup>13</sup>C-<sup>1</sup>H dipolar couplings are completely governed by the orienting axis with respect to the magnetic field. In solution or the isotropic phase, due to tumbling of molecules, the anisotropic chemical shifts observed in the mesophase vanish. Thus the order parameter values derived from <sup>13</sup>C NMR provide information at the molecular (local) level which is correlated with the molecular structure of the mesogen.

The 2D proton encoded local field (PELF)77-79 scheme (Fig. S57, ESI<sup> $\dagger$ </sup>) is employed for extracting the <sup>13</sup>C<sup>-1</sup>H dipolar couplings of the terminal alkyl chains of the KTC, HTC and OTC mesogens as it provides better resolution for aliphatic carbons. The experimental details are provided in the ESI.<sup>†</sup> The 2D PELF spectra for the three mesogens are shown in Fig. S58, ESI† and the corresponding extracted 1D dipolar slices are plotted in Fig. S59-S61, ESI.<sup>†</sup> The <sup>13</sup>C NMR data of the terminal alkyl chains for KTC, HTC and OTC are compared with a recently reported mesogen<sup>23</sup> where the alkyl chain is located at the lateral position of the thiophene ring. In particular, the alignment-induced chemical shift values of carbons that are linked to the core unit versus the carbons of the chains located at the lateral position can provide qualitative information about the chain ordering. Table S1, ESI<sup>†</sup> lists the terminal chain carbon chemical shift values of the KTC and HTC mesogens in solution. The chemical shift assignment is completed by comparing the structurally similar compounds in the literature.<sup>31</sup> For HTC, the n-hexyl chain carbon chemical shifts are identified by



Fig. 7 2D SAMPI-4 spectra of mesogens in various phases. (a) KTC in the nematic phase (98 °C), (b) HTC in the SmC phase (85 °C), (c) OTC in the SmC phase (96 °C), (d) OTPC in the SmC phase (166 °C) and (e) BTC in the nematic phase (130 °C). Thiophene methine carbon contours are indicated in red color.

considering the HTC aliphatic region. In other words, the dodecyloxy chain is common for both the mesogens whereas the *n*-hexyl chain is present in only HTC. For the static 1D  $^{13}\mathrm{C}$  NMR, again the chemical shift values of the terminal chain carbons of KTC are

 Table 4
 Orientational order parameter for phenyl and thiophene rings of five mesogens<sup>a</sup>



		CCI	H bond	angles	_			Calculated	Calculated dipolar oscillation frequencies (kHz)				
Mesogen	Ring	$\theta_{\rm b}$	$\theta_{\rm b}$ $\theta_{\rm c}$		Szz		$S_{xx} - S_{yy}$ b		с	d	а	RMSD (kHz)	
ктс	Ι	119	.8	120.8	0.5	$49 \pm 0.022$	$0.056\pm0.009$	2.39	2.14	1.28	1.26	0.02	
	II	120	.4	120.7	0.5	$51\pm0.024$	$0.050\pm0.007$	2.20	2.12	1.27	1.27	0.01	
HTC	Ι	119	.6	120.5	0.6	$38\pm0.023$	$0.062\pm0.009$	2.82	2.56	1.48	1.46	0.04	
	II	120	.5	120.7	0.6	$50\pm0.019$	$0.070\pm0.006$	2.65	2.59	1.53	1.52	0.01	
OTC	Ι	119	.8	120.6	0.7	$29\pm0.020$	$0.068\pm0.007$	3.13	2.87	1.69	1.67	0.05	
	II	120	.6	120.9	0.7	$43 \pm 0.023$	$0.076\pm0.008$	2.95	2.85	1.74	1.73	0.01	
BTC	Ι	119	.8	120.6	0.6	$01\pm 0.024$	$0.058\pm0.009$	2.59	2.37	1.39	1.37	0.02	
	II	120	.4	120.8	0.6	$07\pm0.022$	$0.060\pm0.008$	2.47	2.36	1.42	1.41	0.01	
OTPC	Ι	119	.5	118.6	0.7	$48\pm0.021$	$0.072\pm0.008$	3.33	3.65	1.68	1.72	0.03	
	II	119	.1	118.8	0.7	$57\pm0.019$	$0.075\pm0.007$	3.54	3.65	1.72	1.72	0.01	
			CCH l	oond an	gles			Calcula	ted dipolar os	cillation frequ	iencies (kHz)		
Mesogen	Ring	β	$\theta_{\mathbf{B}}$	$\theta_{\mathbf{C}}$	$\theta_{\rm D}$	Szz	$S_{xx} - S_{yy}$	В	С	D	А	RMSD (kHz)	
KTC	III	0.5	106.9	40.0	32.2	$0.510\pm 0.$	012 $0.053 \pm 0.012$	004 5.29	4.39	7.20	0.72	0.01	
HTC	III	17.0	122.5	58.5	_	$0.753 \pm 0.$	$0.079 \pm 0.079 \pm 0.0000$	009 2.42	2.79	1.45	1.20	0.06	
OTC	III	17.0	122.7	58.0	_	$0.830\pm0.$	022 $0.065 \pm 0.022$	008 2.47	2.74	1.61	1.28	0.02	
BTC	III	7.5	114.6	45.6	_	$0.550\pm 0.$	012 $0.033 \pm 0.012$	006 3.74	2.99	0.92	0.82	0.04	
	IV	7.5	118.4	48.7	33.3	$0.471\pm 0.$	010 $0.008 \pm 0.001$	003 2.18	1.84	8.86	0.74	0.05	
OTPC	TIT	18	1147	45.5		$0.900 \pm 0$	$010  0.078 \pm 0.000$	005 5 70	4.25	1 16	1 20	0.02	

<sup>*a*</sup> Ring I (KTC/HTC/OTC/BTC/OTPC): a = C1, b = C2, c = C3, d = C4. Ring II (KTC/HTC/OTC/BTC): a = C6, b = C7, c = C8, d = C9. Ring II (OTPC): a = C5, b = C6, c = C7, d = C8. Ring III (KTC/HTC/OTC/BTC): A = C11, B = C12, C = C13, D = C14. Ring III (OTPC): A = C9, B = C10, C = C11, D = C12.

used for identifying the *n*-hexyl chain of HTC. In a recent work,  $2^{3}$ we examined a  $\pi$ -conjugated thiophene based mesogen in which the *n*-hexyl chain is located at the lateral position. In this work, the *n*-hexyl chain carbons (HTC) in the liquid crystalline phase showed a different trend compared to the terminal chain carbons. In the reported mesogen, the hexyl chain is away from the long axis as it is positioned at the lateral location while the terminal chains are along the long axis. Accordingly, the *n*-hexyl chain carbons of the reported mesogen showed positive sign for alignment-induced chemical shifts whereas the terminal chain carbons of the same mesogen exhibited the usual negative sign. In the present work, the aliphatic carbons of the HTC mesogen exhibited alignmentinduced chemical shifts with a negative sign. This is in sharp contrast to the reported  $\pi$ -conjugated mesogen where the *n*-hexyl chain carbons in the liquid crystalline phase showed positive sign for the alignment-induced chemical shift values. Interestingly, the solution <sup>13</sup>C NMR values of the *n*-hexyl chain of the reported mesogen as well as the n-hexyl chain of HTC are comparable whereas the <sup>13</sup>C chemical shifts in the liquid crystalline phase show a dramatically different trend. In HTC, as the n-hexyl chain is at the terminal location and in the liquid crystalline phase, it orients along the long axis. However, for the reported mesogen,<sup>23</sup> the orientation of the hexyl chain which is at the lateral location is different. It is also clear from earlier studies that the methylene carbons that predominantly have trans conformation and orient with respect to the long axis show negative alignment-induced chemical shift values while those with cis conformation and away from the long axis exhibit a positive trend. Using the <sup>13</sup>C-<sup>1</sup>H

dipolar couplings the order parameters of the terminal chains of HTC, KTC and OTC are calculated. It is clear from Table S1, ESI† that the order parameter values follow an established style in concurrence with trends observed from alignment induced chemical shift values of terminal chain carbons.

The mesophase transition temperatures of mesogens provide scope for understanding the structure-property relationship. For structurally close mesogens i.e. KTC, HTC and OTC, the melting transition varies between 83-97 °C while the clearing temperatures are in the range of 116-123 °C. With the introduction of an alkyl chain *i.e.* the hexyl chain for HTC and octyl chain for OTC, an increase in the mesophase range is noticed. Furthermore, due to increase in the length of the molecule, the aspect ratio increases from KTC to OTC, and as a result, the tendency for layer ordering increases. In the case of KTC, only the nematic phase is noticed whereas for HTC and OTC, the smectic C phase is observed as monotropic and enantiotropic respectively in addition to the nematic phase. For the case of BTC, the melting and clearing temperatures are high due to the rigid bithiophene ring. Interestingly, despite increase in the length of the molecule, the smectic phase is not seen in BTC. For OTPC also, the melting and clearing temperatures are quite high similar to BTC but smectic polymesomorphism is noticed. Thus OTPC exhibits enantiotropic SmC, monotropic SmB and crystal E phases. The most interesting feature is that despite the very low mesophase range (8.5  $^{\circ}$ C), the appearance of smectic polymesomorphism could be attributed to the absence of flexible and polarizable ester units. The high

melting and clearing temperatures are a clear indication of the overall rigidity of the mesogen due to the direct link between the phenyl as well as thiophene rings. Thus, insertion of bithiophene produces the highest mesophase range with an enantiotropic nematic mesophase.

# 4. Conclusion

Five mesogens in which thiophene is at one end of the core and a dodecyloxy chain at the other terminus were synthesized either by Suzuki coupling or direct arylation. The common feature of the synthesized mesogens was the presence of two phenyl rings and a thiophene ring in the core. The HOPM and DSC investigations revealed that mesogens with a terminal alkyl chain exhibited polymesomorphism. The appearance of smectic phases in HTC, OTC and OTPC was due to the high aspect ratio of the molecules since the alkoxy and alkyl chains at both ends result in segregation of the aliphatic chains from the rigid core units as supported by XRD investigation. The orientational order parameters of the constituent rings as well as the terminal alkyl chain were determined from <sup>13</sup>C-<sup>1</sup>H dipolar couplings from <sup>13</sup>C NMR studies. For KTC, the order parameters of both the phenyl rings were 0.55 whereas for the thiophene ring, the value was 0.51. In the case of HTC, the phenyl ring order parameter values were 0.638 (ring I) and 0.65 (ring II) and 0.753 for the thiophene ring. For OTC, the values were 0.729 and 0.743 for the phenyl rings and 0.83 for the thiophene ring. The notable feature of the <sup>13</sup>C NMR study was about mesogens in which the alkyl chain was present on the terminal thiophene ring, which showed higher order parameters than the corresponding phenyl rings. If the alkyl chain, on the other hand, was absent or if thiophene was connected to other thiophene rings directly, the order parameter of the thiophene was lower than that of the corresponding phenyl rings. These variations were rationalized by considering the location of the long axis with respect to the substituent on the thiophene ring. Importantly, the <sup>13</sup>C NMR data of the terminal chains in the liquid crystalline phase were compared with a thiophene mesogen in which the *n*-hexyl chain is located at the lateral position. The n-hexyl chain carbons of the reported mesogen showed positive sign for alignment-induced chemical shifts whereas the aliphatic carbons of the HTC mesogen exhibited a negative sign. Quite remarkably, the solution <sup>13</sup>C NMR values of the *n*-hexyl chain of the reported mesogen as well as the *n*-hexyl chain of HTC are similar, whereas a distinct difference in the liquid crystalline phase was noticed. The stark contrasting trend was attributed to their location leading to different kinds of orientation with respect to the long axis. Thus, this study delivered interesting structure-property and orientational information on the core as well as the terminal chains of thiophene and phenyl ring based mesogens.

# Conflicts of interest

There are no conflicts to declare.

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