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Electronic Supplementary Information:

2-Octyl Thiophene based Three Ring Mesogens: Solid state ^{13}C NMR and XRD Investigations

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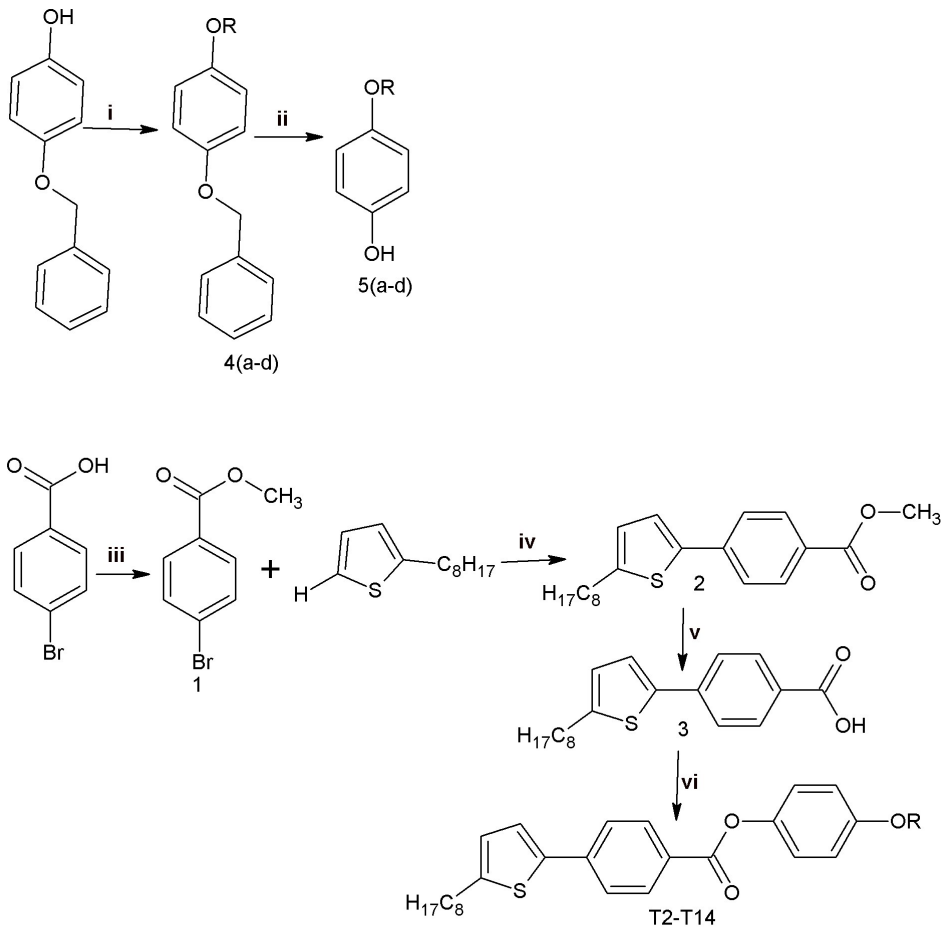
Scheme-1



OR= C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$

Reagents and Conditions: i) RBr, KOH, EtOH, reflux ii) THF, Ammonium formate, Pd/C iii) MeOH, H_2SO_4, reflux iv) $Pd(OAc)_2$, $PCy_3.HBF_4$, pivalic acid,K_2CO_3, DMAc, v) KOH, EtOH, reflux, vi) 4-alkoxy phenol, DCC/DMAP.

Experimental Section

Synthesis of 4-bromomethylbenzoate (1)

4-Bromobenzoic acid 5g dissolved in 50 mL methanol in a 250 mL two neck RB and kept for reflux 20 minutes and con.H_2SO_4 (5 mL) added drop wise using pressure dropping funnel.[1] The reaction was refluxed for 4 hrs and monitored by TLC. After completion of the reaction the white colour compound was precipitate out in the solution. It was filtered and washed with 10% NaOH solution. The obtained compound was dried and recrystallized in isopropanol. Yield 76%, m.p-81°C.

FT-IR (KBr, cm^{-1}): 2997, 2850 ($C-H_{str}$), 1715 ($C=O_{str}$), 1439 ($C-H_{ben}$), 1248, ($C-O-C_{asym\ \&\ sym\ str}$). 842. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.37, 131.72, 131.12, 129.06, 128.04 and 52.29.

Synthesis of 4-n-alkoxy 4-(5-octyl-2-thienyl)-benzoates (T2-T14)

The esters were prepared by the reaction between appropriate 4-n-alkoxy 4-(5-octyl-2-thienyl) benzoic acids with alkoxy phenols using DCC/DMAP reagent with good yields.[2] The starting methyl 4-(5-octylthiophen-2-yl) benzoate was prepared in a single step coupling with 2-octylthiophene and 4-bromo methyl benzoate using palladium acetate as a catalyst by direct arylation method.[5]

Methyl 4-(5-octylthiophen-2-yl) benzoate (2)

In a representative experiment 2-octylthiophene (6.0 g, 0.0152M) and methyl 4-bromo benzoate (3.15 g, 0.0152M) dissolved in 25 mL anhydrous N, N-dimethylacetamide, K_2CO_3 (1.5 eq, 0.02M, 3.14 g), Pd $(OAc)_2$ (2 mol%, 68 mg), pivalic acid (30 mol%, 465 mg), tricyclohexylphosphine tetrafluorobotate ($PCy_3.HBF_4$) (4 mol%, 223 mg) were added. The reaction mixture was stirred for 14 hrs at 110 °C under nitrogen atmosphere. The progress of

the reaction monitored by TLC. The obtained solid was dissolved in 100 mL dichloromethane (DCM) washed with 10% HCl; The organic layer was dried over anhydrous Na_2SO_4, and concentrated in a vacuo to afford crude ester which was purified by column chromatography using hexane and ethyl acetate as an eluent in 1:10. The compound was recrystallized from methanol. Colorless solid obtained. Yield 81%, m.p-92.2 °C, FT-IR (KBr, cm^{-1}): 2956, 2922 ($C-H_{str}$), 1717($C=O_{str}$), 1562 ($C=C_{str}$ aromatic), and 1279 ($C-O-C_{asym\ \&\ sym\ str}$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03-7.98 (d, J=8.0 Hz, 2H), 7.63-7.58 (d, J=8.0, 2H), 7.23 (d, *J* = 4.0 Hz, 1H), 6.77 (d, *J* = 4.0 Hz, 1H), 3.91 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.70 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.43-1.21 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.86, 147.57, 140.25, 139.05, 130.22, 128.20, 125.41, 124.96, 124.26, 52.07, 31.87, 31.62, 30.32, 29.34, 29.22, 29.10, 22.67 and 14.11.

4-(5-octylthiophen-2-yl) benzoic acid (3)

In a typical experiment, 2g of (6.05 mm) methyl 4-(5-octylthiophen-2-yl) benzoate placed in 250 mL single necked RB equipped with double wall condenser dissolved in 100 mL of ethanol was added to the flask and 2.5 eq, 0.8 g of KOH soluble in 20 mL of distilled water was added.[1] The resulting solution was refluxed for 2 hrs, then the solution was allowed to cool to room temperature and neutralized with 10% dil.HCl to get white precipitate which was filtered using vacuum, the solid obtained was purified by recrystallized from methanol. The colorless solid was obtained. Yield: 81%, m.p-155 °C, 224.8°C (TI-N), 214.3 °C (TN-SmC); FT-IR (KBr, cm^{-1}): 3014, 2972 ($C-H_{str}$), 2665, 2547 ($O-H_{str}$ of carboxilic acid) 1682 ($C=O_{str}$ of carboxylic acid), 1603 and 1577 ($C=C_{str}$ aromatic), 1426 ($C-H_{ben}$), 1256 and 1167 ($C-O-C_{asym\ \&\ symstr}$ of ester and ether respectively; ^1H NMR (400 MHz, DMSO-d_6): δ 8.32(s, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 3.5 Hz, 1H), 6.90 (d, *J* = 3.3 Hz, 1H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.71-1.52 (m, 4H), 1.27 (m, *J* = 17.6 Hz, 8H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR ppm (DMSO-d_6): δ 167.40, 147.13, 139.86,

138.47, 130.62, 129.40, 126.61, 125.55, 125.18, 31.71, 31.52, 29.93, 29.14, 29.04, 28.88, 22.54 and 14.42.

Synthesis of 4-(dodecyloxy) phenyl 4-(5-octylthiophen-2-yl) benzoate (T12)

In a representative experiment, 4-(5-octylthiophen-2-yl) benzoic acid (0.6g, 0.0018 mol) and 4-(dodecyloxy) phenol (0.51 g, 0.0018 mol) were dissolved in 50 mL dichloromethane (DCM) and 4-dimethylamino pyridine (DMAP) (22 mg, 0.00018 mol) were placed in 100 mL two necked RB at 0 °C. After 10 minutes, dicyclohexylcarbodiimide (DCC) (0.37 g, 0.0018 mol) dissolved in dichloromethane (DCM) was added to the RB.[3] The reaction allowed to stirring for an hour. After that the reaction was transferred to room temperature and continued for 14 hrs. N, N´-dicyclohexyl urea precipitated out was filtered off and the organic solution was taken into separating funnel and washed twice with 5% KOH solution followed by distilled water. The obtained compound was purified by column chromatography on silica gel (hexane-EtOAc 10:1 as an eluent). The resulted solid was recrystallized from n-heptane. Similar procedure was used for synthesis of T2, T4, T6, T8, T10 and T14 mesogens.

Synthesis of 1-(benzyloxy)-4-(octyloxy) benzene (4a)

4-(benzyloxy) phenol (5g, 0.025M) dissolved in 100 mL ethanol and KOH 3.5g (2.5 eq, 0.0625 M) dissolved in 25 mL distilled water refluxed for 30 min, 1-bromooctane (4.3 mL, 0.025M) was added drop wise using pressure equalizing dropping funnel.[4] The progress of the reaction was monitored by TLC, the reaction mixture was poured into the distilled water and the obtained solid was filtered and recrystallized from isopropanol. Yield 85%, m.p-73.8 °C. Similar procedure was used for other homologue decyloxy, dodecyloxy, and tetra decyloxy benzylated alkoxy compounds.

FT-IR (KBr, cm^{-1}): 3036 (aromatic C-H_{str}), 2955, 2918(C-H_{str}), 1511(C=C_{str} aromatic), 1385, 1072 (C-O-$C_{asym\&symstr}$).^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.42 (d, *J* = 7.3 Hz, 2H), 7.39-7.36 (m, *J* = 10.1, 4.8 Hz, 3H), 7.32 (d, J=10.0 Hz, 2H), 6.92 (d, J=10Hz, 2H), 5.08 (s, 2H), 3.86 (t, *J* = 6.6 Hz, 2H), 1.75 (m, *J* = 7.9 Hz, 2H), 1.33 (m, *J* = 14.4 Hz, 2H), 1.30 (m, 2H), 1.26 (m, 2.5 Hz, 6H), 0.90 (t, J=6.5Hz, 3H); ^{13}C-NMR ppm ($CDCl_3$): δ 153.0, 152.86, 137.42, 128.64, 127.96, 127.59, 115.87, 115.46, 70.77, 68.69, 32.03, 29.78, 29.54, 26.17, 22.81 and 14.26.

1-(benzyloxy)-4-(decyloxy) benzene (4b). Yield 85%, m.p-79.4 °C, FT-IR (KBr, cm^{-1}): 3062, 3028 (aromatic C-H_{str}), 2954, 2906 (C-H_{str}), 1516 C=C_{str}, 1386,1030 (C-O-$C_{asym\&symstr}$); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.43 (d, J=7.0 Hz, 2H), 7.41 (m, J=7.5Hz, 1H), 7.37 (d, J=7.5Hz, 2H), 6.88 (d, J=7.5 Hz, 2H), 6.81 (d, J=10 Hz, 2H), 5.01 (s, 2H), 3.89 (t, J=6.0 Hz, 2H), 1.74 (m, J=7.2 Hz, 4H), 1.30 (m, 4H), 1.26 (m, 8H), 0.88 (t, 6.0 Hz, 3H); ^{13}C-NMR ppm ($CDCl_3$): δ 153.40, 152.91, 137.42, 128.63, 127.95, 127.64, 115.88, 115.47, 70.78, 68.71, 31.98, 29.66, 29.51, 26.15 and 14.22.

1-(benzyloxy)-4-(dodecyloxy)benzene (4c). Yield 84%, m.p-80.5 °C, FT-IR (KBr, cm^{-1}): 3011, 2957, 2925(C-H_{str}), 1519(C=C_{str} aromatic), 1489, 1285 (C-H_{ben}), 1170, 1025(C-O-$C_{asym\&symstr}$); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.45 (d, *J* = 7.2 Hz, 2H), 7.41 (m, *J* = 8.2, 6.7 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.33 (d, *J* = 10.0 Hz, 2H), 6.91(d, *J* = 10.0 Hz, 2H), 5.06 (s, 2H), 3.93 (t, J=6.0 Hz, 2H), 1.79 (m, *J* = 15.9, 10.7 Hz, 4H), 1.35 (m, *J* = 7.1 Hz, 10H), 1.30 (dd, *J* = 15.9, 10.7 Hz, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR ppm ($CDCl_3$): δ 153.64, 152.95, 137.46, 128.66, 127.98, 127.98, 127.60, 115.90, 115.49, 70.79, 68.71, 31.75, 29.48, 25.87, 22.75 and 14.19.

1-(benzyloxy)-4-(tetradecyloxy)benzene (4d). Yield 80%, m.p-84.5 °C, FT-IR (KBr, cm^{-1}):3016 (aromatic C-H_{str}), 2918, 2851(C-H_{str}), 1508(C=C_{str}), 1161, 1057(C-O-$C_{asym\&asymstr}$);

^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.43 (d, *J* = 7.3 Hz, 2H), 7.41 (m, *J* = 7.3 Hz, 1H), 7.35 (d, 7.0 Hz 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.01(s, 2H), 3.89 (t, *J* = 6.5 Hz, 2H), 1.75(m, 4H), 1.43 (m, 4H), 1.26 (m, 16H), 0.88 (t, *J* = 5.9 Hz, 3H); ^{13}C-NMR ppm ($CDCl_3$): δ 153.54, 152.85, 137.37, 128.88, 127.50, 115.81, 115.40, 70.71, 68.64, 31.96, 29.70, 26.09, 22.73 and 14.16.

4-Ethoxyphenol, 4-butoxyphenol, 4-(hexyloxy)phenol are procured from Aldrich (USA).

Synthesis of 4-(octyloxy) phenol (5a)

The compound 1-(benzyloxy)-4-octyloxy)benzene 3g and 10 eq of ammonium formate dissolved in 100 ml THF and 10% Pd/C (0.3g) was added and stirred at room temperature for 12 hrs under nitrogen atmosphere. The product purity was checked by TLC. After completion of the reaction the solid Pd/C was filtered by celite powder. Similar procedure was used for 4-(decyloxy) phenol, 4-(dodecyloxy) phenol, and 4-(tetradecyloxy) phenol.

4-(octyloxy) phenol (5a). Yield 80%, m.p-74.5 °C, FT-IR (KBr, cm^{-1}): 3316 ($O\text{-}H_{str}$), 3079, 3038(aromatic $C\text{-}H_{str}$), 2940 ($C\text{-}H_{str}$), 1512 ($C{=}C_{str}$ aromatic), 1278, 1239($C\text{-}O\text{-}C_{asym}\&_{symstr}$), 827; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (q, *J* = 8.8 Hz, 4H), 4.86 (s, 1H), 3.89 (t, *J* = 6.5 Hz, 2H), 1.87-1.64 (m, 2H), 1.54-1.16 (m, 10H), 0.88 (t, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.29, 149.39, 116.05, 115.72, 68.88, 31.92, 29.60, 29.58, 29.43, 29.38, 29.34, 26.06, 22.70 and 14.13.

4-(decyloxy)phenol (5b). Yield 78%, m.p-80.5 °C, FT-IR (KBr, cm^{-1}): 3380 ($O\text{-}H_{str}$), 2974, 2921, 1514 (aromatic $C{=}C_{str}$), 1472, 1230, 1100 ($C\text{-}O\text{-}C_{asym\&symstr}$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.76 (q, *J* = 9.0 Hz, 4H), 5.19 – 4.77 (s, 1H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.82-1.65 (m, 2H), 1.52-1.15 (m, 14H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.25, 149.38, 116.06, 115.72, 68.88, 31.93, 29.61, 29.59, 29.44, 29.38, 29.35, 26.06, 22.71 and 14.15.

4-(dodecyloxy) phenol (5c). Yield 85%, m.p-80.0 °C, FT-IR (KBr, cm^{-1}): 3346 ($O-H_{str}$), 2986 ($C-H_{str}$), 1525 (aromatic $C=C_{str}$), 1278, 1094 ($C-O-C_{asym\&symstr}$; ^1H NMR (500 MHz, $CDCl_3$): δ 6.71 (q, *J* = 9.0 Hz, 4H), 5.44 (s, 1H), 3.89 (t, *J* = 6.7 Hz, 2H), 1.81-1.65 (m, 2H), 1.52-1.08 (m, 18H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CHCl_3$): δ 153.23, 149.50, 116.17, 115.81, 68.99, 32.04, 29.78, 29.76, 29.72, 29.70, 29.53, 29.48, 29.46, 26.14, 22.81 and 14.25.

4-(tetradecyloxy)phenol (5d). Yield 78%, m.p-81.5 °C, FT-IR (KBr, cm^{-1}): 3342 ($O-H_{str}$), 2923 ($C-H_{str}$), 2856,($C-O-C_{asym\&symstr}$) 1260, 1170; ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.77 (q, *J* = 9.0 Hz 4H), 5.04 (s, 1H), 3.89 (t, *J* = 6.7 Hz, 2H), 1.74 (m, 2H), 1.30 (m, 12H), 1.26 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C-NMR ppm ($CDCl_3$): δ 153.35, 149.35, 116.00, 115.60, 68.80, 31.93, 29.67, 29.59, 26.06, 22.70 and 14.12.

WAXS and SAXS of T10 mesogen:

Wide-angle and small-angle X-ray scattering measurements were carried out on XEUSS SAXS/WAXS system using a Genixmicro source from Xenocs operated at 50 kV and 0.6 mA. The Cu Kα radiation (λ = 1.54 Å) was collimated with a FOX2D mirror and two pairs of scatterless slits from Xenocs. The 2D-patterns were recorded on a Mar345 image plate and processed using Fit2D software. These measurements were made in the transmission mode. Silver behenate was used as standard materials for calibration of the scattering vectors of SAXS and WAXS. Mar 345 dtb image plate detector was set at 1050 mm and 221.75 mm from the sample in the direction of the beam for SAXS and WAXS data collections, respectively. XEUSS SAXS/WAXS system is equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature controller. The Linkam hot stage was

connected to the LNP 95 cooling system, which cools the stage to liquid nitrogen temperature. The flow of nitrogen was automatically adjusted with the help of T95 controller.

Table 1: Powder X-ray diffraction data of T10 mesogen

T (ºC)	d_1 (Å)	d_2 (Å)	d_1/L
135	37.03	4.61	0.96
133	37.43	4.55	0.97
130	36.33	4.58	0.95
120	35.84	4.55	0.93
110	35.84	4.53	0.93
100	35.84	4.50	0.93
95	37.03	4.49	0.96
93	39.63	4.44	1.03
90	42.11	4.44	1.10
80	42.11	4.44	1.10

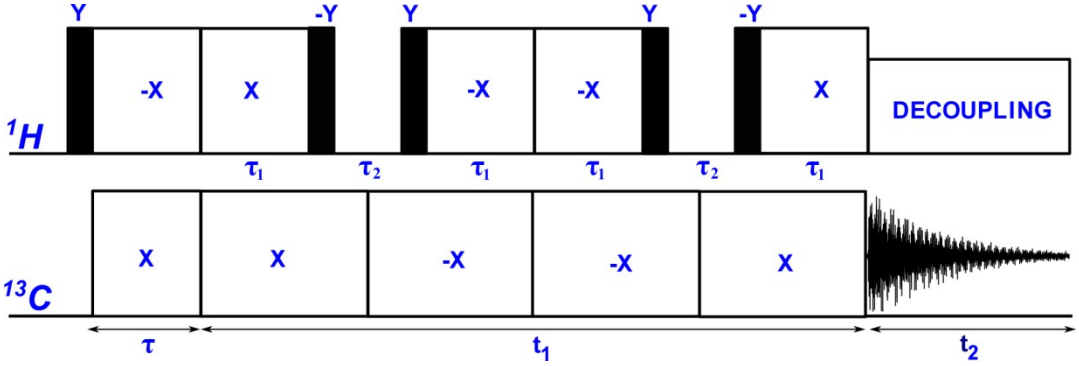


Figure 1: SAMPI-4 pulse sequence used for obtaining the 2D-SLF spectrum in the mesophase. Here τ is cross-polarization (CP) contact time. During the t_1 period, the heteronuclear ^{13}C-^{1}H dipolar couplings are evolved and the homonuclear ^{1}H-^{1}H dipolar couplings are suppressed by "magic sandwich" pulses. Finally ^{13}C signals acquired during t_2 period with the heteronuclear decoupling by SPINAL-64 pulse sequence. Here the darker boxes represent 90° pulses.

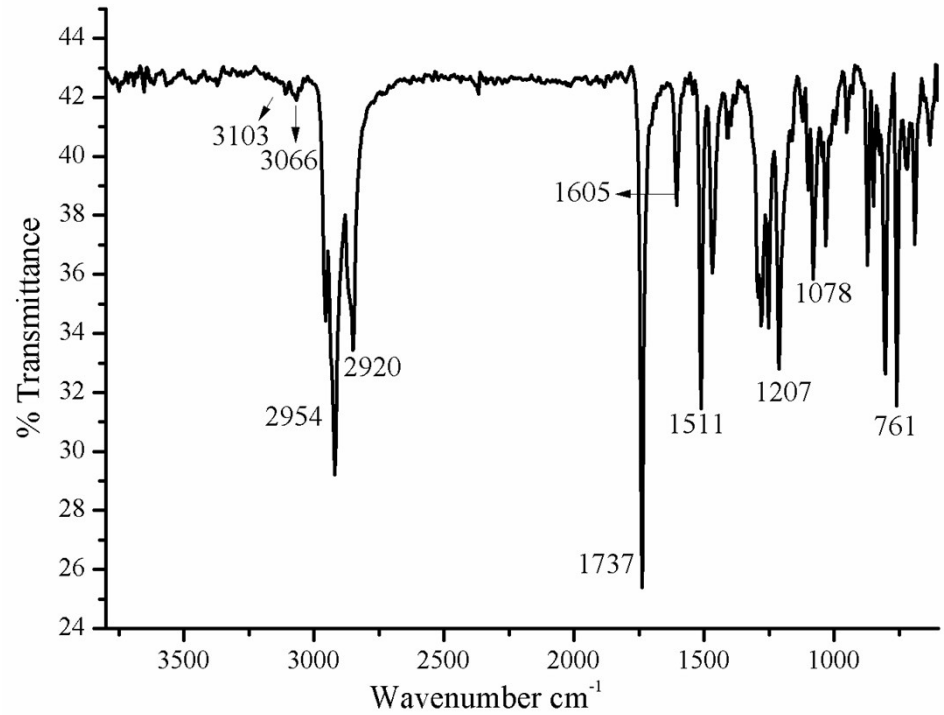


Figure 2: FT-IR spectrum of T10 mesogen.

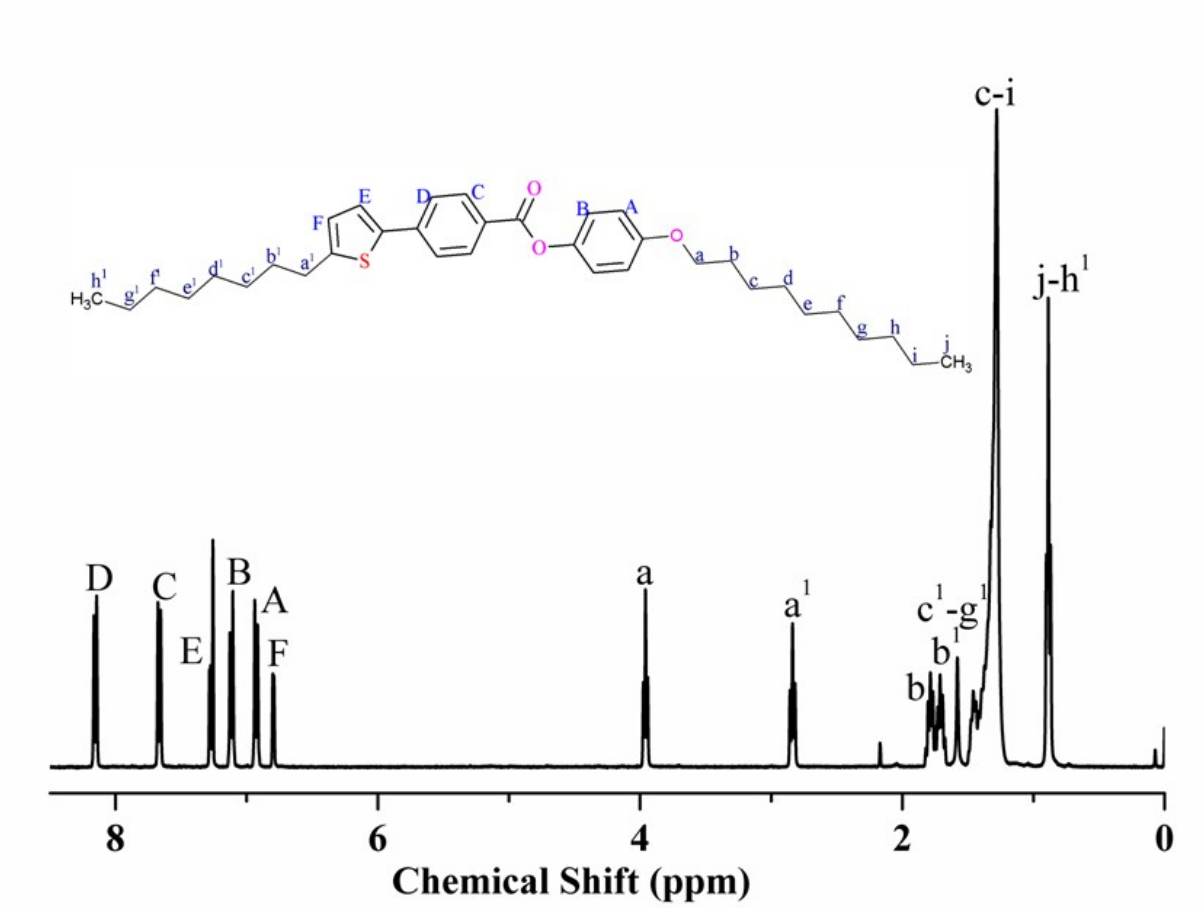
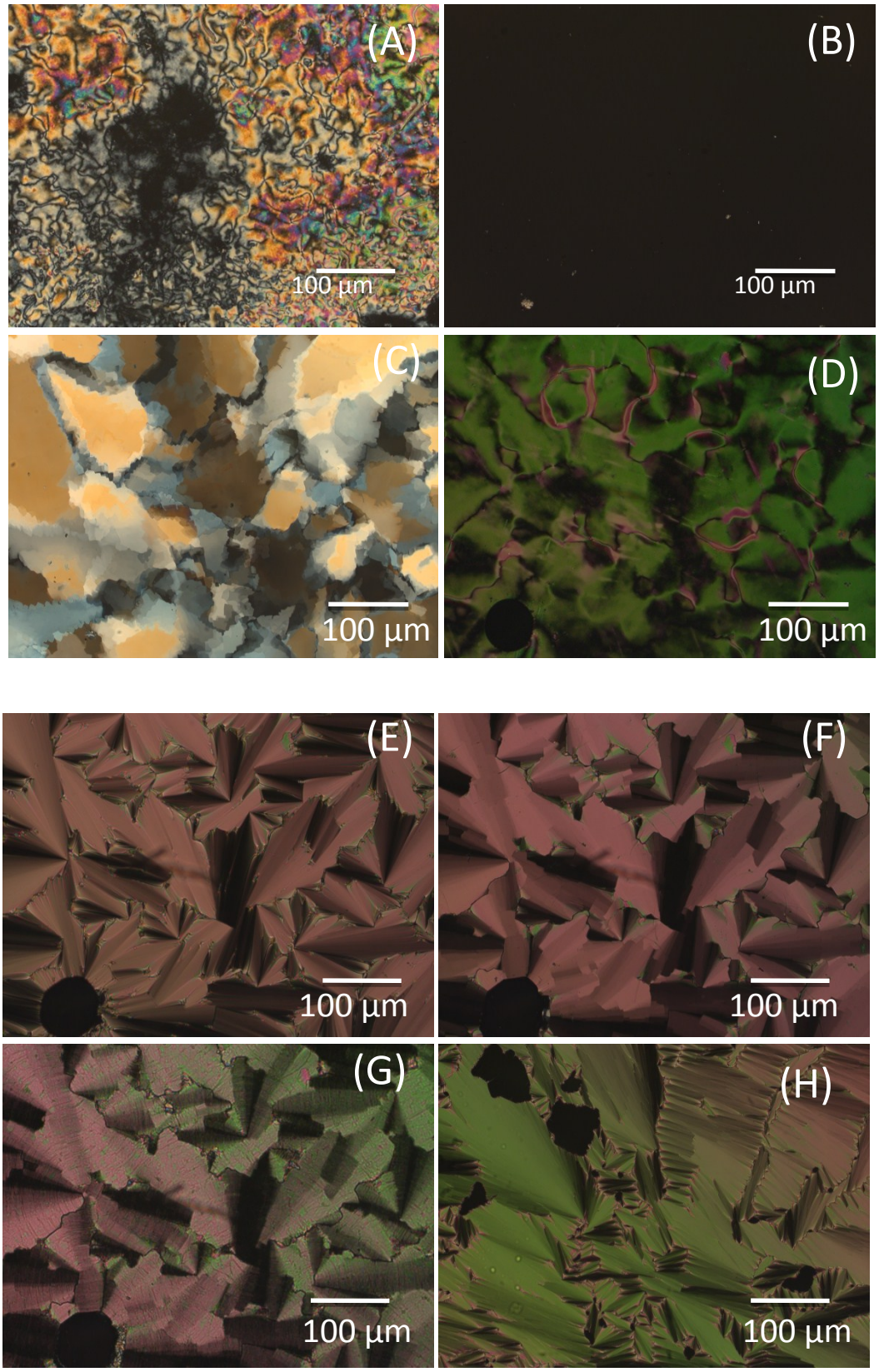


Figure 3: ^{1}H NMR spectrum of T10 mesogen.


(A)
100 µm
(B)
100 µm
(C)
100 µm
(D)
100 µm
(E)
100 µm
(F)
100 µm
(G)
100 µm
(H)
100 µm

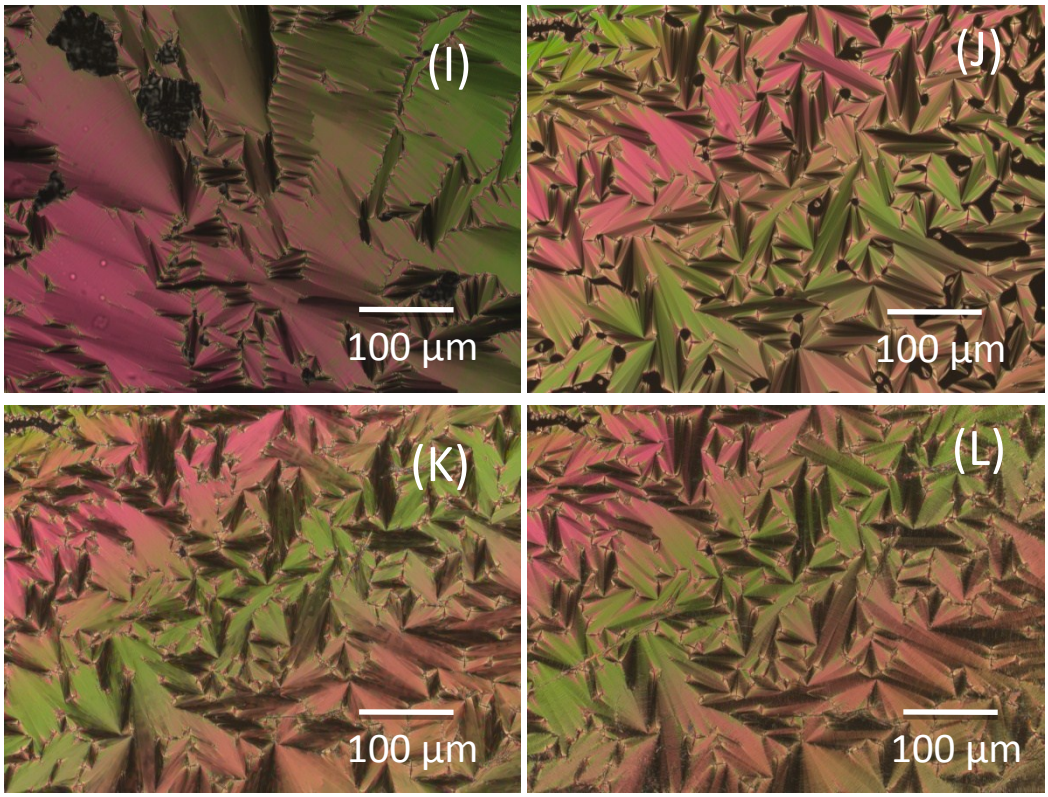


Figure 4: HOPM (A) T2- Nematic phase at 155.2 °C (B) Smectic A phase at 131.0 °C, (C) Platelet texture (Crystal E phase) at 111.0 °C (D) T4 mesogen- Nematic phase at 148.6 °C (E) Smectic A phase at 134.4 °C (F) Smectic B phase at 95.6 °C (G) Crystal E phase at 41.0 °C (H) T8 mesogen- Smectic B phase at 94.2 °C, HOPM (I) T8 mesogen-Crystal E at 62.4 °C (J) T14 mesogen-Smectic A phase at 132.8 °C (K) Smectic C phase at 121.3 °C (L) Smectic B phase at 90.2 °C.

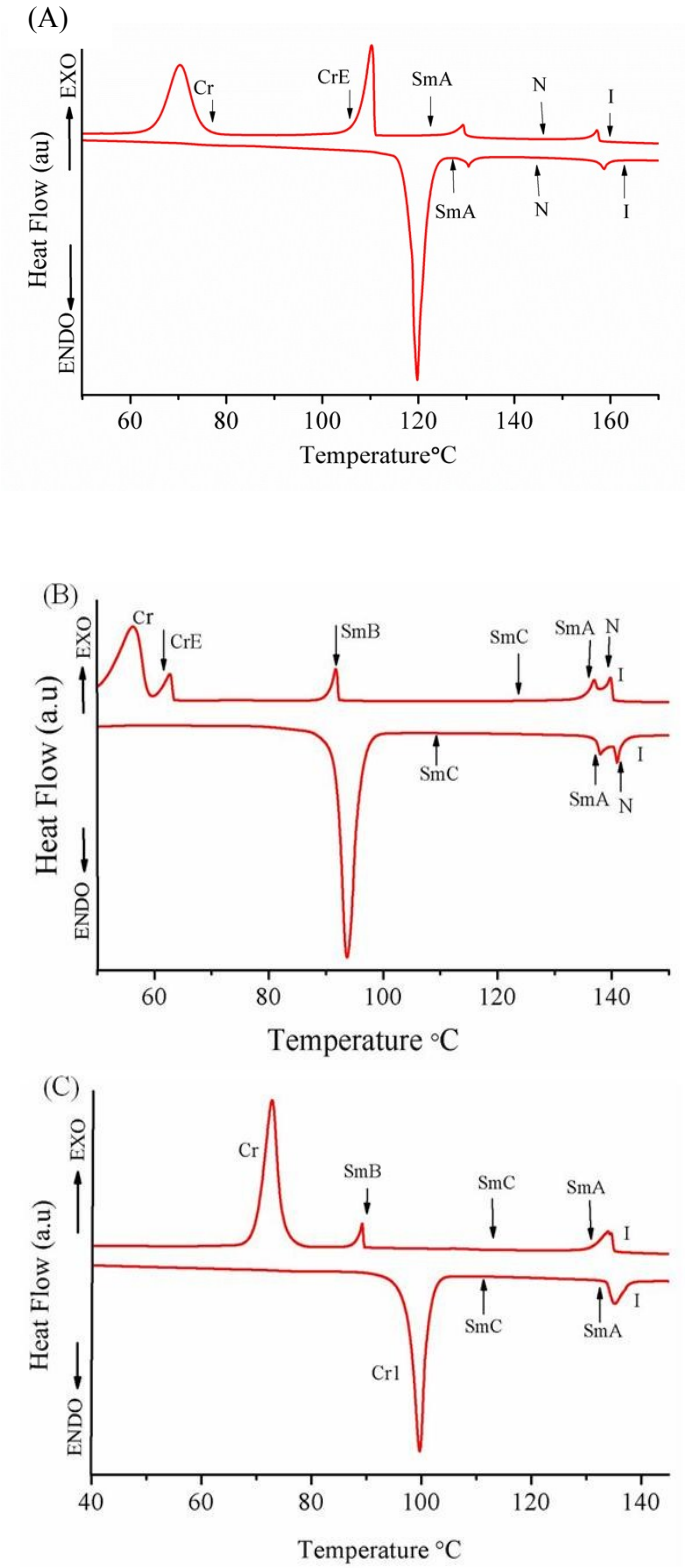


Figure 5: DSC scans of (A) T2 (B) T10 (C) T14 mesogens.

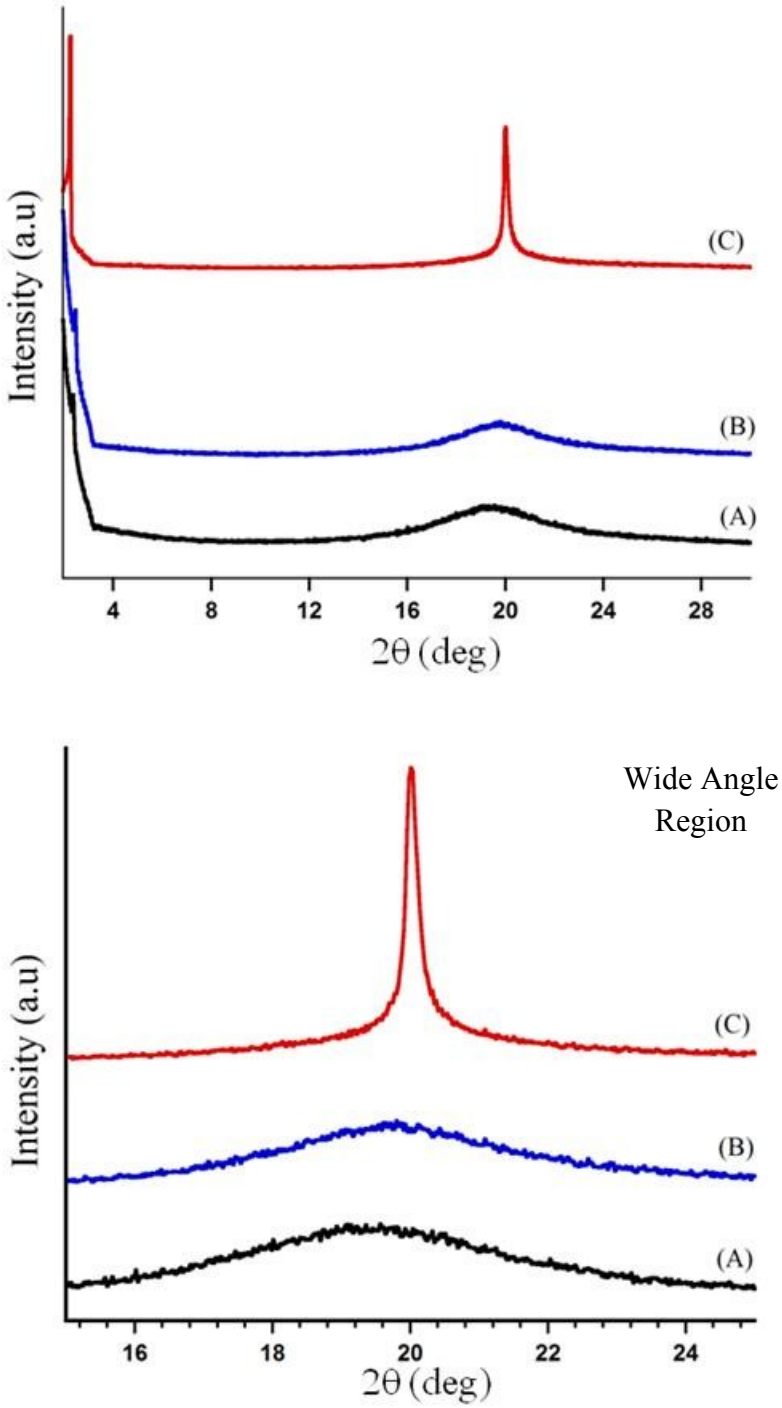


Figure 6: High-resolution powder X-ray diffraction patterns for T10 at (A) 135 °C (B) 110 °C (C) 90 °C.

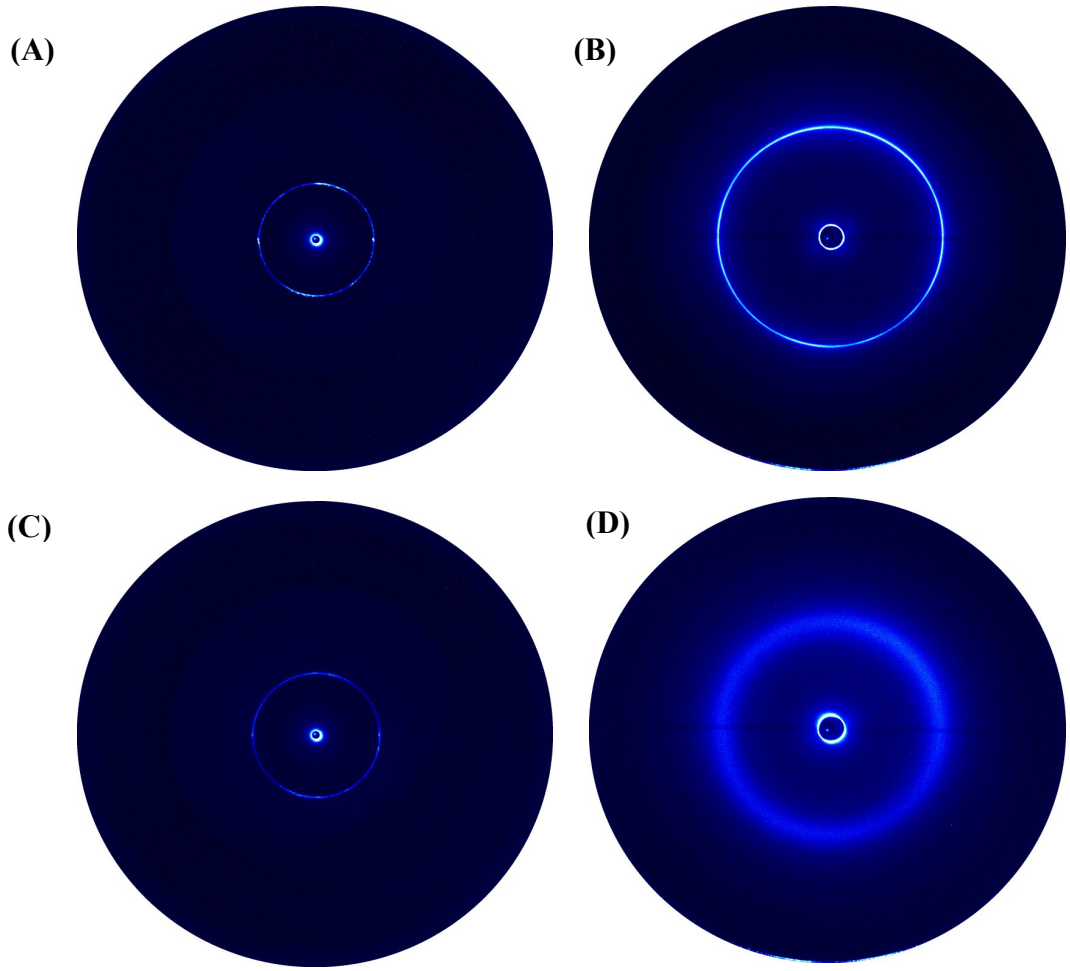


Figure 7: 2D XRD images of T10 mesogen at 90ºC: (A) small angle region, (B) wide angle region in SmB phase. At 120ºC: (C) small angle region, (D) wide angle region in SmC phase.

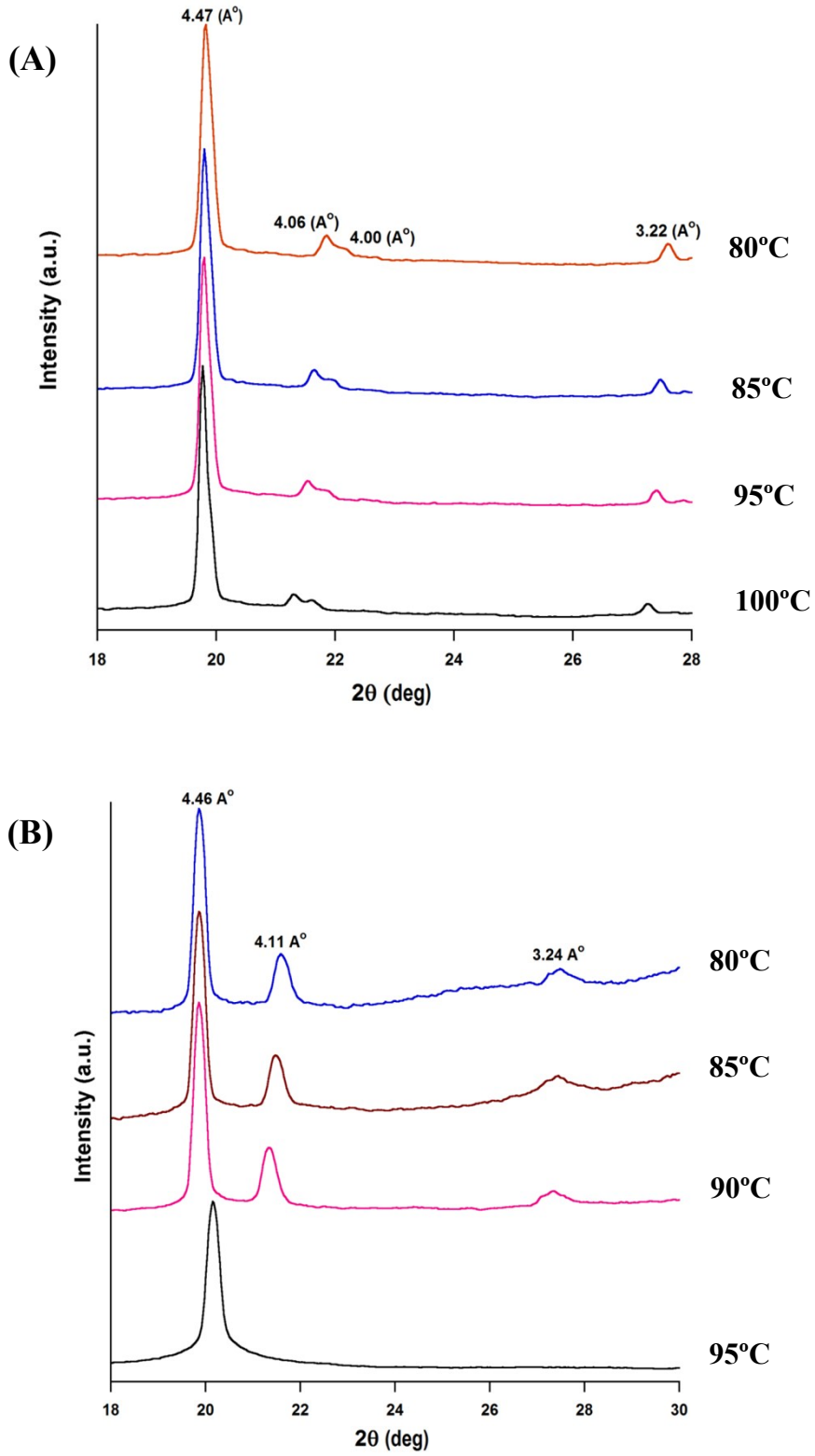


Figure 8: XRD profile of (A) T2 and (B) T4 mesogens in the wide angle region.

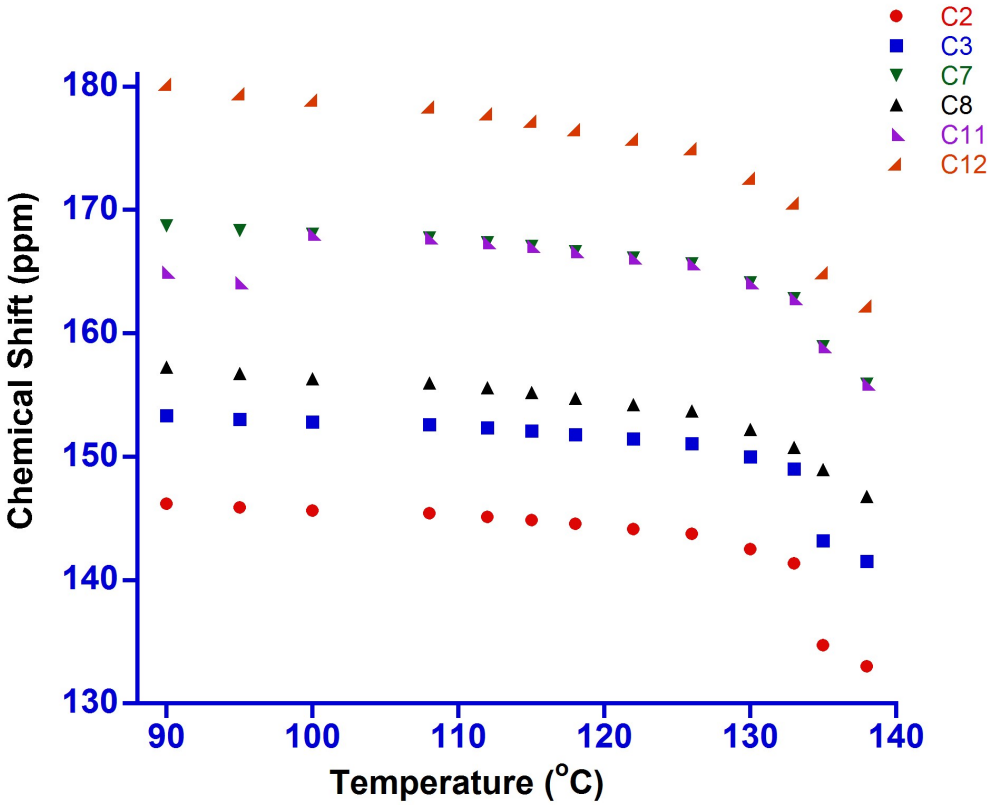


Figure 9: ^{13}C NMR chemical shifts at different temperatures in liquid crystalline state.

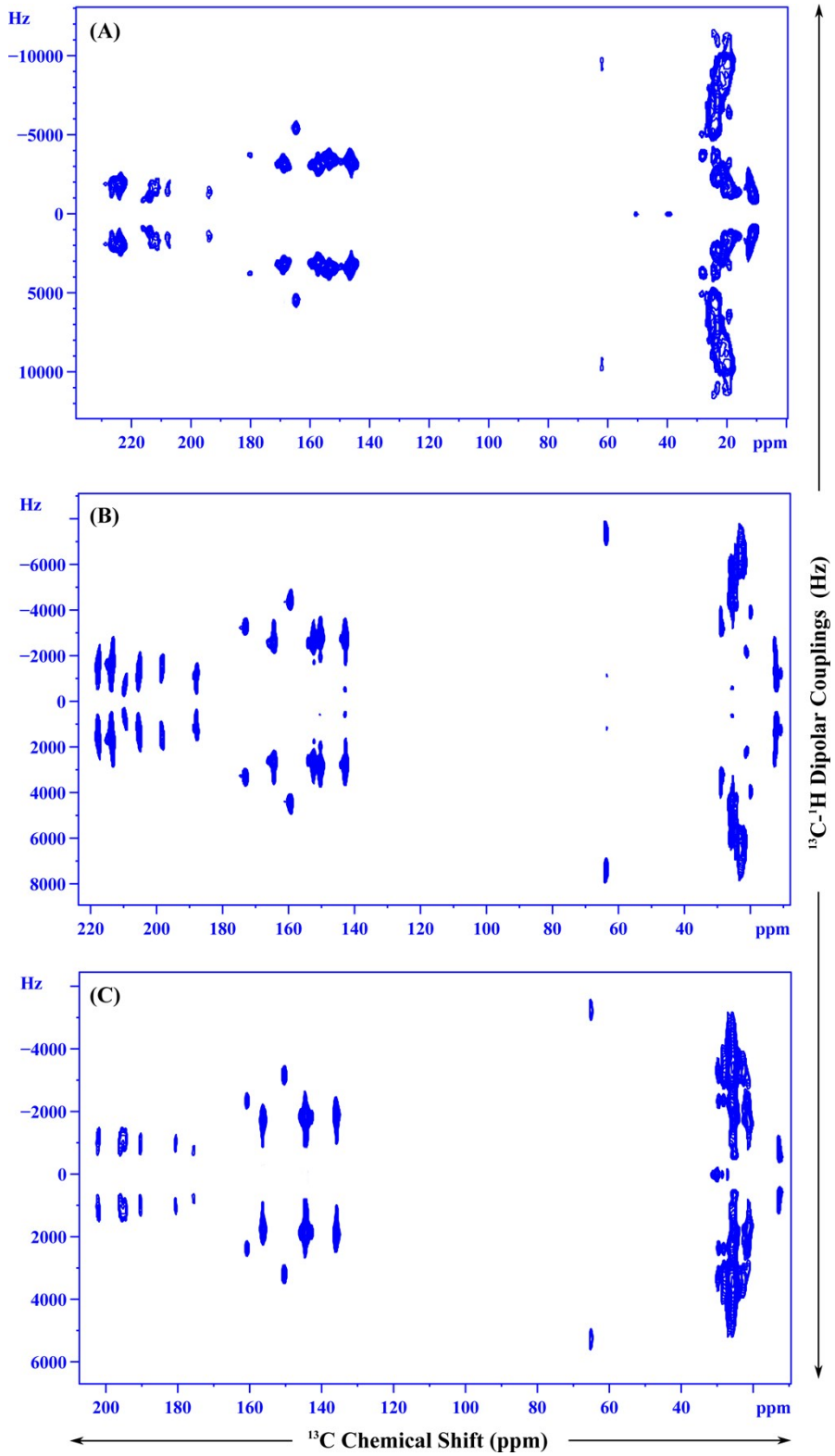


Figure 10: 2D SAMPI-4 spectra of T10 in liquid crystalline phases at (A) 90 °C, (B) 133 °C and (C) 138 °C.

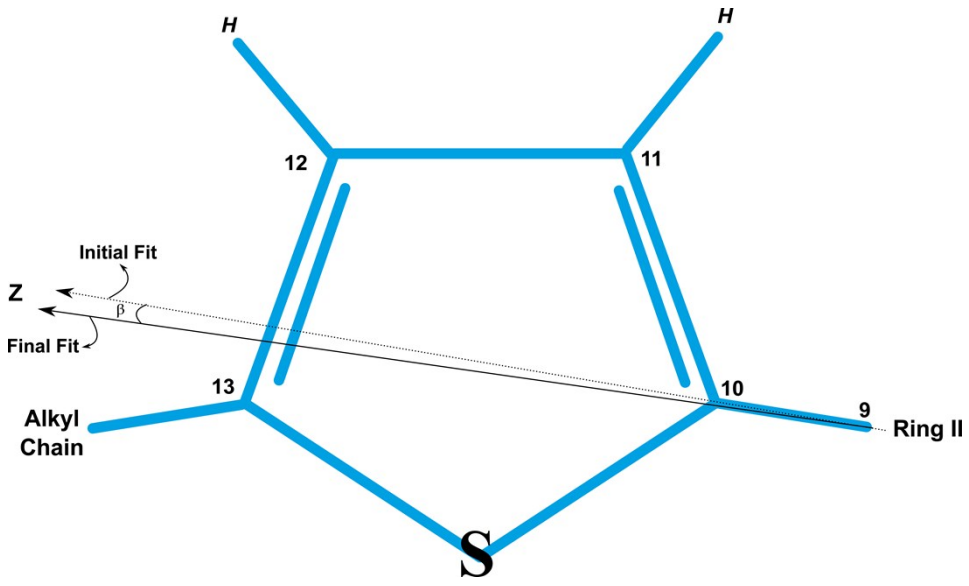


Figure 11: Model of thiophene for arriving at the order parameter from dipolar couplings.

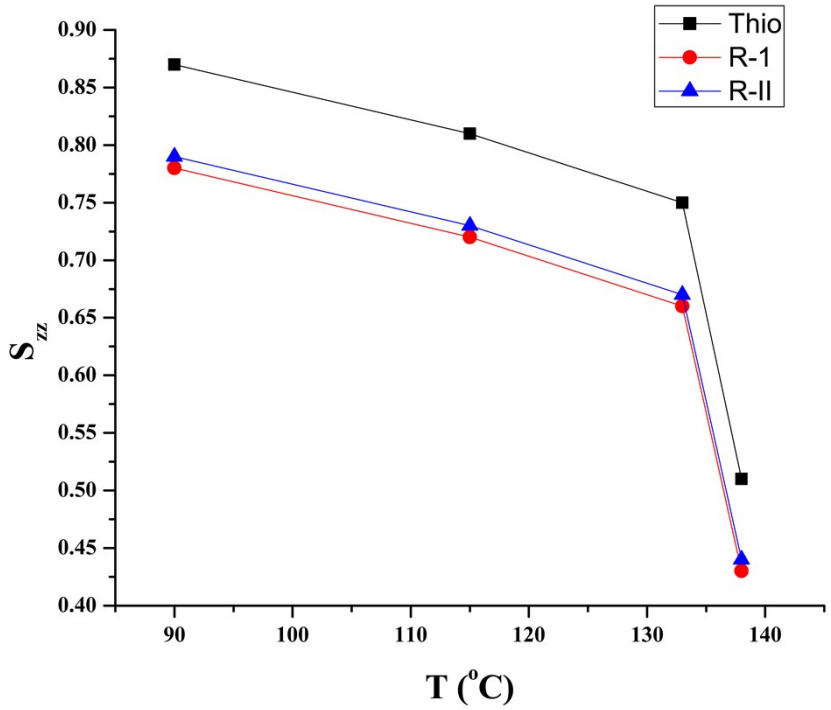


Figure 12: Orientational order parameters of T10 mesogen at different temperatures in liquid crystalline phase.

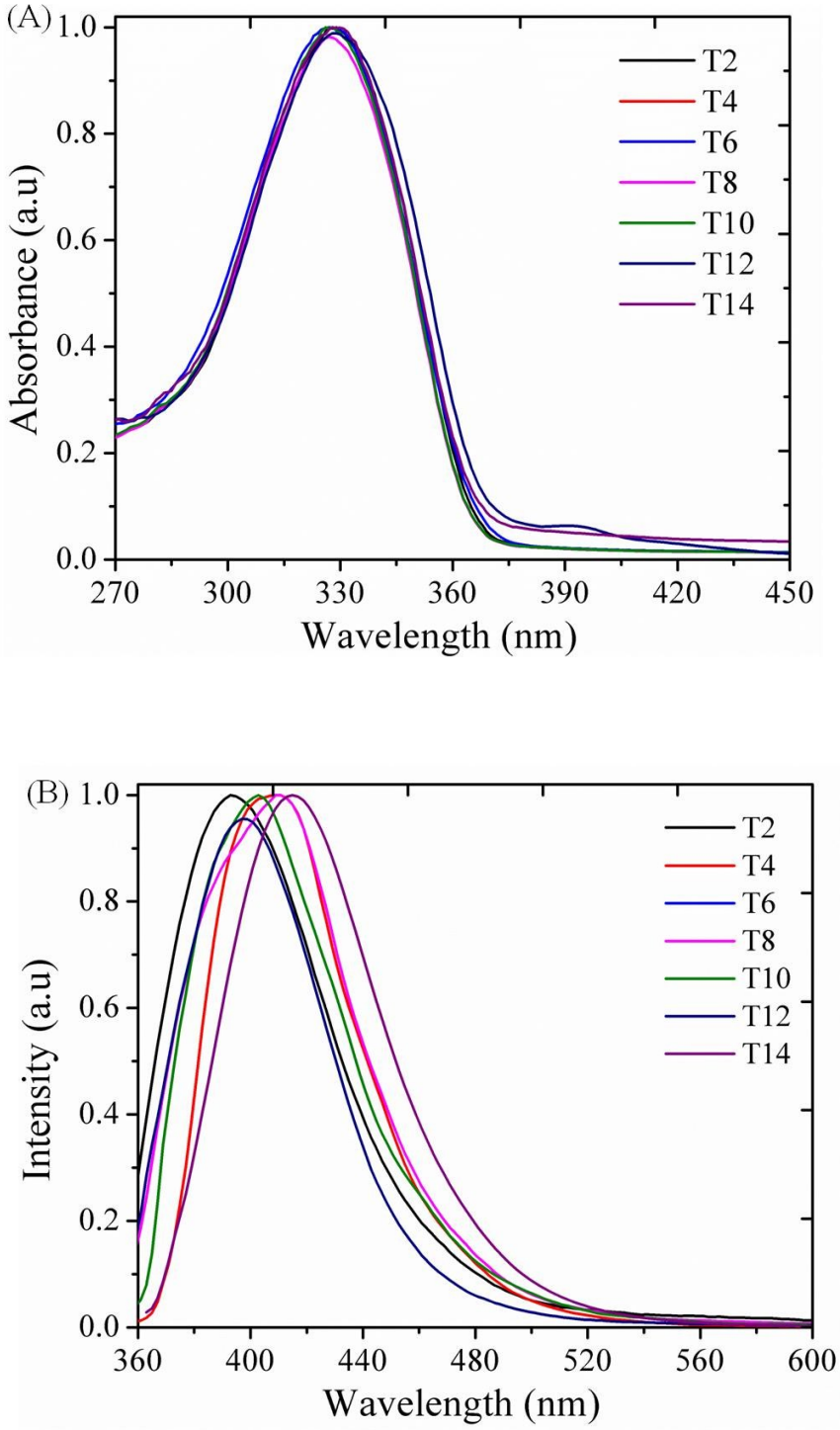


Figure 13: UV-vis (A) absorption (B) emission spectrum of mesogens in chloroform solution.

ESI-REFERENCES:

1. W. Greene, *Protecting Groups in Organic Synthesis*, John Wiely & Sons. New York, 1999.
2. B. Neises, W. Steglich, *Angew. Chem. Int. Ed*., 1978, **17**, 522-524.
3. G. Buchi, S. M. Weinreb, *J. Am. Chem. Soc*., 1971, **93**, 746.
4. M. Alaasar, M. Prehm, M. Brautzsch, and C. Tschierske*, J. Mater. Chem. C*, 2014, **2**, 5487–5501.
5. B. Lie´gault, D. Lapointe, L. Caron, A. Vlassova, and K. Fagnou, *J. Org. Chem.* 2009, **74**, 1826–1834.