Supporting Information

Benzylidenehydrazine Based Room Temperature Columnar Liquid Crystals

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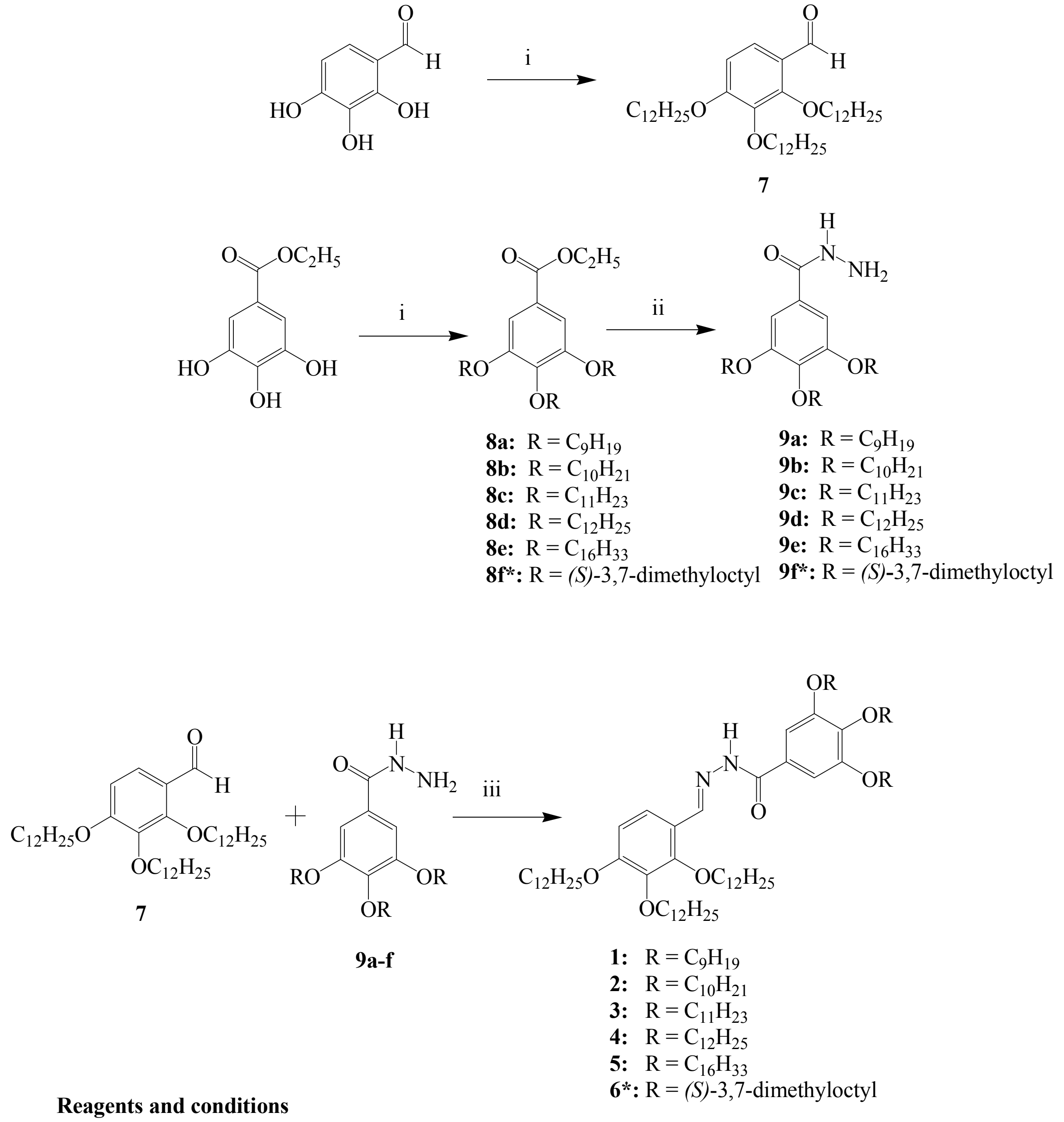
Contents

1. Methods

The starting materials were obtained either from Aldrich or Lancaster Company and used as received. All solvents were purified and dried by standard methods prior to use. The crude samples were purified by column chromatographic technique using either silica gel (400 mesh) or neutral aluminium oxide as stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). Investigation of the mesomorphic properties was carried out by polarizing microscopy (Optiphot-2, Nikon) on a hot stage (FP 82 HAT, Mettler), differential scanning calorimetry (DSC, DSC-7, Perkin-Elmer), X-ray diffraction (XRD) of surface aligned samples (HI-Star, Siemens; alignment was achieved by slow cooling a drop of the isotropic liquid below the clearing temperature on a glass substrate; the incident X-ray beam was nearly parallel to the glass plate). Infrared spectra (IR) were measured as KBr discs on Perkin Elmer Spectrum 1000 FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ using Bruker AMX-400 (400 MHz) spectrometer. All chemical shifts are reported in δ (ppm) using the TMS as an internal reference. CD spectra were recorded with a Jasco J-810 spectropolarimeter.

2. Synthesis



8a: R = C_9H_{19}
8b: R = $C_{10}H_{21}$
8c: R = $C_{11}H_{23}$
8d: R = $C_{12}H_{25}$
8e: R = $C_{16}H_{33}$
8f*: R = *(S)*-3,7-dimethyloctyl

9a: R = C_9H_{19}
9b: R = $C_{10}H_{21}$
9c: R = $C_{11}H_{23}$
9d: R = $C_{12}H_{25}$
9e: R = $C_{16}H_{33}$
9f*: R = *(S)*-3,7-dimethyloctyl

1: R = C_9H_{19}
2: R = $C_{10}H_{21}$
3: R = $C_{11}H_{23}$
4: R = $C_{12}H_{25}$
5: R = $C_{16}H_{33}$
6*: R = *(S)*-3,7-dimethyloctyl

Reagents and conditions
i) *n*-Bromoalkane, anhyd. K_2CO_3, DMF, 85 °C, 12 h (85-90%)
ii) NH_2-NH_2.H_2O, EtOH, reflux, 12 h (80%)
iii) EtOH, AcOH (cat), reflux, 2 h (75-78%)

Scheme S1. Synthesis of compounds **1-6**.

2.1 Synthesis of 2,3,4-*n*-tridodecyloxybenzaldehyde (7).

A mixture of 2,3,4-trihydroxy benzaldehyde (2g, 12.97 mmol, 1 equiv.), anhyd. K_2CO_3 (10.76, 77.86 mmol, 6 equiv.) and *n*-bromododecane (10.66, 79.64 mmol, 3.3 equiv.) was taken in dry DMF and stirred at 80 °C for 12 h under nitrogen atmosphere. The reaction mixture was cooled poured into ice-water and extracted with dichloromethane (2 × 25 ml). The combined extracts were washed with water, brine, dried over anhyd. Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 5-10% ethyl acetate-hexanes yielded the desired product.[S1]

7: Colorless solid; yield: 78 %; m.p.: 37 °C; IR (KBr pellet): ν_{max} in cm^{-1} 2917, 2849, 1695, 1583, 1119; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.26 (s, 1H, CHO), 7.57 (d, 1H, *J* = 8.0 Hz, Ar), 6.72 (d, 1H, *J* =10 Hz, Ar), 4.2 (t, 2H, *J* = 6.0 Hz, 1 × OCH_2), 4.1-3.94 (m, 4H, 2 × OCH_2), 1.88 -1.26 (m, 60H, 30 × CH_2), 0.88 (t, 9H, *J* = 6 Hz, 3 × CH_3); MS (FAB+): m/z calcd for $C_{43}H_{78}O_4$ (M+1): 659.6. Found: 659.2.[S1]

2.2 Ethyl 3,4,5-trialkoxybenzoates (8a-f) and 3,4,5-trialkoxybenzhydrazides (9a-f).

These compounds were synthesized using the procedure described previously.[S2]

2.3 *N*-(2,3,4-Tridodecyloxybenzylidene)-*N'*-3,4,5-trialkyloxybenzoylhydrazines 1-5 and 6*

General procedure. A mixture of **9** (0.7 mmol, 1 equiv.), **7a-f** (1.2 mmol, 1.5 equiv.) and catalytic amount of glacial acetic acid (2 drops) in ethanol was refluxed for 2h. Yellow color solid obtained upon cooling was filtered, washed with ethanol and further purified by repeated crystallization from a mixture of EtOH:CH_2Cl_2 (9:1).

1: Pale yellow semi-solid; yield: 72%; IR (KBr pellet): ν_{max} in cm^{-1} 3226, 2927, 2855, 1651, 1265; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.91 (s, 1H, N=CH), 8.45 (s, 1H, NH), 7.82 (s, 1H, Ar), 7.05 (s, 2H, Ar), 6.71 (s, 1H, Ar), 4.07 – 3.94 (m, 12H, 6 × OCH_2), 1.83 – 0.86 (m, 120H, 6 × CH_3, 51 × CH_2); MS (FAB+): m/z calcd for $C_{77}H_{138}N_2O_7$: 1203.1. Found: 1203.1; Anal. calcd for $C_{77}H_{138}N_2O_7$: C, 76.82; H, 11.55; N, 2.33. Found: C,76.87; H, 11.40; N, 2.20.

2: Pale yellow semi-solid; yield: 75%; IR (KBr pellet): ν_{max} in cm^{-1} 3212, 2927, 2855, 1640, 1264; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.80 (s, 1H, N=CH), 8.45 (s, 1H, NH), 7.83 (s, 1H, Ar), 7.09 (s, 2H, Ar), 6.68 (s, 1H, Ar), 4.21 – 3.84 (m, 12H, 6 × OCH_2), 1.91 – 0.81 (m, 126H, 6 × CH_3, 54 × CH_2); MS (FAB+): m/z calcd for $C_{80}H_{144}N_2O_7$: 1245.1. Found: 1245.9; Anal. calcd for $C_{80}H_{144}N_2O_7$: C, 77.11; H, 11.65; N, 2.25. Found: C,77.24; H, 11.41; N, 1.97.

3: Pale yellow semi-solid; yield: 74%; IR (KBr pellet): ν_{max} in cm^{-1} 3214, 2925, 2854, 1645, 1264; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.87 (s, 1H, N=CH), 8.45 (s, 1H, NH), 7.81 (s, 1H, Ar), 7.05 (s, 2H, Ar), 6.72 (s, 1H, Ar), 4.25 – 3.85 (m, 12H, 6 × OCH_2), 1.95 – 0.84 (m, 132H, 6 × CH_3, 57 × CH_2); MS (FAB+): m/z calcd for $C_{83}H_{151}N_2O_7$ (M+1): 1288.1. Found: 1288.31; Anal. calcd for $C_{83}H_{150}N_2O_7$: C, 77.39; H, 11.74; N, 2.17. Found: C,77.51; H, 12.04; N, 2.40.

4: Pale yellow solid; yiled: 71%; IR (KBr pellet): ν_{max} in cm^{-1} 3216, 2925, 2854, 1638, 1265; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.88 (s, 1H, N=CH), 8.5 (s, 1H, NH), 7.32 (s, 1H, Ar), 7.01 (s, 2H, Ar), 6.6 (s, 1H, Ar), 4.2 – 3.9 (m, 12H, 6 × OCH_2), 1.84 – 0.86 (m, 138H, 6 × CH_3, 60 × CH_2); MS (FAB+): m/z calcd for $C_{86}H_{156}N_2O_7$: 1329.2. Found: 1329.3; Anal. calcd for $C_{86}H_{156}N_2O_7$: C, 77.65; H, 11.82; N, 2.11. Found: C, 77.63; H, 12.01; N, 1.82.

5: Pale yellow solid; yield: 74%; IR (KBr pellet): ν_{max} in cm^{-1} 3218, 2926, 2854, 1653, 1265; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.89 (s, 1H, N=CH), 8.48 (s, 1H, NH), 7.89 (s, 1H, Ar), 7.1 (s, 2H, Ar), 6.70 (s, 1H, Ar), 4.34 – 3.94 (m, 12H, 6 × OCH_2), 1.81 – 0.86 (m, 162H, 6 × CH_3, 72 × CH_2); ^{13}C NMR (100MHz, $CDCl_3$): 166.30, 151.37, 150.96, 152.70, 152.65, 146.67, 141.24, 139.97, 129.82, 124.82, 110.53, 108.72, 108.14, 104.4, 74.76, 73.70, 73.57, 69.57, 69.30, 68.88, 60.95, 32.01, 30.42, 30.36, 29.80, 29.68, 29.59, 29.52, 29.44, 26.24, 26.21, 26.16, 22.78, 14.51, 14.19; MS (FAB+): m/z calcd for $C_{98}H_{180}N_2O_7$: 1497.4. Found: 1497.1; Anal. calcd for $C_{98}H_{180}N_2O_7$: C, 78.55; H, 12.11; N, 1.87. Found: C,78.33; H, 12.29; N, 1.71.

6*: Pale yellow semi-solid; yield: 78%; IR (KBr pellet): ν_{max} in cm^{-1} 3213, 2925, 2854, 1636, 1264; ^1H NMR (400MHz, $CDCl_3$): δ 8.90 (s, 1H, N=CH), 8.49 (s, 1H, NH), 7.85 (s, 1H, Ar), 7.01 (s, 2H, Ar), 6.65 (s, 1H, Ar), 4.20 – 3.89 (m, 12H, 6 × OCH_2), 1.89 – 0.89 (m, 126H, 12 × CH_3, 42 × CH_2, 6 × CH); MS (FAB+): m/z calcd for $C_{80}H_{144}N_2O_7$: 1245.1. Found: 1245.9; Anal. calcd for $C_{80}H_{144}N_2O_7$: C, 77.11; H, 11.65; N, 2.25. Found: C,77.40; H, 11.52; N, 1.98.

3. XRD Studies

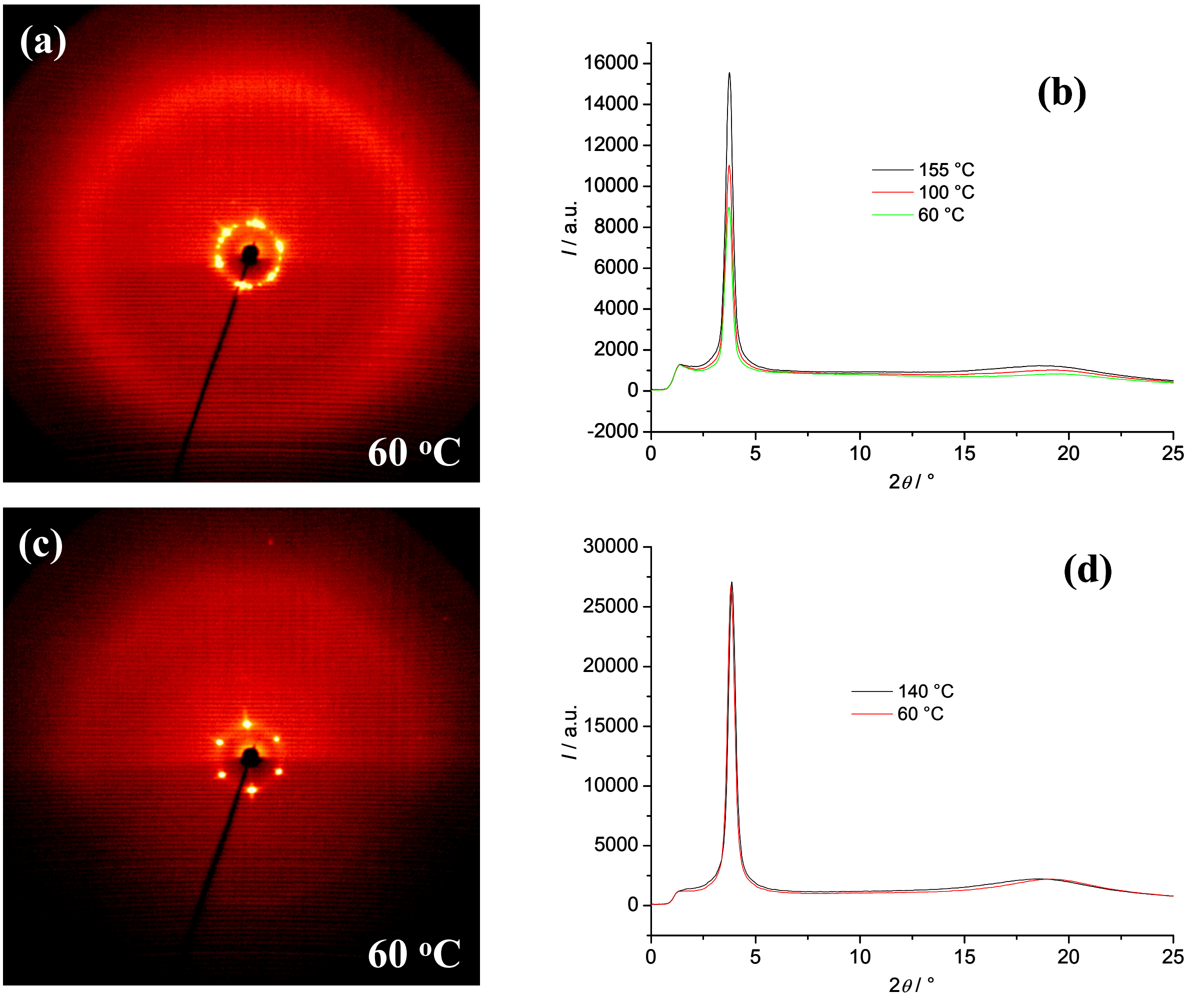


Figure S1: X-ray diffraction patterns of partially aligned samples of (a) the Col_h-phase of compound **3** and (c) the Col_h*-phase of compound **6*** at 60 °C; θ-scans of the diffraction patterns of (b) **3** and (d) **6***.

Table S1. Indexation of XRD pattern of compounds **1, 3** and **6***.

Compd.	Phase (T/ ^{o}C)	d/nm	Lattice parameters (nm)	Intensity	Miller indices *hk*
1	Col$_h$ (155)	2.25	a = 2.62	s	10
		0.47		diff	–
	Col$_h$ (100)	2.29	a = 2.64	s	10
		0.45		diff	–
3	Col$_h$ (155)	2.40	a = 2.73	s	10
		0.47		diff	–
	Col$_h$ (100)	2.40	a = 2.74	s	10
		0.45		diff	–
	Col$_h$ (60)	2.48	a = 2.75	s	10
		0.45		diff	–
6*	Col$_h$ (140)	2.28	a = 2.63	s	10
		0.47		diff	–
	Col$_h$ (60)	2.30	a = 2.67	s	10
		0.46		diff	–

Table S2: Calculations of molecular volume (V_{mol}), volume of the hypothetical unit cells (V_{cell}) and number of molecules in these unit cells (n_{cell}).[a]

Compound	T/°C	V_{cell} [nm^3]	V_{mol} [nm^3]	$n_{\mathrm{cell,cryst}}$	$n_{\mathrm{cell,liqu}}$	n_{cell}[b]
1	155	2.79	1.91	1.46	1.15	1.30
1	100	2.72	1.91	1.42	1.12	1.27
3	155	3.03	2.06	1.47	1.16	1.31
3	60	2.95	2.06	1.43	1.13	1.28
6*	140	2.82	1.98	1.42	1.12	1.27

[a] V_{cell} = volume of the unit cell defined by the dimensions $a^2 \times \sin(60°) \times h$ ($h = d$ at the maximum of wide angle scattering); V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[S3] $n_{\mathrm{cell,cryst}}$ = number of molecules in the unit cell, calculated according to $n_{\mathrm{cell}} = V_{\mathrm{cell}}/V_{\mathrm{mol}}$ (average packing coefficient in the crystal is $k = 0.7$;[S4] $n_{\mathrm{cell,liqu}}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{\mathrm{cell,liqu}} = 0.55/0.7 \times n_{\mathrm{cell,cryst}}$; n_{cell} = in the LC phase estimated as the average of that in the $n_{\mathrm{cell,cryst}}$ and $n_{\mathrm{cell,liqu}}$.

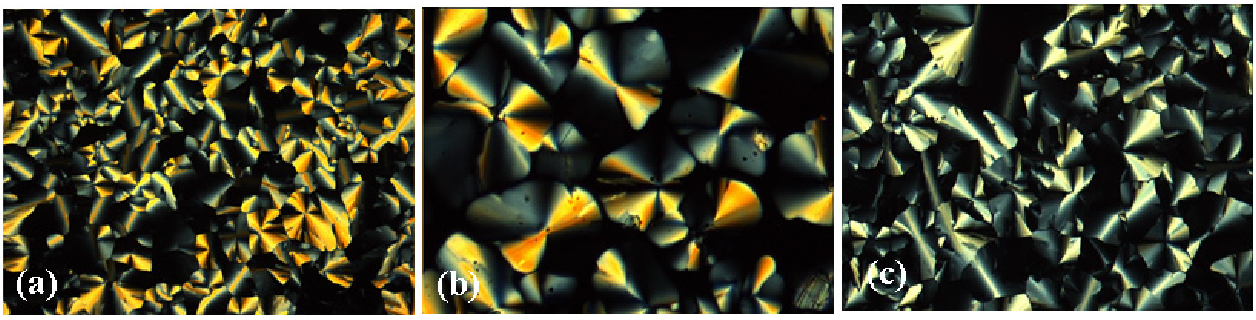


Figure S2: Optical texture observed on a untreated glass slide at different temperatures of compounds (a) **4** at 154 °C, (b) **1** at 155 °C and (c) **2** at 103 °C

4. Circular Dichroism Analysis

Table S3: CD maxima and their respective intensities for compound **6***.

T/ °C	λ_{max}/nm	Intensity/mdeg
23	363.5	-4.8
30	363.5	-5.1
40	363.6	-5.3
50	363.7	-6.2
60	363.3	-8.1
70	363.3	-8.6
80	362.6	-9.8
90	362.8	-10.9
100	362.5	-11.7
110	362.2	-12.6
120	361.9	-14.1
130	360.8	-14.3
140	361.1	-15.2
150	-	-
160	-	-
165	-	-

5. DSC plots

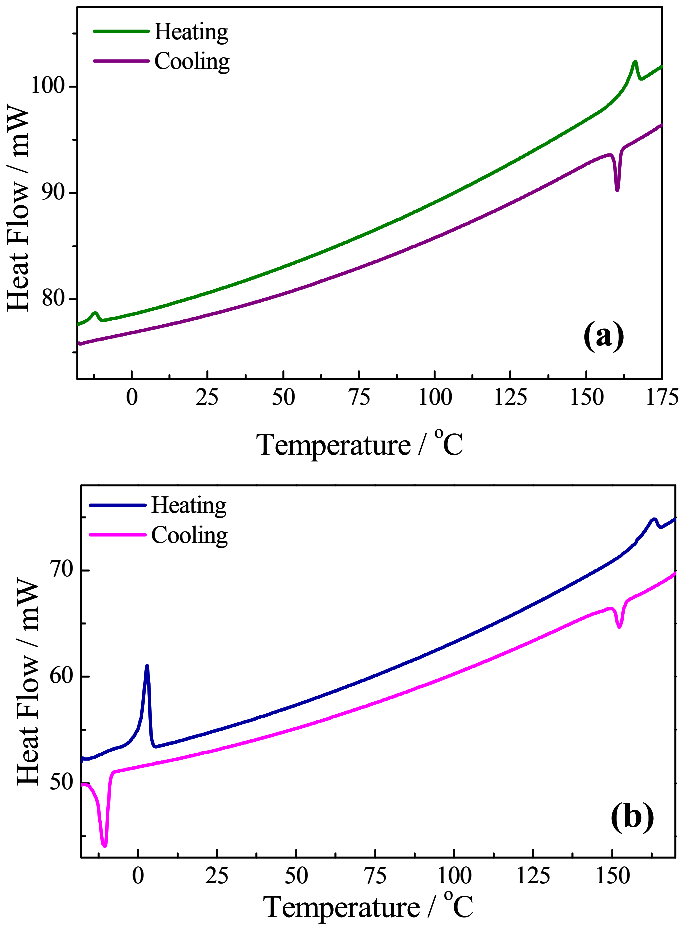


Figure S3: DSC thermoplots of room temperature liquid crystals (a) **1** and (b) **3**.

6. References

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