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Molecular Order and Mesophase Investigation of Thiophene based Forked Mesogens

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ABSTRACT

Thiophene based rod-like molecules constructed from a three phenyl ring core and terminal dialkoxy chains recognized as forked mesogens are synthesised and their mesophase properties as well as the molecular order are investigated. The synthesized forked mesogens would serve as model compounds for tetracatenar or biforked mesogens. Based on the position of the thiophene link with rest of the core, 2-substituted and 3-substituted mesogens are realised in which the length of the terminal alkoxy chains are varied. The mesophase properties are evaluated with a hot-stage polarising microscope and differential scanning calorimetry. For both the homologs, the appearance of either nematic phase alone or in conjunction with smectic C phase is noticed depending on the length of the terminal alkoxy chains. The existence of layer ordering characteristic of smectic C phase is confirmed for a representative mesogen using the variable temperature powder X-ray diffraction. The high-resolution solid-state^{13}C NMR measurements of C_{12} homologs of the two series revealed orientational order parameters of all the rings of the core as well as terminal chains in liquid crystalline phase. For both the homologs, due to the asymmetry of the ring I, the order parameter value is higher in contrast to ring II, ring III as well as thiophene ring. The chemical shifts and ^{13}C-^{1}H dipolar couplings of OCH_2 carbons of the terminal dodecyloxy chains provided contrasting conformations reflecting the orientational constraints. Further, the investigations also revealed that the mesophase range as well as the tendency for layer ordering is higher for 3-sbustituted mesogens as against 2-substituted homologs.

Introduction

Thermotropic liquid crystals with rod-like core are known as calamitic mesogens while the discotics are built with the disc-like core.[1-4] The poly catenar mesogens are a distinct class of molecules which are considered as an intermediate shape to rod-like as well as discotic systems.[5-7] These mesogens are designed to have a lengthy rod-like core with multiple alkoxy chains at both the terminal positions and are recognized for rich polymesomorphism covering nematic, smectic, columnar and cubic phases.[5-7] The remarkable feature of these mesogens is the influence of (i) number and length of the alkoxy chains and (ii) the ratio of phenyl rings versus alkoxy chains on mesophase sequence, as well as the phase transition temperatures.[7] The biforked mesogens are also known as tetracatenar mesogens possess two alkoxy chains at both ends of the core unit.[8,9] If the molecule, on the other hand, has two alkoxy chains at one end of the core, they are termed as forked mesogens. For instance, Nguyen and coworkers[10-11] examined the mesophase characteristics of three ring based forked mesogens with a terminal cyano group and found smectic A phase. Our group has been involved in the development of thiophene mesogens with an aim of investigating the orientational constraints of thiophene moiety in liquid crystalline phases employing the high-resolution solid-state ^{13}C NMR spectroscopy.[12-14] Thiophene has emerged as an important structural moiety for functional organic materials and there is an increasing research activity on thiophene based thermotropic liquid crystals owing to their use in opto electronics as well as photonic applications. [15-17]The current work deals with the forked mesogens in which thiophene ring is positioned at one end of the core unit. Two series of mesogens are synthesized from 2 or 3-thiophene carboxylic acid with additional three phenyl rings in the core besides dialkoxy chains at one terminal. By varying the length of the terminal chains, six mesogens are synthesized and the mesophase characteristics are accomplished by hot-stage polarizing microscope (HOPM) and differential scanning calorimetry (DSC). The existence of smecticC mesophase for one of the homologue is confirmed by variable temperature X-ray diffraction (VT-XRD) where a change in layer spacing with lowering of temperature is observed.

The high-resolution solid-state ^{13}C NMR has emerged as a powerful tool for structural characterization of topologically different thermotropic liquid crystals.[12-14,18-20] The utility of 2D separated local field (SLF) based experiments for finding the molecular topology as well as the molecular order of thermotropic liquid crystals is highlighted in a recent review.[21] In this work, the 1D and 2D solid state ^{13}C NMR technique is employed for examining the orientational order of thiophene based forked mesogens. The investigations reveal higher mesophase range as well as the tendency for layer ordering for 3-substituted mesogens as against 2-substituted series. Further, dramatic lowering of nematic to isotropic transition temperature (~110-130 °C) is noticed for the synthesized molecules in contrast to structurally similar four ring mesogen with one alkoxy chain. Additionally, the examination of order parameter values determined from ^{13}C NMR investigations of thiophene as well as phenyl rings in mesophase supports the asymmetry of the ring I as reflected in the value of local order parameter.

EXPERIMENTAL SECTION

The experimental details of intermediates and final mesogens (E)-4-(((4-((3,4-bis(alkoxy)benzoyl)oxy)phenyl)imino) methyl)phenylthiophene-2-carboxylates (7a-7d) and (E)-4-(((4-((3,4-bis(alkoxy)benzoyl)oxy)phenyl)imino) methyl)phenylthiophene-3-carboxylates (8a-8d) along with spectral data is furnished in Supporting Information (SI).

Materials

4-hydroxy benzaldehyde, 3, 4-dihydroxy benzaldehyde, 2- thiophene carboxylic acid, 3-thiophene carboxylic acid, 4-nitro phenol, n-bromohexane, n-bromooctane, n-bromo decane and n-bromododecane, N, N'-dicyclohexylcarbodiimide (DCC), N, N- dimethylamino pyridine (DMAP) and palladium on charcoal (Pd/C, 10%), were purchased from Aldrich

(USA) and used without further purification. N, N'-dimethyl formamide (DMF), tetrahydrofuran (THF), ethanol, methanol, dichloromethane, ethyl acetate, chloroform, diethyl ether, n-hexane, n-heptane, acetone, acetonitrile, ethyl methyl ketone (EMK), isopropanol, anhydrous potassium carbonate, anhydrous sodium sulphate, sodium chloride, celite-540, hydrochloric acid were obtained from Merck (India) and used as received. Sodium phosphate monobasic dihydrate ($NaH_2PO_4.2H_2O$) and sodium chlorite ($NaClO_2$) from Loba Chemie (Mumbai) and used as such.

Instrumental Details

FT-IR spectra of all of the compounds were recorded by an ABB BOMEM MB3000 spectrometer using KBr pellets. 1D^{13}C NMR spectra of the compounds were recorded on Bruker Avance-III HD 400 MHz at room temperature using tetramethylsilane as an internal standard in $CDCl_3$. The nature of the mesophase and the temperature of occurrence of different phases were examined by using Carl Zeiss Axiocam MRC5 optical polarizing microscope equipped with a Linkam THMS 600 stage with a TMS 94 temperature controller. The photographs were taken using an Imager A2M digital camera. Differential scanning calorimetry traces were recorded by a DSC Q200 instrument with a heating rate of 10 °C per minute in a nitrogen atmosphere and the samples were subjected to two heating and two cooling cycles.

Variable temperature powder X-ray diffraction studies were carried out on un-oriented samples filled in Lindemann capillary of diameter of 1mm (Hampton Research, Aliso Viejo, CA, USA) using Cu K α (λ= 1.54 Å) radiation from PANalytical instrument (DY 1042-Empyrean) 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).[22]The gas phase molecular geometry of 8d mesogen was optimized by DFT-based Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3YLP) method employing 6-31G* basis set Gaussian 09W suite of programs.[23-25]

Solid state NMR measurements

The solid-state NMR experiments were performed on a Bruker Avance III HD 400 WB NMR spectrometer (9.4 T) equipped with a Bruker double resonance 4 mm WVT MAS probe. The ^{1}H and ^{13}C resonance frequencies were 400.07 and 100.61 MHz, respectively. All the measurements in the liquid crystalline phases of the samples were recorded under static condition. The fine powder samples were packed in a 4 mm Zirconia rotor with Teflon spacer and Zirconia cap. Initially the samples were heated from room temperature to the isotropic phase and then slowly cooled to the respective mesophases to achieve sample alignment. The 1D ^{13}C NMR spectra in mesophases were obtained by cross-polarization (CP) scheme with a contact time of 3 ms and 62.5 kHz of radio frequency (RF) field strength on both the ^{1}H and ^{13}C channels. The other parameters were: number of scans 512 and 1024 respectively, for 7d and 8d mesogens and recycle delay 8 s. SAMPI-4 pulse sequence[26] employed to get high resolution 2D SLF spectrum under static condition (Figure S1 of Supporting Information). Our earlier work demonstrated the utility of SAMPI-4 pulse scheme for variety of liquid crystalline samples.[12-14,27,28] 2D SAMPI-4 spectra were obtained for 7d and 8d mesogens using the following parameters: CP contact time τ =3 ms/3ms, t_1 increments =100/82, number of scans=28/100. The recycle delay of 15s/11s was employed to minimize the RF heating effect. The data were zero filled in both the t_2 and t_1 dimensions, yielding a 4096 × 256 real matrix. A shifted sine bell window function was applied to the time domain data and the spectrum was processed in the phase sensitive mode. In all the experiments, ^{1}H 90º pulses were of duration 4 μs and SPINAL-64[29]heteronuclear decoupling was applied during ^{13}C acquisition with a proton nutation frequency of 30 kHz. Sample heating was performed by running the bearing air through a heating coil and the sample temperature was calibrated from ^{207}Pb NMR chemical shift of Pb(NO_3)$_2$.[30]The ^{13}C chemical shift was referenced externally relative to the adamantine methine resonance at 29.5 ppm.

Results and Discussion

The molecular structures of synthesized mesogens are shown in Scheme 1. The mesogenic series are constructed by condensing either 4-formylphenyl thiophene-2-carboxylate or 4-formylphenyl thiophene-3-carboxylate and dialkoxy two ring amine in ethanol under microwave condition.[31]To realize the forked mesogens, at one end of the core, two alkoxy chains are placed while the other terminus has thiophene ring. Further, the aromatic rings of the core are connected through ester and azomethine groups. By varying the length of the terminal alkoxy chains, four mesogens for each series are synthesized. The main objective of the investigation is to find the influence of second alkoxy chain on the mesophase transition temperatures as well as the phase sequence. Further, the role of second alkoxy chain on the local order parameters of the phenyl rings are investigated using ^{13}C NMR spectroscopy. For the ring I which has two alkoxy chains, the order parameter is directly influenced by the asymmetry of the ring. The forked mesogens are structurally simple and serve as model compounds for tetracatenar (biforked) mesogens.[5-7]Thus investigation of the structure-property relation of forked mesogens would simplify the course of understanding the mesophase properties as well as the molecular order of polycatenar mesogens which are known for their excellent polymesomorphism.[5-9] The synthesized mesogens are structurally characterized by FT-IR, solution ^{1}H and ^{13}C NMR spectroscopy (Figure S2-S7 of Supporting Information).

MesophaseCharacterization

The mesophase properties are evaluated by HOPM (Figure1) and further confirmed by DSC (Figure 2). In each series, four mesogens are synthesized in which the terminal chain has C_6, C_8, C_{10} and C_{12} carbons(7 a-d and 8 a-d). In the case of 2-thiophene series (7 a-d), all the mesogens showed nematic phase on heating and cooling cycles. Additionally, a monotropic smectic C phase is noted for C_{10} and C_{12} homologs. In other words, enantiotropic nematic phase for all the homologs, and monotropic smectic C phase for higher homologs (C_{10} and C_{12}) is observed. For the 3-thiophene series too (8 a-d), all homologs showed nematic phase whereas enantiotropic smectic C phase is additionally seen for C_{10} and C_{12} homologs. In HOPM, on cooling the sample from isotropic phase, typically either marble or birefringent threaded texture characteristic of the nematic phase is noticed.[32] For those homologs where the transition from nematic to smectic C mesophase is observed, transition bars are seen followed by smectic schlieren texture (Figure 1).[33] Table 1 lists the melting (crystal-mesophase) and clearing temperatures (nematic-isotropic) of the synthesized mesogens. It is apparent from the Table 1 that the crystal to mesophase transitions are in the range of ~ 110-134 °C while the clearing transitions are found to be ~ 135-165 °C across the series. With increase in terminal chain length, a decrease in clearing temperatures is observed. A comparison of mesophase range of both the series indicates higher values for 3-substituted homologs.

To understand the influence of second alkoxy chain on mesophase transition temperatures, a recently reported structurally similar mesogenwith one terminal alkoxy chain is considered.[34]In view of the reported mesogens have a dodecyloxy chain at the terminal position, the discussion is limited to C_{12} homologs of both the series. For 2-thiophene series, remarkably, the clearing temperature showed a reduction of ~ 138 °C whereas mere ~6 °C decrease in the crystal to mesophase transition is observed. For the case of 3-thiophene series, lowering of nematic to isotropic temperature is found to be ~113 °C while a ~30 °C decrease in the crystal to mesophase transition is noticed. Further, the reported mesogens exhibited only enantiotropic nematic phase whereas for forked mesogens, either monotropic or enantiotropic smectic C phase is observed for higher homologs. Thus, the additional curvature imparted by the presence of second alkoxy chainfavour layer ordering. Also the increase in aliphatic chains favour segregation of incompatible parts of the forked mesogens, i.e. separation of flexible aliphatic chains from rigid aromatic units result in layer ordering characteristic of smectic C phase.[35]

The mesophase properties obtained from HOPM are further confirmed by DSC heating and cooling cycles (Figure 2 and S8-S11 of Supporting Information). Table 1 lists the transition enthalpy values which are in concurrence with HOPM results. The N-I transition enthalpy values are in the range 0.14-0.24 (kcal/mole) whereas crystal to smectic C phase data is typically higher than the N-I transition values.[36] Despite the presence of two alkoxy chains at the terminal position, the appearance of enantiotropic mesophases in the forked mesogens is attributed to the lengthy rod-like core with four rings i.e. three phenyl and one thiophene ring. The presence of smectic C phase is further proved by variable temperature X-ray diffraction experiments. Since the C_{10} and C_{12} homologs of 3-thiophene series only exhibit enantiotropic smectic C phase, the XRD studies are limited toC_{12} homologue (8d) only where (Figure 3) an intense sharp reflection in the small angle region and broad hump at the wide angle region (125°C) is detected. These reflections are characteristics of layer order arising from smectic phases exhibited by rod-like molecules.[37]In order to realize the length of the molecule (L=39.87Å), the energy optimized structure by DFT of the C_{12} homologue (8d) is used (Figure 4). Table 2 lists the layer spacing (d) as well as wide-angle reflection for the 8d in the temperature range 105 to 125 °C (Figure S12 of Supporting Information). To find the nature of the smectic phase, the d/L ratio measured at different temperatures is enlisted in Table 2. As the d/L values decrease with lowering of temperature, the phase is assigned as tilted smectic phase. Further, the broad hump in the wide angle region (Figure 3) indicates the absence of in-plane order and liquidlike nature of the molecules within the layer.[38] These features strongly suggest that the mesophase under observation is tilted fluid phase i.e.

smectic C mesophase. The tilt angle measured from the d/L values in the temperature span of 105-125 °C is in the range of ~ 18-25°.[39]

^{13}C NMR studies in liquid crystalline phase

As stated earlier, the main focus of the investigation is to find the orientational order of all the rings of the core unit as well as terminal chains. To fulfill the objective, 1D as well as 2D ^{13}C NMR spectroscopy experiments of two representative mesogens (7d and 8d) belonging to each series are carried out in liquid crystalline phase. By making use of ^{13}C-^{1}H dipolar couplings from the 2D experiments, the order parameters of all the rings of the core unit are determined. Since the ring I has three substituents, the order parameter of it reflects the asymmetry of the ring.[40] Further, the ^{13}C NMR experiments would also throw light on the orientational constraints of thiophene ring with reference to substitution pattern since the thiophene is linked to rest of the core either at 2- or 3-position.

To accomplish the structural characterization of ^{13}C NMR spectra of mesogens in liquid crystalline phase, the complete assignment of ^{13}C NMR spectra of them in solution is essential. Thus the solution ^{13}C NMR spectra of 7d and 8d mesogens recorded in $CDCl_3$at room temperature are shown in Figure 5A and 5B. The spectrum shows well-resolved lines with varying chemical shifts as well as intensities in the range 14-166 ppm. Since the mesogen has four rings in the core unit and two dodecyloxy chains at the terminal, many lines in the span of 14-166 ppm are noticed. The ^{13}C chemical shift assignment of all the carbons is attempted first by iterating the spectrum with ChemDraw software followed by verifying them with the values arrived by group contribution approach.[41]The assignment is further refined by making use of DEPT,^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC data (Figures S13-S24 of Supporting Information). Table 3 shows the chemical shift values of all the carbons of 7d and 8d mesogens. Due to the asymmetry of the ring I, the spectrum has morenumber of quaternary carbons.

The static ^{13}C NMR spectrum of 2-thiophene mesogen (7d) in nematic phase measured at 124 °C is shown in Figure 6A. Molecules exhibiting liquid crystalline property in the mesophase align with respect to the magnetic field. The alignment is governed by the sign of the anisotropic magnetic susceptibility tensor. Molecules with positive sign would align parallel to the magnetic field while those with negative sign favour perpendicular orientation.[42,43]The alignment of the molecules in the magnetic field results in sharp lines with well resolved peaks as indicated by the spectrum. The peaks arising from core unit carbons are noticed from 134-216 ppm in nematic phase as against 14-166 ppm in solution. The increase in the chemical shift values in nematic phase is due to parallel alignment of the molecules in the magnetic field.[42,43]For the case of terminal dodecyloxy chains, in solution NMR, the lines are noted in the range 14-70 ppm. However, in the nematic phase, the ^{13}C spectrum of the terminal chain carbons is different owing to the anisotropic environment in the mesophase. In other words, the variation in chemical shifts of the dodecyloxy chains positioned at C1 and C2 of ring I arise due to change in their orientations with respect to ordering axis. Accordingly, one of the OCH_2 carbon of dodecyloxy chains (C1 position) shows a marginal decrease in chemical shift values while the OCH_2 carbon of other chain (C2 position) exhibits a significant increase. The variation in ^{13}C chemical shifts of OCH_2 and CH_2 carbons of both the chains in solution as well as in nematic phase are listed in Table4. Thus the change in chemical shift values of terminal dodecyloxy chains provides further insight into the location of long axis in the nematic phase. In solution phase, due to tumbling of molecules, the anisotropic effects which are seen in nematic phase vanish. As a result, the difference in the chemical shift values of OCH_2 and other carbons of dodecyloxy chains in nematic phase emerge as observed in the spectrum. For the core unit carbons, the peaks in the range 134-216 ppm show achange in intensity pattern. Similar to solution ^{13}C NMR spectrum, the C3 and C6 of core unit show distinct values in nematic phase. For the rest of the phenyl rings of the core, intense peaks in the range 140-160 ppm are noticed. Among them, the peak appeared at 146.9 ppm is more intense indicating the overlapping of other carbons of the core unit. The high resolution of the spectrum (7d) in mesophase enables the identification of almost all the carbons and accordingly, 21 carbons of the core unit are more or less clearly seen (Figure 6A). Further, with the use of the 2D spectrum which is discussed in later part of the section, all the assignment of the carbons is accomplished. Despite many carbons in the core unit, the high resolution of the spectrum aided by well spread chemical shifts due to the structural heterogeneity of the constituent moieties, the assignment could be achieved. In other words, the presence of thiophene, 1-4-disubstitued phenyl rings,1,2,4-trisubstituted phenyl ring as well as linking units in the mesogenic core, a wide span of the chemical shifts (134-216 ppm) in the spectrum is noticed.

For 3-thiophene homolog (8d), the ^{13}C NMR is acquired in thesmectic C phase (Figure 6B) at 116 °C. Similar to the 2-thiophene homolog, in this case also the assignment of all the core unit carbons is achieved with the help of 2D spectrum. Table3 lists the chemical shift values of the solution as well as static ^{13}C NMR data of 8d. The major difference between 2 and 3- substituted thiophenes (7d *vs* 8d) is the linking of the III phenyl ring of the core to thiophene position. This variation resulted in a great change in the contour pattern in 2D spectrum (Figure 7). For the terminal dodecyloxy chains, similar to 2-thiophene isomer (7d), the difference in chemical shift values of OCH_2 is noted in smectic C phase.

Orientational order parameters

To determine the order parameter values of all the rings of the core unit of both the mesogens (7d and 8d), the static 2DSLF measurements are carried out (Figure 7) in respective mesophases. In the case of 3-thiophene homologue (8d), the spectrum measured in smectic C phase at 116 °C (Figure 7B) shows well resolved contours which not only differ in chemical shifts but also the ^{13}C-^{1}H dipolar couplings. Based on the ^{13}C-^{1}H dipolar coupling values, the 2D spectrum of the core unit can be classified into three regions. For example, ^{13}C-^{1}H dipolar couplings in the range 1.0-1.52kHz appear from quaternary carbons of ester carbonyl and thiophene ring and the phenyl ring I carbons. The other phenyl ring quaternary carbons i.e. ring II and III, showed values in the range 2.25-2.55kHz. The methine carbons of the rings II and III are found to be ~ 3.0 kHz whereas the ring I carbons are seen~ 3.65 kHz. The thiophene^{13}C-^{1}H dipolar couplings, however, appeared in the range 4.8-6.4 kHz while the imine carbon gave a contour at 203.0 ppm with a dipolar coupling value of 5.28 kHz. From these values, it clear that for the ring I, the quaternary ^{13}C-^{1}H dipolar coupling values are 1.11-1.25 kHz, whereas the CH dipolar coupling value is 3.68 kHz. For the ring II and III, on the other hand, the quaternary carbon dipolar coupling values are 2.28 to 2.54 kHz whereas the methine dipolar couplings are 2.99-3.20 kHz. In other words, the dipolar couplings of quaternary carbons are higher for ring II and III while the methine carbon dipolar couplings are high for ring I. These changes are direct consequence of the influence of long axis on the phenyl rings (I-III). Yet another variation is about the dipolar coupling values of the thiophene ring. As stated earlier, the ^{13}C-^{1}H dipolar coupling values of methine carbons of thiophene ring are highest (4.8-6.4 kHz) in contrast to other carbons including imine linking unit. These large variations within the thiophene suggest that the long axis is passing through the thiophene ring in such a way that among the three methine carbons, two are in similar orientation while the third one experiences different orientation. It is enriching to note that the 2D SLF spectrum could provide a convincing quantum of information about the variation in the orientation of different moieties of the core unit in the liquid crystalline phase.

Yet another remarkable feature that can be acknowledged on inspection of 2D spectra of 7d and 8d is the orientation of methine carbons of thiophene ring reflected on the contour pattern. For instance, in solution ^{13}C NMR, the chemical shift values of C20 and C21 methine carbons of 7d and 8d are more or less similar while a ~ 9 ppm difference is noted for C19 methine carbon. In liquid crystalline phase, on the other hand, the three methine carbons not only show variation in chemical shift values but also as in ^{13}C-^{1}H dipolar couplings. This suggests that the location of thiophene ring in mesogens (7d & 8d) is very sensitive to long axis resulting in strikingly different contours with large variation in C19-C21 carbons of thiophene ring. In the spectrum, for 7d, the methine carbons are seen in the range 164-182 ppm while the dipolar couplings appeared in the span of 4.3-7.35 kHz. For the case of 8d, the chemical shifts of thiophene methine carbons are observed in the range 143-161 ppm whereas the dipolar couplings are found to be 4.80 to 6.40 kHz. Also in contrast to phenyl ring methine carbons of the respective mesogens (7d and 8d), the thiophene carbons show higher dipolar couplings which enable their identification straight forward. These changes suggest that the location of carboxylic ester on thiophene has profound influence on dipolar couplings (Table 3). Further, the variation in chemical shifts as well as dipolar couplings of the thiophene is also influenced by the mesophase in which the measurements are carried out. For 7d, the spectrum is recorded in nematic phase while for 8d the experiment is performed in smectic C phase.

In general, the 2D SLF experiments provide ^{13}C-^{1}H dipolar oscillation frequencies from which the ^{13}C-^{1}H dipolar couplings can be extracted for a given molecular geometry (phenyl or thiophene ring) as per the reported procedure.[14,27,28,44,45] These extracted ^{13}C-^{1}H dipolar couplings can be related to the order parameters of particular ring by considering the local symmetry. For, 1-4 disubstituted phenyl ring, the D_2 symmetry enables two order parameters namely S_{zz} and S_{xx}-S_{yy} whereas for 1,2,4-trisubstituted phenyl ring, the C_s symmetry demands at least three order parameters viz. S_{zz}, S_{xx}-S_{yy} and S_{xz}. Thus the experimental ^{13}C-^{1}H dipolar couplings are related the order parameters of the core unit of forked mesogensby the following equation[46,47]

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

where $K = -h\gamma_H\gamma_C/4\pi^2 r^3{}_{CH}$, with γ_H and γ_C are the gyromagnetic ratios of ^{1}H and ^{13}C nuclei respectively and r_{CH} is the inter nuclear distance between them, θ_x, θ_y and θ_z are angles that r_{CH} forms with the respective coordinate axes of the system which are the local axes defined on the molecular fragment under consideration. The standard bond distances r_{CH}=1.1 Å for the *C–H* bond and r_{CC}=1.4 Å for the *C–C* bond are considered during the fitting. Also, the C-C-H bond angles are found to be necessary to slightly vary around 120° to arrive at the best fit.[48] For ring-I, the z-axis is considered along the C1-C4 bond (para axis) and x-axis is the in-plane axis perpendicular to z. The three local order parameters namely, S_{zz}, S_{xx}-S_{yy}, and S_{xz} describe the orientation of this rigid fragment of the core unit for both the mesogens. The data fitting revealed a good agreement between calculated and experimental values for methine carbons only and attempts to incorporate the quaternary carbons in the fitting procedure showed large deviation which could be due to non-planar geometry of ring I. The calculated order parametersof the ring I for both the mesogensare listed in Table5. For rings II and III which are 1,4-disubstituted phenyl rings and possess effective D_2 symmetry, the S_{xz}=0 in the equation 1. By using the equation 1, the order parameter values of ring II and ring III are calculated to be 0.86 and 0.82 respectively and for thiophene ring, on the other hand, the value is 0.69 (Table 6). For the thiophene ring due to irregular pentagonal geometry, like phenyl ring I, three order parameters are required for an arbitrary choice of the axis system.[28,49] The z-axis is considered along the C17-C18 bond for 7d and 8d mesogens by which the thiophene is directly connected to the rest of the mesogen. The bond angles and bond distances computed from the energy minimized structure of thiophene for 7d and 8d mesogens are utilized (Figure 4 and Figures S25, S26of Supporting Information). Here, the fit is initiated using only three methine carbons to find two order parameter namely, S_{zz} and S_{xx}–

S_{yy} with an expectation that the other order parameter is likely to be small. Further, the efficiency of the fit is enhanced by introducing an angle β between the z-axis and the C17-C18 bond. A plot of temperature versus alignment induced shifts(AIS) (Figures S27 and S28 of Supporting Information) shows abrupt change at nematic to smectic C indicating first order nature of the transition in concurrence with DSC data.

Figures S29 and S30 of Supporting Information shows the 2D Proton Encoded Local Field (PELF) pulse sequence and spectra for 7d and 8d mesogens respectively in the region 14-80 ppm covering the terminal dodecyloxy chains. Since PELF provides better resolution for aliphatic carbons this method is adopted for screening the ^{13}C-^{1}H dipolar couplings of terminal dodecyloxy chains which are tabulated in Table 4. This table also lists the chemical shift values of terminal chain carbons in solution as well as in mesophase for both 7d and 8d mesogens. As observed earlier, the remarkable feature of the ^{13}C NMR of OCH_2 carbons in mesophase is clear distinction of orientation of dodecyloxy chains attached to C1 and C2 carbons of the ring I. The chemical shift differences in solution NMR for OCH_2 carbons of dodecyloxy chains is 0.29 ppm. In mesophase on the other hand, the OCH_2 carbons shows a difference of 8.6 ppm. Further, the OCH_2 arising from dodecyloxy chain attached to phenyl ring at para position shows lower value whereas the OCH_2 of the dodecyloxy chain attached to meta position show increase in value (Table 4). The rest of the methylene carbons of both chains show decrease in chemical shift value in contrast to solution spectra. Similarly, the terminal methyl carbons of both chains gave single contour whose value in contrast to solution is lower. The 2D spectrum shows 13 contours accounting for 24 carbons of both the chains. The assignment of chemical shift values of all the dodecyloxy chain carbons is carried out by following the earlier reports of mesogens that have alkoxy chains in the phenyl ring.[50,51] For instance, the variation in OCH_2 carbons of the dodecyloxy chains of 7d indicates that both the chains are experiencing different orientation with respect to long axis. Fung et al.[52-56] earlier carried out ^{13}C NMR studies of biforked mesogens and mesogens with four ring core unit with lateral alkoxy chains, where the difference in orientation for OCH_2 carbons chains attached to phenyl ring are noticed. This is explained based on the fact that the OCH_2 attached to meta position is in mostly in cis conformation, where as the one placed at para position is predominantly in trans conformation. The contrasting profile of OCH_2 carbons as against rest of the methylene carbons further indicates that methylene carbons of both the dodecyloxy chains are in trans conformation. These chemical shift changes are also supported by the negative sign of the order parameters except for meta OCH_2 carbon. For example, the typical values of order parameters of 7d mesogen arein the range of -0.019 to -0.177 except for meta OCH_2 carbon for which the order parameter is 0.026. Similar trends are also noticed for 8d mesogen (Table4). It is clear from the 2D NMR studies that the introduction of second alkoxy chain in the meta position of phenyl ring I, the location of long axis changes (Figure 8). Further based on the HOPM and DSC data, it is clear that the mesophase transitions experience drastic reduction in view of the flexibility imparted to the overall molecule by the introduction of second alkoxychain at the meta position of the ring I. It is important to note that Fung et al. [52-55]could not determine the order parameter of the core unit of ring to which alkoxy chains are attached due to the overlapping of signals. However, in the present case, due to the high resolution achieved from the 2D spectrum, the order parameter of ring I as well as other rings of the core unit could be carried out for 7d as well as 8d mesogens.

It is clear from Tables 5 and 6 that the order parameter values are not same for phenyl as well as thiophene rings. Further, relatively lower values observed for 7d than 8d are due to the fact that the measurements of 8d are carried out in smectic C phase while for 7d the experiments are performed in nematic phase. In all the cases, the order parameter of ring-II of the core is found to be higher than other rings which suggest that the long-axis of molecules is more or less collinear to C_2 axis of ring-II. Also the thiophene ring shows lower value than respective phenyl rings order parameters in both the cases (7d and 8d) as they are located at one end of the mesogen.

Conclusions

Two series of forked mesogens with a thiophene ring in the core were synthesized from 2/3-thiophene carboxylic acid. Depending on the position of the carboxylic acid in the thiophene, 2 and 3 homolog series were realized in which the terminal dialkoxy chain length was varied between 6-12 even carbons. The HOPM and DSC investigations indicated the presence of enantiotropic nematic as well as smectic C phases for higher homologs. The VT-XRD studies further confirm the tilted fluid nature of the smectic phase. A detailed ^{13}C NMR investigation of two representative homologs belonging to each series is carried out. For 2-thiophene homolog, measurements were performed in nematic phase while for 3-thiophene mesogen, the NMR spectra were recorded in smectic C phase. The 2D SLF measurements of the mesogens in mesophase provided well resolved contours with ^{13}C-^{1}H dipolar couplings. The important observations of the ^{13}C NMR investigation include (i) asymmetry of the phenyl ring I leading to three order parameters (ii) the dependence of chemical shifts as well as ^{13}C-^{1}H dipolar couplings of thiophene methine carbons on the substitution i.e. 2- versus 3-substitution and (iii) contrasting conformational profile of OCH_2 carbons of dialkoxy terminal chains. Thus the investigation provided complete profile of order parameter of core unit as well as terminal chain carbons. The orientational constraints mapped from the ^{13}C-^{1}H dipolar couplings of the mesogens in liquid crystalline phase demonstrate the greater utility of ^{13}C NMR for probing the molecular structure as well as the order for forked mesogens.

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SUPPORTING INFORMATION

It contains synthetic details, spectral data (FT-IR, NMR) of intermediates and final mesogens, figures of SAMPI-4 pulse sequence, DSC scans of final mesogens,VT-XRD plot of 8d mesogen, 1D and 2D solution NMR spectra for 7d and 8d mesogens, planar and energy optimized structures of 7d mesogen, thiophene models, plot of AIS as a function of temperature for 7d and 8d mesogens and PELF experimental details. This material is available free of charge via the Internet at http://pubs.acs.org

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Table 1: Transition Temperatures and Enthalpy values of Synthesized Mesogens (7a-7d) and (8a-8d) in the second heating cycle.

Mesogen Code	Transition temperatures (°C) and enthalpy values in parenthesis (∆H kcal/mol)			Mesophase range
7a	Cr-N 133.87 (10.05)	-	N-I 154.41 (0.24)	20.54 (N)
7b	Cr-N 130.62 (11.17)	-	N-I 149.28 (0.15)	18.66 (N)
7c	Cr-N 125.27 (11.97)	-	N-I 142.19 (0.14)	16.92 (N)
7d	Cr-N 118.25 (11.89)	-	N-I 135.66 (0.15)	17.41 (N)
8a	Cr-N 123.82 (11.86)	-	N-I 165.62 (0.18)	44.32 (N)
8b	Cr-N 121.30 (8.99)	-	N-I 156.35 (0.20)	32.53 (N)
8c	Cr-SmC 117.09 (8.18)	SmC-N 123.25 (0.10)	N-I 144.21 (0.20)	6.16 (SmC) 20.96 (N)
8d	Cr-SmC 111.88 (12.00)	SmC-N 129.71 (0.47)	N-I 141.19 (0.17)	17.83 (SmC) 11.48 (N)

Cr: crystallisation;SmC: smectic C;N: nematic; I: isotropic

Table 2: Powder X-ray Diffraction Data of Mesogen 8d.

T (°C)	d_1 (Å)	d_2(Å)	d_1/L
125	36.98	4.55	0.92
115	36.61	4.52	0.92
105	36.16	4.48	0.91

Table 3: ^{13}C NMR Data of core unit for 7d and 8d mesogens in solution and liquid crystalline phases

	7d (124 ºC)				**8d (116 ºC)**			
Carbon No.	**Solution (ppm)**	**CS (ppm)**	**AIS (ppm)**	**^{13}C-^{1}H DOF (kHz)**	**Solution (ppm)**	**CS (ppm)**	**AIS (ppm)**	**^{13}C-^{1}H DOF (kHz)**
1	153.9	176.2	22.3	1.24	153.9	187.8	33.9	1.44
2	148.7	165.7	17.0	1.19	148.7	202.7	54.0	1.11
3	112.0	135.2	23.2	3.51	114.6	138.9	24.3	3.68
4	121.6	158.6	37.0	1.41	121.5	174.5	53.0	1.25
5	124.4	133.9	9.5	4.17	124.4	138.9	14.5	3.68
6	114.7	135.2	20.5	3.51	111.9	138.9	27.0	3.68
7	165.2	206.3	41.1	0.61	165.2	215.4	50.2	1.09
8	149.4	211.5	62.1	1.59	149.4	226.1	76.7	2.28
9	121.8	142.9	21.1	2.53	121.9	148.5	26.6	3.20
10	122.1	146.9	24.8	2.30	122.2	153.4	31.2	2.99
11	149.4	215.8	66.4	1.51	149.3	226.1	76.8	2.28
12	159.1	194.3	35.2	4.26	159.2	203.0	43.8	5.28
13	134.0	194.3	60.3	1.70	133.9	208.2	74.3	2.54
14	130.1	156.6	26.5	2.42	130.1	163.1	33.0	3.06
15	122.5	146.9	24.4	2.30	122.5	153.4	30.9	2.99
16	153.0	194.3	41.3	1.18	153.1	231.4	78.3	2.29
17	160.2	204.1	43.9	0.67	160.7	215.4	54.7	1.09
18	132.6	167.5	34.9	0.90	132.6	167.2	34.6	1.51
19	135.0	170.9	35.9	5.10	126.6	150.5	23.9	6.34
20	128.1	164.2	36.1	4.38	128.2	143.3	15.1	5.02
21	133.8	181.8	48.0	7.33	134.4	160.9	26.5	4.83

CS: chemical shift; AIS: alignment induced shift; DOF: dipolar oscillation frequencies

Table 4:^{13}C NMR data of dodecyloxy chain for 7d and 8d mesogens in solution and liquid crystalline phases

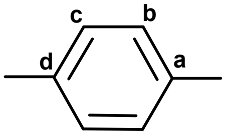
7d (124 ºC)						8d (116 ºC)					
Carbon No	**Solution (ppm)**	**CS (ppm)**	**AIS (ppm)**	**D_{CH} (kHz)**	**S_{CH}**	**Carbon No**	**Solution (ppm)**	**CS (ppm)**	**AIS (ppm)**	**D_{CH} (kHz)**	**S_{CH}**
a	69.09	77.30	8.21	-0.59	0.026	a	69.08	78.80	9.72	-0.61	0.027
a’	69.38	68.70	-0.68	3.69	-0.163	a’	69.35	67.30	-2.05	4.84	-0.213
b	29.21	26.90	-2.31	1.72	-0.076	b,b’	29.21	24.70	-4.51	4.63	-0.204
b’	29.21	25.10	-4.11	4.01	-0.177	c,c’	26.01	22.10	-3.91	2.89	-0.127
c,c’	26.02	22.00	-4.02	2.59	-0.114	d,d’	29.21	25.60	-3.61	2.29	-0.101
d,d’	29.23	25.40	-3.83	2.25	-0.099	e,e’	29.41	26.10	-3.31	3.32	-0.146
e,e’	29.45	25.70	-3.75	2.97	-0.131	f,f’	29.45	26.10	-3.35	3.32	-0.146
f,f’	29.67	26.30	-3.37	2.36	-0.104	g,g’	29.67	27.40	-2.27	1.84	-0.080
g,g’	29.71	26.70	-3.01	1.93	-0.085	h,h’	29.75	27.70	-2.05	1.47	-0.065
h,h’	29.75	28.40	-1.35	2.11	-0.093	i,i’	29.08	23.40	-5.68	2.04	-0.090
i,i’	29.10	23.20	-5.9	2.05	-0.090	j,j’	31.96	30.40	-1.56	1.27	-0.056
j,j’	31.97	29.80	-2.17	1.49	-0.066	k,k’	22.73	22.10	-0.63	0.88	-0.039
k,k’	22.73	21.80	-0.93	1.11	-0.049	l,l’	14.18	13.50	-0.68	0.42	-0.019
l,l’	14.16	13.30	-0.86	0.44	-0.019						

CS: chemical shift; AIS: alignment induced shift; D_{CH}: Dipolar coupling; S_{CH}:Bond order parameter

Table 5: Orientational order parameters of phenyl ring-I for the mesogens 7d and 8d at 124 and 116 ºC respectively.[a]

Mesogens	**Bond Angles**			S_{zz}	S_{xx}-S_{yy}	S_{xz}	**Calculated dipolar oscillation frequencies (kHz)**			**RMSD (kHz)**
	θ_3	**θ_5**	**θ_6**				**C-3**	**C-5**	**C-6**	
7d	121.0	120.0	121.8	0.76	-0.102	-0.090	3.51	4.17	3.51	0.002
8d	121.0	121.8	121.8	0.80	-0.122	-0.081	3.68	3.68	3.68	0.001

Table 6: Orientational order parameters of phenyl (ring-II and ring-III) and thiophene rings for the mesogens 7d and 8d at 124 and 116 ºC respectively.[a]



Mesogens	**Phenyl**	**Bond Angles**		S_{zz}	S_{xx}-S_{yy}	**Calculated dipolar oscillation frequencies (kHz)**				**RMSD (kHz)**
		θ_b	**θ_c**			**b**	**c**	**a[b]**	**d**	
7d	II	119.9	120.8	0.59	-0.058	2.53	2.28	1.36	1.38	0.04
	III	118.8	119.2	0.54	-0.028	2.40	2.30	1.64	1.17	0.07
8d	II	121.1	121.6	0.86	-0.082	3.19	3.00	2.01	2.03	0.01
	III	121.1	121.4	0.82	-0.084	3.08	2.97	2.59	1.94	0.06
Mesogens	**Thiophene**	**β**		S_{zz}	S_{xx}-S_{yy}	**C-18**	**C-19**	**C-20**	**C-21**	**RMSD (kHz)**
7d		5.9		0.48	-0.053	-	5.10	4.42	7.36	0.03
8d		2.3		0.69	-0.073	-	5.03	6.32	4.85	0.02

[a] In the figure above the table, b and c are methine carbons, a and d are quaternary carbons respectively for ring-I and II .

[b] For carbon a in ring III, the contribution of azomethine proton has also been taken in to account.

Figure Captions:

Figure 1: HOPM photographs of 8d (A) marble texture of nematic phase at 138.5°C, (B) transition bars at 129.5°C and (C) broken fan texture of smectic C phase at 126.5°C. 7d (D) threaded texture of nematic phase at 132.9 °C, (E) transition bars at 118.0°C and (F) coexistence of schlieren and broken fan texture of C phase.

Figure 2: DSC heating and cooling scans of (A) 7d and (B) 8d mesogens.

Figure 3: High resolution powder X-ray diffraction profile of 8d in smectic C phase at 125°C with enlarged wide angle region.

Figure 4: (A) Planar and (B) energy optimized structures of 8d mesogen

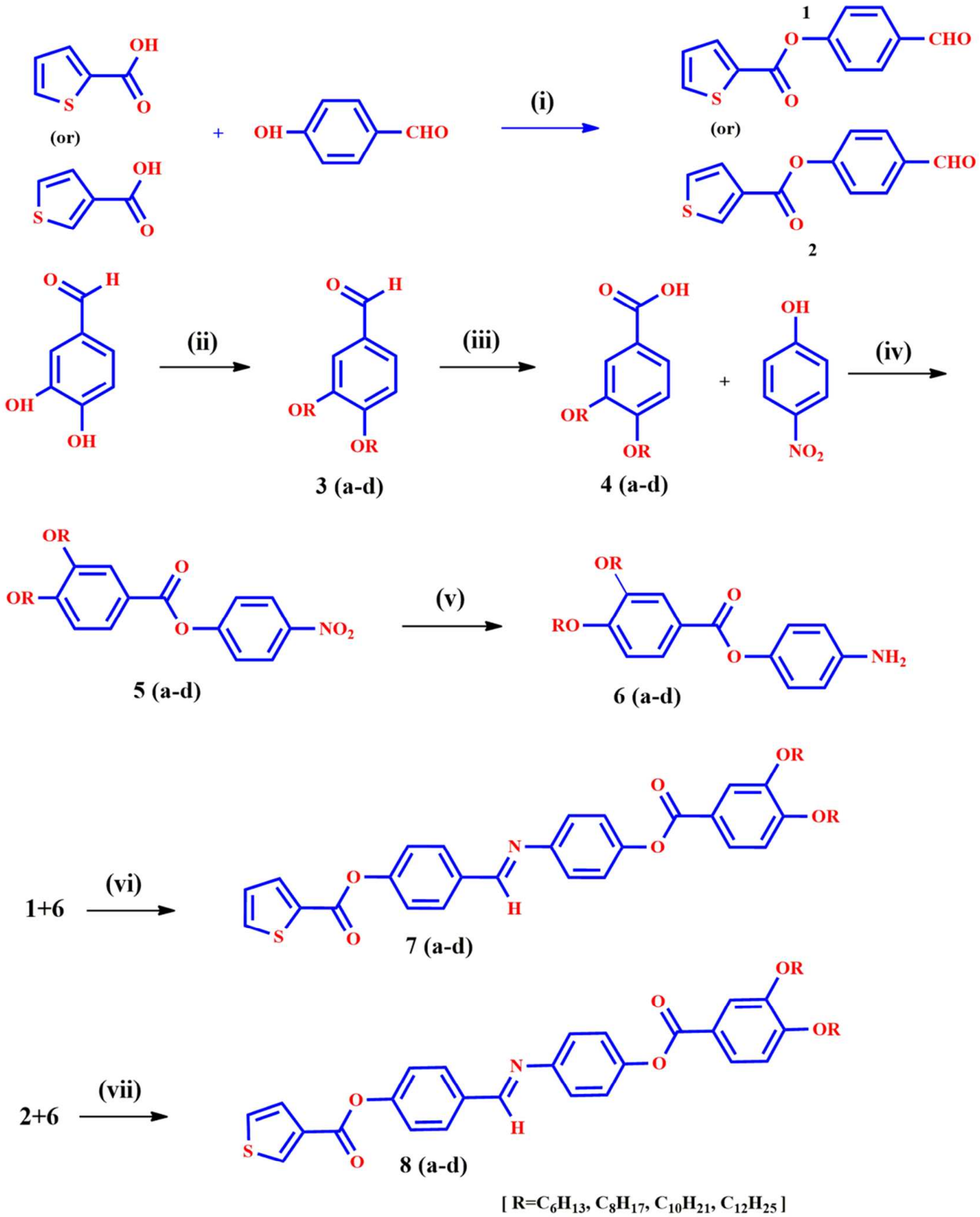
Figure 5: Proton-decoupled solution^{13}C NMR spectra of (A) 7d and (B) 8d mesogens.

Figure 6: Static^{13}C NMR spectra of (A) 7d in nematic phase at 124 °C and (B) 8d in smectic C phase at 116 °C.

Figure 7: 2D SAMPI-4 spectra of (A) 7d in nematic phase at 124 °C and (B) 8d in smectic C phase at 116 °C.

Figure 8: Molecular structures of (A) 7d and (B) 8d mesogens with the projection of long axis.

Scheme 1



i) DCC, DMAP, DCM, RT, ii) n-bromoalkane, K_2CO_3, DMF, 90 °C, iii) $NaClO_2$, $NaH_2PO_4.2H_2O$, H_2O, THF, 0 °C – RT, iv) DCC, DMAP, DCM, RT, v) Pd/C, H_2 gas, THF, RT, vi) and vii) C_2H_5OH, MW.

Figure 1

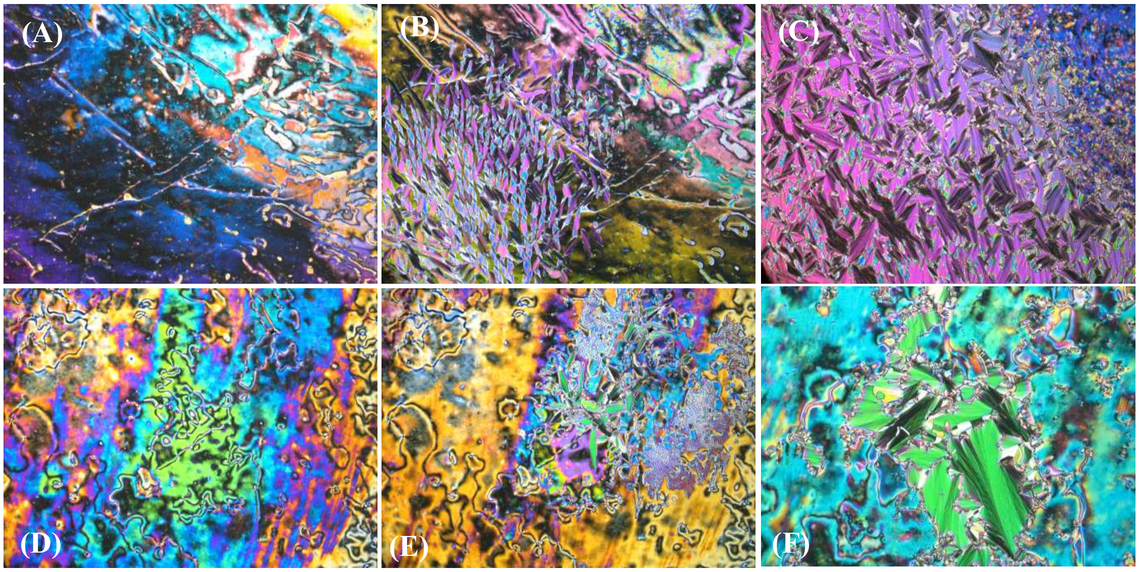


Figure 2

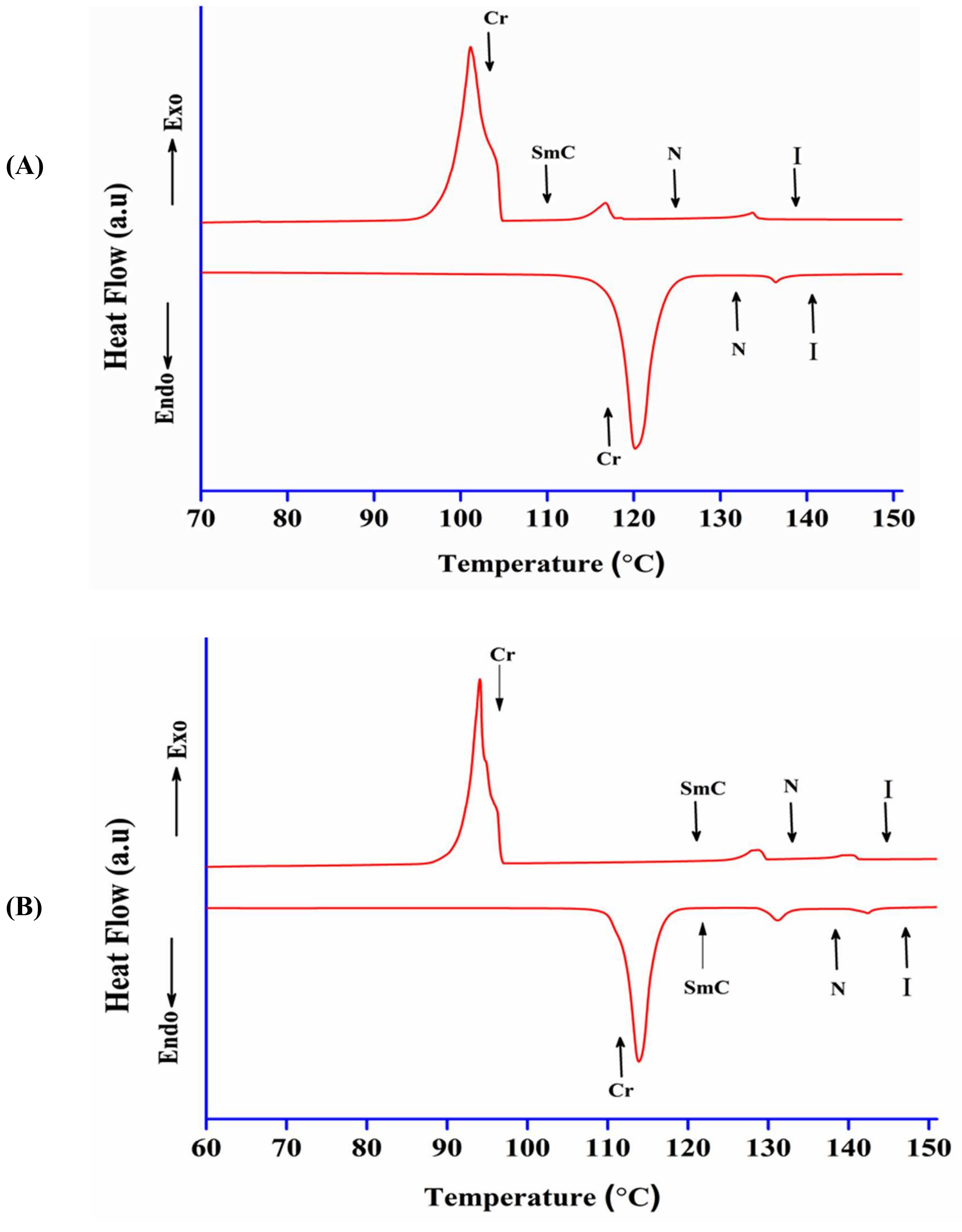
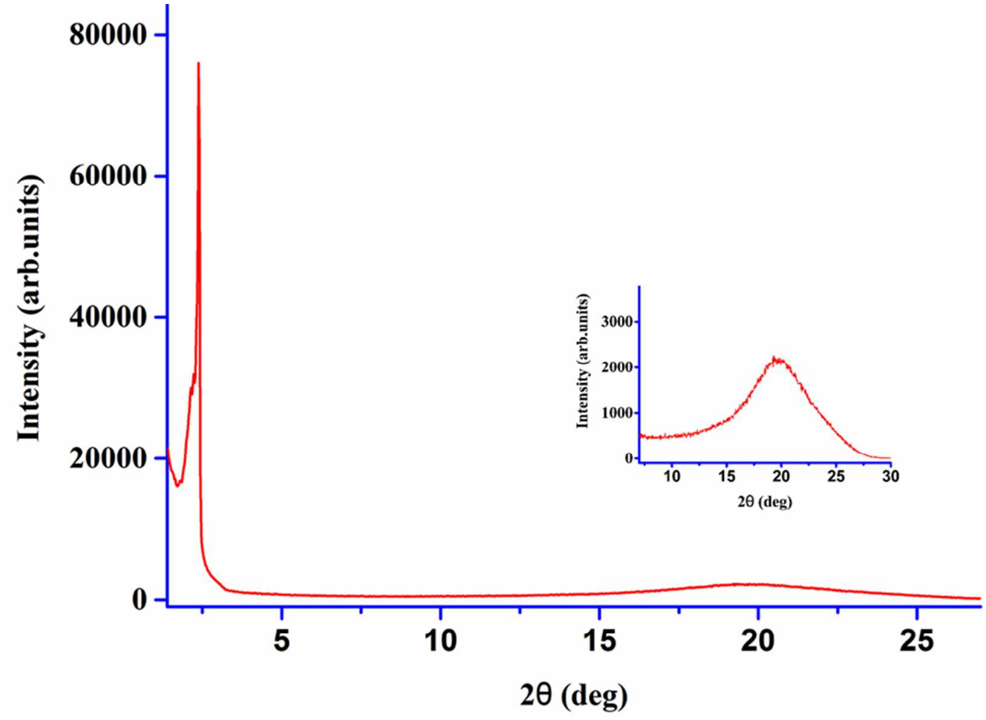

(A)
Cr
SmC
N
I
Exo
Heat Flow (a.u)
Endo
N
I
Cr
70
80
90
100
110
120
130
140
150
Temperature (°C)
(B)
Cr
SmC
N
I
Exo
Heat Flow (a.u)
Endo
SmC
N
I
Cr
60
70
80
90
100
110
120
130
140
150
Temperature (°C)

Figure 3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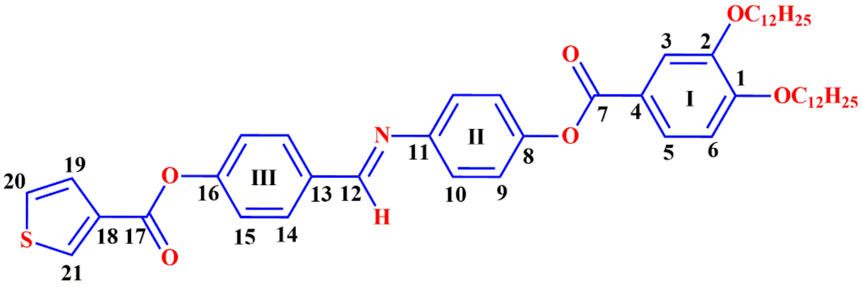
60000
40000
20000
0
Intensity (arb.units)
5
10
15
20
25
2θ (deg)
3000
2000
1000
0
Intensity (arb.units)
10
15
20
25
30
2θ (deg)

Figure 4

(A)


OC12H25
3
2
1
OC12H25
O
7
4
I
N
11
II
8
O
5
6
20
19
O
16
III
13
12
10
9
S
18
17
O
15
14
H
21

(B)

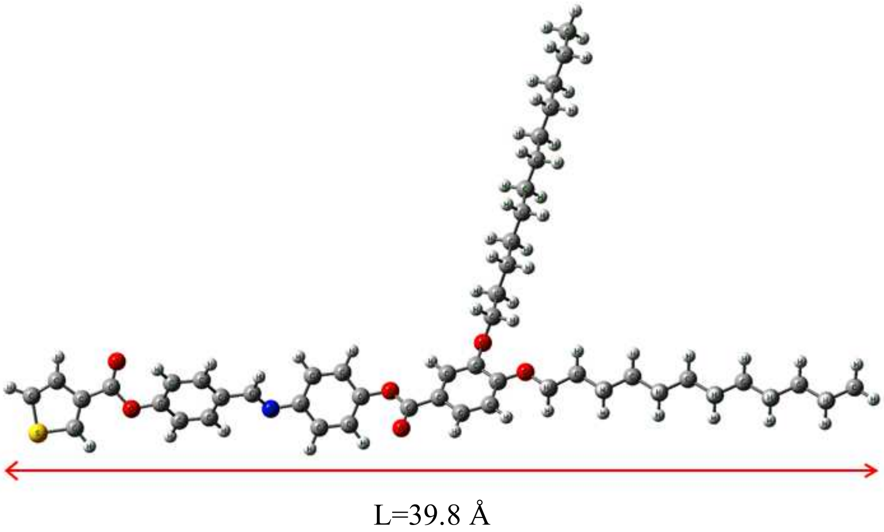

L=39.8 Å

Figure 5

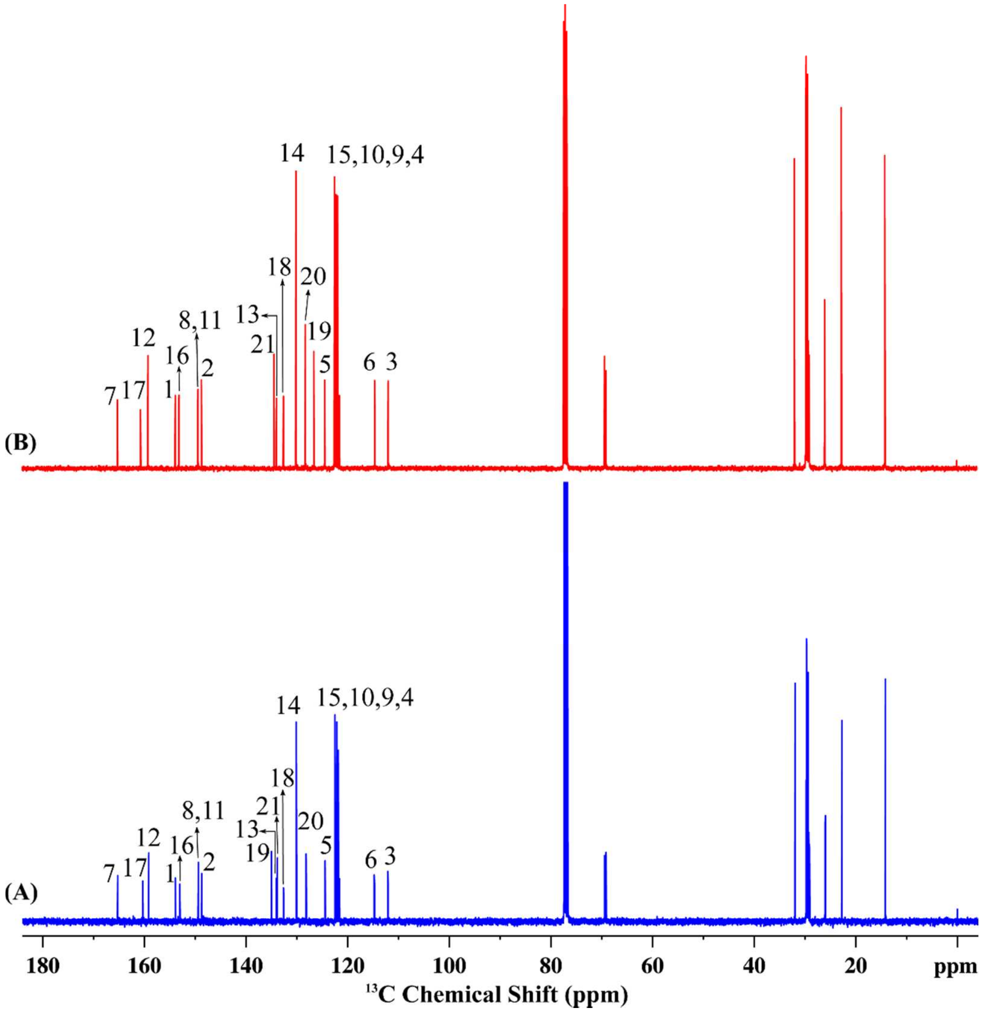

(B)
14
15,10,9,4
18
20
13
8,11
12
21
19
16
5
6
3
2
7
17
1
(A)
14
15,10,9,4
18
21
8,11
13
20
12
16
19
5
6
3
2
7
17
1
180
160
140
120
100
80
60
40
20
ppm
¹³C Chemical Shift (ppm)

Figure 6

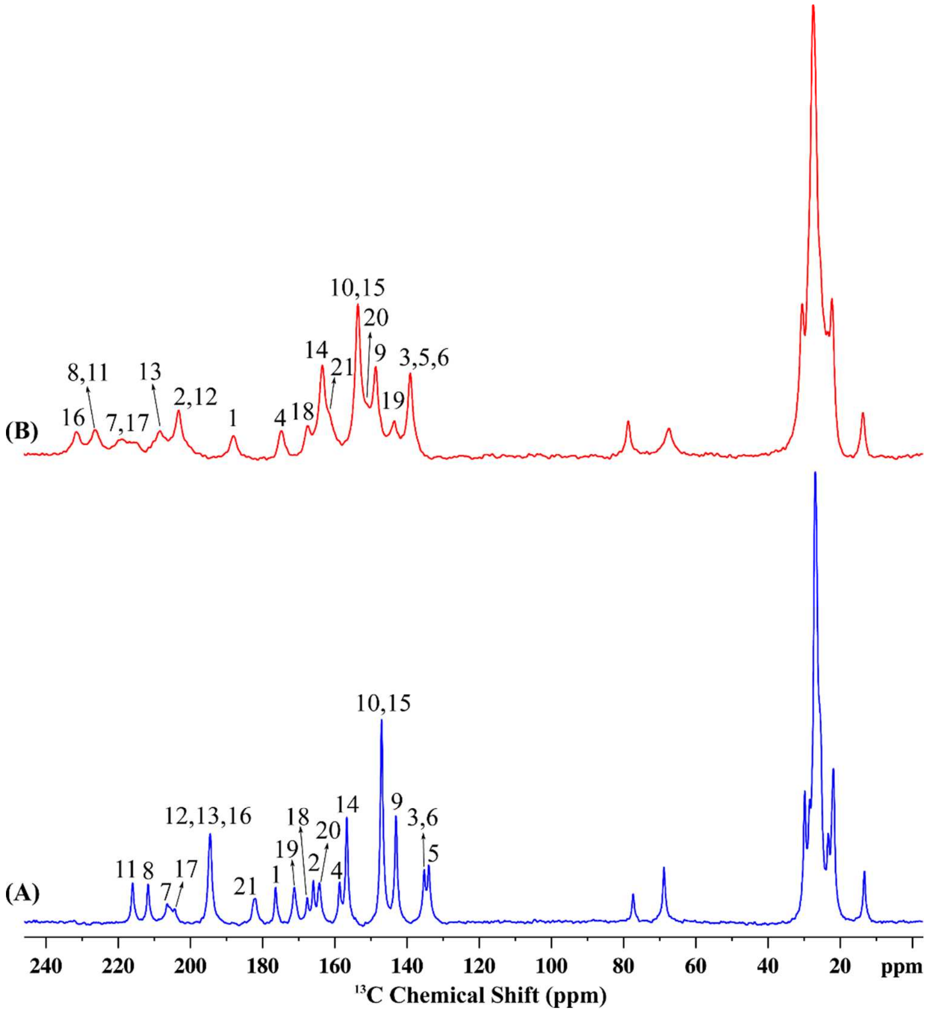
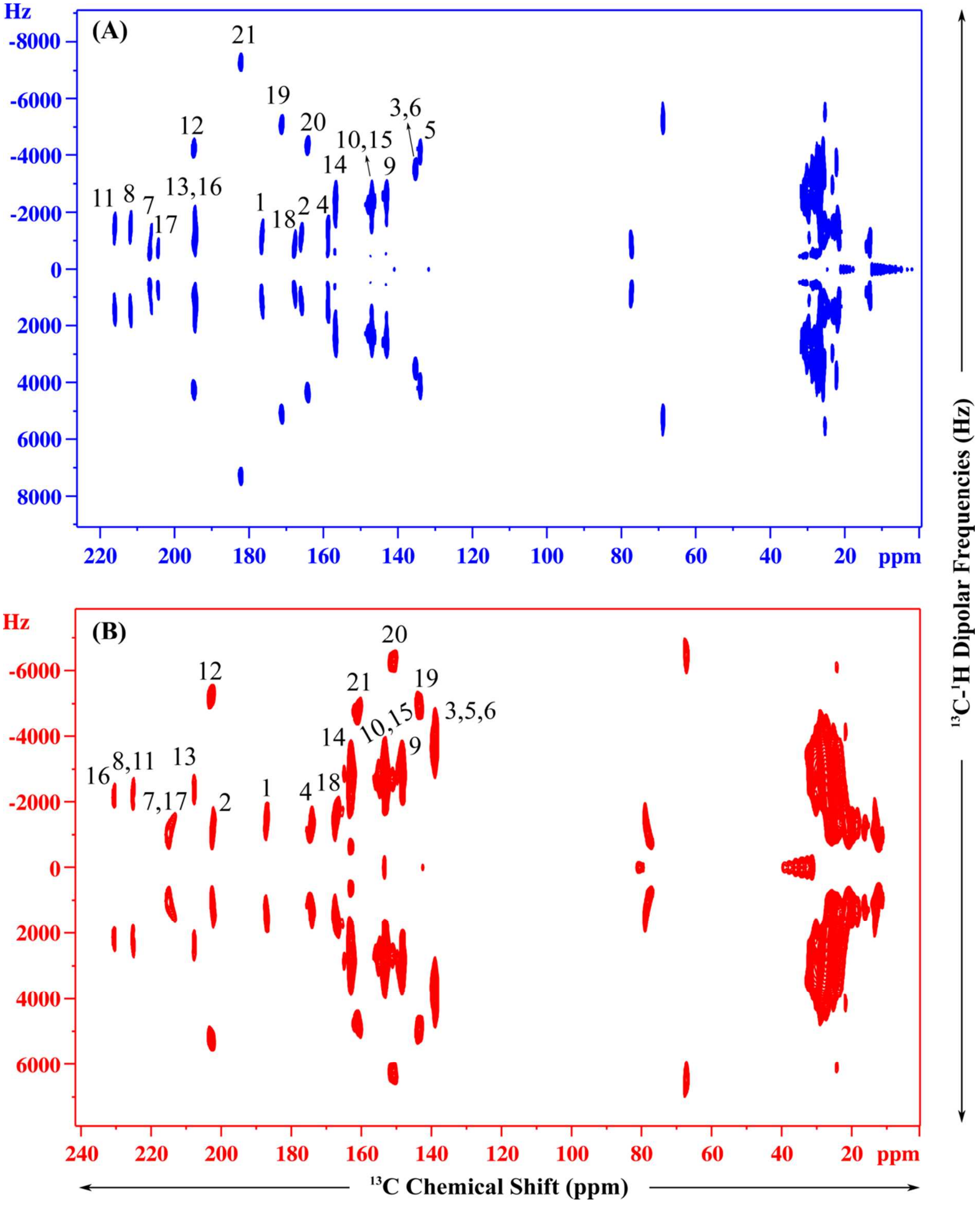

(B)
10,15
20
9
14
21
3,5,6
8,11
13
2,12
19
16
7,17
1
4
18
(A)
10,15
12,13,16
18
14
9
3,6
20
19
5
11
8
17
1
2
21
7
4
240
220
200
180
160
140
120
100
80
60
40
20
ppm
^{13}C Chemical Shift (ppm)

Figure 7


Hz
(A)
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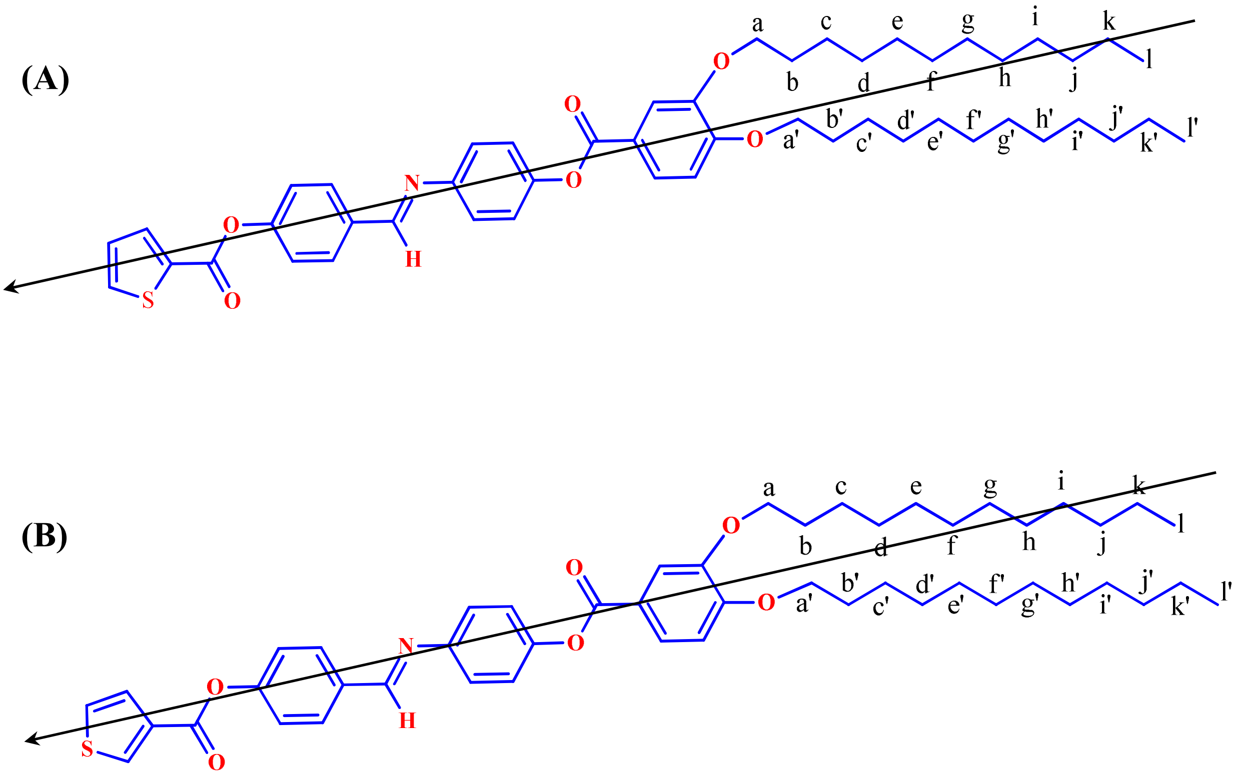
-6000
-4000
-2000
0
2000
4000
6000
8000
21
19
20
12
3,6
5
10,15
14
9
11
8
7
13,16
17
1
18
2
4
220
200
180
160
140
120
100
80
60
40
20
ppm
Hz
(B)
-6000
-4000
-2000
0
2000
4000
6000
20
12
21
19
3,5,6
14
10,15
9
16
8,11
13
7,17
2
1
4
18
240
220
200
180
160
140
120
100
80
60
40
20
ppm
^{13}C Chemical Shift (ppm)
^{13}C-^{1}H Dipolar Frequencies (Hz)

Figure 8


(A)
a
c
e
g
i
k
b
d
f
h
j
l
a'
b'
c'
d'
e'
f'
g'
h'
i'
j'
k'
l'
O
N
H
S
(B)
a
c
e
g
i
k
b
d
f
h
j
l
a'
b'
c'
d'
e'
f'
g'
h'
i'
j'
k'
l'
O
N
H
S

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