Electronic Supplementary Material (ESI) for Soft Matter.

The Effect of Position of (*S*)-2-Octyloxy Tail on the Formation of Frustrated Blue Phase and Antiferroelectric Phase in Schiff Base Liquid Crystals

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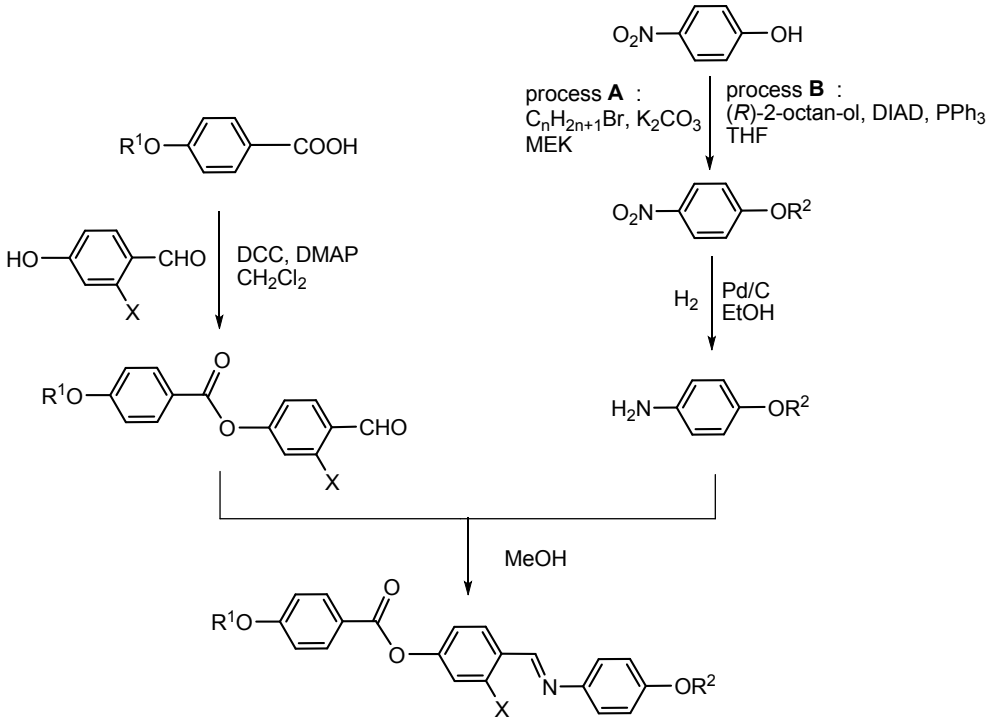
Electronic supplementary information (ESI)

Expermental

General procedures for the synthesis of compounds OH I (n=6-12), OH II (n=6-12), H I (n=7) and H I (n=8)



Compounds	X	R^1	R^2
OH I (n = 6-12)	OH	C_6H_{13}	$-C_nH_{2n+1}$
H I (n = 7)	H		
OH II (n = 6-12)	OH	$C_nH_{2n+1}-$	C_6H_{13}
H II (n = 8)	H		

Scheme 1 Synthetic route to the target compounds.

Characterization of materials

The chemical structure of the target materials were identified by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy using a Bruker Avance DRX 500 NMR spectrometer (Bruker Co., Karlsruhe, Germany). The purity of the final compounds was assessed by thin layer chromatography (TLC), and further confirmed by elemental analysis using a Heraeus Vario EL III analyzer (Elementar Analysenyteme GmbH Co., Hanau, Germany). The carbon and hydrogen analytical data agreed with calculated results within ±1%.

Mesophases were principally identified by microscopic texture of the materials sandwiched between two glass plates under crossed polarizing microscope using Nikon Microphoto-FXA optical microscopy in conjunction with hot stage METTER TOLEDO FP82HT controlled by METTLER FP90 control processor. The phase transition temperatures and corresponding phase transition enthalpies of compounds were determined by differential scanning calorimeter (DSC) using PERKIN- ELMER DSC7 calorimeter under running rates of 3°C min^{-1}. Switching behavior and dielectric permittivity of antiferroelectric smectic phases were measured in homogeneously aligned cells (E. H. C. Co. Japan) using triangular wave method[1]. The sample was filled into the liquid crystal sample cell by capillary action in the isotropic states. Two wires were then pasted separately to the ITO glasses of the sample cell by silver paint. For thinner cells, alignment was achieved by slowly cooling the sample from the isotropic liquid into the smectic mesophase, at rate of 0.1 °C min^{-1} and in the absence of an electric field.[2]

Preparation of materials

The chiral starting materials, (*R*)-2-octanol were purchased from Fluka Co. Chem., Japan, with purity greater than 99%. Thin layer chromatography was performed with

TLC sheets coated with silica; spots were detected by UV irradiation. Silica gel (Merck silica gel 60, 63-200 mesh) was used for column chromatography. The organic solvents were dried and distilled before use. Some intermediates in scheme 1 were prepared according to conventional methods. Detailed synthetic procedures for the intermediates and target materials are described below.

Synthesis of 4-formyl-3-hydroxyphenyl 4'-[(1*S*)-(1-methylheptyl)oxy]benzoate.

A mixture of 2, 4-dihydroxybenzaldehyde (0.28 g, 2.00 mmol), (*S*)-4-(1-methylheptyloxy)benzoic acid (0.50 g, 2.00 mmol), DMAP (0.03 g, 0.21 mmol), DCC (1.24 g, 6.0mmol) and dry CH_2Cl_2 (10 ml) was stirred at room temperature for two days. After work-up procedure, yellow powder (0.47 g) was isolated in 63 % yield by column chromatography over silica gel (63-200mesh) using CH_2Cl_2 as eluent. ^{1}H-NMR ($CDCl_3$): δ (ppm) 11.24 (s, Ar-O**H**, 1H), 9.89 (s, Ar-C**H**O, 1H), 8.11 (d, ArH, 2H, J = 8.5 Hz), 7.14 (d, Ar-**H**, 2H, J = 8.5 Hz), 7.12 (d, Ar-**H**, 1H, J = 8.5 Hz), 7.11 (s, Ar-**H**, 1H), 4.49 (m, -OC**H***, 1H), 1.85-1.25 (m, -C$\mathbf{H}_2$-, CH*C$\mathbf{H}_3$, 13H), 0.89 (t, -CH_2C$\mathbf{H}_3$, 3H, J = 7.0 Hz).

Synthesis of 4-alkoxynitrobenzene.

A mixture of 4-nitrophenol (1.00 g, 7.19 mmol), bromoalkane (7.90 mmol), anhydrous potassium carbonate (2.50 g, 17.97 mmol) and 2-butanone (MEK) (15 mL) was refluxed for 48 h. After work-up procedure, the products as yellow liquid or white solid were isolated in 90-95% yield by column chromatography over silica gel (63-200mesh) using EA/hexane (1:4) as eluent.

Synthesis of 4-alkoxyaniline.

To a solution of compound 4-alkoxynitrobenzene (0.55 mmol) in dry EtOH (10 mL), Pd/C (0.01 g, 0.11 mmol) was added and stirred under hydrogen atmosphere (balloon) for 24 h (monitored by TLC). The reaction mixture was then filtered

through a celite bed. The filtrate was concentrated under reduced pressure to give yellow liquid or white solid in 90-95% yield.

Synthesis of 4-formyl-3-hydroxyphenyl 4-(alkyloxy)benzoate

A mixture of 2,4-dihydroxybenzaldehyde (1.53 mmol), 4-(alkyloxy)benzoic acid (1.20 mmol), DMAP (0.17 mmol), DCC (4.60 mmol) and CH_2Cl_2 (10 mL) was stirred at room temperature for 24 h. After work-up procedure, the products were isolated by column chromatography over silica gel using CH_2Cl_2 as eluent to give white solids in 70-80 % yield.

4-formyl-3-hydroxyphenyl 4-(octyloxy)benzoate.

A white solid. ^{1}H-NMR ($CDCl_3$): δ (ppm) 11.25 (s, Ar-O**H**, 1H), 9.90 (s, Ar-C**H**O, 1H), 8.13 (d, Ar-**H**, 2H, J = 9.0 Hz), 7.62 (d, Ar-**H**, 1H, J = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, J = 8.5 Hz), 6.92 (dd, Ar-**H**, 1H, J = 8.5 Hz, J = 2.0 Hz), 6.89 (d, Ar-**H**, 1H, J = 2.0 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, J = 6.5 Hz), 1.86-1.27 (m, CH$_2$C**H**$_2$CH$_2$, 12H), 0.90 (t, -CH$_2$C**H**$_3$, 3H, J = 7.0 Hz).

4-formyl-3-hydroxyphenyl 4-(nonyloxy)benzoate.

A white solid. ^{1}H-NMR ($CDCl_3$): δ (ppm) 11.25 (s, Ar-O**H**, 1H), 9.90 (s, Ar-C**H**O, 1H), 8.13 (d, Ar-**H**, 2H, J = 9.0Hz), 7.62 (d, Ar-**H**, 1H, J = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, J = 8.5 Hz), 6.92 (dd, Ar-**H**, 1H, J = 8.5 Hz, J = 2.0 Hz), 6.89 (d, Ar-**H**, 1H, J = 2.0 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, J = 6.5 Hz), 1.86-1.27 (m, CH$_2$C**H**$_2$CH$_2$, 14H), 0.90 (t, -CH$_2$C**H**$_3$, 3H, J = 7.0 Hz).

4-formyl-3-hydroxyphenyl 4-(decyloxy)benzoate.

A white solid. ^{1}H-NMR ($CDCl_3$): δ (ppm) 11.25 (s, Ar-O**H**, 1H), 9.90 (s, Ar-C**H**O, 1H), 8.13 (d, Ar-**H**, 2H, J = 9.0Hz), 7.62 (d, Ar-**H**, 1H, J = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, J = 8.5 Hz), 6.92 (dd, Ar-**H**, 1H, J = 8.5 Hz, J = 2.0 Hz), 6.89 (d, Ar-**H**, 1H, J = 2.0 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, J = 6.5 Hz), 1.86-1.27 (m, CH$_2$C**H**$_2$CH$_2$, 16H), 0.90 (t, -CH$_2$C**H**$_3$, 3H, J = 7.0 Hz).

4-formyl-3-hydroxyphenyl 4-(undecyloxy)benzoate.

A white solid. ^{1}H-NMR ($CDCl_3$): δ (ppm) 11.25 (s, Ar-O**H**, 1H), 9.90 (s, Ar-C**H**O, 1H), 8.13 (d, Ar-**H**, 2H, J = 9.0Hz), 7.62 (d, Ar-**H**, 1H, J = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, J = 8.5 Hz), 6.92 (dd, Ar-**H**, 1H, J = 8.5 Hz, J = 2.0 Hz), 6.89 (d, Ar-**H**, 1H, J = 2.0 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, J = 6.5 Hz), 1.86-1.27 (m, CH$_2$C**H**$_2$CH$_2$, 18H), 0.90 (t, -CH$_2$C**H**$_3$, 3H, J = 7.0 Hz).

4-formyl-3-hydroxyphenyl 4-(dodecyloxy)benzoate.

A white solid. ^{1}H-NMR ($CDCl_3$): δ (ppm) 11.25 (s, Ar-O**H**, 1H), 9.90 (s, Ar-C**H**O, 1H), 8.13 (d, Ar-**H**, 2H, J = 9.0Hz), 7.62 (d, Ar-**H**, 1H, J = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, J = 8.5 Hz), 6.92 (dd, Ar-**H**, 1H, J = 8.5 Hz, J = 2.0 Hz), 6.89 (d, Ar-**H**, 1H, J = 2.0 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, J = 6.5 Hz), 1.86-1.27 (m, CH$_2$C**H**$_2$CH$_2$, 20H), 0.90 (t, -CH$_2$C**H**$_3$, 3H, J = 7.0 Hz).

4-[1-(1*S*)-methylheptyloxy]nitrobenzene.

A solution of diisopropyl azodicarboxylate (1.98 mL, 9.98 mmol) and 4-nitrophenol (1.39 g, 9.98 mmol) in 10 mL anhydrous THF was drop by drop to a solution of triphenylphosphine (2.62 g, 9.98 mmol) and (*R*)-2-octanol (1.2 mL, 7.68 mmol) in 15mL anhydrous THF at room temperature with stirring for 24 h. After work-up procedure, this product was isolated by column chromatography over silica gel (63-200mesh) using toluene as eluent. The yellow oil (1.482 g) was obtained in 77% yields. ^{1}H-NMR ($CDCl_3$): δ (ppm) 8.19 (d, Ar-**H**, 2H, J = 3.0 Hz), 6.92 (d, Ar-**H**, 2H, J = 3.0 Hz), 4.48 (m, OC**H***, 1H, J = 6.0 Hz), 1.81-1.30 (m, CH$_2$C**H**$_2$CH$_2$, 13H), 0.89 (t, -CH$_2$C**H**$_3$, 3H, J = 6.6 Hz).

Synthesis of 4-[(1*S*)-1-methylheptoxy]aniline.

This compound was synthesized using the same synthetic method as that described for 4-alkoxyaniline. This product was isolated to give brown oil (0.315 g) in 89% yields. ^{1}H-NMR ($CDCl_3$): δ 6.74 (d, Ar-**H**, 2H, J = 3.0 Hz), 6.60 (d, Ar-**H**, 2H, J = 3.5

Hz), 4.17 (m, OC**H***, 1H), 3.42 (s, N$\mathbf{H}_2$, 2H), 1.72-1.25 (m, $CH_2C\mathbf{H}_2CH_2$, 13H), 0.89 (t,-$CH_2C\mathbf{H}_3$, 3H, *J* = 6.8 Hz).

Synthesis of 3-hydroxy-4-((4-(alkoxy)phenylimino)- phenyl 4'-[(1*S*)-1-methylheptoxy]benzoate, OH I (n=6-12).

A mixture of 4-formyl-3-hydroxyphenyl 4'-[(1*S*)-(1-methylheptyl)oxy]benzoate (0.24 mmol), 4-alkoxyaniline (0.24 mmol) and methanol (10 mL) was refluxed for 4 h until the yellow solid precipitated out. The yellow solid obtained in 60-75% yield was collected by filtration and further purified by repeated recrystallization from methanol.

OH I (n=6) ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz), 6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC$\mathbf{H}_2CH_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C$\mathbf{H}_2$-, CH*C$\mathbf{H}_3$, 21H), 0.89 (t, -$CH_2C\mathbf{H}_3$, 6H, *J* = 7.0 Hz). FT-IR (KBr): 3543, 2924, 2857, 1724, 1610, 1465, 1255 cm^{-1}. Elemental analysis for $C_{34}H_{43}NO_5$(percent): calculated C, 74.83, H, 7.94, N, 2.57; found C, 74.81, H, 7.81, N, 2.49.

OH I (n=7). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz), 6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC$\mathbf{H}_2CH_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C$\mathbf{H}_2$-, CH*C$\mathbf{H}_3$, 23H), 0.89 (t, -$CH_2C\mathbf{H}_3$, 6H, *J* = 7.0 Hz). FT-IR (KBr): 3543, 2924, 2857, 1724, 1610, 1465, 1255 cm^{-1}. Elemental analysis for $C_{35}H_{45}NO_5$(percent): calculated C, 75.10, H, 8.10, N, 2.50; found C, 74.99, H, 8.06, N, 2.35.

OH I (n=8). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.13 (d,

Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz), 6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C**H**$_2$-, CH*C**H**$_3$, 25H), 0.89 (t, -CH$_2$C**H**$_3$, 6H, *J* = 7.0 Hz). FT-IR (KBr): 3543, 2924, 2857, 1724, 1610, 1465, 1255 cm^{-1}. Elemental analysis for $C_{36}H_{47}NO_5$(percent): calculated C, 75.36, H, 8.26, N, 2.44; found C, 75.56, H, 8.03, N, 2.24.

OH I (**n=9**). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz), 6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C**H**$_2$-, CH*C**H**$_3$, 27H), 0.89 (t, -CH$_2$C**H**$_3$, 6H, *J* = 7.0 Hz). FT-IR (KBr): 3543, 2924, 2857, 1724, 1610, 1465, 1255 cm^{-1}. Elemental analysis for $C_{37}H_{49}NO_5$(percent): calculated C, 75.60, H, 8.40, N, 2.38; found C, 75.48, H, 8.59, N, 2.25.

OH I (**n=10**). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz), 6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C**H**$_2$-, CH*C**H**$_3$, 29H), 0.89 (t, -CH$_2$C**H**$_3$, 6H, *J* = 7.0 Hz). FT-IR (KBr): 3543, 2924, 2857, 1724, 1610, 1465, 1255 cm^{-1}. Elemental analysis for $C_{38}H_{51}NO_5$(percent): calculated C, 75.84, H, 8.54, N, 2.33; found C, 76.04, H, 8.67, N, 2.22.

OH I (**n=11**). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, -C**H**=N-, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz),

6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C**H**$_2$-, CH*C**H**$_3$, 31H), 0.89 (t, -CH$_2$C**H**$_3$, 6H, *J* = 7.0 Hz). FT-IR (KBr): 3543, 2924, 2857, 1724, 1610, 1465, 1255 cm^{-1}. Elemental analysis for $C_{39}H_{53}NO_5$(percent): calculated C, 76.06, H, 8.67, N, 2.27; found C, 75.81, H, 8.58, N, 2.08.

OH I (**n=12**). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.62 (s, N=C**H**, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.52 (d, Ar**H**, 2H, *J* = 8.5 Hz), 7.40 (d, Ar**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar**H**, 2H, *J* = 8.5 Hz), 6.95 (m, Ar**H**, 1H), 6.87 (d, Ar**H**, 1H, *J* = 8.5 Hz), 6.81 (d, Ar**H**, 2H, *J* = 8.5 Hz), 3.98 (t, -OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 3.75 (m, -OC**H***, 1H), 1.85-1.25 (m, -C**H**$_2$-, CH*C**H**$_3$, 33H), 0.89 (t, -CH$_2$C**H**$_3$, 6H, *J* = 7.0 Hz). Elemental analysis for $C_{41}H_{55}NO_5$(percent): calculated C, 76.27, H, 8.80, N, 2.22; found C, 76.15, H, 8.78, N, 2.28.

3-hydroxy-4-[(1*S*)-(4-(1-methylheptoxy)phenylimino)methyl]phenyl 4-(alkoxy)benzoate, OH II (n=6-12) Compounds **OH II (n=6-12)** were synthesized using the same synthetic method as that described for compounds **OH I (n=6-12)**. These products were obtained with yellow solids in 85-90% yields.

OH II (n=6). ^{1}H-NMR ($CDCl_3$): δ 13.81 (s, Ar-O**H**, 1H), 8.63 (s, C**H**=N, 1H), 8.14 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.41 (d, Ar-**H**, 1H, *J* = 8.0 Hz), 7.27 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.94 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.88 (d, Ar-**H**, 1H, *J* = 2.5 Hz), 6.81 (d, Ar-**H**, 1H, *J* = 2.0 Hz), 4.38 (m, OC***H**, 1H, *J* = 5.5 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 1.86-1.31 (m, CH$_2$C**H**$_2$CH$_2$, 21H), 0.90 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.8 Hz). FT-IR (KBr): 3544, 2925, 2856, 1725, 1612, 1504, 1457, 1255 cm^{-1}. Elemental analysis for $C_{34}H_{45}NO_5$ (percent): calculated C, 74.83, H, 7.94, N, 2.57; found C, 74.54, H, 8.09, N, 2.33.

OH II (n=7). ^{1}H-NMR ($CDCl_3$): δ 13.81 (s, Ar-O**H**, 1H), 8.63 (s, C**H**=N, 1H), 8.14 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.41 (d, Ar-**H**, 1H, *J* = 8.0 Hz), 7.27 (d, Ar-**H**, 2H, *J* = 8.5 Hz),

6.98 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.94 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.88 (d, Ar-**H**, 1H, *J* = 2.5 Hz), 6.82 (dd, Ar-**H**, 1H, *J* = 2.0 Hz), 4.38 (m, OC***H**, 1H, *J* = 5.5 Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, *J* = 6.5Hz), 1.86-1.31 (m, CH$_2$C**H**$_2$CH$_2$, 23H), 0.90 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.8 Hz). FT-IR (KBr): 3544, 2925, 2856, 1725, 1612, 1504, 1457, 1255 cm^{-1}. Elemental analysis for $C_{35}H_{45}NO_5$ (percent): calculated C, 75.10, H, 8.10, N, 2.50; found C, 74.95, H, 8.26, N, 2.27.

OH II (n=8). ^{1}H-NMR ($CDCl_3$): δ 13.81 (s, Ar-O**H**, 1H), 8.63 (s, C**H**=N, 1H), 8.14 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.41 (d, Ar-**H**, 1H, *J* = 8.0Hz), 7.27 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.94 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.88 (d, Ar-**H**, 1H, *J* = 2.5 Hz), 6.82 (dd, Ar-**H**, 1H, *J* = 2.0 Hz), 4.38 (m, OC***H**, 1H, *J* = 5.5Hz), 4.06 (t, OC**H**$_2$CH$_2$, 2H, *J* = 6.5 Hz), 1.86-1.31 (m, CH$_2$C**H**$_2$CH$_2$, 25H), 0.90 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.8 Hz). FT-IR (KBr): 3544, 2925, 2856, 1725, 1612, 1504, 1457, 1255 cm^{-1}. Elemental analysis for $C_{36}H_{47}NO_5$ (percent): calculated C, 75.36, H, 8.26, N, 2.57; found C, 75.01, H, 8.20, N, 2.55.

OH II (n=9). ^{1}H-NMR ($CDCl_3$): δ 13.80 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.14 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.41 (d, Ar-**H**, 1H, *J* = 8.0 Hz), 7.26 (d, Ar-**H**, 2H, *J* = 8.5Hz), 6.98 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.94 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.88 (d, Ar-**H**, 1H, *J* = 2.0 Hz), 6.82 (dd, Ar-**H**, 1H, *J* = 2.0 Hz), 4.38 (m, -OC***H**, 1H, *J* = 6.0 Hz), 4.06 (t, -OC**H**$_2$CH$_2$-, 2H, *J* = 6.5Hz), 1.86-1.31 (m, -CH$_2$C**H**$_2$CH$_2$-, 27H), 0.90 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.4 Hz). FT-IR (KBr): 3544, 2925, 2856, 1725, 1612, 1504, 1457, 1255 cm^{-1}. Elemental analysis for $C_{37}H_{49}NO_5$ (percent): calculated C, 75.60, H, 8.40, N, 2.38; found C, 75.35, H, 8.27, N, 2.33..

OH II (n=10). ^{1}H-NMR ($CDCl_3$): δ 13.80 (s, Ar-O**H**, 1H), 8.62 (s, C**H**=N, 1H), 8.14 (d, Ar-**H**, 2H, *J* = 9.0Hz), 7.41 (d, Ar-**H**, 1H, *J* = 8.5Hz), 7.26 (d, Ar-**H**, 2H, *J* = 9.0Hz), 6.98 (d, Ar-**H**, 2H, *J* = 9.0Hz), 6.93 (d, Ar-**H**, 2H, *J* = 8.5Hz), 6.87 (d, Ar-**H**, 1H, *J* = 2.5Hz), 6.82 (dd, Ar-**H**, 1H, *J* = 2.0Hz), 4.38 (m, -OC***H**, 1H, *J* = 6.5Hz),

4.05 (t, -OC**H**$_2$CH$_2$-, 2H, *J* = 6.5Hz), 1.86-1.26 (m, -CH$_2$C**H**$_2$CH$_2$-, 29H), 0.89 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.5Hz). FT-IR (KBr): 3545, 2925, 2855, 1725, 1610, 1505, 1457, 1255 cm^{-1}. Elemental analysis for $C_{38}H_{51}NO_5$ (percent): calculated C, 75.84, H, 8.54, N, 2.33 ; found C, 75.20, H, 8.62, N, 2.45..

OH II (n=11). ^{1}H-NMR ($CDCl_3$): δ 13.78 (s, Ar-O**H**, 1H), 8.61 (s, Ar-C**H**=N, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.39 (d, Ar-**H**, 1H, *J* = 8.5Hz), 7.25 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 6.96 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 6.92 (d, Ar-**H**, 2H, *J* = 9.0Hz), 6.86 (d, Ar-**H**, 1H, *J* = 2.0 Hz), 6.80 (dd, Ar-**H**, 1H, *J* = 2.0 Hz), 4.36 (m, -OC***H**, 1H, *J* = 6.5 Hz), 4.04 (t, -OC**H**$_2$CH$_2$-, 2H, *J* = 6.5Hz), 1.84-1.27 (m, -CH$_2$C**H**$_2$CH$_2$-, 31H), 0.88 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.5Hz). FT-IR (KBr): 3544, 2926, 2857, 1725, 1609, 1505, 1456, 1254 cm^{-1}. Elemental analysis for $C_{39}H_{53}NO_5$ (percent): calculated C, 76.06, H, 8.67, N, 2.27; found C, 75.07, H, 8.54, N, 2.35.

OH II (n=12). ^{1}H-NMR ($CDCl_3$): δ 13.79 (s, Ar-O**H**, 1H), 8.61 (s, C**H**=N, 1H), 8.13 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.39 (d, Ar-**H**, 1H, *J* = 8.5 Hz), 7.25 (d, Ar-**H**, 2H, *J* = 8.8 Hz), 6.97 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.92 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.86 (d, Ar-**H**, 1H, *J* = 2.0Hz), 6.80 (dd, Ar-**H**, 1H, *J* = 2.0 Hz), 4.36 (m, -OC***H**, 1H, *J* = 6.0 Hz), 4.04 (t, -OC**H**$_2$CH$_2$-, 2H, *J* = 6.5 Hz), 1.84-1.27 (m, -CH$_2$C**H**$_2$CH$_2$-, 33H), 0.88 (t, -CH$_2$C**H**$_3$, 6H, *J* = 6.4 Hz). FT-IR (KBr): 3545, 2925, 2854, 1724, 1611, 1505, 1456, 1255 cm^{-1}. Elemental analysis for $C_{40}H_{55}NO_5$ (percent): calculated C, 76.27, H, 8.80, N, 2.22; found C, 76.39, H, 8.76, N, 2.27.

4-{[4-(heptyloxy)phenylimino]methyl}phenyl 4'-[(1*S*)-1-methylheptyloxy] benzoate, H I (n=7) This compound was synthesized using the same synthetic method as that described for compounds **OH I (n=6-12)**. This product was isolated to give white solid in 56% yields. ^{1}H-NMR ($CDCl_3$): δ 8.50 (s, C**H**=N, 1H), 8.15 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 7.96 (d, Ar-**H**, 2H, *J* = 8.4 Hz), 7.32 (d, Ar-**H**, 2H, *J* = 8.4 Hz), 7.24 (d, Ar-**H**, 2H, *J* = 8.4 Hz), 6.97 (d, Ar-**H**, 2H, *J* = 9.0 Hz), 6.94 (d, Ar-**H**, 2H, *J* =

9.0 Hz), 4.52-4.47 (m, C**H***CH_3, 1H), 3.99 (t, Ar-OC**H**$_2$-, 2H, *J* = 6.6 Hz), 1.83-1.29 (m, -C**H**$_2$-, CH*C**H**$_3$, 23H), 0.91 (m, -CH_2C**H**$_3$, 6H). FT-IR (KBr): 2926, 2859, 1737, 1610, 1247 cm^{-1}. Elemental analysis for $C_{35}H_{45}NO_4$(percent): calculated C, 77.31, H, 8.34, N, 2.58; found C, 77.46, H, 8.12, N, 2.46.

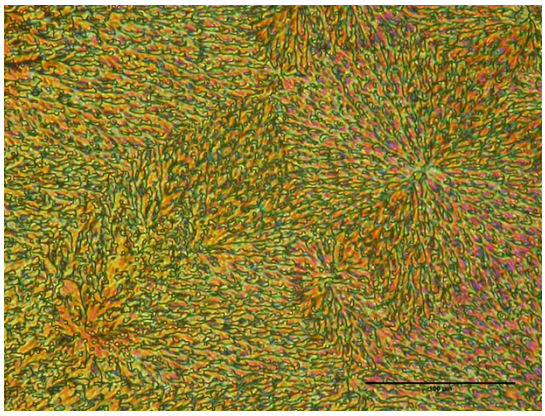
(*E*)-4-(((*R*)-4-(1-methylheptyloxy)phenylimino)methyl)phenyl 4-(octoxy)benzoate, H II (n=8)

Compounds **H II (n=8)** were synthesized using the same synthetic method as that described for compounds **H I (n=7)**. This product was obtained with white solid in 50% yield. ^{1}H-NMR ($CDCl_3$): δ 8.49 (s, C**H**=N, 1H), 8.15 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 7.95 (d, Ar-**H**, 2H, *J* = 8. 5Hz), 7.32 (d, Ar-**H**, 2H, *J* = 8.0 Hz), 7.22 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 6.98 (d, Ar-**H**, 2H, *J* = 8.5 Hz), 6.92 (d, Ar-**H**, 1H, *J* = 8.5 Hz), 4.36 (m, -OC***H**, 1H, *J* = 6.0 Hz), 4.04 (t, -OC**H**$_2$$CH_2$-, 2H, *J* = 6.5 Hz), 1.84-1.30 (m, -CH_2C**H**$_2$$CH_2$-, 25H), 0.89 (t, -$CH_2$C**H**$_3$, 6H, *J* = 5.0 Hz). FT-IR (KBr): 2918, 2866, 1735, 1611, 1505, 1475, 1245 cm^{-1}. Elemental analysis for $C_{36}H_{47}NO_4$ (percent): calculated C, 77.52 , H, 8.94 , N, 2.51; found C, 77.66 , H, 8.81 , N, 2.63.

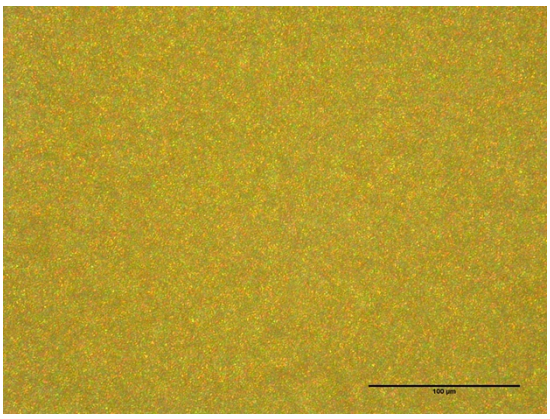
1. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.,*1983, **22**, L661-L663.

2. A. Petrenko and J. W. Goodby, *J. Mater. Chem.,* 2007, **17**, 766-782.

(a)

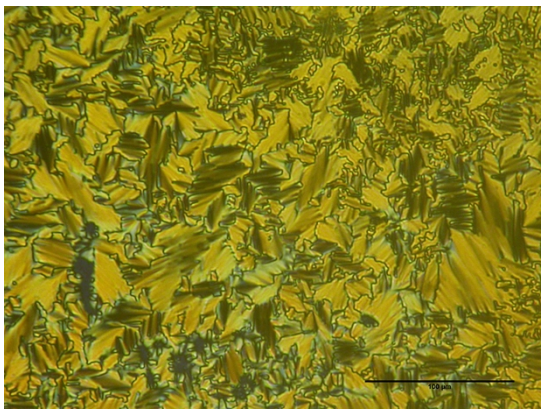


(b)



(c)

(d)



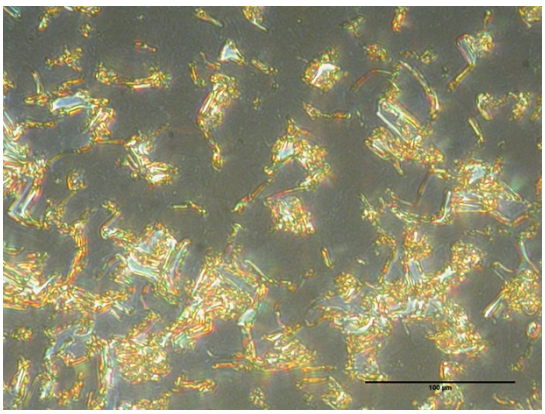
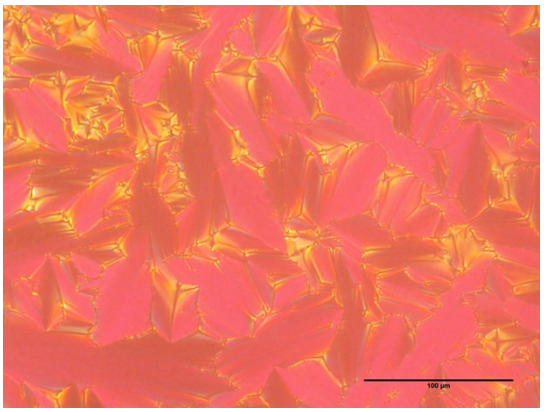
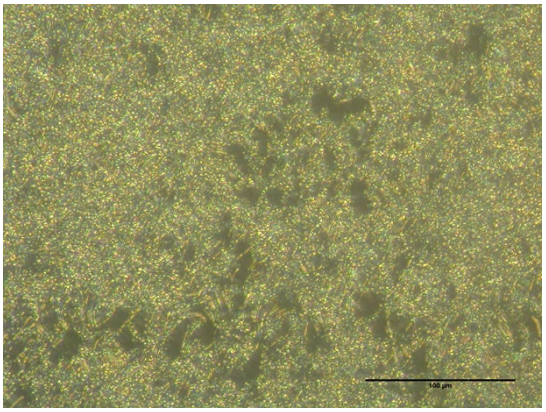


Fig S1. Polarizing optical micrographs: **(a)** compound **OH I (n=7)** exhibited the characteristic of chiral nematic (N^*) thread-like texture at 135.6 °C, in which dark lines connect two *s* =±1/2 point defects or from closed loops; **(b)** compound **OH I (n=7)** showed the focal-conic texture at 89.5 °C, indicating the characteristic of SmA^* phase; **(c)** compound **OH II (n=8)** exhibited chiral nematic (N^*) phase with fan-liked texture at 135.6 °C, indicating the characteristic of strongly twisted material. **(d)** compound **OH II (n=8)** showed the homeotropic (dark) texture of smectic A^* phase at 104.6 °C. (Scale bar: 100 µm)

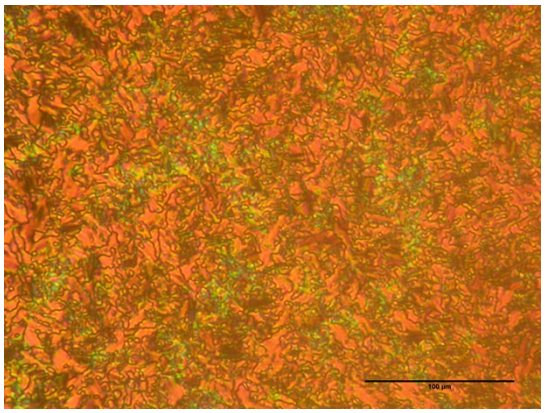
(a)



(b)



(c)



(d)

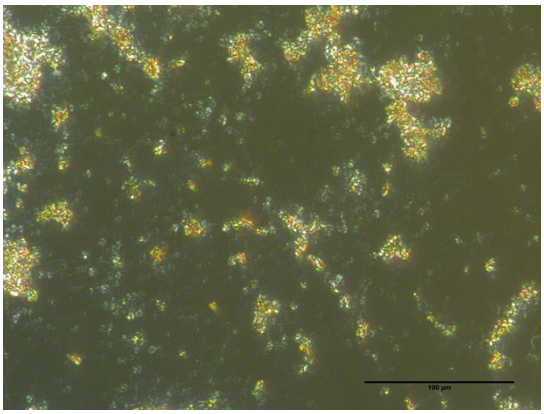


Fig S2. (a) compound **H I (n=7)** exhibited the characteristic of chiral nematic (N^*) fan-liked texture at 136.2 °C; **(b)** compound **H I (n=7)** showed the focal-conic texture and the homeotropic (dark) texture of smectic A^* phase at 89.4 °C, indicating the characteristic of SmA^* phase; **(c)** compound **H II (n=8)** the characteristic of chiral nematic (N^*) fan-liked texture at 130.2 °C; **(d)** compound **H II (n=8)** showed the homeotropic (dark) texture of smectic A^* phase at 117.6 °C. (Scale bar: 100 μm)

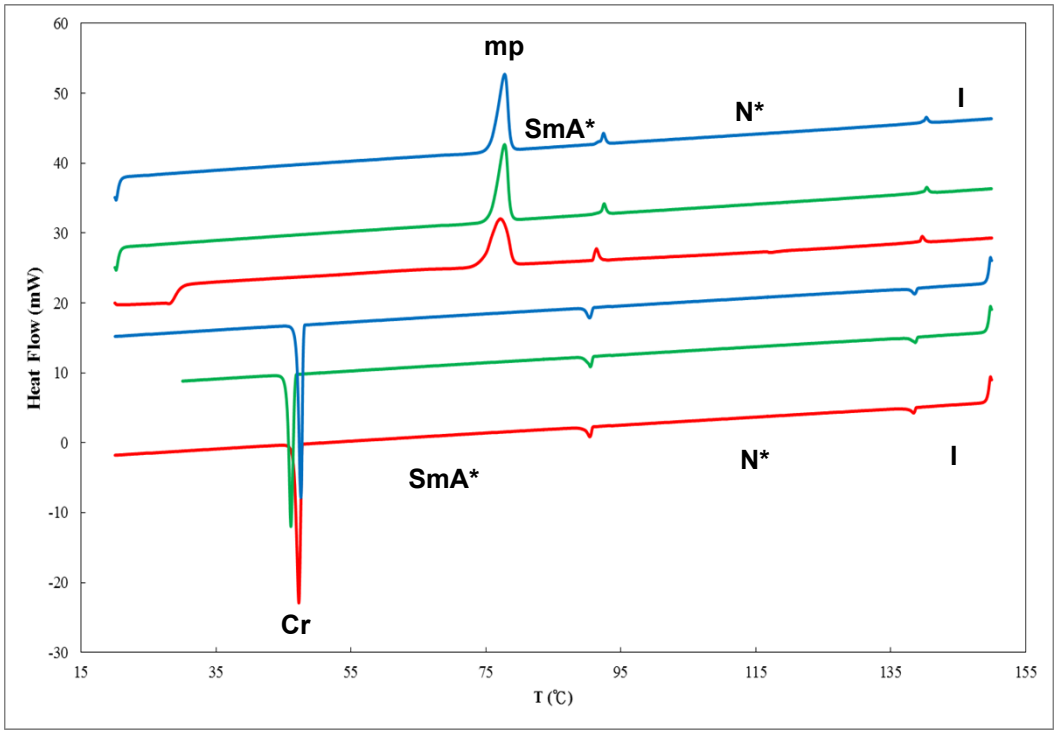


Fig S3. The DSC thermogrames of 1st heating-cooling (red-traces), the 2nd heating-cooling (green-traces) and 3rd heating-cooling (blue-traces) cycles obtained from compound **H I (n=7)**.

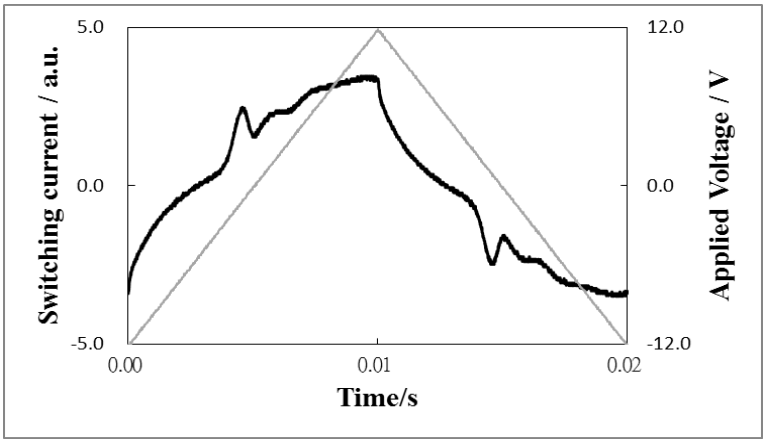


Fig S4. Switching current in a triangle electric field (50 Hz, 5 V_{pp}) in the SmC_A^* phase at 82.0 °C for compound **OH I (n=7)** in 5 μm thickness of homogeneously aligned cell.

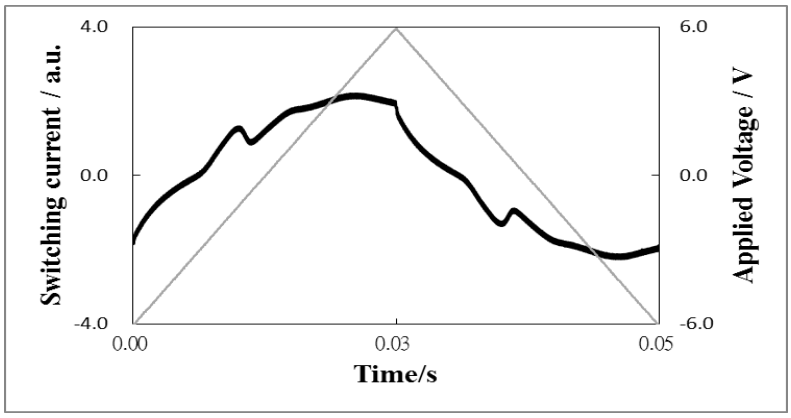


Fig S5. Switching current in a triangle electric field (20 Hz, 4 V_{pp}) in the SmC_A^* phase at 78.0 °C for compound **H I (n=7)** in 5 μm thickness of homogeneously aligned cell.

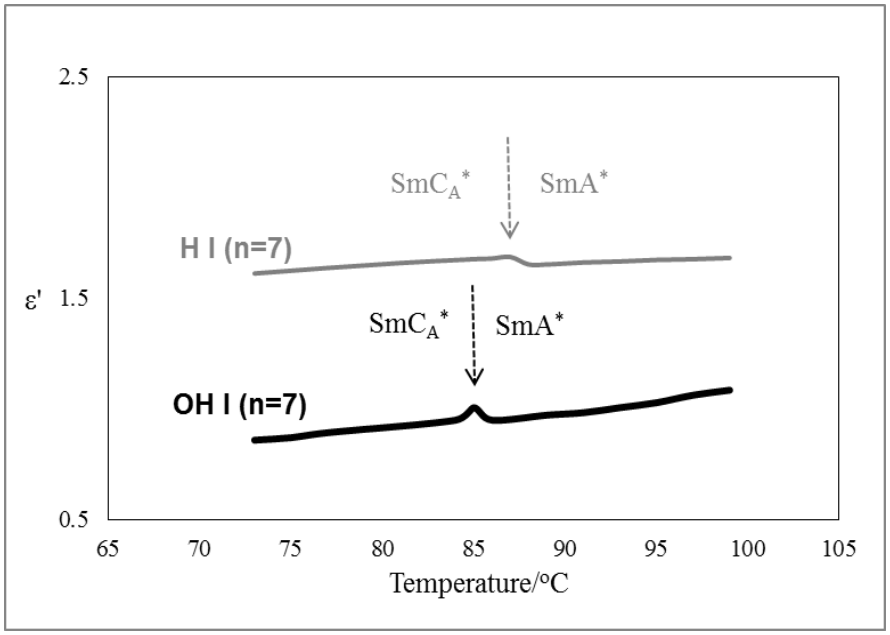


Fig S6. Temperature dependence of the dielectric constant ε′ for compounds **OH I (n=7)** and **H I (n=7)** at 100 Hz in the cell with 25 μm thickness under 1°C min^{-1} cooling process.