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Direct Method to Grasp Molecular Topology of Mesogens through ^{13}C-^{1}H Dipolar Couplings

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EXPERIMENTAL

Materials

3-hydroxy methylbenzoate, 4-hydroxy benzaldehyde, 3,4- dihydroxybenzaldehyde, Bromododecane, 2-fluoro 4-nitrophenol, 4-formyl benzoic acid, N, N′-dicyclohexylcarbodiimide (DCC), 4-dimethylamino pyridine (DMAP), 10% palladium on charcoal (Pd/C), dodecyl benzoic acid, N-Boc-4-amino phenol, 4-hydroxy methyl benzoate, and trifluoroacetic acid were purchased from Aldrich (USA) and used without further purification. iron powder, triethylamine, N, N′-dimethylformamide (DMF), tetrahydrofuran (THF), isopropanol, ethanol, methanol chloroform, n-butyl bromide, thionylchloride, acetonitrile (ACN), ethyl acetate, cyclohexane, calcium chloride (SD Fine, Mumbai, India) were used as received. Dichloromethane, ethyl acetate, diethyl ether, n-hexane, n-heptane, acetone, 1,4-dioxane, toluene, glacial acetic acid, ethyl methyl ketone (EMK), potassium hydroxide (pellets), sodium chloride, ammonium chloride, anhydrous $MgSO_4$, anhydrous potassium carbonate, anhydrous sodium sulphate, sodium hydroxide, sodium bicarbonate, Celite-540 and silica gel (100-200 mesh) and hydrochloric acid were obtained from Merck

(India) and used as such. 4-Aminophenyl 4-(octyloxy)benzoate was a custom made and purchased from Sreeni Labs, Hyderabad (India).

Instrumental conditions

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-III 400 MHz at room temperature using tetramethylsilane as an internal standard in $CDCl_3$. Fourier transform infrared (FT-IR) spectra of all the compounds were recorded by Perkin Elmer UATR TWO spectrometer. The nature of the mesophase and the temperature of occurrence were determined with Carl Zeiss Axiocam MRC5 polarising optical microscope equipped with Linkam THMS 600 stage with TMS 94 temperature programmer. The samples were placed between 12 mm glass cover slips and transferred to heating stage and were heated with a programmed heating rate. The photographs were taken using imager A2M digital camera. DSC measurements were performed with DSC 214 (Netzsch) with a heating rate of 10°C/min. Each sample is subjected to two heating and cooling cycles and the data obtained on second cycle is considered for discussion. Variable temperature powder X-ray diffraction (VTXRD) studies were carried out on unoriented samples (Lindemann capillary; diameter of 1 mm; Hampton Research, Aliso Viejo, CA, USA) using a PANalytical instrument (DY 1042-Empyrean) operating with a linefocused Ni-filtered Cu Kα (λ = 1.54 Å) beam and a linear detector (PIXcel 3D). The sample temperature was controlled with a precision of 0.1°C using a Linkam heater and a temperature controller.[1]

Solid state ^{13}C NMR experiments

All solid-state ^{13}C NMR experiments (under static conditions) in the mesophase are performed on a Bruker AV-III HD WB 400 NMR spectrometer (9.4 T) with an operating frequency of ^{1}H: 400.07 and ^{13}C:100.61 MHz. Bruker 5 mm double resonance VTN static probe is used for the measurements fitted with a 5 mm horizontal solenoid coil. A 4 mm zirconia rotor is used to pack powdered samples, closed with a zirconia cap, inserted into a

5mm glass tube, and placed inside the horizontal coil for the measurement. The mesogens L1 and B1 are heated to the respective isotropic phase and slowly cooled to the mesophase for the measurements. For R1 mesogen, clearing temperature could not be reached due to NMR probe limitation; hence, the sample was heated up to 230 C° and slowly cooled down for the measurement. 1D spectrum at different temperatures is obtained using a standard ramp-CP scheme with a contact time of 3 ms, a radio frequency (rf) power of 50 kHz, typical number of scans of 128/128/196 (R1/L1/B1), and a recycle delay of 8 s. The 2D SAMPI-4 pulse sequence[2] was used to get ^{13}C-^{1}H dipolar couplings associated with ^{13}C Chemical shifts. This sequence's experimental condition and utility in the context of topological variant liquid crystalline systems are highlighted in earlier reports.[3–5] The employed experimental parameters for mesogens R1/L1/B1 were: 1H 90^{o} pulse width: 5 μs, CP contact time τ: 3 ms, the number of t_1 points: 128/128/100, the number of scans: 30/24/64, relaxation delays: 14 s/15 s/15 s (to avoid sample heating). The 2D data matrix of size 4096 × 256 was double Fourier transformed, and the qsine window function was used in both F1 and F2 dimensions. For both 1D and 2D experiments, SPINAL-64 [6] proton decoupling scheme is employed during the carbon acquisition with an rf irradiation of 30 kHz. Bruker BVTB-3500 unit regulated the sample temperature. The chloroform ^{13}C resonance at 77.2 ppm was used as an external reference.[7]

Synthesis of R1, L1 and B1 Mesogens

Synthesis of R1 Mesogen

4-dodecyloxy benzoic acid – 1(A)

This was prepared by a two-step process – (i) In an experiment, 4-hydroxy methyl benzoate (6 g, 0.04 mol) was placed in a 500 ml three necked round bottom flask equipped with stirrer and thermometer. To that, N,N′-dimethylformamide (150 ml) and potassium carbonate (6.21 g, 0.045mol) were added. The resulting mixture was stirred while maintaining the

temperature at 90 ˚C, then n-bromododecane (9.6 ml, 0.04 mol) was added through a pressure equalizing dropping funnel over a period of 30 minutes and the stirring was continued for about 5 hours and then the reaction mixture was allowed to cool to room temperature, poured into a two liter beaker. The contents were diluted with water (250 ml) and then transferred to a 500 ml separating funnel and diethyl ether was added. The ether layer collected was washed twice using 10% potassium hydroxide solution and followed by distilled water. The organic layer was dried with anhydrous sodium sulphate. Upon evaporation of ether, 4-dodecyloxy methyl benzoate resulted as a liquid.[8] (ii) 4-dodecyloxymethyl benzoate (10 g, 0.03 mol) was placed in a one liter single necked round bottom flask equipped with double wall water condenser. Ethanol (250 ml) and potassium hydroxide (4.37 g, 0.075 mol) dissolved in distilled water (250 ml) were added to the flask. The solution was refluxed for two hours and allowed to cool to room temperature and then neutralized with 10% hydrochloric acid to get a white precipitate.[9] The acid was purified by recrystallizing from methanol.

Yield: 80%, m.p-96.5˚C, FT-IR (KBr, cm^{-1}): 2921, 2851 (C-H_{str}), 2558 (O-$H_{str.}$of carboxylic acid), 1681 (C=O_{str} of carboxylic acid), 1605, 1512 (C=C_{str}aromatic), 1467, 1427 (C-H_{ben}), 1255, 1167 (C-O-C $_{asym\&symstr}$ ether); ^{1}H-NMR ppm ($CDCl_3$): 8.05 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.34 (m, 16H), 0.87 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 171.91, 163.86, 132.42, 120.91, 114.27, 68.38, 32.02, 29.76, 29.73, 29.69, 29.65, 29.45, 29.17, 26.06, 22.79 and 14.23.

Preparation of 4-aminophenyl 4-dodecyloxybenzoate – 1(B)

This was also synthesized by two-step process – (i) In an experiment, 4-dodecyloxy benzoic acid (5 g, 0.016 mol) and N-Boc-4-amino phenol (3.41 g, 0.016 mol) were placed in a 250 ml conical flask. To this, dichloromethane (150 ml) was added and the solution was stirred at room temperature with magnetic stirrer. 4-dimethylamino pyridine (0.19 g, 0.0016 mol) was added as a catalyst to the solution. After 10 minutes, dicyclohexylcarbodiimide (3.5 g, 0.017

mol) dissolved in dichloromethane was added to the flask and the solution was allowed to stir for 15 hours.[10] Then the precipitated N, N′-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into separating funnel and then washed with 5% KOH solution (2×100 ml), 10% HCl solution (2×100 ml) and followed by distilled water (3×100 ml).The organic layer collected was dried over anhydrous sodium sulphate. Upon evaporation of solvent, the white solid resulted was purified by recrystallization from isopropyl alcohol. (ii) In an experiment, 4-[(tert-butoxycarbonyl)amino]phenyl dodecyloxybenzoate (3 g, 0.006 mol) was placed in a 250 ml two necked round bottom flask which was kept in an ice bath. Dichloromethane (150 ml) was added to the flask while maintaining the temperature at 0˚C. Then trifluoroacetic acid (8.62 ml, 0.116 mol) was added and the reaction mixture was stirred for two hours.[11] Later it was taken out of the ice bath, saturated sodium bicarbonate solution (50 ml) was added and stirred for 20 minutes. The contents were transferred to a 500 ml separating funnel and dichloromethane was added. The organic layer was washed twice with 1% potassium hydroxide and distilled water respectively. Upon evaporation of dichloromethane, solid 4-aminophenyl 4-dodecyloxybenzoate was resulted. It was purified by recrystallization from heptane.

Yield: 71.5 %, m.p-96˚C, FT-IR (KBr, cm^{-1}): 3460, 3372 (NH_{2str}), 2954, 2919, 2850 (C-H_{str}), 1715 (C=O_{str}), 1629 (NH_{ben}), 1605, 1579, 1513 (C=C_{str} aromatic), 1471, 1420 (C-H_{ben}), 1258, 1191, 1167, 1120 (C-O-C $_{asym\&symstr}$ of ester and ether respectively); ^{1}H-NMR ppm ($CDCl_3$): 8.13 (d, 2H), 6.98 (m, 4H), 6.70 (d, 2H), 4.02 (t, 2H), 3.65 (s, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.34 (m, 12H), 0.89 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 165.66, 163.46, 144.26, 143.23, 132.27, 122.47, 121.88, 115.78, 114.30, 68.38, 32.01, 29.67, 29.48, 29.44, 29.21, 26.09, 22.81 and 14.26.

Synthesis of 4-formylphenyl 4-(dodecyl) benzoate – 1(C)

A mixture of 4-dodecylbenzoic acid (4 g, 0.0137 mol) and 4-hydroxy benzaldehyde (1.68 g, 0.0137 mol) were placed in a conical flask. Dichloromethane (100 ml) was added to the flask and the solution was stirred at room temperature. To this mixture, 4-dimethylamino pyridine (0.17 g, 0.00137mol) was added as a catalyst. After 10 minutes, N, N¹-dicyclohexylcabodiimide (2.98 g, 0.0145 mol) was added to the flask and the solution was allowed to stir for 12 hours.[12] The precipitated N, N′-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into separating funnel, washed sequentially with 5% aqueous acetic acid (2×100 ml), cold 5% aqueous sodium hydroxide (2×100 ml) and distilled water (3×100 ml) and then dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the solid obtained was crystallized from isopropyl alcohol.

Yield: 63.9%, m.p-63°C, FT-IR (KBr, cm^{-1}): 2956, 2918, 2847($C\text{-}H_{str}$), 1739($C{=}O_{str}$),1698(-HC=O), 1601, 1504, 1574 ($C{=}C_{str}$ aromatic),1461($C\text{-}H_{ben}$), 1389, 1265, 1176, 1158(C-O-C $_{asym\&symstr}$ of ester and ether respectively);^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 9.99(s, 1H), 8.10(d, 2H), 7.95(d, 2H), 7.39(d, 2H), 7.32(d, 2H), 2.69(t, 2H), 1.64(m, 2H), 1.36(m, 18H), 0.8(t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm):191.13, 164.66, 155.92, 150.05, 134.04, 131.36, 130.45, 128.90, 126.35, 122.68, 46.08, 36.20, 32.01, 29.75, 29.73, 29.65, 29.54, 29.44, 29.34, 22.78 and 14.22.

Synthesis of four ring Mesogen (R1)

In an experiment, aminophenyl 4-dodecyloxy benzoate (0.79 g, 0.002 mol) and 4-formyl phenyl-4-dodecyl benzoate (0.78 g, 0.002 mol) were taken into a 100 ml conical flask. Few 0.5 ml of ethanol and few drops of acetic acid were added and the flask was placed in a microwave oven (power: 40 W) for 15 minutes.[13] Then it was allowed to cool to room

temperature, the solid obtained was washed with methanol and recrystallized twice from ethyl methyl ketone.

Yield: 70.8%, m.p-93.5˚C, FT-IR (KBr, cm^{-1}): 2953, 2920, 2870 (C-H_{str}), 1731(C=O_{str}), 1624(-C=N_{str}), 1605, 1580, 1509(C=C_{str} aromatic),1470,1417(C-H_{ben}), 1273, 1255, 1237, 1206, 1187, 1170, 1161, 1118(C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 8.49(s, 1H), 8.16(d, 2H), 8.14(d, 2H), 7.97(d, 2H), 7.32(m, 2H), 7.31(m, 2H), 7.26(d, 2H), 7.24(d, 2H), 6.96(d, 2H), 4.04(t, 2H), 2.70(t, 2H), 1.82(m, 2H), 1.67(m, 2H), 1.49(m, 2H), 1.32(m, 34H), 0.88(m, 6H); ^{13}C-NMR ppm ($CDCl_3$): 165.03, 165.87, 163.58, 159.20, 153.50, 149.65, 149.42, 149.29, 133.81, 132.28, 130.31, 130.05, 128.72, 126.68, 122.44, 122.24, 121.79, 121.52, 114.31, 68.42, 36.21, 32.02, 31.25, 29.75, 29.70, 29.67, 29.57, 29.47, 29.36, 29.20, 26.09, 22.80 and 14 25.

Synthesis of L1 Mesogen

Preparation of 4-butoxy benzoic acid – 2(A)

A two-step process was employed for preparing4-butoxy benzoic acid – (i) 4-hydroxy methyl benzoate (18 g, 0.12 mol) and n-butyl bromide (10.78 ml, 0.1 mol) were taken in a 250 ml single necked round bottom flask equipped with a double-wall water condenser. The flask was immersed in an oil bath which was placed on a magnetic stirrer and the temperature was maintained at 85 °C. To that, acetonitrile (ACN) (200 ml) and potassium carbonate (17 g, 0.12 mol) were added. The resulting mixture was stirred for about 20 hours and then the reaction mixture was allowed to cool to room temperature and the solvent was removed using rotavapor. The contents were dissolved in dichloromethane and transferred to 250 ml separating funnel and extracted with water twice (100 ml). The dichloromethane layer was collected and the solvent was evaporated using a rotavapor. The liquid obtained was purified by column chromatography using ethyl acetate: hexane (5: 95 v/v) as eluents.[8] ; (ii)

Methyl 4-butoxybenzoate (17 g, 0.079 mol) was placed in a 500 ml single necked round bottom flask fitted with a double-wall water condenser. Ethanol (200 ml) and potassium hydroxide (9 g, 0.016 mol) were added to the flask. The reaction mixture was refluxed for four hours using oil bath and then cooled to room temperature.[9] It was neutralized with 10% hydrochloric acid to get white precipitate which washed twice with water. The 4-butoxy benzoic acid obtained was purified by recrystallization from cyclohexane.

Yield: 85%, m.p-147.0˚C, FT-IR (KBr, cm^{-1}): 2920, 2852 (C-H_{str}), 2560 (O-$H_{str.}$of carboxylic acid), 1683 (C=O_{str} of carboxylic acid), 1605, 1512 (C=C_{str}aromatic), 1465, 1424 (C-H_{ben}), 1250, 1165 (C-O-C $_{asym\&symstr}$ ether); ^{1}H-NMR ppm ($CDCl_3$): 8.05 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.79 (m, 2H), 1.34 (m, 2H), 0.87 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 171.89, 163.79, 132.32, 120.71, 114.25, 68.30, 32.00, 22.79 and 14.23.

Synthesis of 4-formyl-1,2-phenylenebis(4-butyloxybenzoate) 2(B)

It was also synthesized in two steps – (ii) 4-Butoxy benzoic acid (20 g, 0.1mol) was placed in a 500 ml single necked round bottom flask fitted with a double wall reflux condenser with calcium chloride guard tube, $SOCl_2$ (12 ml, 0.11 mol), and a few drops of DMF were added to the flask.[14] The reaction mixture was refluxed for one hour and the unreacted $SOCl_2$ was removed by vacuum pump to get 4-butoxy benzoyl chloride as liquid. (ii) 3,4-Dihydroxybenzaldehye (7.11 g, 0.05 mol) and triethylamine (15.3 ml, 0.11 mol) dissolved in methyl ethyl ketone (150 ml) was taken in 500 ml two necked round bottom flask fitted with stirrer and cooled in an ice bath at 0 ^{o}C. To this, 4-butoxy benzoyl chloride dissolved in EMK (50 ml) was slowly added drop wise through a dropping funnel for 45 minutes while stirring the contents. The triethylamine salt was filtered and the solvent was removed using rotavapor. The solid obtained was purified by column chromatography using ethyl acetate: hexane (v/v: 10/90) mixture.

FT-IR (KBr, cm^{-1}): 2969.1, 2932.7, 2837.8 (C-H_{str}), 1736.0 (C=O_{str} of ester), 1697.7 (C=O_{str} of aldehyde), 1601.9, 1579.0 (C=C_{str} aromatic), 1421.9(C-H_{ben}), 1262.9, 1241.9, 1167.2, 1100.1, 1044.6 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.99 (d, J = 2.1 Hz, 2H), 7.97 (s, 1H), 7.90 (d, J = 1.9 Hz, 1H), 7.84 (dd, J = 8.3, 1.9 Hz, 1H), 7.55 (d, J = 4.1 Hz, 1H), 6.84 (dd, J = 4.2, 2.0 Hz, 2H), 6.82 (dd, J = 4.4, 2.4 Hz, 2H), 3.97 (t, J = 6.5, 1.9 Hz, 4H), 1.81 – 1.70 (m, 4H), 1.54 – 1.43 (m, 4H), 0.97 (t, J = 7.4, 0.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.22, 163.85, 163.79, 163.71, 163.37, 147.94, 143.57, 134.67, 132.45, 132.40, 127.96, 124.69, 124.37, 120.33, 120.23, 114.35, 114.33, 68.00, 31.08, 19.16, 13.78.

Synthesis of lateral ring Mesogen (L1)

4-Formyl-1,2-phenylenebis(4-butyloxybenzoate) (350 mg,1.12 mol) and 4-aminophenyl 4-(octyloxy)benzoate (383 mg,1.12 mol) were taken in a 250 ml conical flask, and to that 5 ml of ethanol and two drops of acetic acid were added.[13] The contents were heated in microwave oven (100 W) for 10 minutes. The conical flask was cooled to room temperature and the solid was washed with methanol. It was purified by recrystallization in heptane.

FT-IR (KBr, cm^{-1}): 2954, 2874 (C-H_{str}) 1734 and 1727 (C=O_{str} of ester), 1605 (C=N_{str}), 1510 (C=$C_{skeletal}$), 1466, 1420 (C-H_{ben}), 1246, 1163 (C-O-C stretching of ester), 1056, 1109 (C-O-C stretching of ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.17 – 8.13 (m, 2H), 8.03 (d, J = 1.9 Hz, 1H), 8.02 (d, J = 2.4 Hz, 2H), 8.00 (s, 1H), 7.97 (d, J = 1.9 Hz, 1H), 7.84 (dd, J = 8.4, 1.9 Hz, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.25 – 7.22 (m, 2H), 7.00 – 6.95 (m, 2H), 6.86 (dd, J = 4.8, 2.0 Hz, 2H), 6.85 – 6.82 (m, 2H), 4.04 (t, J = 6.6 Hz, 2H), 3.99 (td, J = 6.5, 2.3 Hz, 4H), 1.86 – 1.73 (m, 6H), 1.52 – 1.45 (m, 6H), 1.42 – 1.25 (m, 9H), 0.98 (dd, J = 7.6, 7.1 Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 163.95, 163.76, 163.68, 163.65, 163.59, 158.45, 149.40, 149.19, 145.36, 143.27,

134.78, 132.41, 132.39, 132.30, 127.13, 123.97, 123.57, 122.48, 121.85, 121.52, 120.68, 120.62, 114.33, 114.28, 68.36, 67.99, 31.82, 31.12, 29.34, 29.23, 29.12, 26.00, 22.67, 19.18, 14.11, 13.81.

Synthesis of B1 Mesogen

3-benzyloxy benzoic acid – 3(A)

This was prepared by a two-step process; (i) 3-hydroxy methylbenzoate (15.2 g, 0.1mol) was placed in a 500 ml three neck round bottom flask equipped with stirrer and thermometer. Potassium carbonate (20.7 g, 0.15 mol) and DMF (200 ml) were added to the flask. The resulting mixture was stirred while maintaining the temperature at 90˚C. Then benzyl bromide (11.8 ml, 0.1 mol) was added through a pressure equalizing dropping funnel over a period of 45 minutes and the stirring was continued for 6 hours and then the reaction mixture was allowed to cool to room temperature, poured into a two liter beaker containing 150 ml distilled water.[8] This was neutralized with 10% HCl solution until it turned litmus paper to red color and the solid regenerated was filtered using Buchner funnel and was washed with 10% KOH solution, followed by distilled water and then dried in vacuum oven. (ii) 3-benzyloxy methylbenzoate (19.36 g, 0.08 mol) was placed in a 1000 ml single neck round bottom flask equipped with double wall water condenser. Ethanol (200 ml) and potassium hydroxide solution (11.2 g, 200 ml) in equal volume were added to the flask. The reaction mixture was refluxed for three hours and then allowed to cool to room temperature.[9] It was neutralized with 10% hydrochloric acid to get white solid which was dried and recrystallized from heptane.

Yield: 79.2%, m.p-141˚C, FT-IR (KBr, cm^{-1}): 3006 (aromatic C-H_{str}), 2948 (C-H_{str}), 2880, 2840 (O-H_{Str} of carboxylic acid), 1709 (C=O_{str} of carboxylic acid), 1638, 1590 (C=C_{str} aromatic), 1492, 1382 (C-H_{ben}), 1270, 1155,1106 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-

NMR ppm ($CDCl_3$): 7.76 (d, 1H), 7.74 (s, 1H), 7.47 (m, 1H), 7.41 (d, 2H), 7.37 (d, 2H), 7.35 (m, 1H), 7.24 (m, 1H), 5.12 (s, 2H).

4-formylphenyl 3-(benzyloxy) benzoate – 3(B)

In an experiment, 3-benzyloxy benzoic acid (6 g, 0.026 mol) dissolved in dichloromethane placed in a 250 ml conical flask which was kept on magnetic stirrer and 4-hydroxy benzaldehyde (3.2 g, 0.026 mol) dissolved in THF was added. Then, 4-dimethylaminopyridine [DMAP] (0.3 g, 0.0026 mol) was added as a catalyst. To the reaction flask, N,N′-dicyclohexylcarbodiimide (DCC) (5.97 g. 0.029 mol) was added and stirred for about 15 hours at room temperature.[12] The precipitated N, N′-dicychlohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into separating funnel, washed with 5% aqueous acetic acid (2×100 ml), cold 5% aqueous sodium hydroxide (2×100 ml) and distilled water (3×100 ml) sequentially, dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the solid obtained was recrystallized from methanol and isopropanol mixture.

Yield: 67%, m.p-89.3˚C, FT-IR (KBr, cm^{-1}): 2943, 2881, 2826, ($C\text{-}H_{str}$), 2733 ($C\text{-}H_{str}$ of aldehyde) 1734 ($C{=}O_{str}$), 1693 ($C{=}O_{str}$ of aldehyde), 1588, 1493 ($C{=}C_{str}$ aromatic), 1440,1385 ($C\text{-}H_{ben}$), 1277, 1160 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 10.02 (s,1H), 7.98 (d, 2H), 7.80 (d, 2H), 7.45 (m, 2H), 7.41 (d, 2H), 7.39 (d, 2H), 7.34 (m, 1H), 7.26 (m, 1H), 5.14 (s, 2H); ^{13}C-NMR ppm ($CDCl_3$): 191.04, 164.42, 159.02, 155.77, 136.43, 134.19, 131.38, 130.29, 129.92, 128.78, 128.31, 127.66, 123.01, 122.62, 121.30 and 115.92.

4-formylphenyl 3-hydroxybenzoate – 3(C)

In a representative experiment, 4-formylphenyl 3-(benzyloxy) benzoate (5 g, 0.015mol) dissolved in THF (100 ml) was added to 250 ml three neck round bottom flask which was placed on magnetic stirrer. 10% Pd/C (0.5 g) was slowly added to the solution. The mixture was stirred at room temperature in the presence of hydrogen atmosphere.[15] After the completion of reaction, the mixture was filtered using celite-540 and the solvent was removed under reduced pressure. The solid obtained was purified by column chromatography on silica gel and eluted with a mixture of 40% ethyl acetate in pet ether. Upon evaporation of solvent, solid was formed which was recrystallized from toluene.

Yield: 49.1%, m.p-157˚C, FT-IR (KBr, cm^{-1}): 3291 ($-OH_{str}$), 2724 ($C-H_{str}$ of aldehyde) 1738 ($C=O_{str}$), 1684 ($C=O_{str}$ of aldehyde), 1587, 1490 ($C=C_{str}$ aromatic), 1423, 1394 ($C-H_{ben}$), 1250, 1200, 1150 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm (DMSO-d6): 10.01 (s, 1H), 7.97 (d, 1H), 7.76 (d, 1H), 7.64 (s, 1H), 7.40 (d, 2H), 7.37 (s, 1H), 7.15 (m, 1H), 5.98 (s, -OH).

4-formylphenyl 3-(4-formylbenzoyloxy) benzoate - 3(D)

In a typical experiment, a mixture of 4-formylphenyl 3-hydroxybenzoate (3 g, 0.012 mol) and 4-formyl benzoic acid (1.85 g, 0.012 mol) were placed in a 250 ml conical flask and the flask was kept on magnetic stirrer. THF and DMAP (0.2 g, 0.0012 mol) were added followedby N, N'-dicyclohexyl carbodiimide (DCC) (3.1 g 0.015 mol) dissolved in dichloromethane and stirred for about 15 hours at room temperature.[12] The precipitated N,N′-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (50 ml). On evaporation of solvent the solid formed was taken into separating funnel, dichloromethane was added and was washed with 5% aqueous acetic acid (2×100 ml), cold 5% aqueous sodium hydroxide (2×100 ml), distilled water (3×100 ml) and dried over anhydrous sodium

sulphate. The solvent was removed under reduced pressure and the solid obtained was chromatographed on silica gel using a mixture of 10% ethyl acetate in chloroform as an eluent. The removal of solvent from the eluent gave a solid which was crystallized from EMK.

Yield: 57.7%, m.p-144˚C, FT-IR (KBr, cm^{-1}): 3073 (aromatic C-H_{str}), 2867, 2801 (C-H_{str}), 2757 (C-H_{str} of aldehyde), 1739 (C=O_{str}), 1699 (C=O_{str} of aldehyde), 1595, 1501 (C=C_{str}aromatic), 1442, 1391 (C-H_{ben}), 1258, 1210, 1158 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$) 10.13 (s, 1H), 10.00 (s, 1H), 8.37 (d, 2H), 8.14 (s, 1H), 8.07 (s, 1H), 8.04 (d, 2H), 7.95 (d, 2H), 7.61 (t, 1H), 7.55 (s, 1H), 7.41 (d, 2H); ^{13}C-NMR ppm ($CDCl_3$) 191.59, 191.04, 164.09, 163.62, 155.49, 150.91, 139.87, 134.29, 133.95, 131.42, 130.95, 130.71, 130.15, 129.82, 128.19, 127.48, 123.60 and 122.56.

2-fluoro-1-dodecyloxy-4-nitrobenzene – 3(a)

In an experiment, a mixture of 2-fluoro 4-nitrophenol (3.925 g, 0.025 mol), potassium carbonate (4.14 g, 0.03 mol) and DMF (125 ml) were placed in a 250 ml three necked round bottom flask equipped with stirrer and thermometer. While stirring the reaction mixture at 90˚C, 1-bromododecane (6.15 ml, 0.025 mol) was added through a pressure equalizing dropping funnel for about 40 minutes and the stirring was continued for 5 hours and then the mixture was allowed to cool to room temperature, poured into a 500 ml beaker.[8] The reaction mixture was diluted with distilled water (100 ml) and transferred into a 500 ml separating funnel and then extracted with diethyl ether. The ether layer collected was washed using 10% aqueous potassium hydroxide (2×100 ml) and followed by distilled water (3×100 ml). The organic layer was dried over anhydrous sodium sulphate. Upon evaporation of ether, resulted 4-dodecyloxy 2-fluro nitro compound as dark yellow liquid which was purified by column chromatography using a mixture of 2% ethyl acetate in pet ether as an eluent.

Yield: 78%, m.p-42˚C, FT-IR (KBr, cm^{-1}): 3093 (aromatic C-H_{str}), 2918, 2848 (C-H_{str}), 1606, 1514 (C=C_{str} aromatic), 1464, 1431 (C-H_{ben}), 1350 (-NO_{2str}), 1284, 1215, 1140 (C-O-C $_{asym\&symstr}$ of ether); ^{1}H-NMR ppm ($CDCl_3$): 8.04 (m, 1H), 7.96 (m, 1H), 7.00 (t, 1H), 4.11 (t, 2H), 1.85 (m, 2H), 1.46 (m, 2H), 1.36 (m, 16H), 0.86 (t, 3H).

4-dodecyloxy-3-fluoroaniline – 3(E)

In an experiment, a mixture of 2-fluoro-1-dodecyloxy-4-nitrobenzene (2 g, 0.0058 mol), iron powder (0.98 g), NH_4Cl (0.187 g) dissolved in water were added to the single necked round bottom flask fitted with double wall water condenser.[16] Ethanol (20.9 ml) was added to it and the reaction mixture was refluxed for about 2 hours and was cooled to room temperature, filtered through celite-540. The filtered cake was washed with methanol, and the solution was taken into separating funnel and extracted with diethyl ether, dried over anhydrous $MgSO_4$. The ether solution was concentrated to get a solid material.

Yield: 65.9%, m.p-65˚C, FT-IR (KBr, cm^{-1}): 3430, 3319 (NH_{2str}), 2954, 2919, 2849 (C-H_{str}), 1635 (NH_{ben}), 1589, 1561, 1514 (C=C_{str} aromatic), 1468, 1392 (C-H_{ben}), 1279, 1167, 1146, 1133 (C-O-$C_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 6.76 (m, 1H), 6.43 (m, 1H), 6.33 (m,1H), 3.90 (t, 2H), 3.42 (s, 2H), 1.72 (m, 2H), 1.42 (m, 2H), 1.28 (m, 17H), 0.86 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 162.63, 154.82, 152.88, 141.36, 141.30, 139.56, 139.46, 117.92, 117.90, 110.42, 110.40, 104.24, 104.07, 71.08, 32.02, 29.75, 29.73, 29.69, 29.67, 29.55, 29.49, 29.45, 26.01, 22.78 and 14.20.

Synthesis of Banana Mesogen (B1)

4-Formylphenyl 3-(4-formylbenzoyloxy) benzoate (0.5 g, 0.001 mol) and 4-dodecyloxy-3-fluoroaniline (0.60 g, 0.002 mol) were taken into a 100 ml single necked round bottom flask equipped with double wall water condenser. Few drops of acetic acid, toluene (50 ml) were added to the flask and refluxed for about three hours. Then it was cooled to

room temperature, filtered and washed thrice with methanol, dried in vacuum oven and finally recrystallized from EMK and ethyl acetate respectively.

Yield: 67.3%, m.p-140˚C, FT-IR (KBr, cm^{-1}): 2956, 2916, 2872 (C-H_{str}), 1731 (C=O_{str}),1651, 1628 (-C=N_{str}), 1608, 1576, 1522 (C=C_{str} aromatic), 1470, 1382 (C-H_{ben}), 1281, 1268, 1161 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 8.54 (s, 1H), 8.45 (s, 1H), 8.31 (d, 2H), 8.15 (d, 1H), 8.09 (s, 1H), 8.04 (d, 2H), 7.96 (d, 2H), 7.61 (m, 1H), 7.54 (d, 1H), 7.33 (d, 2H), 7.13 (dd, 1H), 7.07 (m, 2H), 6.99 (d, 2H), 6.97 (m, 1H), 4.04 (t, 4H), 1.83 (m, 4H), 1.46 (m, 4H), 1.35 (m, 33H), 0.87 (t, 6H); ^{13}C-NMR ppm ($CDCl_3$): 164.58, 164.0, 158.02, 157.44, 153.93, 153.14, 151.97, 151.07, 146.57, 145.87, 144.88, 144.17, 140.92, 134.12, 131.11, 131.01, 130.74, 130.08, 129.98, 128.84, 127.97, 127.40, 123.66, 122.22, 117.76, 117.30, 115.17, 115.0, 109.18, 109.02, 69.88, 69.83, 32.01, 29.74, 29.73, 29.68, 29.65, 29.44, 29.33, 29.30, 26.01, 22.79 and 14.22.

Results and Discussion

Mesophase assignment by HOPM, DSC, and XRD study

The complementary techniques like a hot-stage polarizing microscope (HOPM) and differential scanning calorimetry (DSC) are employed for mesophase assignment of synthesized molecules, while XRD is utilized for establishing the layer order typical for smectic mesophases. In HOPM, the samples are heated to an isotropic liquid phase, and on cooling, the texture formed is employed for identifying the liquid crystalline phase. Thus for R1 mesogen, on cooling the isotropic liquid from 258.0°C, the formation of birefringent droplets is noticed, which coalesced to form the marble texture, a typical characteristic of nematic mesophase (Fig. S1A).[17] At 233.2°C, the transition bars across the sample are seen (Fig. S1B), which are the archetype for nematic to SmC phase transition.[18] Upon further lowering of temperature, the SmC phase is noted with characteristic disclinations usually

observed for the SmC phase that appear on cooling from the nematic mesophase (Fig. S1C).[19] Another phase change is noticed at 130.3 °C, where the schlieren texture is seen with difficulty in focusing the texture (Fig. S1D).[7] The phase assignment for the 130.3 °C transitions is arrived at by using DSC and XRD data discussed later in the section. On further cooling, the sample undergoes crystallization at 112.3°C while crystal-to-crystal transition is noticed at 72.6°C. These phase changes are well supported by DSC scans where transitions at diverse temperatures with varying enthalpies are noted (Fig. S2A). It is clear from the DSC scans that all the transitions are enantiotropic as they appear both in heating and cooling cycles. Further, the enthalpy values are in agreement with literature data of rod-like mesogens exhibiting polymesomorphism.[20] Table S1 lists the mesophase transition temperatures and their enthalpy values for the R1 mesogen.

In the case of the L1 mesogen, the HOPM studies confirm the presence of the nematic phase (Fig. S1E). The sample, upon cooling from the isotropic liquid phase (194.5°C), birefringent texture with threads is observed (194.2°C). On further cooling, the formation of nematic schlieren texture is noticed.[17] On lowering the temperature, crystallization of the sample is seen at 73.7°C. These phase changes are confirmed by DSC heating and cooling scans. The DSC measurement concluded that the nematic phase is enantirotropic since the transitions are noted in heating and cooling cycles (Fig. S2B). Table S1 lists the transition temperatures along with their enthalpy values.

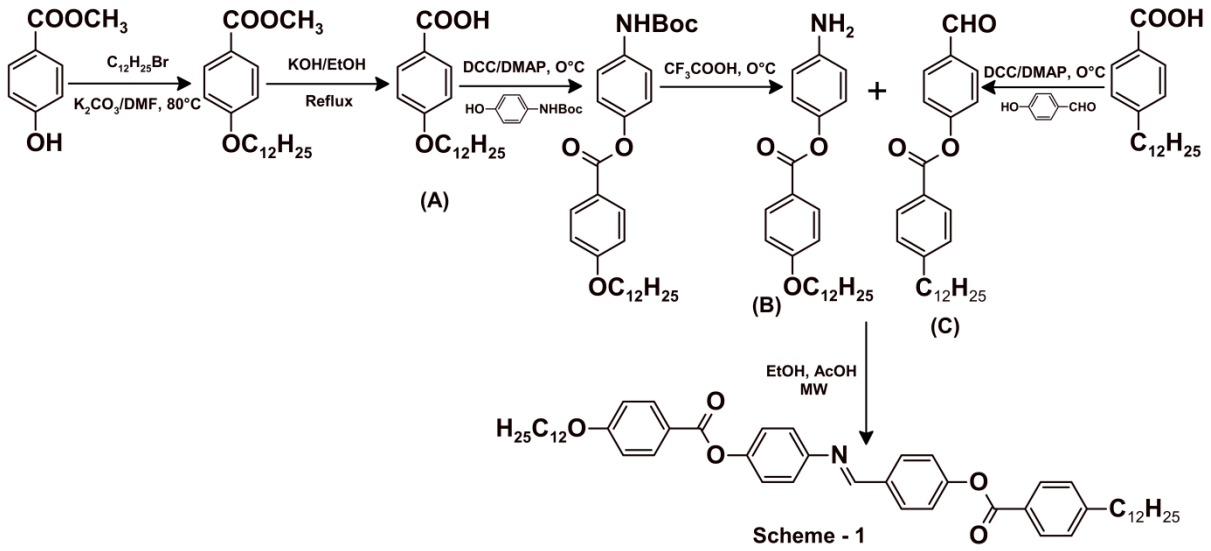
For B1 mesogen, in HOPM, on cooling the isotropic liquid from 155.5°C, the formation of batonnets are noticed at 154.5 °C, which on further cooling, coalesced to form fan texture (151.5°C) typical of SmA phase (Fig. S1F).[17] On further cooling, crystallization of the sample is noted at 109.1°C. In the DSC scan, the crystal to SmA phase transition is noticed at 123.5 °C, and SmA to isotropic phase change is observed at 155.2 °C (Fig. S2C). In the cooling cycle, the isotropic to SmA transition is noted at 154.5°C, and the SmA to

crystal transition is observed at 190.1°C. DSC measurements further support that the SmA mesophase is enantiotropic since the phase is appeared both in heating and cooling cycles. The transition enthalpy values of these phase changes are listed in Table S1. These values are consistent with the literature data on banana mesogens that exhibit SmA mesophase.[21]

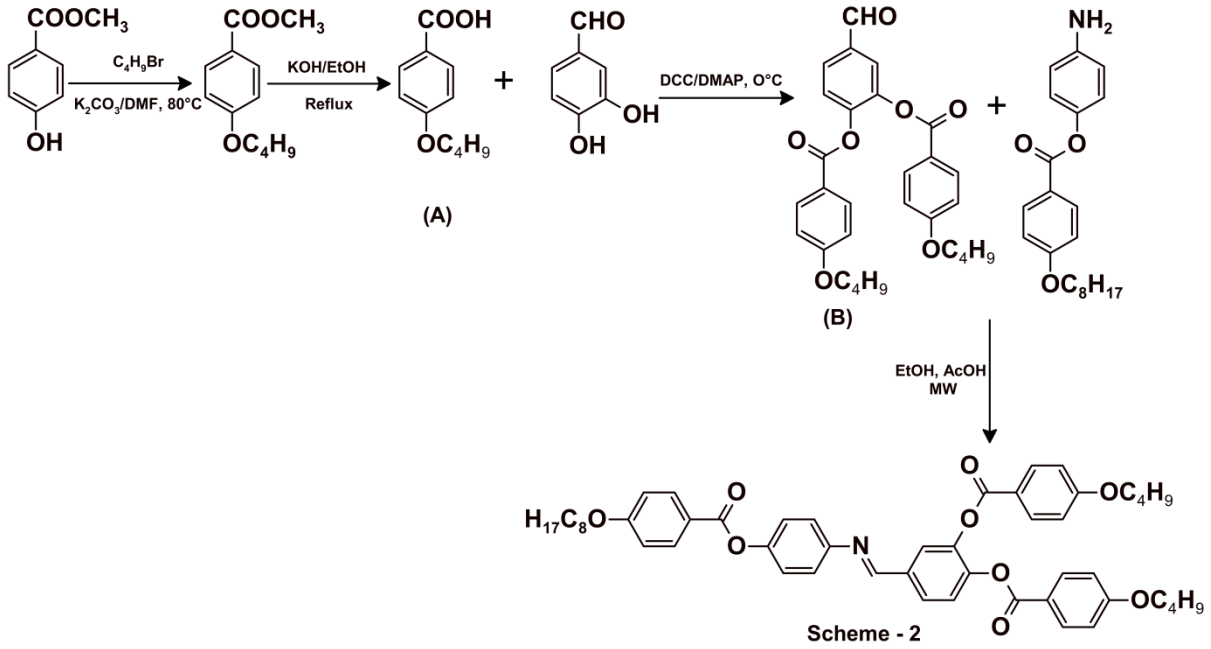
XRD studies further confirm the occurrence of smectic mesophases in R1 mesogen. Fig. S3A shows the XRD plot of R1 mesogen in SmC mesophase measured at 220.0 °C. In the small angle region, sharp and intense peak is noticed at 2θ = 2.518° corresponding to layer spacing (d) of 35.09 Å. In the wide-angle region, however, broad hump is observed at a d-spacing of 4.69 Å (2θ = 18.9°). The appearance of a small angle sharp peak indicates the presence of layer order archetype of smectic mesophase.[22] The wide-angle broad hump denotes the absence of in-plane order and liquid-like arrangements of the molecules. The molecular length (L) of R1 arrived from the quantum chemical calculation is 50.1 Å. The d/L ratio (0.68) is lower than 1, suggesting that the phase is a tilted smectic phase. In view of broad hump in the wide-angle region due to the absence of in-plane order and the d/L ratio being lower than 1, the mesophase is classified as SmC and is consistent with the HOPM observation. The XRD scan measured at 150.0 °C in SmC phase (Fig. S3B) also shows a sharp peak with a similar d value noticed for 220.0 °C. The broad hump at a wide angle region appears at a slightly different value (4.50 Å). An important observation for the 150.0 °C measurements is the presence of a second harmonic peak in the small angle region (2θ = 5.01°), indicating the sharpening of the layer interface. The XRD scan of 120.0 °C (Fig. S3C) shows sharp and intense peak in the small angle region at 2θ = 2.386° corresponding to layer spacing (d) of 37.03 Å and a low intense sharp peak in the wide-angle region. This is in contrast to high-temperature measurements where wide angle region exhibited a broad hump (2θ = 19.77°). Second-order reflection is observed in the small angle region similar to the 150.0 °C XRD scan (2θ = 4.77°) with better sharpness. The change in the d value and a sharp

wide-angle peak clearly indicates variation in the molecular arrangement. A low, intense sharp peak in the wide-angle region shows in-plane order characteristics of higher-order smectic mesophases. In the HOPM study, the schlieren texture is observed with difficulty in focusing at this temperature. In view of the schileren texture and inability to focus the texture in HOPM and sharp peak in the wide-angle region in XRD scan, the mesophase has been assigned as SmI phase.[23] Thus the combined studies of HOPM, DSC and XRD unambiguously confirm the occurrence of nematic, SmC and SmI mesophases for R1 mesogen.

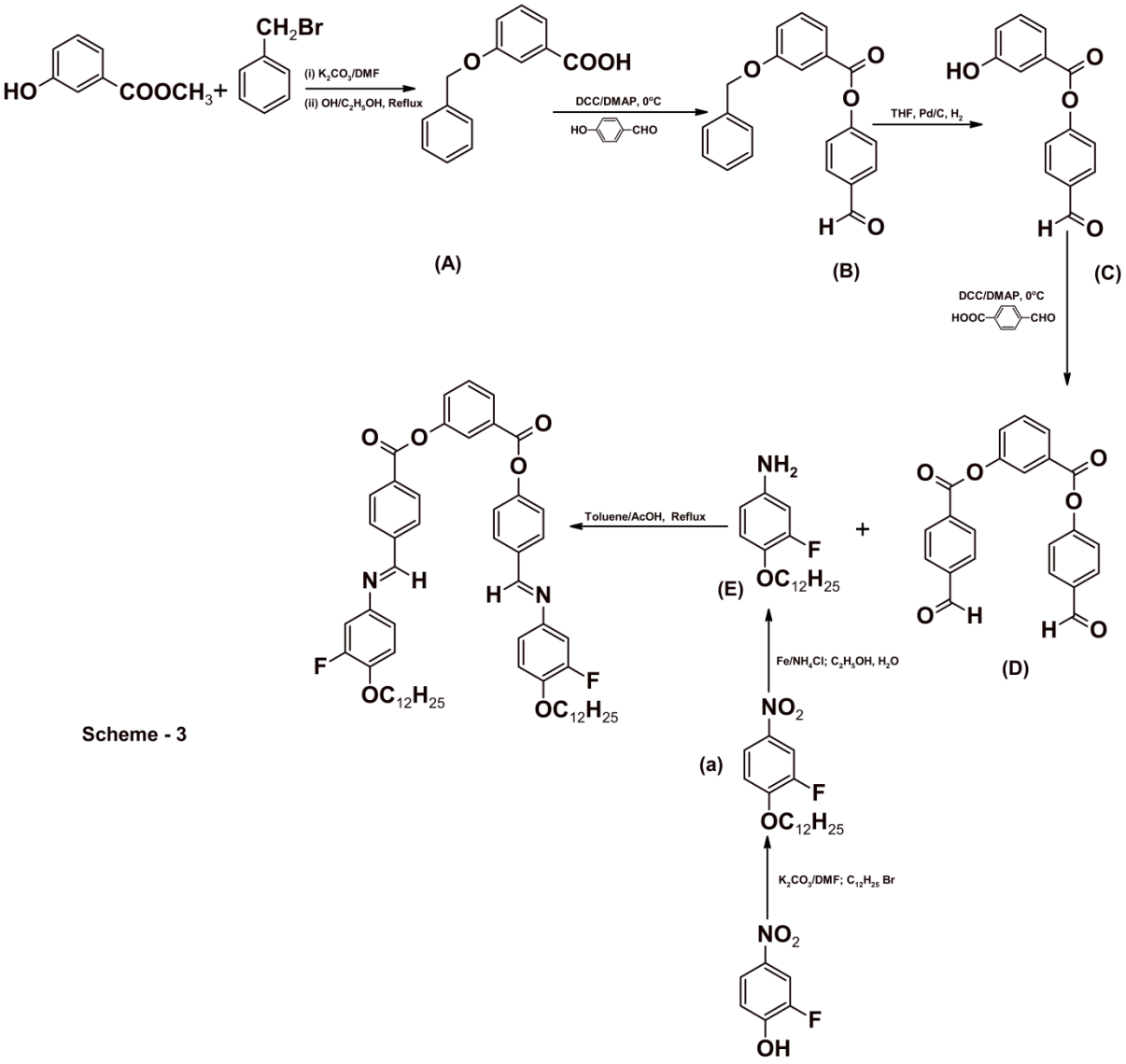
The XRD studies are also carried out for B1 mesogen to confirm the existence of SmA mesophase. The XRD profile of B1 mesogen measured at 130.0 °C is shown in Fig. S3D where in the small angle region, the sharp and intense peak is noted at 2θ = 1.782° with a layer spacing (d) of 49.58 Å. A second-order low intense sharp peak is also seen in the small angle region (2θ = 3.59°), while in the wide-angle region broad hump (2θ = 19.56°) is noticed. The sharp peaks observed in small angle region indicate the layer order typical of smectic mesophase, while the wide-angle diffuse peak advocates the absence of in-plane order and liquid-like arrangement of molecules in the layer.[24] The molecular length (L) measured from the quantum chemical calculation is 46.6 Å. Thus d/L value is equal to 1, indicating the orthogonal nature of the smectic phase. Further, the fluid nature of the phase is reflected in the diffuse peak observed in the wide-angle region. Therefore, the mesophase is confirmed as SmA in line with the HOPM observation where formation of batonnets leading to fan texture is noted.



Scheme S1: Synthetic strategy for realizing R1 mesogen



Scheme S2: Synthetic strategy for L1 mesogen



Scheme - 3

Scheme S3: Synthetic route for making B1 mesogen

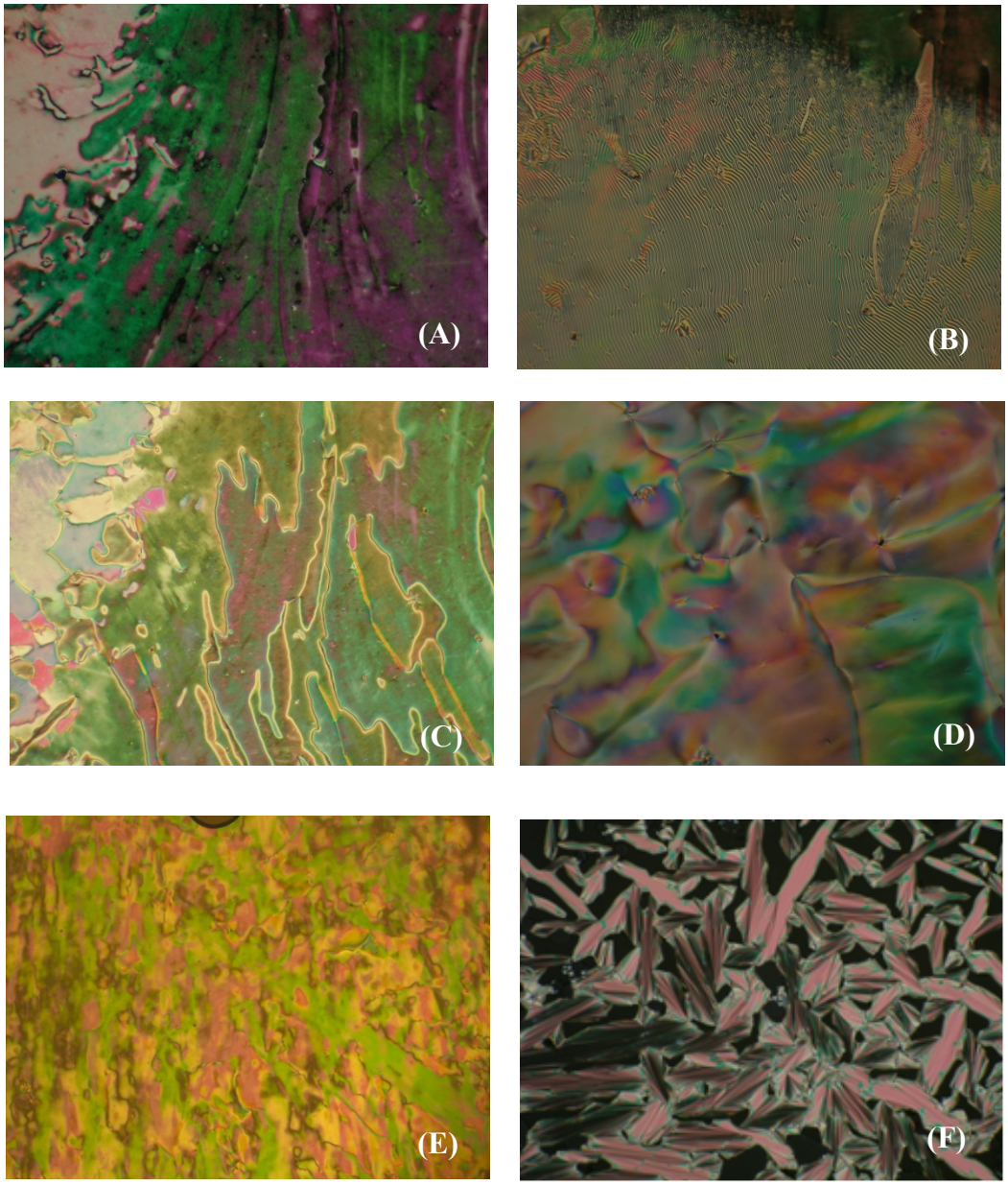


Fig. S1: HOPM images of (A) R1 at 256.0°C in Nematic phase; (B) R1 at 231.0°C transition bars; (C) R1 at 230.0°C in SmC phase; (D) R1 at 125.3°C in SmI phase; (E) L1 at 192.5°C in Nematic phase; (F) B1 at 151.5°C in SmA mesophase

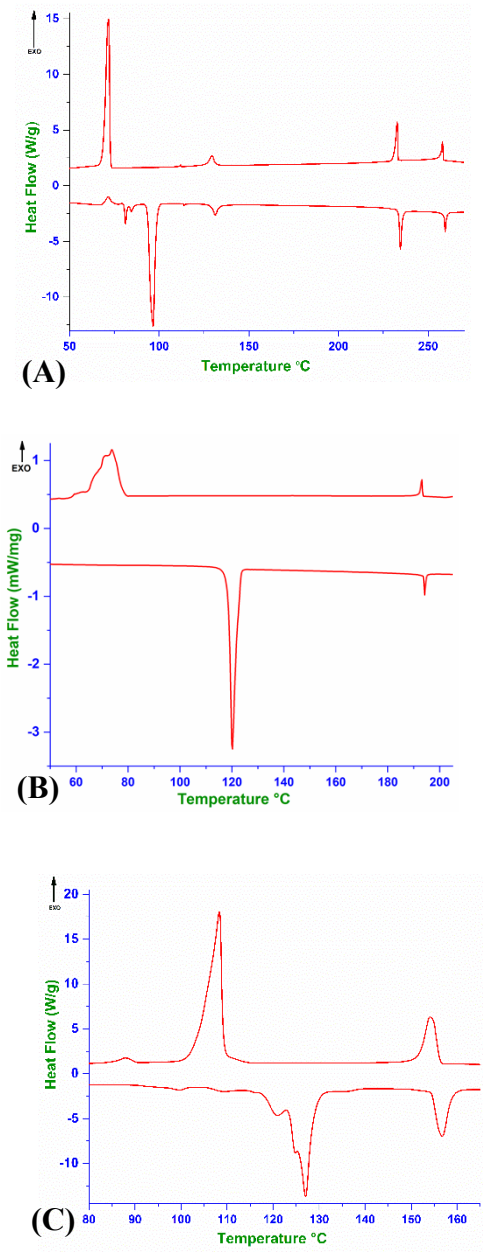


Fig. S2: DSC heating and cooling scans of (A) R1 (B) L1, and (C) B1 Mesogens

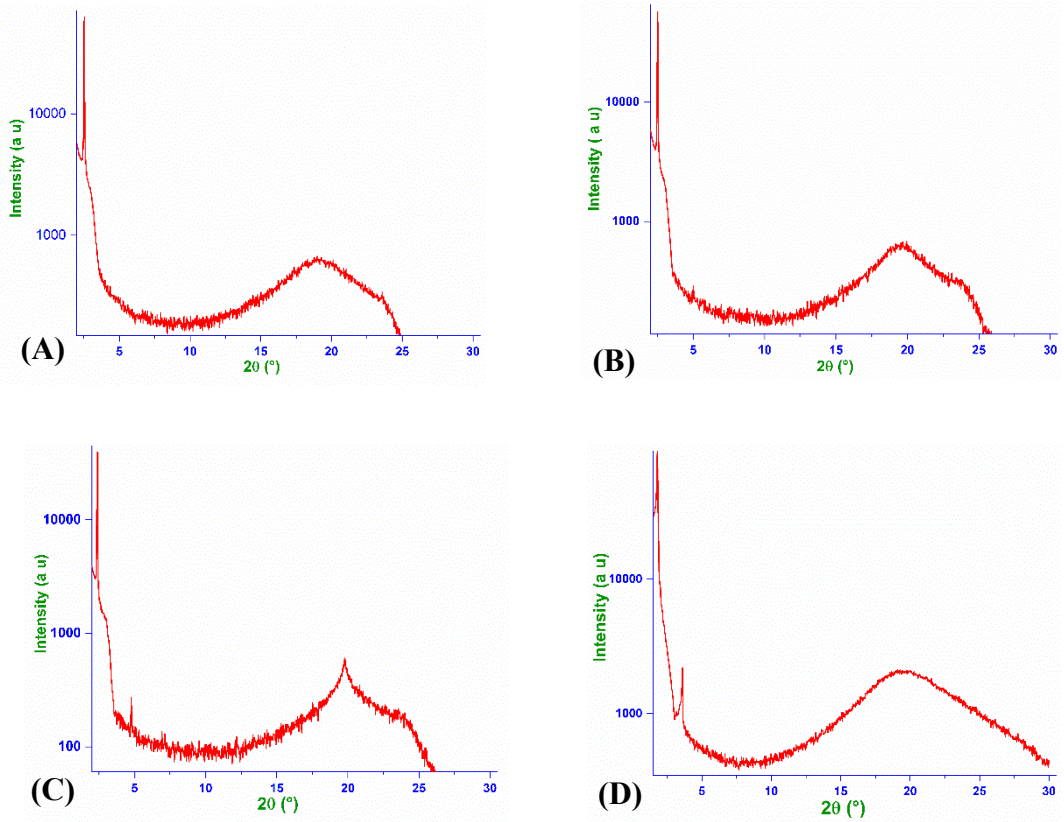


Fig. S3: Powder XRD plots of (A) R1 at 220.0°C in SmC phase; (B) R1 at 150.0°C in SmC phase; (C) R1 at 120.0°C in SmI phase; (D) B1 at 130.0°C in SmA phase

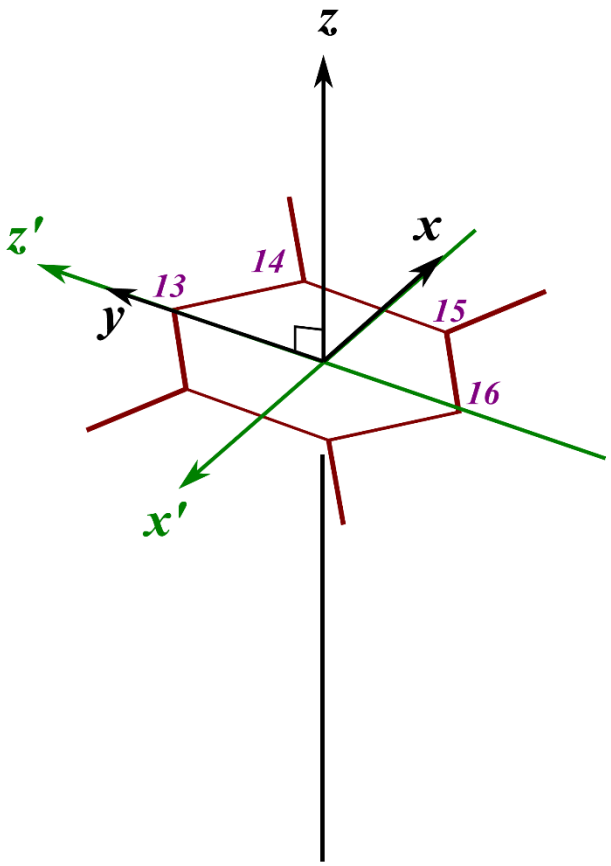


Fig. S4: Model showing the coordinate axes (x,y,z) employed for the determination of orientational order parameter for ring III of L1 mesogen, whereas (x',y',z') indicates conventional coordinate axes.

Table S1: Mesophase transition temepratures and enthalpy values of mesogens

Compound	**$T_{Cry-SmI}$ (°C)**	**$T_{SmI-SmC}$ (°C)**	**T_{SmC-N} (°C)**	**T_{N-Iso} (°C)**	**T_{Iso-N} (°C)**	**T_{N-SmC} (°C)**	**$T_{SmC-SmI}$ (°C)**	**$T_{SmI-Cry1}$ (°C)**	**$T_{Cry1-Cry2}$ (°C)**
R1 Mesogen	93.5 [7.72]	129.2 [0.50]	233.5 [1.12]	258.9 [0.39]	258.0 [0.48]	233.2 [1.13]	130.3 [0.58]	112.3 [0.03]	72.6 [7.94]
	T_{Cry-N} (°C)	**T_{N-I} (°C)**	**T_{I-N} (°C)**	**T_{N-Cry} (°C)**					
L1 Mesogen	120.1 [9.04]	194.4 [0.24]	194.2 [0.26]	73.7 [7.29]					
	$T_{Cry-SmA}$ (°C)	**T_{SmA-I} (°C)**	**T_{I-SmA} (°C)**	**$T_{SmA-Cry}$ (°C)**					
B1 Mesogen	123.5 [8.0]	155.2 [3.2]	154.5 [3.8]	109.1 [13.9]					

Cry – crystal; N- nematic; SmA-smectic A; Smc-smectic C; SmI- smectic I; Iso-isotropic

Table S2: ^{13}C NMR data for the core units of the R1 mesogen in solution and mesophases.[a]

C. No	Soln. (ppm)	105 °C			125 °C			145 °C			205 °C		
		CS (ppm)	AIS (ppm)	DOF (kHz)	CS (ppm)	AIS (ppm)	DOF (kHz)	CS (ppm)	AIS (ppm)	DOF (kHz)	CS (ppm)	AIS (ppm)	DOF (kHz)
1	149.4	233.0	83.6	1.96	229.1	79.7	1.85	226.9	77.5	1.77	221.5	72.1	1.61
2	128.7	159.2	30.5	3.20	157.3	28.6	2.99	156.1	27.4	2.93	153.2	24.5	2.76
3	130.1	166.7	36.6	3.22	164.8	34.7	3.03	163.7	33.6	2.90	160.8	30.7	2.73
4	126.7	207.0	80.3	1.87	202.9	76.2	1.72	201.0	74.3	1.69	196.3	69.6	1.55
5	164.9	224.7	59.8	0.64	221.1	56.2	0.61	219.4	54.5	0.59	215.6	50.7	0.55
6	153.5	238.2	84.7	1.91	234.4	80.9	1.78	232.4	78.9	1.73	226.9	73.4	1.60
7	122.5	156.9	34.4	3.18	155.0	32.5	2.96	153.9	31.4	2.92	151.2	28.7	2.83
8	130.3	167.6	37.3	2.98	165.2	34.9	2.74	163.7	33.4	2.90	160.8	30.5	2.73
9	133.8	218.1	84.3	2.52	214.7	80.9	2.39	212.9	79.1	2.30	208.6	74.8	2.14
10	159.2	208.3	49.1	6.18	206.4	47.2	5.70	205.2	46.0	5.55	201.8	42.6	5.16
11	149.7	233.0	83.3	1.96	229.1	79.4	1.85	226.9	77.2	1.77	221.5	71.8	1.61
12	122.3	156.9	34.6	3.18	155.0	32.7	2.96	153.9	31.6	2.92	151.2	28.9	2.83
13	121.8	150.3	28.5	3.40	149.1	27.3	3.11	148.2	26.4	3.07	145.8	24.0	3.05
14	149.3	236.8	87.5	1.99	233.3	84.0	1.91	231.3	82.0	1.84	226.9	77.6	1.60
15	165.0	224.7	59.7	0.64	221.1	56.1	0.61	219.4	54.4	0.59	215.6	50.6	0.55
16	121.5	199.4	77.9	1.85	195.5	74.0	1.77	193.6	72.1	1.73	189.3	67.8	1.58
17	132.3	169.8	37.5	3.03	167.4	35.1	2.78	166.1	33.8	2.75	162.9	30.6	2.61
18	114.3	144.7	30.4	3.07	143.1	28.8	2.79	142.2	27.9	2.72	139.9	25.6	2.66
19	163.6	242.7	79.1	1.99	238.6	75.0	1.89	236.7	73.1	1.84	232.0	68.4	1.63

[a] Soln.: Solution chemical shift, CS: mesophase chemical shift; AIS: alignment induced chemical shift; DOF: dipolar oscillation frequencies

Table S3: ^{13}C NMR data for the core units of the L1 mesogen in solution and mesophases.[a]

C. No.	Soln.	113 °C			136 °C			159 °C		
	(ppm)	CS (ppm)	AIS (ppm)	DOF (kHz)	CS (ppm)	AIS (ppm)	DOF (kHz)	CS (ppm)	AIS (ppm)	DOF (kHz)
1	163.6	218.3	54.7	1.33	214.2	50.6	1.28	208.0	44.4	1.16
2	114.3	135.0	20.7	2.45	133.2	18.9	2.30	131.0	16.7	2.11
3	132.4	157.7	25.3	2.37	155.4	23.0	2.24	152.6	20.2	2.05
4	121.5	177.7	56.2	1.37	173.6	52.1	1.30	168.4	46.9	1.16
5	164.0	196.8	32.8	0.68	193.9	29.9	0.88	188.9	24.9	0.82
6	145.4	198.0	52.6	0.98	193.9	48.5	0.49	190.3	44.9	0.42
7	127.1	137.5	10.4	2.02	136.4	9.3	1.90	135.0	7.9	1.76
8	124.0	118.7	-5.3	2.00	117.9	-6.1	1.89	116.8	-7.2	1.74
9	134.8	196.5	61.7	1.70	192.8	58.0	1.58	186.8	52.0	1.49
10	123.6	164.9	41.3	2.78	162.2	38.6	2.62	158.6	35.0	2.41
11	143.3	188.0	44.7	0.94	185.6	42.3	0.90	182.7	39.4	0.82
12	163.8	164.9	1.1	0.61	163.9	0.1	0.56	163.0	-0.8	0.50
13	120.7	145.2	24.5	0.99	142.8	22.1	0.92	140.1	19.4	0.85
14	132.4	144.2	11.8	5.26	142.8	10.4	4.86	140.8	8.4	4.36
15	114.3	141.6	27.3	5.30	140.4	26.1	4.88	138.8	24.5	4.34
16	163.6	162.2	-1.4	1.11	161.0	-2.6	1.03	159.0	-4.6	0.95
17	158.5	196.8	38.3	3.42	193.9	35.4	3.15	189.8	31.3	2.81
18	149.4	213.7	64.3	1.32	209.2	59.8	1.29	202.2	52.8	1.17
19	122.5	147.6	25.1	2.20	145.5	23.0	2.04	142.9	20.4	1.84
20	121.8	142.8	21.0	2.35	140.9	19.1	2.19	138.8	17.0	1.97
21	149.2	206.5	57.3	1.37	202.5	53.3	1.33	196.2	47.0	1.19
22	165.0	204.3	39.3	0.56	201.6	36.6	0.45	196.5	31.5	0.39
23	120.6	177.7	57.1	1.37	173.6	53.0	1.30	168.4	47.8	1.16
24	132.3	158.7	26.4	2.14	156.4	24.1	1.99	153.5	21.2	1.78
25	114.3	136.6	22.3	2.19	134.8	20.5	2.07	132.5	18.2	1.87
26	163.6	218.3	54.7	1.33	214.2	50.6	1.28	208.0	44.4	1.16

[a] Soln.: Solution chemical shift, CS: mesophase chemical shift; AIS: alignment induced chemical shift; DOF: dipolar oscillation frequencies

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