Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supporting Information

Development of polar order and tilt in lamellar liquid crystalline phases of bent-core mesogens

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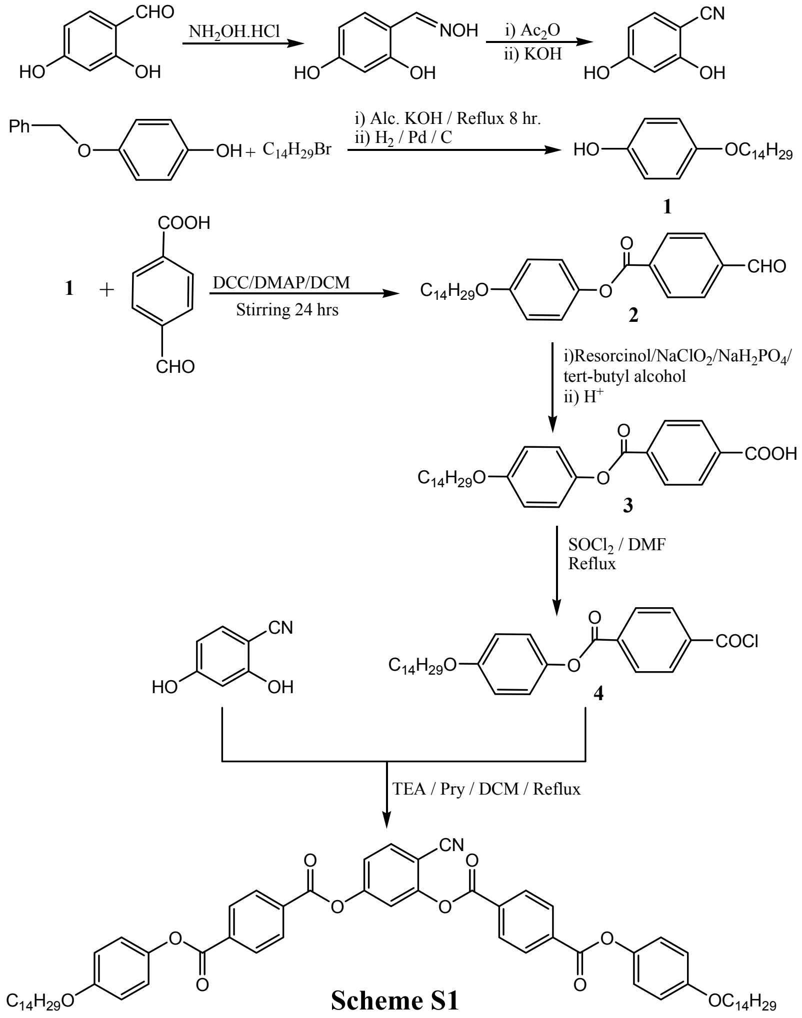
Content

1. Synthesis and analytical data

The structure characterization of the synthesized bent-core compound is based on ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard). Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

Materials: 1-bromotetradecane (Aldrich), 4-benzyloxyphenol (Aldrich), resorcinol (Aldrich), tert-butyl alcohol (Aldrich), sodium chlorite (Aldrich), sodium dihydrogenphosphate (Aldrich), potassium carbonate (Fluka), potassium hydroxide (Merck), 4-formylbenzoic acid (Aldrich), thionylchloride (Aldrich), 1,3-dicycloxylcarbodiimide (DCC; Merck), 4-(*N,N*-dimethylamino)pyridine (DMAP) (Aldrich), 2,4-dihydroxybenzaldehyde (Aldrich) and hydroxylamine hydrochloride (Merck). Chloroform (Merck) and dichloromethane (Merck) were dried separately over calcium chloride (Merck) and distilled before use. Other solvents and chemicals were used without further purification.

The synthetic procedures leading to **1/14** are outlined in Scheme S1. 2,4-Dihydroxybenzonitrile was synthesized according to the procedure described in Ref. S1. 4-(4-*n*-tetradecyloxyphenoxycarbonyl)benzoic acid **3** was prepared using a procedure similar to that one reported in Ref. S2.



Scheme S1

1.1 2,4-Dihydroxybenzonitrile

A solution of 2,4-dihydroxybenzaldehyde (22.5 g, 160 mmol) in ethanol (60 mL) was treated with a concentrated aqueous solution of hydroxylamine hydrochloride (16.7 g, 240 mmol) followed by slow addition of a concentrated aqueous solution of Na_2CO_3. $10H_2O$ (22.9 g, 40 mmol). Crystals were obtained and isolated by filtration. Recrystallisation from water gives 22.3 g (91%) of the 2,4-dihydroxybenzaldoxime. Mp 190–192 °C. The solid was then dissolved and refluxed in of acetic anhydride (90 mL) for 3 h. The solvent was removed under vacuum. The product was recrystallized from ethanol to give 14.0 g (44%) of the acetylated intermediate. This product was treated with aqueous KOH solution (12 g of KOH in 55 mL of water), and the resulting solution was stirred for 3 days at ambient temperature. Careful acidification (pH 2) with dilute sulfuric acid (20 vol%) was followed by extraction with ethyl acetate (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel using ethyl acetate–heptane (20 : 1) as eluent. Yield 7.0 g, 82%. Mp 174–175.5 °C.

1.2 4-(4-n-Tetradecyloxyphenoxycarbonyl)benzoic acid (3)

4-*n*-Tetradecyloxyphenol **1** was prepared by the alkylation of 4-benzyloxyphenol (4.0 g, 20 mmol) with 4-*n*-tetradecylbromide (6.55 g, 24 mmol) followed by deprotection with hydrogen at 40 °C and normal pressure for 24 hours in the presence of 5% Pd–C. 4-Formylbenzoic acid (2.0 g, 13.3 mmol) was acylated with **1** (4.08 g, 13.3 mmol) in the presence of DCC (2.75 g, 13.3 mmol) to give the 4-(4-*n*-tetradecyloxyphenoxycarbonyl)-benzaldehyde **2** (4.0 g, yield 68.5%). The aldehyde **2** was oxidized to the acid **3** as follows: **2** (3.89 g, 8.9 mmol) and resorcinol (1.05 g, 9.5 mmol) were dissolved in tert-butyl alcohol (140 mL). Separately, sodium chlorite (3.80 g, 42.0 mmol) and sodium dihydrogenphosphate (3.04 g, 25.4 mmol) were dissolved in water (30 mL). This aqueous solution was added dropwise with stirring into the solution of **2** over a 10-min period. The pale yellow reaction mixture was then stirred at room temperature overnight. Volatile components were removed under vacuum and the residue was dissolved in water (100 mL). The aqueous solution was acidified to pH 3 by adding 1 N aqueous HCl. The obtained white precipitate was isolated, washed successively with water and hexane, and dried in the air.

1-Benzyloxy-4-n-tetradecyloxybenzene. Yield 84%, m.p. 84-86 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73–7.32 (m, 5H, Ar-H), 6.85 (d, 2H, Ar-H), 6.80 (d, 2H, Ar-H), 3.85 (t, J = 6.6 Hz, 2H, -OCH_2), 1.70–1.64 (m, 2H, -$OCH_2\underline{CH_2}$), 1.50–1.17 (m, 22H, CH_2), 0.82 (t, J = 6.9 Hz, 3H, CH_3).

4-n-Tetradecyloxyphenol (1). Yield 90%, m.p. 84-85 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.70–6.68 (m, 5H, Ar-H), 4.9 (s, 1H, Ar-OH), 3.85 (t, J = 6.6 Hz, 2H, -OCH_2), 1.70–1.63 (m, 2H, -$OCH_2\underline{CH_2}$), 1.50–1.18 (m, 22H, CH_2), 0.82 (t, J = 6.9 Hz, 3H, CH_3).

4-n-Tetradecyloxyphenyl 4-formylbenzoate (2). Yield 64%, m.p. 110-112 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 10.13 (s, 1H, Ar-CHO), 8.33 (d, J = 8.2 Hz, 2H, Ar-H), 8.00 (d, J = 8.4 Hz, 2H, Ar-H), 7.11 (d, 2H, Ar-H), 6.91 (d, 2H, Ar-H), 3.95 (t, J = 8.2 Hz, 2H, -OCH_2), 1.78–1.75 (m, 2H, -$OCH_2\underline{CH_2}$), 1.52–1.24 (m, 22H, CH_2), 0.86 (t, J = 7.0 Hz, 3H, CH_3).

4-(4-n-Tetradecyloxyphenoxycarbonyl)benzoic acid (3). Yield 94%, m.p. 165-168 °C. ^{1}H-NMR (500 MHz, DMSO) δ 8.21 (d, J = 8.6 Hz, 1H, Ar-H), 8.11 (d, J = 8.6 Hz, 1H, Ar-H), 7.19 (d, J = 8.8 Hz, 1H, Ar-H), 6.98 (d, J = 8.8 Hz, 1H, Ar-H), 3.96 (t, *J* = 8.3 Hz, 2H, -OCH_2), 1.73–1.70 (m, 2H, -$OCH_2\underline{CH_2}$), 1.40–1.23 (m, 22H, CH_2), 0.84 (t, *J* = 6.9 Hz, 3H, CH_3).

1.3 4-Cyano-1,3-phenylene bis[4-(4-n-tetradecyloxyphenoxycarbonyl)benzoate] (1/14)

4-(4-*n*-Tetradecyloxyphenoxycarbonyl)benzoic acid (**3**) (0.5 g, 1.09 mmol) was refluxed in excess thionylchloride (1.5 mL) under argon atmosphere, after one hour the excess thionylchloride was removed under vacuum, then 4-cyanoresorcinol (0.08 g, 0.54 mmol), triethylamine (0.22 g, 1.32 mmol) and pyridine (cat.) were dissolved in anhydrous CH_2Cl_2/THF (1:1, 30 mL) and added to the acid chloride and stirring is continued under reflux for 6 hrs. The reaction mixture is then poured into aqueous 1 N HC1 (10 mL). The organic layer was separated and washed twice with saturated aqueous $NaHC0_3$ solution. The combined aqueous washes were back-extracted with 30 mL of CH_2C1_2. The organic extracts were dried over anhydrous Na_2S0_4, filtered, and concentrated under vacuum. The crude products were purified by column chromatography using $CHCl_3$ as eluent followed by two crystallizations from ethanol/chloroform (2:1) mixture to give the desired final compound (**1/14**) as colorless crystals. Yield 0.34 g, 64.15%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40–8.27 (m, 8H, Ar-H), 7.82 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.58 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.36 (dd, *J* = 8.6, 2.2 Hz, 1H, Ar-H), 7.13 (d, 4H, J= 9.3 Hz, Ar-H), 6.93 (d, J= 9.1 Hz, 4H, Ar-H), 3.95 (t, *J* = 6.6 Hz, 4H, -OCH_2), 1.83–1.72 (m, 4H, -$OCH_2\underline{CH_2}$), 1.49–1.15 (m, 22H, CH_2), 0.86 (t, *J* = 6.9 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.43, 163.17, 162.84, 157.20, 157.17, 154.59, 153.28, 144.01, 143.98, 134.91, 134.79, 134.15, 132.56, 132.17, 130.66, 130.50, 130.44, 122.22, 122.19, 120.16, 117.29, 115.22, 115.24, 110.00, 104.54, 68.51, 31.91, 29.70, 29.69, 29.67, 29.65, 29.62, 29.59, 29.41, 29.37, 29.28, 26.05, 22.70, 14.12. Elemental Analysis: Calc. for $C_{63}H_{77}NO_{10}$ C, 75.04; H, 7.69; N, 1.39. Found C, 75.04; H, 7.60; N, 1.38 %.

2. Additional figures

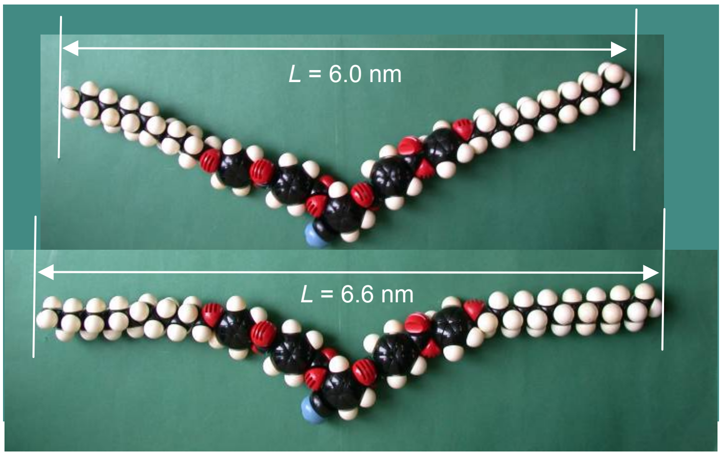


Fig. S1. Molecular conformations used for the determination of the molecular length *L*.

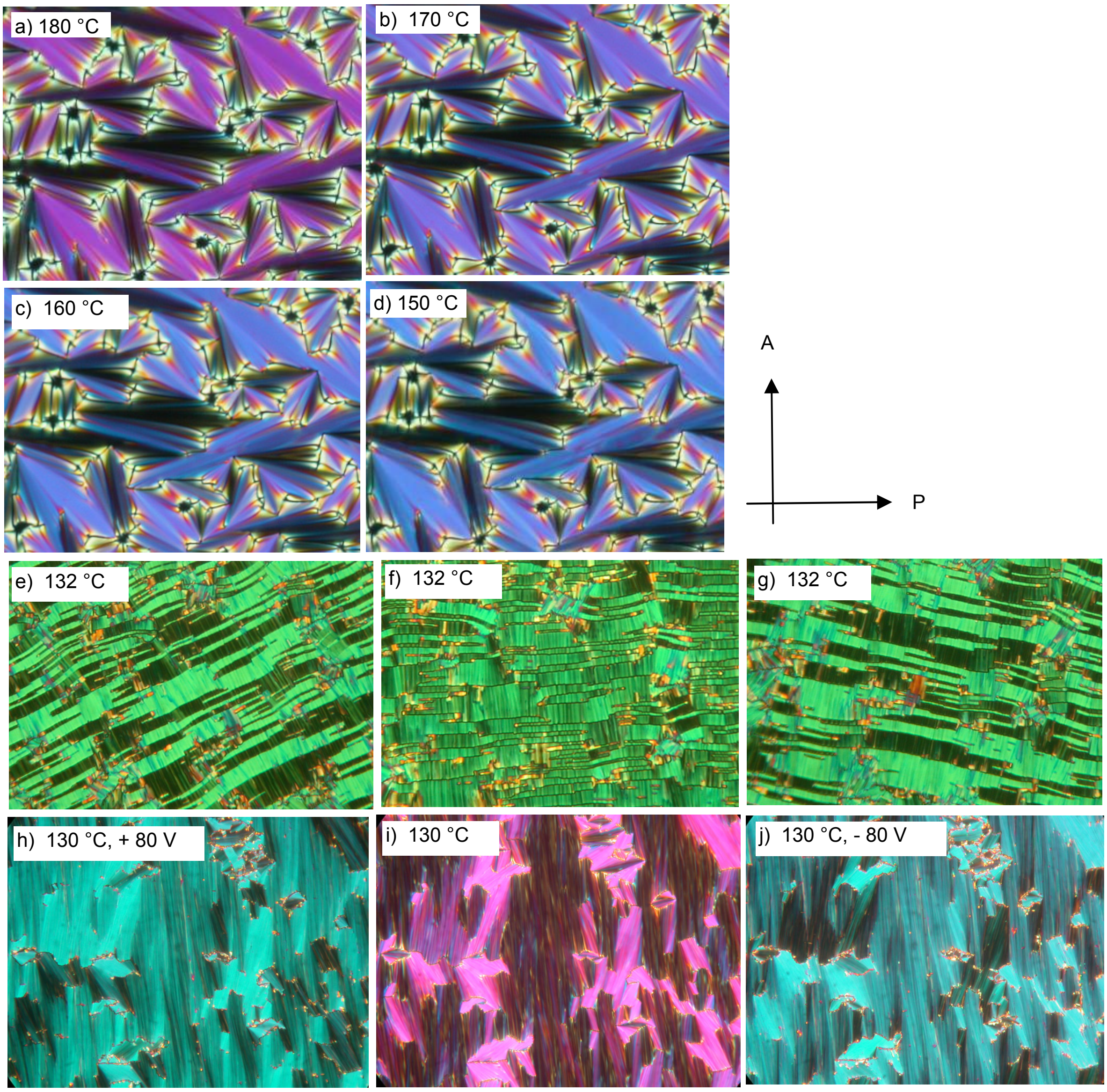


Fig. S2. Textures of a planar aligned sample of compound **1/14** a) in the SmA$_{(P)}$ phase at at T = 180 °C, b) at T = 170 °C, c) at T = 160 °C and d) at T = 150 °C (crossed polarizers) showing the increase of the birefringence; e-g) SmC$_s$P$_A$ phase at T = 132 °C, sample rotated between crossed polarizers e) by -15°, f) 0° and g) + 15 ° (T = 132 °C); h-j) SmCP$_\alpha$ phase at T = 130 °C, i) at 0V and the field induced SmC$_s$P$_F$ states h) at a voltage of +80V and j) at -80 V.

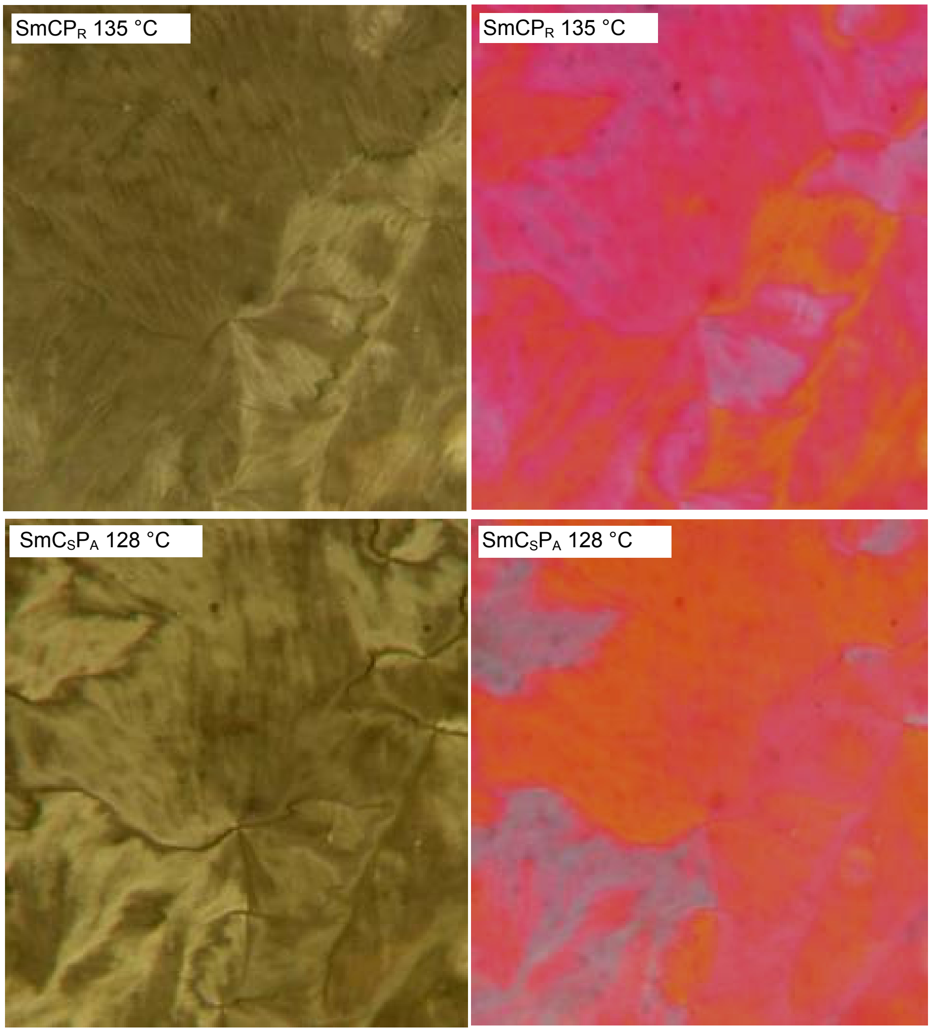


Fig. S3. Enlarged images of the textures of the SmCP$_R$ phase (top) and the SmC$_s$P$_A$ phase (bottom) with (right) and without (left) λ-retarder plate (corresponding to Fig.2 c,d) and g,h).

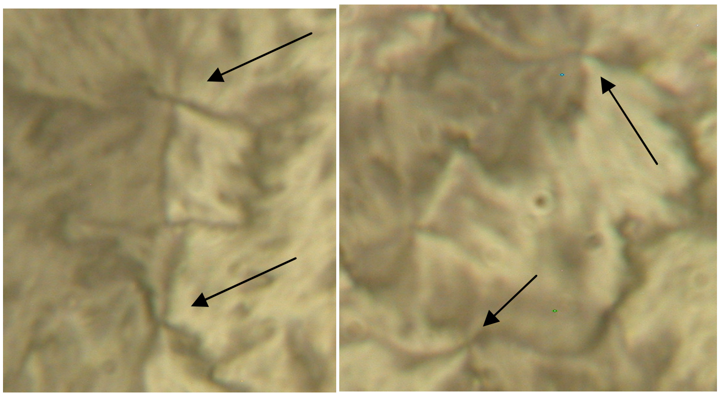


Fig. S4. Homeotropic texture of the SmCP$_R$ phase of compound **1/14** at $T = 139$ °C showing four-brush declinations (π-disclinations, see arrows)

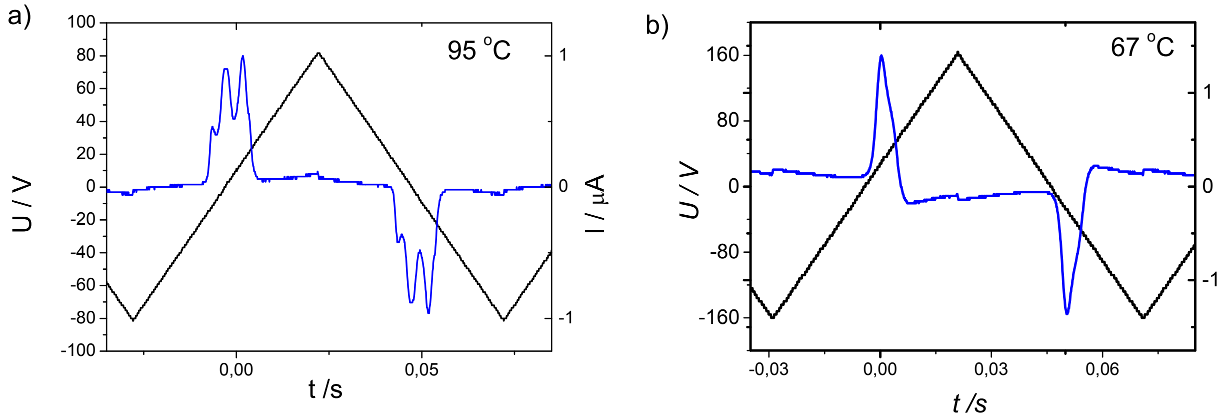


Fig. S5. Switching current response curves of compound **1/14** recorded by applying a triangular wave voltage (160 V_{pp}, 10 Hz, 5 kΩ) to a 6 µm coated ITO cell with homogeneous alignment layer a) in the SmC$_a$'P$_A$ phase at T = 95 °C and b) in the SmC$_a$P$_A$ phase T = 67 °C.

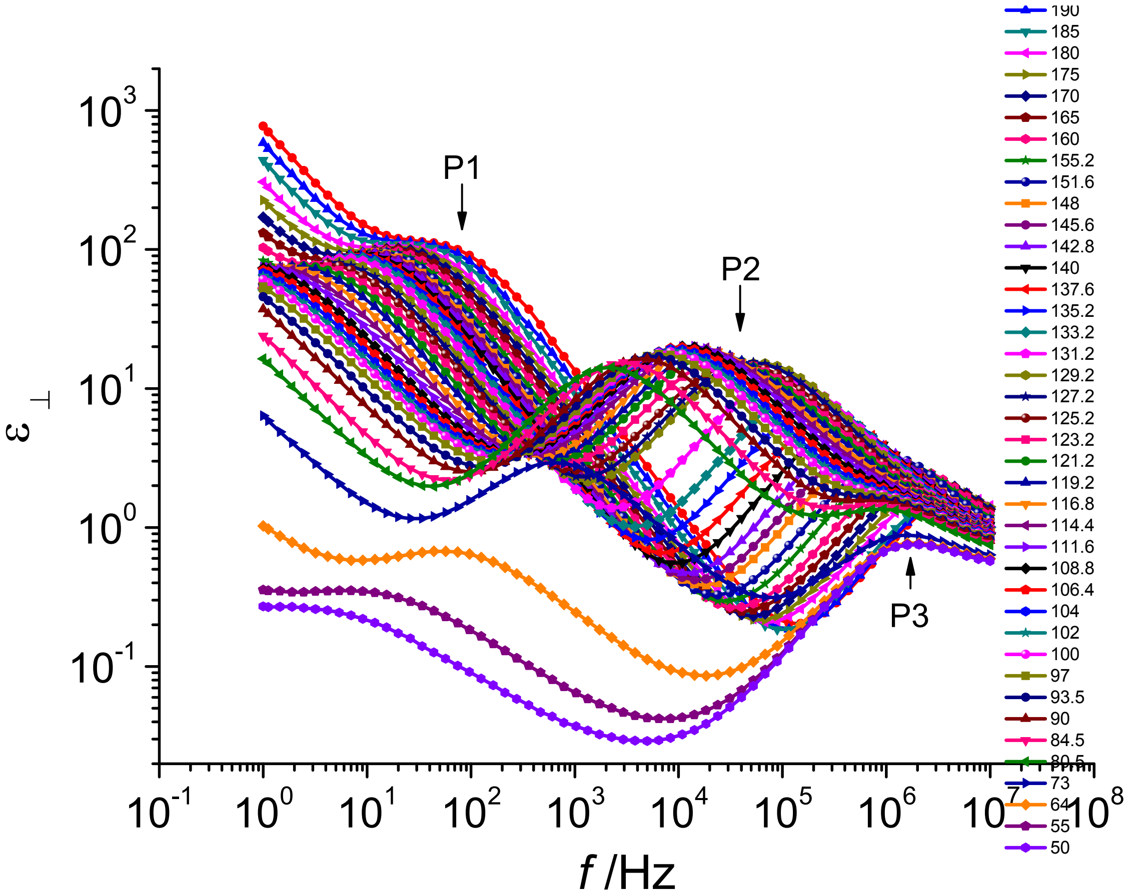


Fig S6. Dielectric investigation of compound **1/14**: Temperature dependence of $\varepsilon''_\perp$ on temperature as observed for a 10 µm planar cell in the frequency range from 1 to 10^6 Hz in the temperature range between 50 and 193 °C (all data).

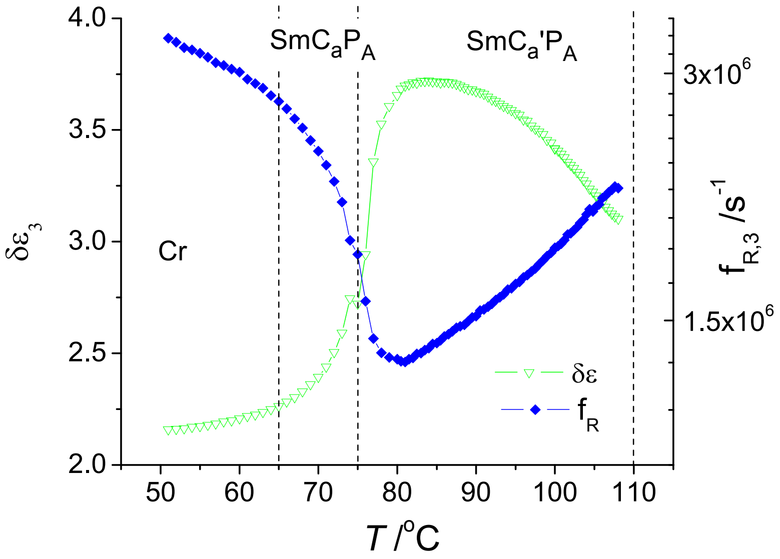


Fig. S7: Temperature dependence of dielectric strength ($\delta\varepsilon_3$) and the relaxation frequency ($f_{R,3}$) for P3, α_3 varying from 0.77 to 0.8 and β_3 was fixed at 1. P3 is assigned to the rotation around the short axis. The sample in the temperature range 60 to 75 °C is in a liquid crystalline phase though it behaves as in glassy state. Data for $\delta\varepsilon_2$ and $f_{R,2}$ are given in Fig 7 of the manuscript.

3. References

S1. I. Wirth, S. Diele, A. Eremin, G. Pelzl, S. Grande, L. Kovalenko, N. Pancenko and W. Weissflog, *J. Mater. Chem.*, 2001, **11**, 1642.

S2. G. S. Lee, Y. J. Lee, S. Y. Choi, Y. S. Park, and K. B. Yoon, *J. Am. Chem. Soc.*, 2000, **122**, 12151.