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Supporting Information

Observation of exceptional 'deVries-like' properties in a conventional Aroylhydrazone based Liquid Crystal

Hemant Kumar Singh[§a], Sachin Kumar Singh[§a], Rajib Nandi[b], D. S. Shankar Rao[c], S. Krishna Prasad[c], Ranjan K. Singh[b], Bachcha Singh[a*]

[a]*Department of Chemistry (Centre of Advance Study), Institute of Science, Banaras Hindu University, Varanasi-221005, India*
[b]*Department of Physics (Centre of Advance Study), Institute of Science, Banaras Hindu University, Varanasi-221005, India*
[c]*Centre for nano and soft matter sciences, Jalahalli, Bangalore - 560013, India*

Email: bsinghbhu@rediffmail.com

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1. General methods

Ethyl 4-hydroxybenzoate, 2,4-dihydroxybenzaldehyde, hydrazine monohydrate, $LiAlH_4$, thionyl chloride, potassium iodide, anhydrous Cs_2CO_3, bromoalkanes purchased from Aldrich Chemicals, USA used as received. All other solvents and reagents were purchased from Merck, India. The solvents were dried using standard methods when required [S1]. Elemental analyses were performed on a CE-440 Exeter Analytical CHN analyser. IR spectra (4000–100 cm^{-1}) were recorded on a Varian 3100 FT-IR Excalibur series spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a JEOL FT-NMR AL 300 MHz spectrometer using tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) thermograms were recorded with a Mettler Toledo TC 15 TA differential scanning calorimeter at the rate of 5.0 K min^{-1} under a nitrogen atmosphere using spec pure grade indium as standard by taking samples in close-lid aluminium pans. The transition temperatures from DSC thermograms have been determined with an accuracy of ±0.1 K. The mesophase type was identified by visual comparison with known phase standards using a Nikon Eclipse LV-100 POL polarizing optical microscope (POM) fitted with a hot stage temperature-controlled LTSE 420 heating stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) with temperature controlling accuracy of 0.1K. For the temperature-dependent Xray diffraction measurements, a PANalytical X'Pert PRO MP X-ray diffractometer [S2] consisting of a focusing elliptical mirror and a fast high resolution detector (PIXCEL) was employed; the wavelength of the radiation in this case also was 0.15418 nm. The profles collected using this apparatus were analyzed using Fityk profile fitting software [S3]. Microwave reactions were performed in a CEM Discover BenchMate single-mode microwave reactor with a new sealed pressure regulation 10-mL pressurized vial with "snap-on" cap and teflon-coated magnetic stir bar. The standard temperature control system for the Discover System consists of a non-contact calibrated infrared sensor, which monitors and controls the temperature conditions of the reaction vessel located in the instrument cavity.

2. Synthesis and analytical data

2.1 Synthesis of ethyl 4-hexadecyloxybenzoate

To a small glass vial containing ethyl 4-hydroxybenzoate (0.017 g, 0.10 mmol), caesium carbonate (0.10 g, 0.30 mmol) and 1-bromohexadecane (30 µL, 0.11 mmol) was added NMP (4 mL). The vial was loosely covered with a rubber septum (Aldrich) and then irradiated under microwave for 30 second. The vial was taken out and again kept back after about 1 min. The process was continued 8/10 times until the reaction gets completed (monitored by TLC). The reaction mixture was cooled and 100 mL of water was added. The compound was extracted with diethyl ether (3x30 mL); the organic layer was washed with water (twice) and brine. The organic solutions were dried over anhydrous $MgSO_4$ and solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate–petroleum ether 1:20) and crystallized from methanol.

Yield: 87%. FT IR (KBr, cm^{-1}): 2935, 2860 (aliphatic C-H), 1718 (ester, C=O), 1609, 1519 (Ph), 1310, 1260 (OPh); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ 7.97 (d, J (H,H)=8.7 Hz, 2H, -C_6H_4), 6.91 (d, J (H,H)=8.7 Hz, 2H, -C_6H_4), 4.31 (q, 2H, -$COOCH_2$), 3.96 (t, 3H, -OCH_2), 1.77 (m, 2H, -$OCH_2C\underline{H}_2$), 1.59 (t, 3H, -$COOCH_2C\underline{H}_3$), 1.37-1.18 (m, 26H, -$[CH_2]_{13}$), 0.87 (t, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.31, 162.79, 131.38, 122.53, 113.82, 68.07, 60.41, 31.89, 29.60, 25.93, 22.61, 14.29, 14.05; Elemental analyses: calculated for $C_{25}H_{42}O_3$ (%), C, 76.87; H, 10.84; Found, C, 76.85; H, 10.87.

2.2 Synthesis of 4-hexadecyloxybenzyl alcohol

Ethyl 4-hexadecyloxybenzoate (0.39 g, 1 mmol) dissolved in dry THF was added slowly to a slurry of $LiAlH_4$ (0.05 g, 1.2 mmol) in dry THF (15 mL) over 1.5 h at 0°C. Upon addition, the mixture was continued to stir at room temperature for 2 h. Reaction mixture was cooled to 0°C and quenched by successive addition of methanol, 15% NaOH, H_2O and stirring continued until H_2 evolution ceased. Reaction mixture was then filtered and the lithium salts rinsed generously with CH_2Cl_2. The filtrate was dried over anhydrous $MgSO_4$ and concentrated to give the title benzyl alcohol.

Yield: 92%. FT IR (KBr, cm^{-1}): 3320 (-OH), 2922, 2854 (aliphatic C-H), 1615, 1515 (Ph), 1308, 1252 (OPh); ^1H NMR (300 MHz, $CDCl_3$) δ = 7.22 (d, J (H,H)= 9.9 Hz, 2H, -C_6H_4), 6.86 (d, J (H,H)=8.4 Hz, 2H, -C_6H_4), 4.65 (d, J (H,H)= 6.0 Hz, 2H, Ar-CH_2-OH), 3.94 (t, 2H, -OCH_2), 1.75-1.25 (m, 28H, -$[CH_2]_{14}$), 0.86 (t, 3H, -CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ =

158.68, 132.90, 128.55, 114.45, 67.96, 64.80, 31.87, 29.54, 29.35, 29.27, 29.21, 25.93, 22.60, 14.12; Elemental analyses: calculated for $C_{23}H_{40}O_2$ (%), C, 79.25; H, 11.57; Found, C, 79.23; H, 11.53.

2.3 Synthesis of 4-hexadecyloxybenzyl chloride

Thionyl chloride (0.1 mL, 1.4 mmol) was added drop wise to a solution of 4-hexadecyloxybenzyl alcohol (0.35 g, 1 mmol) in dry CH_2Cl_2 with a catalytic amount of DMF at 0°C. Upon addition, reaction mixture was allowed to stir for 10-20 min., while monitoring was done through TLC (CH_2Cl_2) for completion of reaction. Reaction mixture was concentrated under reduced pressure and the resulting residue was re-crystallized from acetone to give the title benzyl chloride.

Yield: 82%. FT IR (KBr, cm^{-1}): 2925, 2855 (aliphatic C-H), 1612, 1520 (Ph), 1310, 1252 (OPh); ^1H NMR (300 MHz, $CDCl_3$) δ = 7.26 (d, J (H,H)= 8.4 Hz, 2H, $-C_6H_4$), 6.85 (d, J (H,H)=8.7 Hz, 2H, $-C_6H_4$), 4.56 (s, 2H, Ar-CH_2-Cl), 3.92 (t, 2H, $-OCH_2$), 1.77-1.25 (m, 28H, $-[CH_2]_{14}$), 0.89 (t, 3H, $-CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.43, 130.25, 129.69, 114.78, 68.32, 46.52, 32.15, 29.71, 29.55, 29.21, 26.25, 22.72, 14.28; Elemental analyses: calculated for $C_{23}H_{39}ClO$ (%), C, 75.27; H, 10.71; Found, C, 75.23; H, 10.73.

2.4 Synthesis of ethyl 4-[(4'-(hexadecyloxy)benzyloxy]benzoate

To a thoroughly degassed suspension of Cs_2CO_3 (0.49 g, 1.5 mmol) in DMF (3 mL) was added ethyl 4-hydroxybenzoate (0.085 g, 0.5 mmol) and the mixture was irradiated under microwave for 30 sec. at 70°C after which, 4-hexadecyloxybenzyl chloride (0.18 g, 0.5 mmol) was added and the mixture was irradiated for next 30 sec. The process was continued 3/4 times until the reaction gets completed (monitored by TLC). Reaction mixture was cooled to room temperature and was poured into cold water. The precipitate was collected by suction filtration and purified by flash column chromatography using ethyl acetate and hexane (1:9) followed by re-crystallization from acetone to give the title compound.

Yield: 80%. IR (KBr, cm^{-1}): 2923, 2850 (aliphatic C-H), 1717 (ester, C=O), 1610, 1523 (Ph), 1317, 1272 (OPh); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ 7.96 (d, J (H,H)=8.7 Hz, 2H, $-C_6H_4$), 7.35 (d, J (H,H)=8.4 Hz, 2H, $-C_6H_4$), 6.93 (d, J (H,H)=8.7 Hz, 2H, $-C_6H_4$), 6.87 (d, J (H,H)=8.4 Hz, 2H, $-C_6H_4$), 5.05 (s, 2H, Ar-CH_2-O-Ar), 4.31 (q, 2H, $-COOCH_2$), 3.94 (t, 3H, $-OCH_2$), 1.77 (m, 2H, $-OCH_2\underline{CH_2}$), 1.45-1.27 (m, 26H, $-[CH_2]_{13}$), 0.89 (t, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 166.36, 162.47,159.21, 131.53, 129.29, 127.97, 123.10, 114.61, 114.35, 69.97, 68.05, 60.60, 31.89, 29.54, 28.32, 26.07, 22.65, 14.39, 13.10; Elemental analyses: calculated for $C_{32}H_{48}O_4$ (%), C, 77.38; H, 9.74; Found, C, 77.35; H, 9.77.

2.5 Synthesis of 4-[(4'-(hexadecyloxy)benzyloxy]benzohydrazide

The ethyl 4-[(4'-(hexadecyloxy)benzyl)oxy]benzoate (0.25 g, 0.5 mmol,) was mixed with hydrazine mono hydrate (2 mL) drop wise with continuous stirring. The reaction mixture was irradiated under microwave for 5 min. with 60 sec. of pulse. The vial was cooled to room temperature and the white solid thus obtained was washed with water several times and dried under vacuum. The crude product was recrystallized from absolute ethanol.

Yield: 82%. IR (KBr, cm^{-1}): 3420 ν_a (N-H), 3318 ν_s (N-H), 2922, 2855 (aliphatic C-H), 1653 (amide-I, C=O), 1572 (amide-II, N-H), 1618, 1514 (Ph), 1342, 1251 (OPh), 1015 (N-N); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ 7.68 (d, J (H,H)=8.7 Hz, 2H, $-C_6H_4$), 7.32 (m, J (H,H)=8.4 Hz, 3H, $-C_6H_4$/NH; NH merge with $-C_6H_4$), 6.97 (d, J (H,H)=8.7 Hz, 2H, $-C_6H_4$), 6.90 (d, 2H, J (H,H)=8.4, $-C_6H_4$), 5.03 (s, 2H, Ar-CH_2-O-Ar), 4.09 (b, 2H, $NHN\underline{H}_2$), 3.95 (t, 2H, $-OCH_2$), 1.76 (m, 2H, $-OCH_2C\underline{H}_2$), 1.61-1.25 (m, 26H, $-[CH_2]_{13}$), 0.87 (t, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 168.35, 161.75, 159.22, 129.21, 128.63, 127.90, 124.96, 114.85, 114.61, 69.95, 68.06, 31.85, 29.56, 29.37, 29.31, 29.23, 26.05, 22.68, 14.12; Elemental analyses: calculated for $C_{30}H_{46}N_2O_3$ (%), C, 74.65; H, 9.61; N, 5.80; Found, C, 74.62; H, 9.64;N, 5.82.

2.6 Synthesis of 4-(tetradecyloxy)-2-hydroxybenzaldehyde

To a solution of 2,4-dihydroxybenzaldehyde (0.14 g, 1.0 mmol) in NMP (2 mL) was added 1-bromotetradecane (0.27 mL, 1.0 mmol) and Cs_2CO_3 (1.3 g, 4.0 mmol).The reaction mixture was irradiated for 30 second of pulse for 4-5 times until the reaction gets completed (monitored by TLC). The residue was filtered off and dilute hydrochloric acid (6 N) was added to the filtrate until the point of neutralization and the product was then extracted twice with $CHCl_3$ (50 mL portions). The chloroform extract was concentrated to obtain a white solid, which was purified by column chromatography over SiO_2 eluting first with n-hexane and then with a mixture of n-hexane and chloroform (v/v, 1/1); evaporation of this purified extract finally yielded 4-(tetradecyloxy)-2-hydroxybenzaldehyde as a white solid.

Yield: 82 %. IR (KBr, cm^{-1}): 3452 (-OH), 2937, 2854 (aliphatic C-H), 1687 (aldehyde, C=O), 1609, 1562 (Ph), 1319, 1245 (-OPh); ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ 11.22 (s, 1H, -OH), 9.87 (s, 1H, -CHO), 7.65 (d, J(H,H)=8.7 Hz, 1H, -C_6H_3), 6.97 (d, J(H,H)=8.7 Hz, 1H, -C_6H_3), 6.92 (s, 1H, -C_6H_3), 4.09 (t, 2H, -OCH_2), 1.85-1.26 (m, 24H, -$[CH_2]_{12}$), 0.89 (t, 3H, -CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ_c 195.48, 163.96, 163.17, 134.95, 132.48, 118.57, 110.85, 68.46, 31.92, 29.63, 25.95, 22.67, 14.12; Elemental analyses: calculated for $C_{21}H_{34}O_3$ (%), C, 75.41; H, 10.25; Found, C, 75.43; H, 10.27.

2.7 Synthesis of N-(4-(tetradecyloxy)-2-hydroxybenzylidene)-4'((4''(hexadecyloxy) benzyl)oxy)benzohydrazide (BSac-1416)

BSac-1416 was prepared by irradiating together absolute ethanol solution of 4-(tetradecyloxy)-2-hydroxybenzaldehyde (0.17 g, 0.5 mmol) and 4-((4'-(hexadecyloxy)benzyl)oxy)benzohydrazide (0.24 g, 0.5 mmol) for ~ 5 min. (30 second x10) in the presence of few drops of acetic acid and leaving solution overnight in the vial closed with rubber septum. The microcrystalline colourless solid was filtered off by suction, thoroughly washed with cold ethanol and recrystallized from a mixture of absolute ethanol and dried at room temperature.

Yield: 83 %. IR (KBr, cm^{-1}): 3415 ν_s (O-H), 3247 ν_s (N-H), 2924, 2854 (aliphatic C-H), 1645 (amide-I, C=O), 1583 (amide-II, N-H), 1610, 1516, 1474 (Ph), 1539, 1280, 1255 (OPh); ^{1}H NMR (300 MHz, $CDCL_3$/DMSO-d^6, 30°C): δ 11.71 (s, 1H, -OH), 11.03 (s, 1H, -NH), 8.42 (s, 1H, -CH=N), 7.89 (d, J_1(H,H)=6.0 Hz, 2H, -C_6H_4), 7.11 (m, 6H, -C_6H_4), 6.49 (s, 1H, -C_6H_3), 6.44 (d, J_1(H,H)=8.1 Hz, 2H, -C_6H_3), 5.04 (s, 2H, Ar-CH_2-O-Ar), 3.96 (t, 4H, J_1(H,H)=6.0 Hz, -OCH_2), 1.78 (m, 4H, -$OCH_2C\underline{H}_2$), 1.44-1.27 (m, 48H, -$[CH_2]_{24}$), 0.88 (t, J_1(H,H)=6.6 Hz, 6H, -CH_3); ^{13}C NMR (75 MHz, $CDCL_3$/DMSO-d^6, 30°C): δ_c 162.91, 161.28, 159.73, 158.44, 148.13, 131.61, 129.01, 128.62, 127.39, 113.34, 106.25, 101.24, 69.23, 66.34, 31.18, 28.80, 28.63, 28.52, 28.40, 25.20, 21.93, 13.47; Elemental analyses: calculated for $C_{51}H_{78}N_2O_5$ (%), C, 76.65; H, 9.84; N, 3.51; Found, C, 76.59; H, 9.83; N, 3.57.

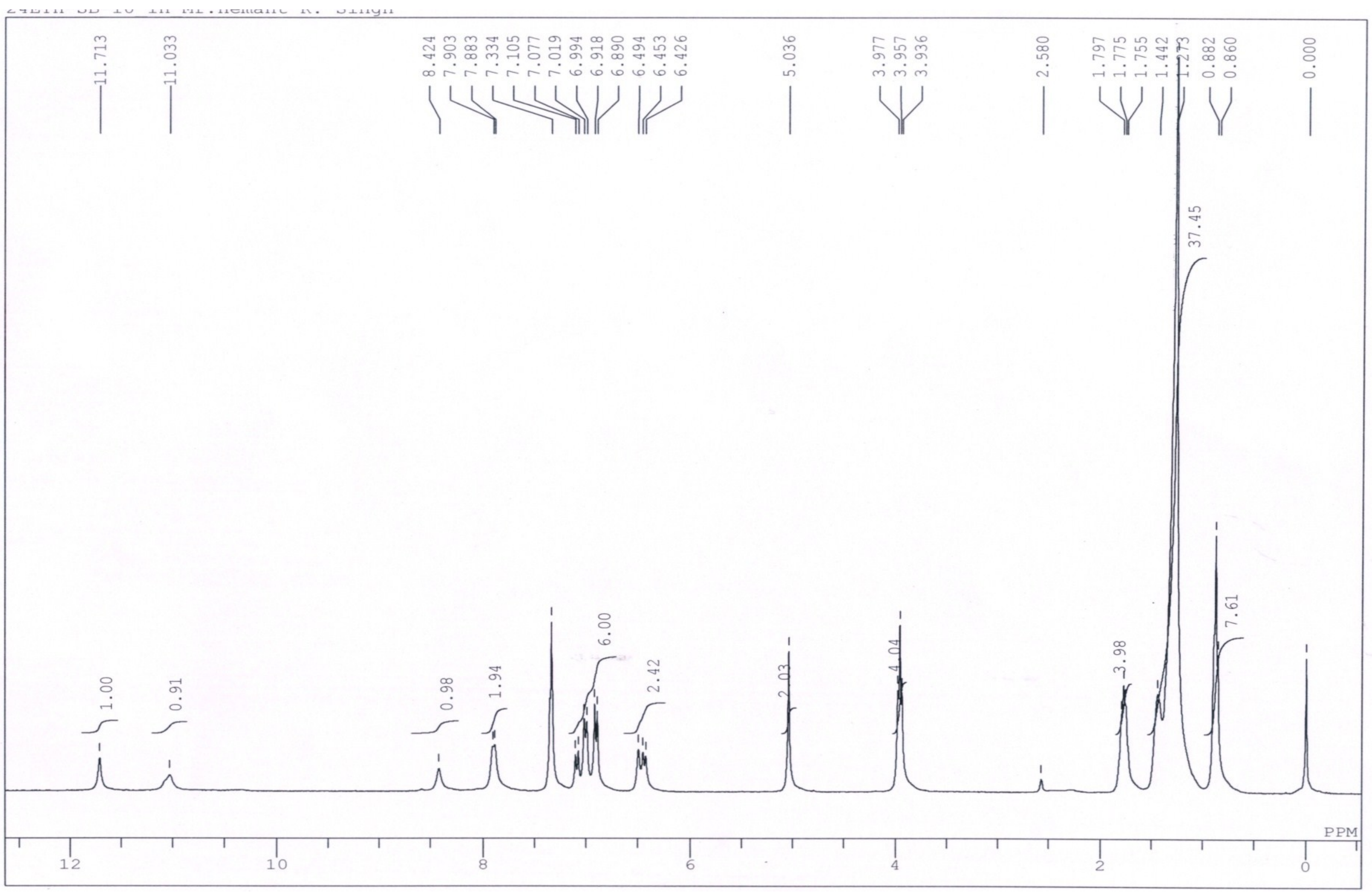

Fig. SI 1 ^{1}H NMR spectrum of N-(4-(tetradecyloxy)-2-hydroxybenzylidene)-4'((4''(hexadecyloxy)benzyl)oxy)benzohydrazide (BSac-1416)

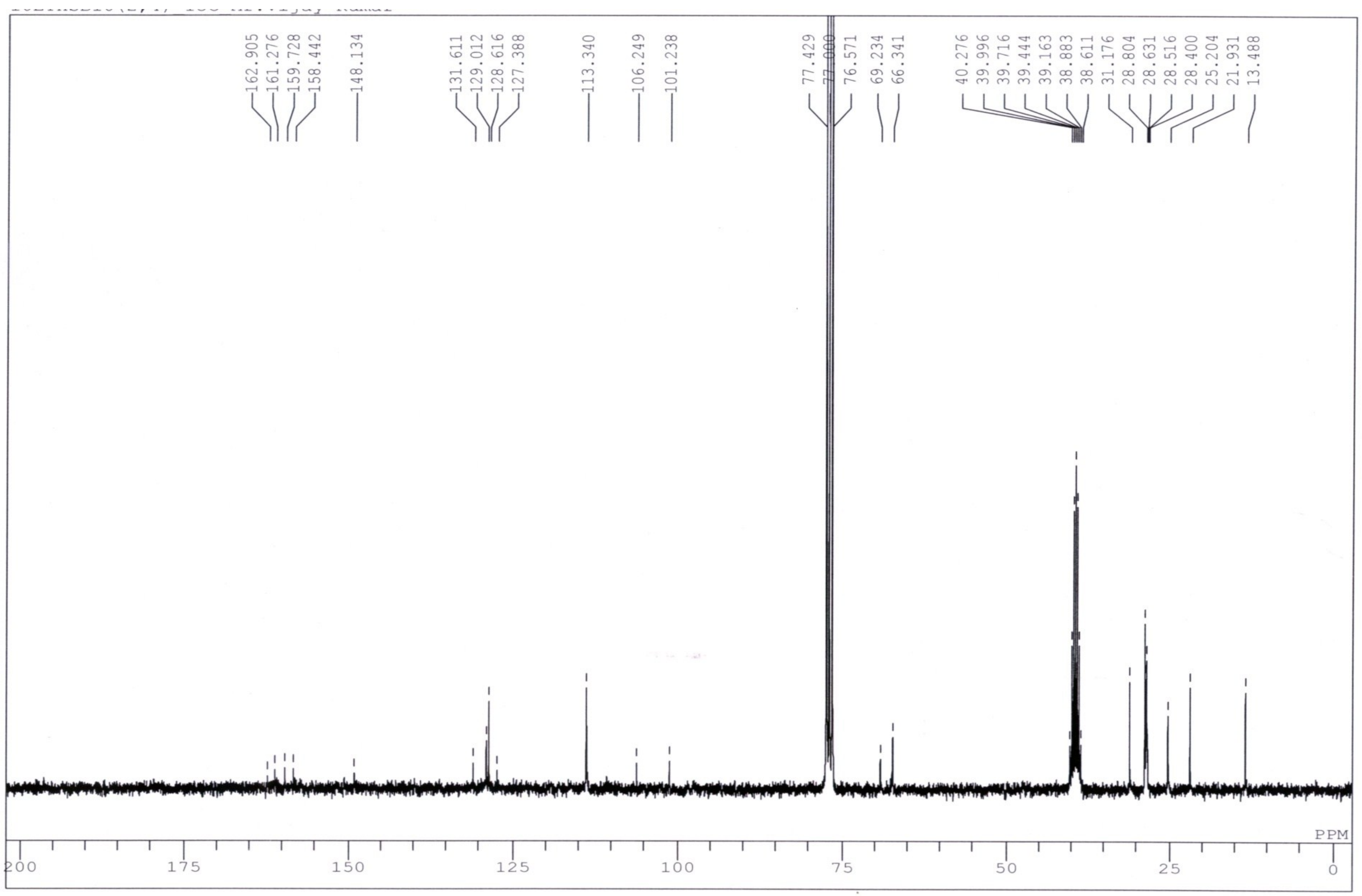

Fig. SI 2 ^{13}C NMR spectrum of N-(4-(tetradecyloxy)-2-hydroxybenzylidene)-4'((4''(hexadecyloxy)benzyl)oxy)benzohydrazide (BSac-1416)

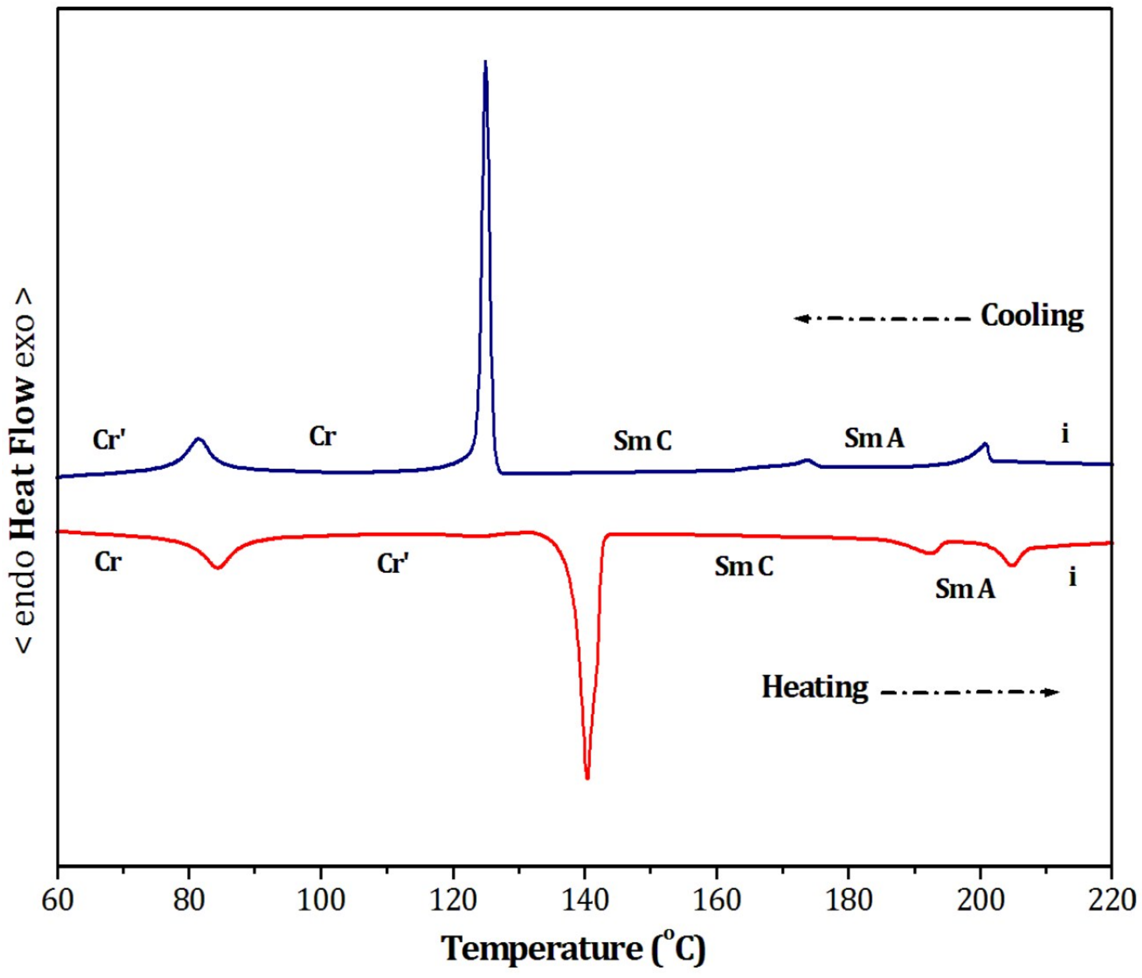

Fig. SI 3 DSC thermogram of BSac-1416

Table SI 1. Phase transitions, enthalpies and entropies of $BSac_{1416}$		
Compound	Heating	cooling
$BSac_{1416}$	Cr 84.31 (8.25; 23.07) Cr' 140.26 (38.50; 93.13) SmC 192.39 (2.57; 5.51) SmA 204.71 (3.11; 6.51) i	i 200.79 (-2.39; -5.05) SmA 173.50 (-0.73; -1.63) SmC 125.24 (-33.32; -83.64) Cr 81.53 (-6.59; -18.59) Cr'
Abbreviations: Cr, Cr'= crystal; Sm C= Smectic C mesophase; Sm A= Smectic A mesophase; i= isotropic liquid. The transition temperatures (°C), enthalpies and entropies are determined by DSC at the scan rate of 5°C/min.		

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