

## Supporting information

### The biaxial smectic ( $\text{SmA}_b$ ) phase in nonsymmetric liquid crystal dimers comprising two rodlike anisometric segments: an unusual behavior

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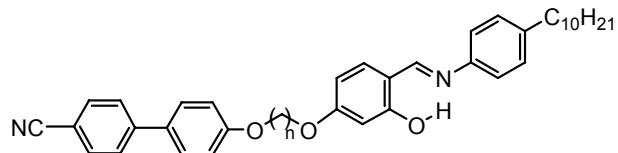
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#### I. General Information

The crude samples, especially the intermediates were purified by column chromatographic technique using silica gel as a stationary phase, whereas the target molecules were purified by recrystallisation technique. Thin layer chromatography (TLC) technique, performed on aluminum sheets pre-coated with silica gel (Merck, Kieselgel 60, F<sub>254</sub>), was employed to assess the purity of the intermediates. IR spectra were recorded using a Perkin-Elmer1000 FTIR spectrometer. <sup>1</sup>H NMR & <sup>13</sup>C NMR spectra were recorded using Bruker Aveance series DPX-200 (200MHz) or BrukerAMX-400 (400MHz) spectrometers. For <sup>1</sup>H NMR spectra, the chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Mass spectra was recorded on a Jeol-JMS-600H spectrometer in FAB<sup>+</sup> mode using 3-nitrobenzyl alcohol as a liquid matrix. Elemental analyses were carried out using a Eurovector EA3000 series CHNOS analyzer. The transitional behavior of target molecules was investigated with the aid of an optical polarizing microscope (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Melter FP90 or FP82HT). The transition temperatures and associated enthalpies were determined by differential scanning calorimetry (Perkin Elmer DSC7). Optical observations were made using either clean untreated glass slides or treated for homogeneous or homeotropic alignment of molecules. X-Ray diffraction studies were carried on powder samples in Lindemann capillaries with CuK<sub>α</sub> radiation using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focusing optics.

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**Table:** Phase sequence, transition temperatures<sup>a</sup> ( °C) and the corresponding enthalpies (J/g) of **1a-e** series.  
 • = Phase exists; - = Phase does not exist (applicable to all the phase characterization tables)



Dimer	n	Cr	Heating Cooling	SmC <sub>a</sub>	Heating Cooling	SmA <sub>b</sub>	Heating Cooling	SmA	Heating Cooling	N	Heating Cooling	I
<b>1a</b>	5	•	110.2 [67.9] 82.5 [64.3]	-	- 96.5 <sup>b</sup>	•		•	128.0 <sup>b</sup> 127.1 <sup>b</sup>	•	141.3 [1.1] 140.8 [1.1]	•
<b>1b</b>	6	•	109.5 [61.3] 76.7 [58.6]	•	- 109.5 <sup>b</sup>	-		•	161.5 <sup>b</sup> 160.9 <sup>b</sup>	•	182.5 [7.6] 181.3 [7.6]	•
<b>1c</b>	7	•	96.99 [52.6] 66.1 [46.1]	-		•	- 88.2 <sup>b</sup>	•	- 91.3 [0.01]	•	140.4 [0.9] 140.1 [0.9]	•
<b>1d</b>	8	•	108.5 [66.5] 75.7 [64.0]	-		-		-		•	165.4 [8.0] 164.6 [8.0]	•
<b>1e</b>	10	•	110.8 [71.3] 84.8 [63.3]	-		-		•	123.0 <sup>b</sup> 124.6 <sup>b</sup>	•	157.8 [8.9] 157.2 [8.9]	•

<sup>a</sup> Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycle at a rate of 5 °C/min.

<sup>b</sup> The phase transition was observed under polarizing microscope but was too weak to get recognized in DSC.

## II. Experimental

### The procedure for the synthesis of 4'-(n-(4-formyl-3-hydroxyphenoxy)pentyloxy)biphenyl-4-carbonitriles (**2a**) : As a representative case

A mixture of 4-( $\omega$ -bromopentyloxy)-2-hydroxybenzaldehyde (5.1 mmol, 1 equiv.), 4'-hydroxy-4-biphenyl carbonitrile (5.1 mmol, 1.0 equiv.), sodium bicarbonate (6.1 mmol, 1.2 equiv.), catalytic amount of potassium iodide and acetone (20 ml) was refluxed for 48 h. The product obtained on evaporation of solvent was poured into water and extracted with dichloromethane (2 x 100 ml). The combined organic extracts were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of solvent furnished the crude product that was purified by column chromatography using silica gel (100-200 mesh). The eluent used was a mixture of dichloromethane and hexanes (1:1). Yield: 65-75%.

**2a:** A white solid; R<sub>f</sub> = 0.35 in 20% EtOAc-hexanes; mp: 124-126 °C; IR (KBr pellet): ν<sub>max</sub> in cm<sup>-1</sup> 2949, 2216, 1626, 1494 and 1215; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.47 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.69 (d, J = 8.5 Hz, 2H, Ar), 7.63 (d, J = 8.3 Hz, 2H, Ar), 7.52 (d, J = 8.7 Hz, 2H, Ar), 7.42 (d, J = 8.6 Hz, 1H, Ar), 6.99 (d, J = 8.6 Hz, 2H, Ar), 6.52 (d, J = 8.7 Hz, 1H, Ar), 6.42 (d, J = 2.1 Hz, 1H, Ar), 4.08-4.02 (m, 4H, 2 × OCH<sub>2</sub>)

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and 1.85-1.22 (m, 6H,  $3 \times \text{CH}_2$ ); MS (FAB $^+$ ): m/z for  $\text{C}_{25}\text{H}_{23}\text{NO}_4$ , Calculated: 401.2, Found: 401.6.

General procedure for the synthesis of 4'-(n-(4-n-(decyl)phenylimino)methyl)-3-hydroxyphenoxy)alkoxy)biphenyl-4-carbonitriles (**1a-e**)

A mixture of 4-*n*-decylaniline **3** (0.42 mmol, 1 equiv.), salicylaldehyde **2a-e** (0.42 mmol, 1 equiv.), absolute ethanol (10 ml) and few traces of acetic acid was refluxed (2 h) until the yellow solid precipitated out. The crude product obtained was collected by filtration and repeatedly washed with absolute ethanol. It was further purified by repeated recrystallisation with a mixture of dichloromethane-ethanol (1:9) until a constant isotropic phase transition temperature was obtained. Yield: Quantitative.

**1a:** A yellow solid; IR (KBr pellet):  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  2917, 2849, 2237, 1626, 1496 and 1196;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.9 (s, 1H, OH), 8.51 (s, 1H,  $\text{CH}=\text{N}$ ), 7.69 (d,  $J = 8.4$  Hz, 2H, Ar), 7.64 (d,  $J = 8.4$  Hz, 2H, Ar), 7.4 (d,  $J = 8.4$  Hz, 2H, Ar), 7.24 (d,  $J = 8.4$  Hz, 1H, Ar), 7.19-7.00 (m, 4H, Ar), 6.99 (d,  $J = 8.8$  Hz, 2H, Ar), 6.48-6.45(m, 2H, Ar), 4.04-4.00(m, 4H,  $2 \times \text{OCH}_2$ ), 2.62 (t,  $J = 7.7$  Hz, 2H,  $1 \times \text{CH}_2$ ), 1.85-1.26 (m, 22H,  $11 \times \text{CH}_2$ ), and 0.88 (t,  $J = 6.4$  Hz, 3H,  $1 \times \text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 164.4, 163.6, 160.3, 159.8, 145.6, 145.3, 141.7, 133.65, 132.6, 131.3, 129.4, 128.3, 127.1, 120.7, 119.1, 115.1, 112.8, 110.1, 107.8, 101.7, 68.1, 68.0, 35.5, 31.9, 31.5, 29.6, 29.5, 29.3, 29.1, 29.0, 25.8, 22.7 and 14.1; MS (FAB $^+$ ): m/z for  $\text{C}_{41}\text{H}_{48}\text{N}_2\text{O}_3$ , Calculated: 616.4, Found: 616.4; Elemental analysis: Calculated (Found): C 79.9 (80.3) ; H 7.9 (7.4); N 4.5 (4.4).

**1b:** A yellow solid; IR (KBr pellet):  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  2917, 2849, 2237, 1626, 1496 and 1196;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.9 (s, 1H, OH), 8.51 (s, 1H,  $\text{CH}=\text{N}$ ), 7.68 (d,  $J = 8.6$  Hz, 2H, Ar), 7.63 (d,  $J = 8.6$  Hz, 2H, Ar), 7.4 (d,  $J = 8.4$  Hz, 2H, Ar), 7.24 (d,  $J = 8.4$  Hz, 1H, Ar), 7.19-7.00 (m, 4H, Ar), 6.99 (d,  $J = 8.8$  Hz, 2H, Ar), 6.48-6.45(m, 2H, Ar), 4.04-4.00(m, 4H,  $2 \times \text{OCH}_2$ ), 2.62 (t,  $J = 7.7$  Hz, 2H,  $1 \times \text{Ar-CH}_2$ ), 1.85-1.26 (m, 24H,  $12 \times \text{CH}_2$ ), and 0.88 (t,  $J = 6.8$  Hz, 3H,  $1 \times \text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 164.1, 163.4, 160.5, 159.8, 145.9, 145.3, 141.5, 133.3, 132.5, 131.4, 129.4, 128.4, 127.1, 120.8, 119.1,

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115.2, 113.2, 110.1, 107.4, 101.7, 68.1, 35.5, 31.9, 31.5, 29.6, 29.5, 29.3, 29.1, 29.0, 25.8, 22.7 and 14.1; MS (FAB<sup>+</sup>): m/z for C<sub>42</sub>H<sub>50</sub>N<sub>2</sub>O<sub>3</sub>, Calculated: 630.4, Found: 630.7; Elemental analysis: Calculated (Found): C 79.8 (80.2); H 7.8 (7.4); N 4.4 (4.5).

**1c:** A yellow solid; IR (KBr pellet):  $\nu_{\max}$  in cm<sup>-1</sup> 2917, 2849, 2237, 1626, 1496 and 1196; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  13.9 (s, 1H, OH), 8.52 (s, 1H, CH=N), 7.68 (d, *J* = 8.6 Hz, 2H, Ar), 7.62 (d, *J* = 8.5 Hz, 2H, Ar), 7.52 (d, *J* = 8.7 Hz, 2H, Ar), 7.23 (d, *J* = 8.3 Hz, 1H, Ar), 7.19-7.01 (m, 4H, Ar), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 6.48-6.44 (m, 2H, Ar), 4.04-4.00 (m, 4H, 2 × OCH<sub>2</sub>), 2.62 (t, *J* = 7.3 Hz, 2H, 1 × Ar-CH<sub>2</sub>), 1.83-1.26 (m, 26H, 13 × CH<sub>2</sub>), and 0.88 (t, *J* = 6.6 Hz, 3H, 1 × CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.2, 163.6, 160.5, 159.8, 145.6, 145.3, 141.5, 133.5, 132.6, 131.3, 129.4, 128.3, 127.1, 120.7, 119.1, 115.1, 113.0, 110.1, 107.6, 101.7, 68.1, 35.5, 31.9, 31.5, 29.6, 29.5, 29.3, 29.1, 29.08, 26.0, 22.7 and 14.1; MS (FAB<sup>+</sup>): m/z for C<sub>43</sub>H<sub>52</sub>N<sub>2</sub>O<sub>3</sub>, Calculated: 644.4, Found: 644.6; Elemental analysis: Calculated (Found): C 80.1 (80.4); H 8.1 (7.7); N 4.3(4.3).

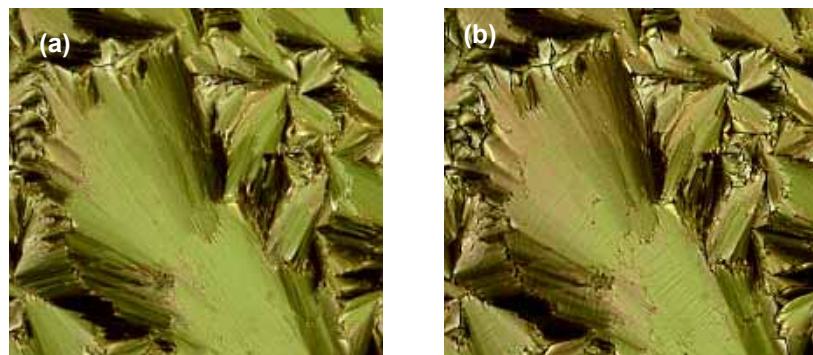
**1d:** A yellow solid; IR (KBr pellet):  $\nu_{\max}$  in cm<sup>-1</sup> 2920, 2848, 2237, 1625, 1495 and 1192; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  13.9 (s, 1H, OH), 8.52 (s, 1H, CH=N), 7.69 (d, *J* = 8.5 Hz, 2H, Ar), 7.62 (d, *J* = 8.3 Hz, 2H, Ar), 7.52 (d, *J* = 8.6 Hz, 2H, Ar), 7.23 (d, *J* = 8.3 Hz, 1H, Ar), 7.19-7.01 (m, 4H, Ar), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 6.48-6.44 (m, 2H, Ar), 4.04-4.00 (m, 4H, 2 × OCH<sub>2</sub>), 2.62 (t, *J* = 7.3 Hz, 2H, 1 × Ar-CH<sub>2</sub>), 1.83-1.26 (m, 28H, 14 × CH<sub>2</sub>), and 0.88 (t, *J* = 6.6 Hz, 3H, 1 × CH<sub>3</sub>); MS (FAB<sup>+</sup>): m/z for C<sub>44</sub>H<sub>54</sub>N<sub>2</sub>O<sub>3</sub>, Calculated: 658.4, Found: 658.6; Elemental analysis: Calculated (Found): C 80.2 (79.9); H 8.3 (8.6); N 4.3(4.2).

**1e:** A yellow solid; IR (KBr pellet):  $\nu_{\max}$  in cm<sup>-1</sup> 2920, 2850, 2237, 1625, 1495 and 1192; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  13.89 (s, 1H, OH), 8.51 (s, 1H, CH=N), 7.68 (d, *J* = 8.5 Hz, 2H, Ar), 7.63 (d, *J* = 8.6 Hz, 2H, Ar), 7.52 (d, *J* = 8.8 Hz, 2H, Ar), 7.23 (d, *J* = 8.4 Hz, 1H, Ar), 7.21-7.00 (m, 4H, Ar), 6.99 (d, *J* = 8.8 Hz, 2H, Ar), 6.48-6.44 (m, 2H, Ar), 4.04-4.00 (m, 4H, 2 × OCH<sub>2</sub>), 2.62 (t, *J* = 7.5 Hz, 2H, 1 × Ar-CH<sub>2</sub>), 1.83-1.26 (m, 32H, 16 × CH<sub>2</sub>), and 0.88 (t, *J* = 6.6 Hz, 3H, 1 × CH<sub>3</sub>); MS (FAB<sup>+</sup>): m/z for C<sub>46</sub>H<sub>58</sub>N<sub>2</sub>O<sub>3</sub>,

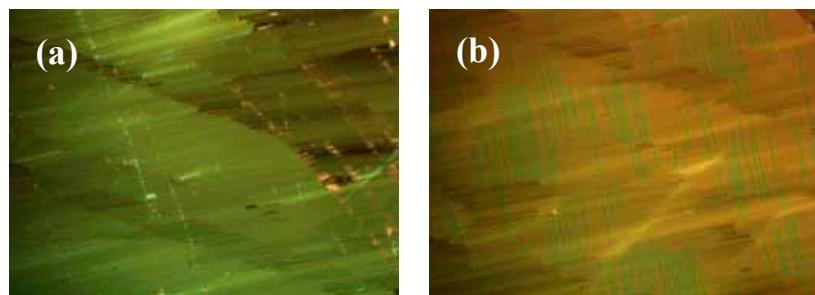
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Calculated: 686.4, Found: 686.3; Elemental analysis: Calculated (Found): C 80.4 (80.4) ; H 8.5 (8.3); N 4.1 (4.1).

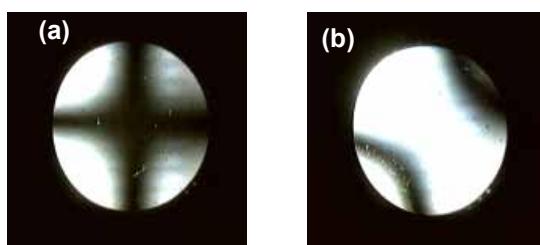
**III. Liquid crystal phase characterization data:**



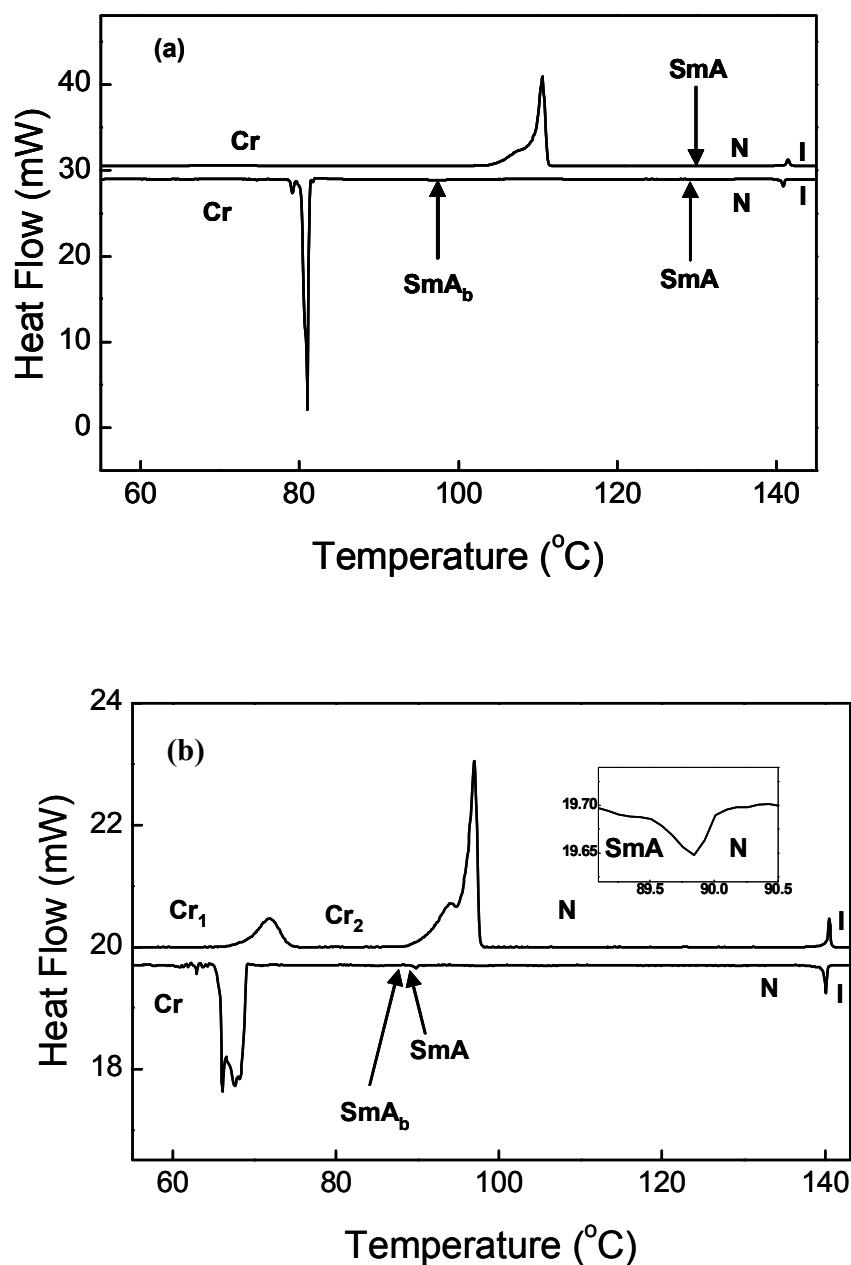
**S1:** Photomicrograph of the POM textures obtained for the dimer **1a** when slides treated for planar orientation (unrubbed) were used: (a) focal conic texture obtained at 98 °C for SmA<sub>d</sub> phase and (b) fine striations appear across the focal conic texture at 90 °C for SmA<sub>db</sub> phase.



**S2:** Photomicrograph of the POM textures obtained for the dimer **1c** when slides treated for planar orientation (unidirectionally rubbed) were used: (a) focal conic texture of the SmA<sub>d</sub> phase (90 °C) and (b) focal conics superposed fine striations appear across the texture at 80 °C for SmA<sub>db</sub> phase.

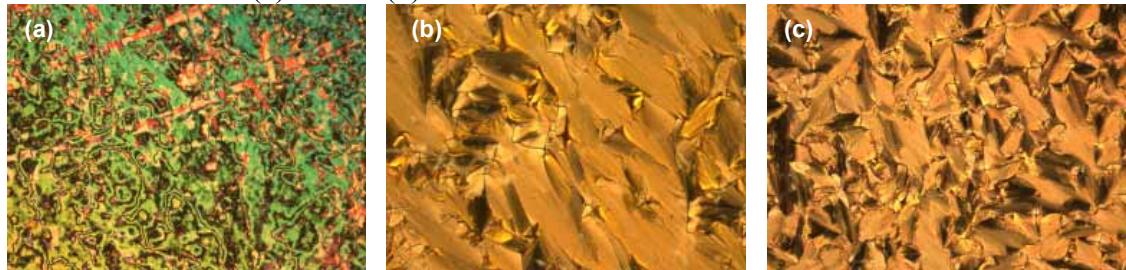


**S3:** Microphotograph of the conoscopic patterns obtained for the homeotropically aligned sample **1a**: (a) the SmA<sub>d</sub> phase at 123.6 °C; (b) the SmA<sub>db</sub> phase at 94.8 °C, notice that the isogryres are well separated.

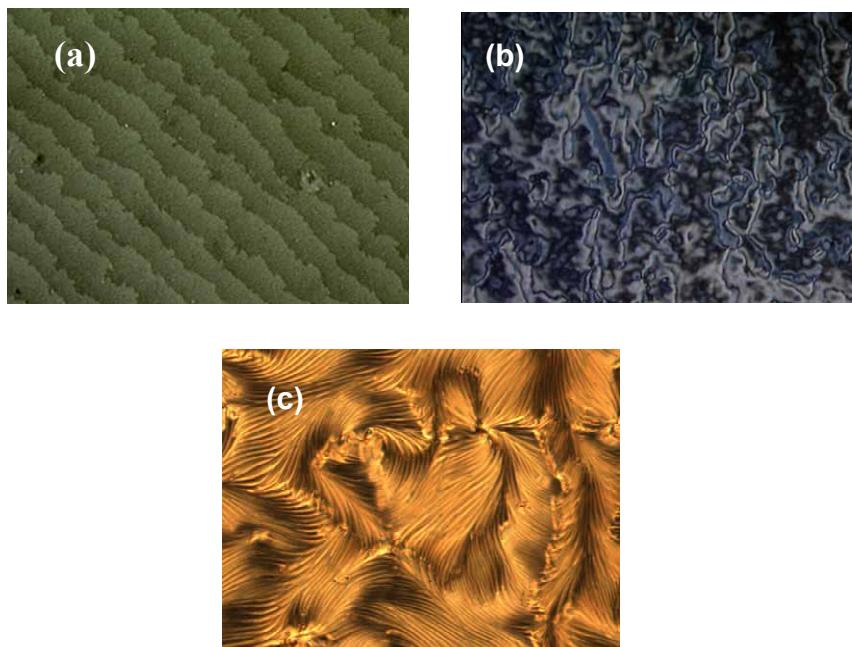


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**S4:** DSC thermogram obtained during first heating and cooling cycle at the rate of 5 °C min<sup>-1</sup> for the dimer (a) **1a** and (b) **1c**.



**S5:** Microphotograph of the textures observed while cooling from the isotropic phase in slides treated for planar orientation for the dimer **1b**. (a) Marble texture for N phase at 179 °C; (b) focal conic texture for SmA<sub>d</sub> phase at 127 °C and (c) broken focal conic texture for SmC<sub>a</sub> phase at 97.5 °C.



**S6:** Photomicrograph of the POM textures obtained for the SmC<sub>a</sub> phase for the homeotropically aligned sample **1b**: (a) a stripe pattern (occurring just below the SmA-SmCa transition); (b) schlieren texture consisting of both two- and four-brush defects and (c) hatched schlieren texture.