Supplemental information

Effect of lactate group in the chiral chain of new compounds exhibiting short-pitch cholesteric or TGBA phase

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1. Synthesis of intermediates

^{1}H NMR spectra were recorded on Varian VNMRS 300 instrument; deuteriochloroform ($CDCl_3$) and hexadeuteriodimethyl sulfoxide (DMSO-d_6) were used as solvents and signals of the solvent served as internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. The signals were identified by APT, gCOSY and gHMBC experiments. Elemental analyses were carried out on Elementar vario EL III instrument. The purity of final compound was checked by HPLC analysis (high-pressure pump ECOM Alpha; column WATREX Biospher Si 100, 250 × 4 mm, 5 μm; detector WATREX UVD 250) and were found to be >99.8 %. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm). Enantiomeric purity of chiral compounds was confirmed by chiral HPLC system (chiral column: Daicel Chiralpak AD-3, 150 × 4.6 mm I.D., 3 μm).

Potassium 4′-butanoylbiphenyl-4-carboxylate (**2a**)

Butanoyl chloride (53.3 g, 0.5 mol) was added drop-wise with stirring to an ice-cooled mixture of biphenyl (77.0 g, 0.5 mol) and anhydrous $AlCl_3$ (78.0 g, 0.58 mol) in 300 ml of 1,2-dichloroethane. The reaction mixture was stirred for 2 days at laboratory temperature. The resulting dark mixture was poured into ice (ca. 600 g)/conc. hydrochloric acid (100 ml) mixture, the organic layer was separated and washed with water. Dark solution was then cooled in the refrigerator to -25 °C and yellow crystals were filtered off, crystallised from chloroform and dried in the vacuum chamber drier. The yield was 81.8 g (73 %). The 80.0 g portion of dry 4-butanoylbiphenyl was dissolved in 1,2-dichloroethane (100 ml) and added in small portions into

the stirred cooled (0°C) mixture of dry $AlCl_3$ (173.0 g, 1.30 mol) and oxalyl chloride (100.0 g, 0.79 mol) in 300 ml of dry 1,2-dichloroethane. The reaction mixture was then stirred at room temperature for 4–6 h, and the resulting mixture was poured into ice (ca. 600 g)/conc. hydrochloric acid (100 ml) mixture. The organic layer was separated, evaporated to dryness and mixed with 10% solution of potassium hydroxide. The white precipitate was filtered off, washed with ethanol and dried. Yield 76.5 g (70 %). ^{1}H NMR (DMSO-d_6) (free acid): 8.02–8.13 (4H, m, H-3, H-5, H-3′, H-5′), 7.70–7.90 (4H, m, H-2, H-6, H-2′, H-6′), 3.04 (2H, t, J=6.7, CH_2CO), 1.64 (2H, m, C**H**$_2CH_3$), 0.90 (3H, t, J=6.8, CH_3).

Potassium 4′-pentanoylbiphenyl-4-carboxylate (**2b**)

Carboxylate **2** was prepared by the same procedure as carboxylate using valeroyl chloride (60.3 g, 0.5 mol) as acylating agent. Yield 81.7 g (52 %). ^{1}H NMR (DMSO-d_6) (free acid): 8.05–8.16 (4H, m, H-3, H-5, H-3′, H-5′), 7.65–7.87 (4H, m, H-2, H-6, H-2′, H-6′), 3.0 (2H, t, J=6.7, CH_2CO), 1.22–1.65 (2H, m, 2×CH_2), 0.89 (3H, t, J=6.8, CH_3).

4′-Butylbiphenyl-4-carboxylic acid (**3a**)

Carboxylate **1** (76.5 g, 0.25 mol) and of potassiumhydroxide (20.0 g, 0.36 mmol) was added to a mixture of 200 ml of ethylene glycol and of hydrazine hydrate (70 ml, 1.4 mol) and toluene (200 ml). The reaction was refluxed and the water was separated using in Dean–Stark trap. The mixture was boiled for 6 hr, then residual hydrazine and about 100 ml of ethylene glycol was evaporated. The cold residuum was mixed with water, precipitate was filtered off. Filtered solid material was acidified with hydrochloric acid and washed with water. The product was crystallised from chloroform/acetic acid mixture (10:1) and washed with *n*-hexane. Yield 49.6 g (78 %). ^{1}H NMR (DMSO-d_6): 8.0 (2 H, d, J=8.8, H-3, H-5), 7.77 (2 H, d, J=8.8, H-2, H-6), 7.64 (2 H, d, J=8.2, H-2′, H-6′), 7.31 (2 H, d, J=8.2, H-3′, H-5′), 2.62 (2 H, t, J=7.6, CH_2Ar), 1.58 (2 H, quin, J=7.6, C**H**$_2CH_2Ar$), 1.32 (2 H, quin, J=7.6, C**H**$_2CH_3$), 0.90 (3 H, t, J=7.3, CH_3).

4′-Pentylbiphenyl-4-carboxylic acid (**3b**)

Carboxylic acid **4** was prepared following the procedure described for carboxylic acid **3a**. Starting from carboxylate **2** (81.7 g, 0.25 mol), 46.5 g (68 %) of acid **4** was obtained. ^{1}H NMR (DMSO-d_6): 8.08 (2 H, d, J=8.8, H-3, H-5), 7.79 (2 H, d, J=8.8, H-2, H-6), 7.68 (2 H, d, J=8.2, H-2′, H-6′), 7.35 (2 H, d, J=8.2, H-3′, H-5′), 2.64 (2 H, t, J=7.6, CH_2Ar), 1.56 (2 H, quin, J=7.6, C**H**$_2CH_2Ar$), 1.25–1.33 (4 H, m, $(CH_2)_2$), 0.89 (3 H, t, J=6.9, CH_3).

4’-Hydroxybiphenyl-4-carboxylic acid (**5**)

Solution of biphenyl-4-yl acetate (53.0 g, 0.25 mol) in 1,2-dichloroethane (200 ml) was added dropwise into a cooled (0°C, ice-water bath) vigorously stirred mixture of dry $AlCl_3$ (53.0 g, 0.40 mol) and oxalyl chloride (30 ml g, 0.34 mol) in 300 ml of dry 1,2-dichloroethane. The reaction mixture was stirred for 4 h and let warm to room temperature. Finally, it was let stand overnight. The resulting mixture was poured into ice (ca. 800 g)/conc. hydrochloric acid (100 ml) mixture. The yellow organic layer was separated and the solvent evaporated under reduced pressure. The residue was mixed with ethanolic solution of sodium hydroxide (1.0 l, 4%) and boiled for 30 min. After cooling to ca. 0°C, the white precipitate was filtered off, washed with ethanol, acidified with hydrochloric acid and washed with water. Dried product was recrystallized from acetic acid. Yield 45.5 g (84 %). 7.96 (2 H, d, *J*=8.7, H-3, H-5) 7.71 (2 H, d, *J*=8.7, H-2, H-6) 7.58 (2 H, d, *J*=8.4, H-2´, H-6´) 6.87 (2 H, d, *J*=8.4, H-3´, H-5´).

3’-Chloro-4’-hydroxybiphenyl-4-carboxylic acid (**6**)

A mixture of 4’-hydroxybiphenyl-4-carboxylic acid (**5**) (50.0 g, 0.23 mol) and conc. sulphuric acid (3 ml) was refluxed in methanol (500 ml) for 1 h and then the solvent was evaporated using rotatory evaporator. Solid residue was dissolved in ethyl acetate (2 l) and sulphuryl chloride (27.5 ml, 0.34 mol) was added dropwise, but quickly, with stirring. The reaction mixture was gently refluxed for 1 h. The resulting cooled mixture was slowly poured into saturated solution of sodium bicarbonate (1 l), organic layer was separated and washed with water. After removal of solvent, solid residue was crystallized from ethanol. Crystallized solid was then dissolved in ethanol at ca. 60 °C and the saturated ethanolic solution of sodium hydroxide (200 ml) was added with stirring. After cooling, the precipitated solid was filtered off, washed with cold ethanol, acidified with hydrochloric acid and washed with water. Crude acid **6** was purified by crystallization from methanol. Yield 46.5 (80 %). ^{1}H NMR (DMSO-d_6): 7.98 (1 H, d, *J*=8.2, H-3, H-5), 7.75–7.86 (3 H, m, H-2, H-6, H-2’), 7.71 (1 H, dd, *J*=8.8, 2.3, H-6’) 7.26 (1 H, d, *J*=8.8, H-5‘).

3’-Chloro-4’-[(methoxycarbonyl)oxy]biphenyl-4-carbonyl chloride (**7**)

Acid **6** (18.0 g, 72.4 mmol) was dissolved in a solution of NaOH (7.2 g, 0.18 mol) in water (100 ml), cooled to 0 °C, and methyl chloroformate (11.4 g, 0.12 mol) was added dropwise under stirring and keeping the temperature below 0 °C. The resulting mixture was stirred for 30 min at 5 °C, and then poured onto crushed ice. After acidification with conc. HCl to pH=2, the precipitate was filtered and washed with cold water (50 ml). Protected acid was recrystallized from acetone and dried in the vacuum chamber drier. Dried protected acid was suspended in dry dichloromethane (200 ml) with a few drops of DMF. Oxalyl chloride (30 ml, 0.34 mmol) was added dropwise with stirring to this mixture. Reaction mixture was stirred for until the clear solution was formed and the evolution of gas stopped (ca. 1 h). Evaporation of solvent yielded

20.0 g (85%) of acid chloride **7** which was used in the next step of the synthesis without purification. ^{1}H NMR ($CDCl_3$): 8.22 (2 H, d, *J*=8.8, H-3, H-5), 7.35–7.74 (3 H, m, H-2, H-6, H-2'), 7.55 (1 H, dd, *J*=8.8, 2.1,H-6'), 7.37 (1 H, d, *J*=8.8, H-5'), 3.98 (3 H, s, CH_3).

(*S*)-1-(Hexyloxy)-1-oxopropan-2-yl 3'-chloro-4'-hydroxybiphenyl-4-carboxylate (**9a**)

Solution of the acid chloride **7** (9.4 g, 29.0 mmol) in dry dichloromethane (200 ml) was added drop wise with stirring to the cooled mixture (0 °C) of hexyl lactate (**8a**) (6.0 g, 34.4 mmol) and pyridine (20 ml) in dry dichloromethane (200 ml) and stirred for additional 3 h. Then the reaction mixture was refluxed for 3 h and finally poured into 5% aq HCl (300 ml). The organic layer was separated, washed with water and dried with anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the resulting viscous oil was dissolved in THF (250 ml) and cooled to -20 °C. To this solution, aqueous ammonium hydroxide (10 ml, 25%, 65.0 mmol) was added drop wise with stirring. The reaction was let warm to room temperature and the progress of hydrolysis was monitored by TLC (CH_2Cl_2 : acetone, 99 : 1). After ca. 1.5 h, the reaction mixture was poured into diluted HCl (200 ml, 1 : 15) and extracted with diethylether (3 × 150 ml). Combined organic layers were washed with water, brine and dried with anhydrous sodium sulphate. After removal of the solvent, the crude product was purified by column chromatography on silica (CH_2Cl_2 : acetone, 99.5 : 0.5, R_f = 0.3). Yield 7.4 g (63 %). ^{1}H NMR ($CDCl_3$) 8.12 (2 H, d, *J*=8.8, H-3, H-5), 7.53–7.64 (3 H, m, H-2, H-6, H-2'), 7.43 (1 H, dd, *J*=8.8, 2.1, H-6'), 7.10 (1 H, d, *J*=8.8, H-5'), 5.79 (1 H, s, OH), 5.34 (1 H, q, *J* = 6.95, C*H), 4.03–4.30 (2 H, m, C*HCOOC**H**$_2$), 1.55–1.77 (5 H, m, COOCH_2C**H**$_2$, C*C**H**$_3$), 1.15–1.42 (6 H, m, $(CH_2)_3$), 0.87 (3 H, t, *J* = 6.7, CH_2C**H**$_3$).

(*S*)-1-{[(*S*)-1-(Hexyloxy)-1-oxopropan-2-yl]oxy}-1-oxopropan-2-yl 3'-chloro-4'-hydroxybiphenyl-4-carboxylate (**9b**)

Carboxylate **9b** was prepared analogously as reported for carboxylate **9a**. The reaction of acid chloride **7** (5.0 g, 15.38 mmol) and (*S*)-hexyl 2-[((*S*)-2-hydroxypropanoyl)oxy]propanoate (4.6 g, 18.67 mmol) and subsequent hydrolysis by ammonium hydroxide (5 ml, 25%, 32.5 mmol) yielded 4.4 g (60 %) of **9b**. ^{1}H NMR ($CDCl_3$) 8.15 (2 H, d, *J*=8.8, H-3, H-5), 7.50–7.65 (3 H, m, H-2, H-6, H-2'), 7.44 (1 H, dd, *J*=8.8, 2.1, H-6'), 7.10 (1 H, d, *J*=8.8, H-5'), 5.82 (1 H, s, OH), 5.42 (1 H, q, *J*=7.0, CH*), 5.20 (1 H, q, *J*=7.0, CH*´), 4.10–4.34 (2 H, m, CH*COOC**H**$_2$), 1.75 (3 H, d, *J*=7.0, C**H**$_3$CH*), 1.63 (2 H, quin. *J*=7.1, COOCH_2C**H**$_2$), 1.55 (3 H, d, *J*=6.2, C**H**$_3$CH*), 1.15 - 1.44 (6 H, m, $(CH_2)_3$), 0.89 (3 H, t, *J*=6.7, CH_2C**H**$_3$).

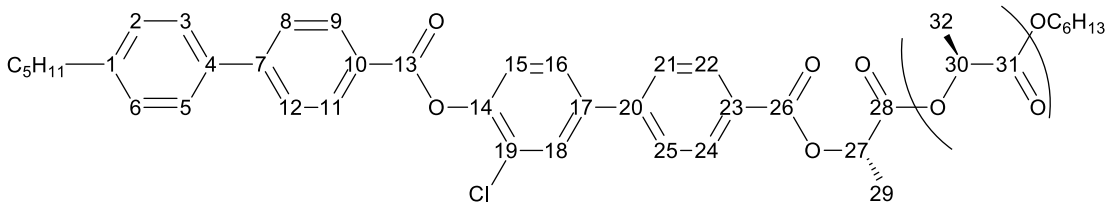

Figure S1: Numbering of nuclei used for NMR signal assignment for **DCL** and **DCLL**.

2. Synthesis of the final products

(*S*)-1-(Hexyloxy)-1-oxopropan-2-yl 4'-[(4'-butylbiphenyl-4-carbonyl)oxy]-3'-chlorobiphenyl-4-carboxylate (**DCL4/6**)

The carboxylate **9a** (3.7 g, 9.1 mmol) and acid **3a** (2.4 g, 9.4 mmol) were dissolved in dry dichloromethane (150 ml), and *N*,*N*´-dicyclohexylcarbodiimide (DCC) (2.0 g, 9.7 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.3 g, 2.5 mmol) were added. The mixture was stirred at room temperature for 24 h and then filtered. The filtrate was evaporated and the residue purified by column chromatography (silica gel, dichloromethane – acetone, 99.7 : 0.3) and recrystallized from hexane to get 5.3 g (91 %) of **DCL4/6**. ^{1}H NMR ($CDCl_3$) 8.30 (2 H, d, *J*=8.8, H-9, H-11), 8.17 (2 H, d, *J*=8.8, H-22, H-24), 7.75 (2 H, d, *J*=8.8, H-8, H-12), 7.74 (1 H, d, *J*=2.3, H-18), 7.66 (2 H, d, *J*=8.2, H-3, H-5), 7.52–7.64 (3 H, m, H-16, H-21, H-25), 7.40 (1 H, d, *J*=8.8, H-15), 7.31 (2 H, d, *J*=8.2, H-2, H-6), 5.35 (1 H, q, *J* = 7.0, C*H), 4.03–4.30 (2 H, m, C*HCOOC**H**$_2$), 2.67 (2 H, t, *J*=7.6, CH_2Ar), 1.55–1.75 (7 H, m, C**H**$_2$$CH_2$Ar, $COOCH_2$C**H**$_2$, C*C**H**$_3$), 1.15–1.51 (8 H, m, 4×CH_2), 0.71–1.06 (6 H, m, 2×CH_2C**H**$_3$). ^{13}C NMR ($CDCl_3$): 170.83 (s, C-28), 165.62 (s, C-26), 164.22 (s, C-13), 147.23 (s, C-17), 146.40 (s, C-7), 143.84 (s, C-20), 143.57 (s, C-1), 139.17 (s, C-14), 131.84 (s, C-4), 130.98 (s, C-9, C-11), 130.52 (s, C-22, C-24), 129.09 (s, C-18), 128.86 (s, C-23), 128.42 (s, C-21, C-25), 127.67 (s, C-10), 127.07 (s, C-5), 126.70 (s, C-12, C-16), 126.64 (s, C-8), 126.56 (s, C-19), 124.31 (s, C-15), 114.98 (s, C-2, C-6), 69.32 (s, C-27), 65.58 (s, CH_2O), 35.68 (s, CH_2Ar), 33.42 (**C**$H_2CH_2CH_3$), 31.68 (**C**$H_2CH_2CH_3$), 28.48 (s, **C**H_2CH_2O), 25.77 (s, **C**$H_2CH_2CH_2O$), 22.69 (s, **C**H_2CH_3), 17.13 (s, C-29), 14.13 (s, CH_2**C**H_3). Elemental analysis for $C_{39}H_{41}ClO_6$ (641.19): calcd. C 73.05, H 6.45, O 14.97; found: C 73.55, H 6.50, O 14.87.

(*S*)-1-(Hexyloxy)-1-oxopropan-2-yl 4'-[(4'-pentylbiphenyl-4-carbonyl)oxy]-3'-chlorobiphenyl-4-carboxylate (**DCL5/6**)

Preparation of compound **DCL5/6** was analogous to the preparation of compound **DCL4/6**. Reaction of carboxylate **9a** (3.7 g, 9.1 mmol) with acid **3b** (2.5 g, 9.3 mmol) in dry dichloromethane (150 ml) in the presence of dicyclohexylcarbodiimide (2.0 g, 9.7 mmol) and DMAP (0.3 g, 2.5 mmol) yielded 5.0 g (85 %), (column chromatography: dichloromethane – acetone, 99.7 : 0.3). ^{1}H NMR ($CDCl_3$) 8.30 (2 H, d, *J*=8.8, H-9, H-11), 8.15 (2 H, d, *J*=8.8, H-22,

H-24), 7.76 (2 H, d, *J*=8.8, H-8, H-12), 7.73 (1 H, d, *J*=2.3, H-18), 7.66 (2 H, d, *J*=8.2, H-3, H-5), 7.53–7.62 (3 H, m, H-16, H-21, H-25), 7.41 (1 H, d, *J*=8.8, H-15), 7.31 (2 H, d, *J*=8.2, H-2, H-6), 5.36 (1 H, q, *J* = 7.0, C*H), 4.08–4.38 (2 H, m, C*HCOOCH$_2$), 2.67 (2 H, t, *J*=7.6, CH$_2$Ar), 1.54–1.76 (7 H, m, CH$_2$CH$_2$Ar, COOCH$_2$CH$_2$, C*CH$_3$), 1.12–1.50 (10 H, m, 5×CH$_2$), 0.73–1.03 (6 H, m, 2×CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$): 170.85 (s, C-28), 165.63 (s, C-26), 164.21 (s, C-13), 147.25 (s, C-17), 146.40 (s, C-7), 143.84 (s, C-20), 143.57 (s, C-1), 139.17 (s, C-14), 131.83 (s, C-4), 130.99 (s, C-9, C-11), 130.57 (s, C-22, C-24), 129.09 (s, C-18), 128.88 (s, C-23), 128.44 (s, C-21, C-25), 127.65 (s, C-10), 127.07 (s, C-5), 126.70 (s, C-12, C-16), 126.64 (s, C-8), 126.56 (s, C-19), 124.31 (s, C-15), 114.98 (s, C-2, C-6), 69.32 (s, C-27), 65.55 (s, CH$_2$O), 35.67 (s, CH$_2$Ar), 31.85 (**C**H$_2$CH$_2$CH$_3$), 31.70 (**C**H$_2$CH$_2$CH$_3$), 28.50 (s, **C**H$_2$CH$_2$O), 25.76 (s, **C**H$_2$CH$_2$CH$_2$O), 22.70 (s, **C**H$_2$CH$_3$), 17.15 (s, C-29), 14.15 (s, CH$_2$**C**H$_3$). Elemental analysis for C$_{40}$H$_{43}$ClO$_6$ (655.22): calcd. C 73.32, H 6.61, O 14.65; found: C 73.57, H 6.56, O 14.56.

(*S*)-1-{[(*S*)-1-(Hexyloxy)-1-oxopropan-2-yl]oxy}-1-oxopropan-2-yl 3'-chloro-4'-[(4'-pentylbiphenyl-4-carbonyl]oxy)biphenyl-4-carboxylate (**DCLL5/6**)

Preparation of compound **DCLL5/6** was analogous to the preparation of compound **DCL4/6**. Reaction of carboxylate **9b** (4.4 g, 9.2 mmol) with acid **3b** (2.5 g, 9.3 mmol) in dry dichloromethane (150 ml) in the presence of dicyclohexylcarbodiimide (2.0 g, 9.7 mmol) and DMAP (0.3 g, 2.5 mmol) yielded 5.1 g (76 %), (column chromatography: dichloromethane – acetone, 99.7 : 0.3). ^{1}H NMR (CDCl$_3$) 8.30 (2 H, d, *J*=8.8, H-9, H-11), 8.17 (2 H, d, *J*=8.8, H-22, H-24), 7.75 (2 H, d, *J*=8.8, H-8, H-12), 7.72 (1 H, d, *J*=2.3, H-18), 7.66 (2 H, d, *J*=8.2, H-3, H-5), 7.50–7.61 (3 H, m, H-16, H-21, H-25), 7.41 (1 H, d, *J*=8.8, H-15), 7.31 (2 H, d, *J*=8.2, H-2, H-6), 5.42 (1 H, q, *J*=7.0, CH*), 5.20 (1 H, q, *J*=7.0, CH*´),4.08–4.38 (2 H, m, C*HCOOCH$_2$), 2.67 (2 H, t, *J*=7.6, CH$_2$Ar), 1.54–1.80 (10 H, m, CH$_2$CH$_2$Ar, COOCH$_2$CH$_2$, 2×C*CH$_3$), 1.10–1.49 (10 H, m, 5×CH$_2$), 0.75–1.07 (6 H, m, 2×CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$): 170.95 (s, C-31), 170.80 (s, C-28), 165.85 (s, C-26), 164.27 (s, C-13), 147.21 (s, C-17), 146.41 (s, C-7), 143.81 (s, C-20), 143.55 (s, C-1), 139.11 (s, C-14), 131.87 (s, C-4), 130.97 (s, C-9, C-11), 130.51 (s, C-22, C-24), 129.05 (s, C-18), 128.82 (s, C-23), 128.44 (s, C-21, C-25), 127.65 (s, C-10), 127.02 (s, C-5), 126.71 (s, C-12, C-16), 126.63 (s, C-8), 126.57 (s, C-19), 124.32 (s, C-15), 114.97 (s, C-2, C-6), 69.75 (s, C-27), 69.42 (s, C-30), 65.57 (s, CH$_2$O), 35.65 (s, CH$_2$Ar), 31.88 (**C**H$_2$CH$_2$CH$_3$), 31.67 (**C**H$_2$CH$_2$CH$_3$), 28.49 (s, **C**H$_2$CH$_2$O), 25.78 (s, **C**H$_2$CH$_2$CH$_2$O), 22.68 (s, **C**H$_2$CH$_3$), 17.03 (s, C-29), 16.95 (s, C-32), 14.11 (s, CH$_2$**C**H$_3$). Elemental analysis for C$_{43}$H$_{47}$ClO$_8$ (727.28): calcd. C 71.01, H 6.51, O 17.60; found: C 71.07, H 6.55, O 17.66.

3. **Experimental results**

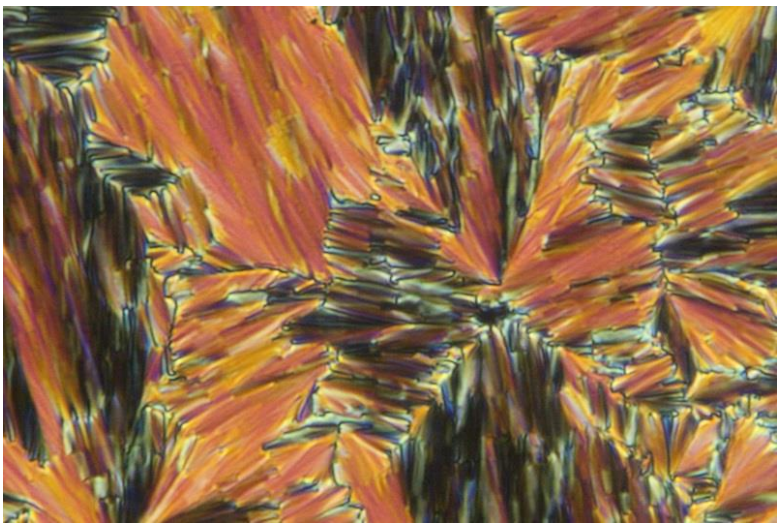

Figure S2

Texture of **DCL4/6** in cell with homoetropic anchoring (HT cell).

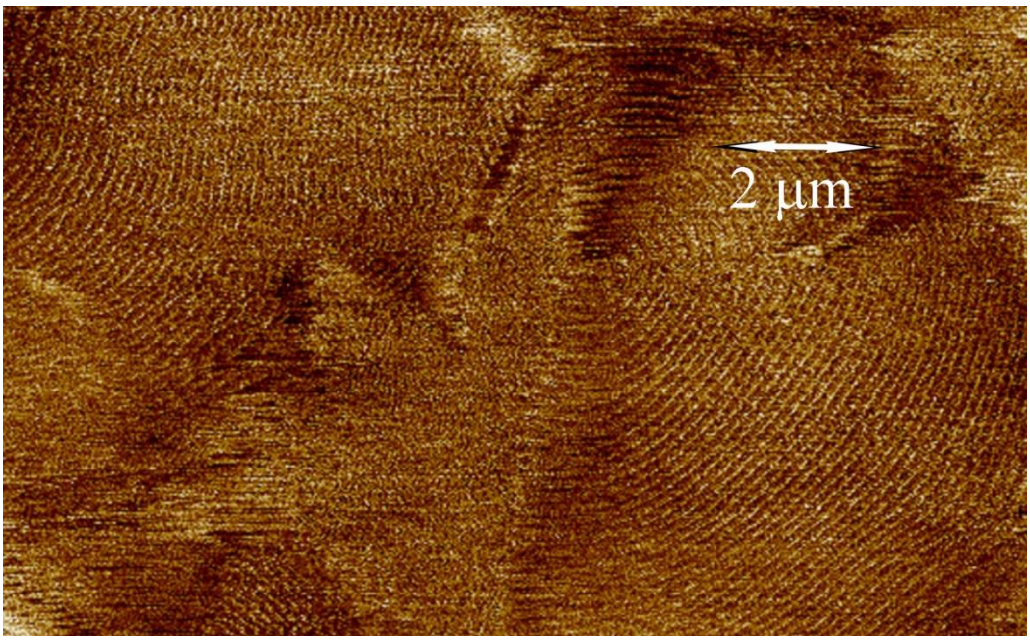

Figure S3

AFM picture on **DCL4/6** film at T=70ºC.

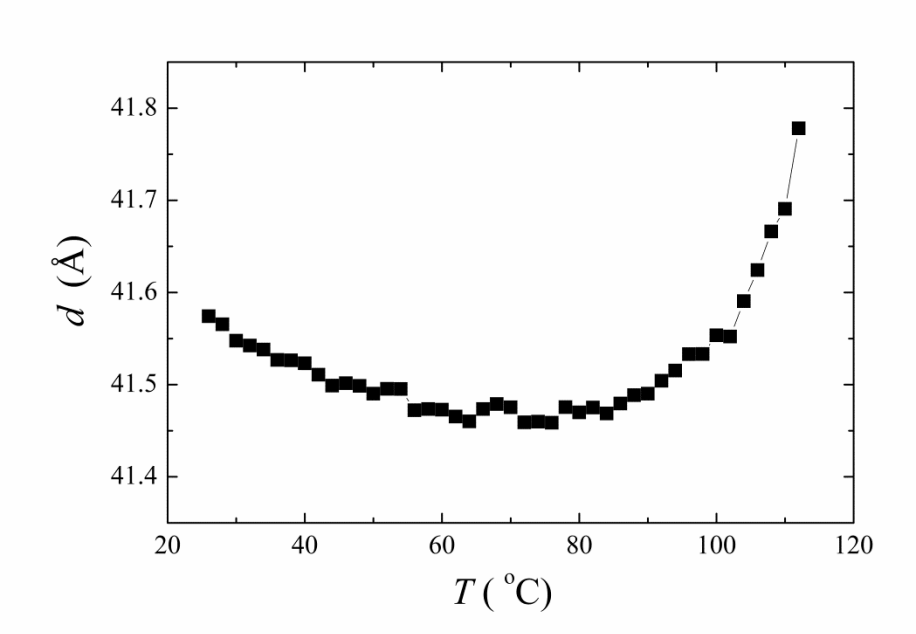

Figure S4

The temperature dependence of the layer spacing in the TGBA phase of **DCLL5/6**.

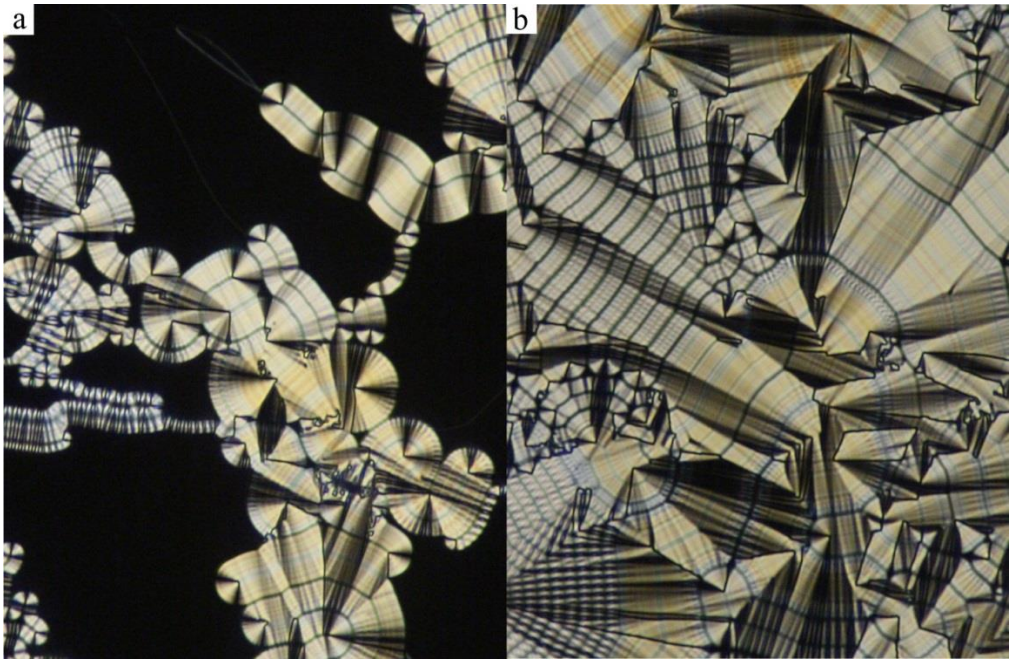

Figure S5

The texture in HG cell induced by the applied electric field of 10 V/μm for **DCL5/6** at T=40ºC, (a) 2 seconds and (b) 10 seconds after the switching-on the field.

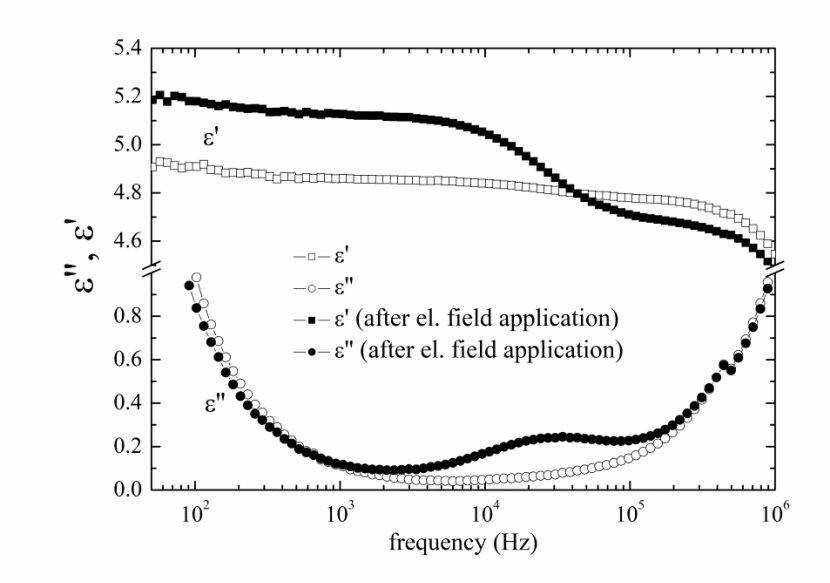

Figure S6

Real, ε', and imaginary, ε'', parts of permittivity for **DCL4/6** in HG cell before (open symbols) and after the electric field application (solid symbols), at temperature T=75ºC. During the measurements after the electric field application, the homeotropic alignment can be partially arranged. Positive dielectric anisotropy can be demonstrated.

4. Oily streaks in the applied electric field

In short-pitch cholesteric phase the chirality of material is strong. It leads to relatively compact so-called "cholesteric layers" as discussed in [S2, S3, S4]. In cells with planar anchoring "cholesteric layers" are generally parallel to glass plates forming uniform domain. Such domains are sometime divided by elongated stripes called oily streaks [S3, S4]. The structural model of oily streaks was proposed e.g. in [S3, S4, S5]. In [S5] oily streaks were classified by the dimensionless parameter of the oily streak width ξ, which is the ratio of oily streak width, d, and sample thickness h, i.e. $\xi = \frac{d}{h}$. Our observations show that for narrow streaks, $\xi < 1$, no modulation is seen along the streak. It was explained in [S5] that narrow thin streak is situated within uniform "cholesteric layers" and there is no influence of the anchoring energy. On the other hand, for wide streaks, $\xi > 1$, we observed additional modulation (Fig. S6). In the following we try to connect this modulation to the formation of an array of focal domains (FD) similarly as outlined in [S6].

Model of oily streak was proposed in [S3, S4, S5]. Oily streak is composed of two parallel π-disclinations in the "cholesteric layer" system, separated by the distance d [S5]. In the case of wide streak the layers between disclinations are not parallel to glass plates but touch surfaces by an angle decreasing with the distance from the center of the streak. Outside of the streak width the "cholesteric layers" are parallel to glass plates and the surface energy is zero.

As we discuss our observations just qualitatively, we will suppose for simplicity that over the distance d between disclinations the surface energy will not change and it can be characterized by some mean value surface energy w_a. So the mean anchoring energy of the oily-streak can be estimated to be $2w_a dL$, with L the length of the streak. The number 2 corresponds to two sample surfaces. The self-energy of π-disclinations is [S2]:

$\frac{\pi\widetilde{K}}{2} ln\left(\frac{R}{r_c}\right)$,

where $\widetilde{K}$ is the bend elastic constant of short-pitch cholesteric material and it is expressed by bend elastic constant of cholesteric K_{33} as $\widetilde{K} = \frac{3}{8}K_{33}$ [S2]. Then the approximate energy of the streak can be estimate as:

$$L\left(\pi\widetilde{K} ln\left(\frac{R}{r_c}\right) + w_a d\right). \qquad (1)$$

The observed modulation of the streak is the consequence of lowering streak energy, namely the surface anchoring energy when the anchoring energy is not small. In such a case we expect that the parallel π-disclinations can be transformed to the system of FD with elliptical focal conics in the plane of the oily strike (see Figure S6) similarly as discussed in [S6].

Let the focal conics have semi-axes $a = \frac{d}{2}$ and b (Figure S6). We again suppose that "cholesteric layers" touch the surface by some angle just over the surface of elliptical FD. The mean anchoring energy over the elliptic surface is then $2\pi\frac{d}{2}bw_a$ taking in account again two sample surfaces. The energy of the elliptical focal domain is given e.g. in [S4]:

$$E_{FD} = 4\pi\frac{d}{2}(1-e^2)\boldsymbol{K}(e^2)\left[\widetilde{K} ln\frac{d\sqrt{1-e^2}}{r_c} - \Lambda\right],$$

with $\Lambda = 2\widetilde{K} + \overline{K}$ and $\boldsymbol{K}(x)$ is the complete elliptic integral of the first kind. The constant $\overline{K}$ characterizes the contribution to the elastic energy due to Gaussian layer curvature [S4].

Over the length of streak, L, the number of FD is given as:

$n = \frac{L}{2b+l}$. Again b is the minor semi-axis of FD and l is the distance between neighboring FD (see Fig. S6(b,c)). Then the energy of the system of FD which form oily streak can be written as:

$$n\left(E_{FD} + 2\pi\frac{d}{2}bw_a\right). \qquad (2)$$

The transformation of the structure of the streak to the system of FD will be possible when the energy (2) of the streak with FD is lower as compared with the energy (1) of the streak without FD, i.e.:

$$L\left(\pi\widetilde{K} ln\left(\frac{R}{r_c}\right) + w_a d\right) > n\left(E_{FD} + 2\pi\frac{d}{2}bw_a\right). \qquad (3)$$

This inequality gives the lower limit for the mean surface anchoring energy w_a:

$$w_a > \frac{E_{FD} - (2b+l)\frac{\pi \bar{K}}{2} ln\left(\frac{R}{r_c}\right)}{(4db + 2dl - \pi db)}. \qquad (4)$$

Note that for the transformation of the streak to the system of focal domains (streak modulation) the length of line defects increases while the surface where "cholesteric layers" are not tangential to it (zero anchoring energy) decreases. So the transformation of the streak to modulated structure occurs for w_a satisfying the above inequality.

In order to obtain a numerical estimation of the w_a limit from inequality (4), we take $R \approx h$, where $h \approx 5$ μm is the sample thickness. The core radius of dislocation is taken as $r_c \approx 0.001$ μm. From our observation (see Fig. S5) we obtain $d = 2a \approx 6.25$ μm and $2b \approx$ 2.08 μm, i.e. $b \approx 1.04$ μm. Moreover the separation l of FD seems to be small, so for the purpose of our estimation we consider $l \approx 0$. As for elastic constants we take $K_{33} \approx 10^{-11}$ J/m what is typical value for nematics and $\bar{K} \approx 0$ what gives the maximum estimation of the FD energy [S4]. Then using inequality (4) we obtain the limiting value of w_a for which the streak modulation starts to be possible as:

$w_a \approx 2 \times 10^{-5}$ J/m^2.

Therefore we can expect for mean anchoring energies greater than the above value streaks will be modulated. The value of estimated anchoring energy corresponds to some medium strength anchoring (for comparison of anchoring energies see e.g. [S7]). Therefore for stronger anchoring the modulation by FD will usually occur.

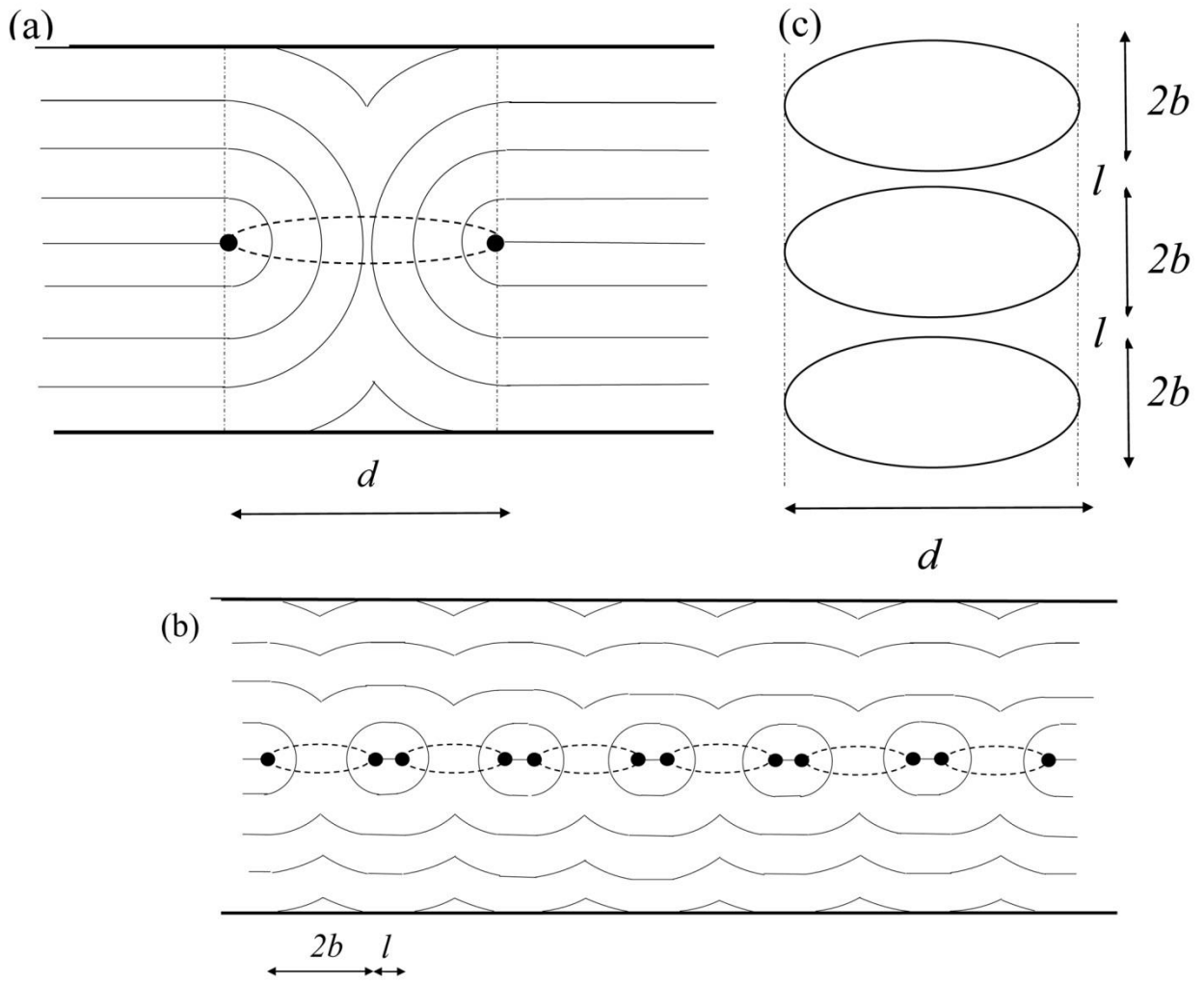

Figure S6

Schematic drawing of oily streak modulation: (a) Layer structure on the cross-section of oily streak reminding Fig. 3 in [S4, S5]. Ellipse (dashed line) represents a focal domain having a major semi-axis $a=d/2$ where d is the oily streak width. Black dots are intersections of the ellipse with the plane of figure. Within the strike width limited by dotted-and-dashed lines the "cholesteric layers" are curved while outside of strike width layers are uniform and parallel to surfaces.

(b) Side view of oily streak. Streak is modulated along its length by focal domains the ellipses of which are represented by dashed lines. In this view widths of ellipses are $2b$ with b as a minor semi-axis of focal domains. Parameter l is the distance of neighbor ellipses and black dots are again intersections of the ellipses with the plane of figure.

(c) Top view of oily strike of the width d. Oily strike is modulated by the system of focal domains (ellipses) as in Figure C.III.6(b) given in [S6].

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