Supporting Information

Modulated SmA_b phases formed by anchor shaped liquid crystalline molecules

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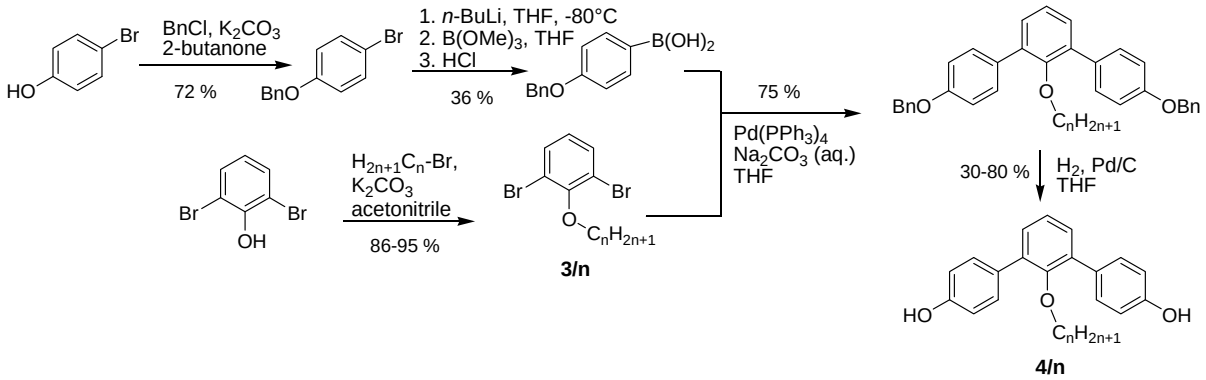
1 Synthesis and analytical data

1.1 General

All starting materials were obtained from ABCR, Aldrich, Fluka or Merck and used as received. Solvents were purified and dried by standard methods prior to use. The crude products were purified by column chromatography using silica gel 60 (40-63 μm, Merck) as stationary phase. The structure characterization of the synthesized compound is based on ^{1}H-, ^{13}C-NMR (Varian Unity 500 and VRX 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard). Mass spectra were taken on Finnigan LCQ (electrospray, spray-voltage 6.7 kV, sheath gas nitrogen). Microanalyses were performed using a Leco CHNS-932 elemental analyser.

1.2 Preparation of the 2´-*n*-alkoxy-*m*-terphenyl-4,4´´-diols 4/*n*



Scheme S1. Synthesis of the 2´-*n*-alkoxy-*m*-terphenyl-4,4´´-diols **4/*n***

The synthetic procedures leading to the *m*-terphenyl diols **4/*n*** is outlined in Scheme S1. 4-Benzyloxybenzene boronic acid was prepared as described in ref.[S1,S2], 2,6-dibromophenol was synthesized as described in ref.[S3] and 2,6-dibromo-1-*n*-hexyloxybenzene **3/6** was obtained according ref. [S4]

2,6-Dibromo-1-*n*-octadecyloxybenzene 3/18 [S3]

A mixture of 2,6-dibromophenol (1 g, 3.97 mmol), 1-*n*-bromooctadecane (1.39 g, 4.17 mmol), K_2CO_3 (1.10 g, 7.94 mmol) and acetonitrile (50 ml) were stirred for 20 hours under reflux. Then water was added and the mixture was extracted three times with diethyl ether. The combined organic phases were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. Yield: 1.72 g (86 %), white solid, mp.: 39-41 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.48 (d, ^{3}J (H,H) = 7.8, 2H, Ar-H), 6.83 (t, ^{3}J (H,H) = 7.9, 1H, Ar-H), 3.99 (t, ^{3}J (H,H) = 6.6, 2H, O-CH_2-), 1.85 (m, 2H, O-CH_2-CH_2-), 1.51 (m, 2H, O-CH_2-CH_2-CH_2-), 1.25 (m, 28H, -CH_2-), 0.87 (m, 3H, -CH_3).

2,6-Dibromo-1-*n*-docosyloxybenzene 3/22

Synthesized from 2,6-dibromophenol (1 g, 3.97 mmol) 1-*n*-bromodocosane (1.6 g, 4.17

mmol), K_2CO_3 (1.10 g, 7.94 mmol) in acetonitrile (50 ml). Crystallized from $CHCl_3$/MeOH; Yield: 1.91 g (86 %), white solid, mp.: 54 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.47 (d, ^3J (H,H) =8.1, Ar-H), 6.82 (t, ^3J (H,H) = 8.1, 1H, Ar-H), 3.98 (t, ^3J (H,H) = 6.6, 2H, O-CH_2-), 1.86 (m, 2H, O-CH_2-CH_2-), 1.24 (m, 38H, -CH_2-), 0.86 (m, 3H, -CH_3).

2'-*n*-Hexyloxy-*m*-terphenyl-4,4''-diol 4/6[S5]

A mixture of 4-(tert-butyldimethylsilyloxy)benzene boronic acid (1.44 g, 3.75 mmol), **3/6** (2.12 g, 9.0 mmol), a catalytic amount of $Pd(PPh_3)_4$ (43 mg, 0.03 mmol), glyme (60 ml) and sat. aq. $NaHCO_3$ (40 ml) was refluxed for 8 h under an argon atmosphere. After cooling to room temperature the solvent was evaporated and the residue was extracted with methylene chloride. Combined organic phases were washed with water and brine, dried over sodium sulphate and the solvent was evaporated. The crude product was dissolved in methanol. To this solution KOH was added and then refluxed for 3 hours to the complete removal of the protection groups. After evaporation of the solvent chloroform was added and washed with water and dried over sodium sulphate. The crude product was purified by column chromatography ($CHCl_3$/MeOH (100:2) and crystallized from $CHCl_3$. Yield: 0.71 g (52 %), yellowish solid, mp: 151°C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.48 (d, ^3J (H,H) = 7.9, 4H, Ar-H), covered by $CHCl_3$, 2H, 7.17 (m, 1H, Ar-H), 6.86 (d, ^3J (H,H) = 7.9, 4H, Ar-H), 4.67 (s, 2H, -OH), 3.17 (t, ^3J (H,H) = 6.3, 2H, O-CH_2-), 1.12 (m, 4H, -CH_2-), 0.94 (m, 4H, O-CH_2-CH_2-CH_2), 0.87 (t, ^3J (H,H) = 7.4, 3H, -CH_3).

2'-*n*-Octadecyloxy-*m*-terphenyl-4,4''-diol 4/18

4,4´´-Dibenzyloxy-2´-n-octadecyloxy-m-terphenyl. A mixture of 4-benzyloxybenzene boronic acid (1.87 g, 8.18 mmol), **3/18** (1.72 g, 3.41 mmol), a catalytic amount of $Pd(PPh_3)_4$ (43 mg, 0.03 mmol), glyme (60 ml) and sat. aq. $NaHCO_3$ (40 ml) was refluxed for 8 h under an argon atmosphere. After cooling to room temperature the solvent was evaporated and the residue was extracted with methylene chloride. Combined organic phases were washed with water and brine, dried over sodium sulphate and the solvent was evaporated. The crude product was purified by column chromatography using chloroform/petroleum ether (1:1) as eluent and crystallized from $CHCl_3$/MeOH. Yield: 1.21 g (50 %), white solid, mp: 71°C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.53 (d, ^3J (H,H) = 8.7, Ar-H), 7.45 (m, 4H, Ar-H), 7.38 (t, ^3J (H,H) =7.5, Ar-H), 7.32 (d, ^3J (H,H) = 7.3, 2H, Ar-H), 7.17 (m, 1H, Ar-H), 7.01 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 5.09 (s, 4H, O-CH_2-Ph), 3.18 (t, ^3J (H,H) = 6.2, 2H, O-CH_2-), 1.23 (m, 28H, -CH_2-), 0.93 (m, 4H, O-CH_2-CH_2-CH_2), 0.86 (t, ^3J (H,H) = 6.8, 3H, -CH_3).

2'-n-Octadecyloxy-m-terphenyl-4,4''-diol **4/18.** A suspension of 4,4´´-dibenzyloxy-2´-*n*-octadecyloxy-*m*-terphenyl (1.21 g, 1.7 mmol) and a catalytic amount of Pd/C (10 % Pd, 40 mg) in 30 ml THF was flushed with hydrogen. The mixture was shaken at 40 °C and 2.8 bar for 48 h, followed by filtration off the catalyst and evaporation off the solvent. The crude product was purified by flash chromatography (silica gel, $CHCl_3$/MeOH) and crystallised from $CHCl_3$/petroleum ether. Yield: 0.68 g (75.3 %), white solid, mp: 115 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.47 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 7.17 (m, 1H, Ar-H), 6.85 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 3.17 (t, ^3J (H,H) = 6.4, 2H, O-CH_2-), 1.24 (m, 28H, -CH_2-), 0.94 (m, 4H, O-CH_2-CH_2-CH_2), 0.86 (t, ^3J (H,H) = 6.5, 3H, -CH_3).

2'-*n*-Docosyloxy-m-terphenyl-4,4''-diol 4/22

4,4´´-Dibenzyloxy-2´-n-docosyloxy-m-terphenyl. Synthesized as described for **4/6** using 4-benzyloxybenzene boronic acid (1.10 g, 4.83 mmol), **3/22** (1.13 g, 2.01 mmol), a catalytic amount of $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), glyme (60 ml) and sat. aq. $NaHCO_3$ (40 ml). Yield: 1.17 g (76 %), white solid, mp: 64 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.53 (d, ^3J

(H,H) = 8.7, Ar-H), 7.45 (m, 4H, Ar-H), 7.38 (t, ^3J (H,H) =7.4, Ar-H), 7.32 (d, ^3J (H,H) = 7.3, 2H, Ar-H), 7.18 (m, 1H, Ar-H), 7.01 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 5.09 (s, 4H, O-CH_2-Ph), 3.18 (t, ^3J (H,H) = 6.2, 2H, O-CH_2-), 1.24 (m, 36H, -CH_2-), 0.93 (m, 4H, O-CH_2-CH_2-CH_2), 0.86 (t, ^3J (H,H) = 6.7, 3H, -CH_3).

2'-n-Docosyloxy-m-terphenyl-4,4''-diol **4/22:** Synthezied as described for **4/18** using 4,4´´-dibenzyloxy-2´-*n*-docosyloxy-*m*-terphenyl (1.2 g, 2.04 mmol) and a catalytic amount of Pd/C (10 % Pd, 20 mg) in 30 ml THF. Yield: 0.75 g (63 %), white solid, mp: 115 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.47 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 7.17 (m, 1H, Ar-H), 6.85 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 4.67 (s, 2H, -OH), 3.17 (t, ^3J (H,H) = 6.4, 2H, O-CH_2-), 1.23 (m, 36H, -CH_2-), 0.93 (m, 4H, O-CH_2-CH_2-CH_2), 0.86 (t, ^3J (H,H) = 6.8, 3H, -CH_3).

1.3 Preparation of the benzoic acids

4-(4-*n*-Alkoxybenzoyloxy)benzoic acids [S6,S7], and 4-(3-flouro-4-(4-*n*-octyloxybenzoyloxy)-benzoic acid[S8] were obtained by known methods.

1.4 Compounds 1/*n*, 1F/22 and 2/22

General procedure of the esterification using DCC (A). The **4/*n*** (1 equ.), the appropriate benzoic acid (2 equ.) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP) were dissolved in dry dichloromethane and stirred for 10 minutes. To this mixture *N,N'*-dicyclohexylcarbodiimide (DCC) (2.6 equ.) was added and stirring was continued for 24 hours at room temperature. The reaction mixture was washed with water and dried over sodium sulphate and filtered. After evaporation of the solvent the crude product was purified by column chromatography using chloroform/petroleum ether (1:1) as eluent and crystallized from chloroform/ethanol and/or chloroform/petroleum ether.

General procedure of the esterification via the benzoyl chlorides (B). The appropriate benzoic acid (1 equ.) was heated under reflux in a large excess of thionyl chloride for 2 h. Excess of thionyl chloride was removed by distillation at first under normal pressure, then under vacuum (bath temperature <150 °C). The resulting acid chloride was dissolved in dry dichloromethane, and appropriate **4/*n*** (0.5 equ.) was added. To this clear solution a catalytic amount of 4- (*N,N*-dimethylamino)pyridine (DMAP) or pyridine and triethylamine (1.3 equ.) were added, and the reaction mixture was refluxed for 4 h at room temperature under an argon atmosphere. The reaction mixture was washed with a 1M HCl solution and a saturated $NaHCO_3$ solution and dried over Na_2SO_4. After evaporation of the solvent the product was purified by column chromatography using chloroform as an eluent and crystallized from chloroform/ethanol and/or chloroform/petroleum ether.

2´-*n*-Hexyloxy-1,1´:3´,1´´-terphenyl-4,4´´-diyl-bis[4-(4-*n*-octyloxybenzoyloxy)benzoate] (1/6)

Synthesized from **4/6** (200 mg, 0.55 mmol) and 4-(4-*n*-octyloxybenzoyloxy)benzoic acid (448 mg, 1.21 mmol) using procedure A with DCC (296 mg, 143 mmol) and DMAP (30 mg, 0.24 mmol) in CH_2Cl_2 (30 ml). Yield: 120 mg (20 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 500MHz): δ = 8.31 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 8.16 (d, ^3J (H,H) = 8.8, 4H, Ar-H), 7.70 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 7.4 (m, 6H, Ar-H), 7.30 (d, ^3J (H,H) = 8.5, 4H, Ar-H) , 7.00 (d, ^3J (H,H) = 8.8, 4H, Ar-H), 4.06 (t, ^3J (H,H) = 6.4, 4H, O-CH_2-), 3.26 (t, ^3J (H,H) = 6.2, 2H, O-CH_2-), 1.83 (m, 4H, O-CH_2-CH_2-), 1.47 (m, 4H, -CH_2-), 1.4 - 1.3 (m, 16H, -CH_2-), 1.23 (m, 2H, -CH_2-), 1.15 (m, 2H, -CH_2-), 1.00 (m, 4H, -CH_2-), 0.90 (t, ^3J (H,H) = 6.9, 6H, -CH_3), 0.81

(t, ^3J (H,H) = 7.3, 3H, -CH_3); ^{13}C-NMR ($CDCl_3$, 125MHz): δ = 164.43, 164.33, 163.82, 155.37, 154.24, 150.07, 136.46, 135.32, 132.40, 131.78, 130.61, 130.31, 126.97, 124.20, 122.09, 121.20, 120.98, 114.41, 73.34, 68.38, 31.77, 31.33, 29.80, 29.29, 29.19, 29.06, 25.96, 25.45, 22.62, 22.49, 14.06, 13.96; ESI-MS (CH_2Cl_2, MeOH, LiCl): *m/z* calcd. for $[M+Li]^+$ $C_{68}H_{74}O_{11}Li$: 1073.54, found: 1073.55; anal. calcd. for $C_{68}H_{74}O_{11}$: C 76.52 H 6.99 found: C 76.45 H 6.85 %.

2´-*n*-Octadecyloxy-1,1´:3´,1´´-terphenyl-4,4´´-diyl-bis[4-(4-*n*-octyloxybenzoyloxy)-benzoate] (1/18)

Synthesized from **4/18** (210 mg, 0.39 mmol) and 4-(4-*n*-octyloxybenzoyloxy)benzoic acid (323 mg, 0.87 mmol) using procedure A with DCC (211 mg, 1.03 mmol) and DMAP (21 mg, 0.17 mmol) in CH_2Cl_2 (30 ml). Yield: 330 mg (73 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400MHz): δ = 8.29 (d, ^3J (H,H) = 8.9, 4H, Ar-H), 8.14 (d, ^3J (H,H) = 8.9, 4H, Ar-H), 7.68 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 7.37 (m, 6H, Ar-H), 7.26 (d, ^3J (H,H) = 7.4, 4H, Ar-H), 6.97 (d, ^3J (H,H) = 8.9, 4H, Ar-H), 4.04 (t, ^3J (H,H) = 6.5, 4H, O-CH_2-), 3.25 (t, ^3J (H,H) = 6.2, 2H, O-CH_2-), 1.82 (m, 4H, O-CH_2-CH_2-), 1.47 (m, 6H, -CH_2-), 1.47 (m, 6H, -CH_2-), 1.4 -1.2 (m, 48H, -CH_2-), 0.98 (m, 4H, -CH_2-); ^{13}C-NMR ($CDCl_3$, 125MHz): δ = 164.42, 164.30, 163.82, 155.38, 154.24, 150.07, 136.47, 135.32, 132.40, 131.78, 130.61, 130.32, 126.96, 124.20, 122.07, 121.21, 120.97, 114.41, 73.37, 68.38, 31.89, 31.78, 29.84, 29.73, 29.71, 29.69, 29.63, 29.62, 29.52, 29.33, 29.30, 29.19, 29.07, 25.96, 25.80, 22.65, 22.63, 14.08, 14.07; ESI-MS (CH_2Cl_2, MeOH, LiCl): *m/z* calcd. for $[M+Li]^+$ $C_{80}H_{98}O_{11}Li$: 1241.73, found: 1241.79; anal. calcd. for $C_{80}H_{98}O_{11}$: C 77.76 H 7.99 found: C 77.55 H 7.87 %.

2´-*n*-Docosyloxy-1,1´:3´,1´´-terphenyl-4,4´´-diyl-bis[4-(3-fluoro-4-*n*-octyloxybenzoyloxy)-benzoate] (1F/22):

The benzoyl chloride was prepared using procedure B from 4-(3-flouro-4-(4-*n*-octyloxybenzoyloxy)benzoic acid (200 mg, 0.50 mmol) and $SOCl_2$ (30 ml), followed by addition of **4/22** (150 mg, 0.25 mmol), triethylamine (0.06 ml, 0.65 mmol), DMAP (30 mg, 0.24 mmol) in CH_2Cl_2 (30 ml). Yield: 120 mg (35 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400MHz): δ = 8.29 (d, ^3J (H,H) = 8.6, 4H, Ar-H), 7.96 (m, 2H, Ar-H), 7.90 (dd, ^3J (H,F) = 11.3, ^4J (H,H) = 2.4, 2H, Ar-H), 7.68 (d, ^3J (H,H) = 8.6, 4H, Ar-H), 7.37 (m, 6H, Ar-H), 7.28 (d, ^3J (H,H) = 8.6, 4H, Ar-H), 7.03 (dd, ^3J (H,H) = 8.4, ^4J (H,F) = 8.4, 2H, Ar-H), 4.12 (t, ^3J (H,H) = 6.6, 4H, O-CH_2-), 3.24 (t, ^3J (H,H) = 6.2, 2H, O-CH_2-), 1.86 (m, 4H, O-CH_2-CH_2-), 1.48 (m, 4H, O-CH_2-CH_2-CH_2-), 1.4-1.1 (m, 52H, -CH_2-), 0.97 (m, 4H, O-CH_2-CH_2-CH_2-), 0.86 (m, 9H, -CH_3); ^{13}C-NMR ($CDCl_3$, 125MHz): δ = 164.35, 163.46, 163.44, 155.09, 154.23, 152.91, 152.29, 152.21, 150.94, 150.04, 136.49, 135.30, 131.83, 130.61, 130.32, 127.53, 127.50, 127.19, 124.21, 121.96, 121.27, 121.19, 117.93, 117.77, 113.49, 113.48, 73.37, 69.50, 31.89, 31.76, 29.83, 29.73, 29.71, 29.68, 29.67, 29.62, 29.61, 29.51, 29.32, 29.25, 29.19, 29.16, 28.96, 25.84, 25. 79, 22.65, 22.61, 14.07, 14.05; ^{19}F-NMR (CDCl3, J/Hz, 200 MHz): δ = -133.73 (t, ^3J (F,H) = 9.2); ESI-MS (CH_2Cl_2, MeOH, LiCl): *m/z* calcd. for $[M+Li]^+$ $C_{84}H_{104}F_2O_{11}Li$: 1333.77, found: 1333.79; anal. calcd. for $C_{84}H_{104}F_2O_{11}$: C 75.95 H 7.90 found: C 75.83 H 7.73 %.

2´-*n*-Docosyloxy-1,1´:3´,1´´-terphenyl-4,4´´-diyl-bis[4-(4´-*n*-hexyloxybiphenyl-4-yl)carboxylate] (2/22)

The acid chloride was prepared using procedure B from 4´-*n*-hexyloxybiphenyl-4-carboxylic

acid (150 mg, 0.50 mmol) and $SOCl_2$ (30 ml), followed by addition of **4/22** (150 mg, 0.25 mmol), triethylamine (0.06 ml, 0.65 mmol), DMAP (30 mg, 0.24 mmol) in CH_2Cl_2 (30 ml). Yield: 90 mg (34 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 500MHz): δ = 8.19 (d, ^3J (H,H) = 8.4, 4H, Ar-H), 7.63 (m, 8H, Ar-H), 7.53 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 7.31 (d, ^3J (H,H) = 7.5, 2H, Ar-H), 7.24 (d, ^3J (H,H) = 8.6, 4H,Ar-H), 6.94 (d, ^3J (H,H) =8.7, 4H, Ar-H), 3.95 (t, ^3J (H,H) = 6.5, 4H, O-CH_2-), 3.20 (t, ^3J (H,H) = 6.2, 2H, O-CH_2-), 1.75 (m, 4H, O-CH_2-CH_2-) 1.42 (m, 4H, O-CH_2-CH_2-CH_2-), 1.4-1.1 (m, 46H, -CH_2-), 0.92 (m, 4H, O-CH_2-CH_2-CH_2-), 0.85 (t, ^3J (H,H) = 6.2, 6H, -CH_3), 0.80 (t, ^3J (H,H) = 6.9, 3H, -CH_3); ^{13}C-NMR ($CDCl_3$, 125MHz): δ = 165.09, 159.58, 154.25, 150.19, 145.97, 136.36, 135.36, 131.98, 130.70, 130.58, 130.30, 128.35, 127.55, 126.57, 124.19, 121.26, 114.98, 73.34, 68.15, 31.89, 31.57, 29.85, 29.75, 29.72, 29.68, 29.63, 29.33, 29.20, 25.80, 25.70, 22.65, 22.58, 14.08, 14.00; ESI-MS (CH_2Cl_2, MeOH, LiCl): *m/z* calcd. for $[M+Li]^+$ $C_{78}H_{98}O_7Li$: 1153.75, found: 1153.78; anal. calcd. for $C_{78}H_{98}O_7$: C 81.63 H 8.61 found: 81.56 H 8.61 %.

2. Investigation methods

The mesomorphic properties were investigated by polarising microscopy (POM; Optiphot 2, Nikon in conjunction with a heating stage FP82HT, Mettler), differential scanning calorimetry (DSC; DSC-7, Perkin Elmer). XRD patterns were recorded with a 2D detector (HI-STAR, Siemens). Ni filtered and pin hole collimated CuK_α radiation was used. The exposure time was 15 min and the sample to detector distance was 8.8 and 26.9 cm for small angle and wide angle scattering experiments, respectively. Samples were aligned by slow cooling (rate: 1 K min^{-1} – 0.1 K min^{-1}) of a small droplet of the compound on a glass plate and takes place at the sample–air interface. The samples were held on a temperature-controlled heating stage.

3. Additional Data

3.1 DSC traces

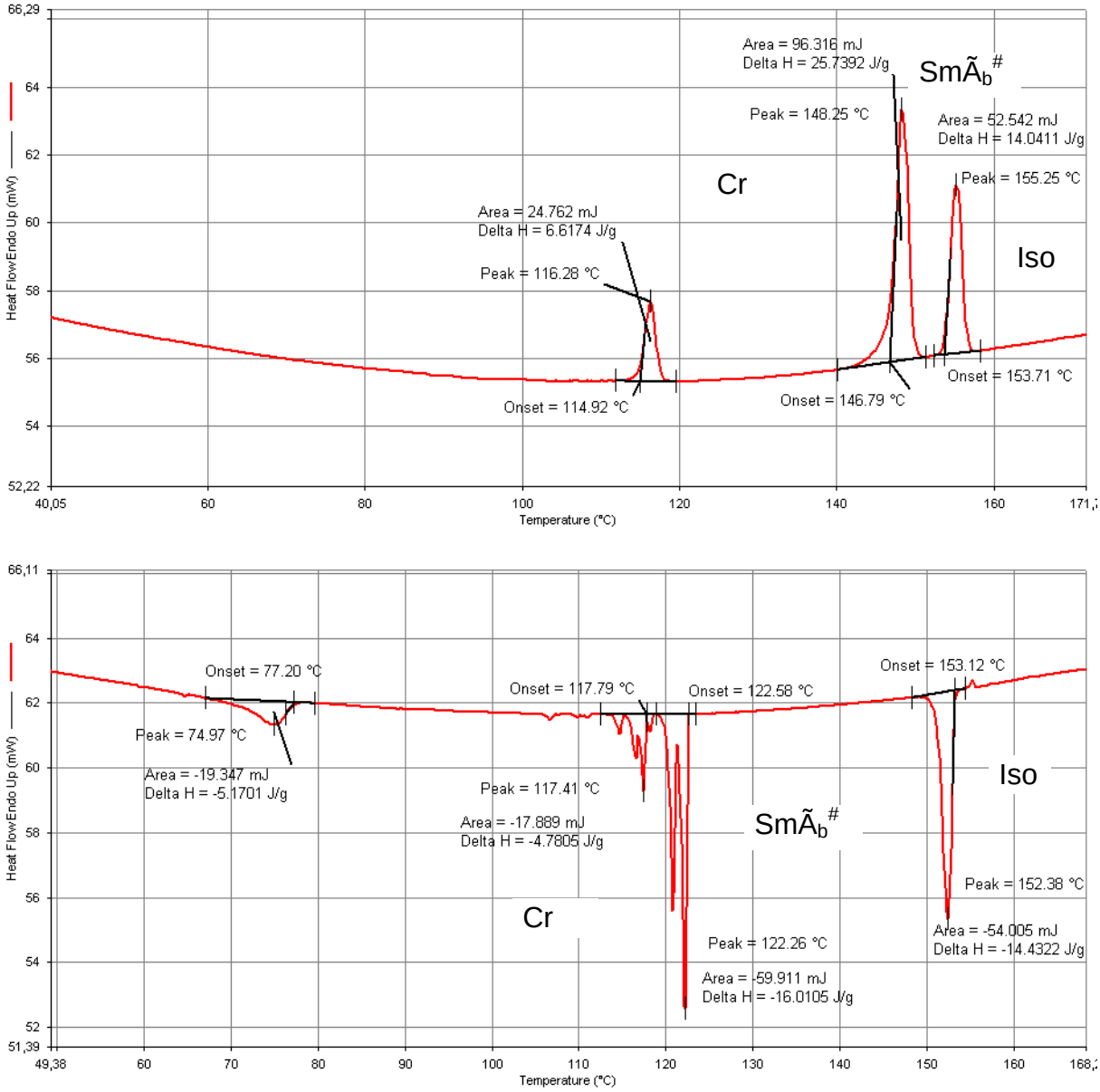


Fig. S1. DSC heating (top) and cooling scans (bottom) of **1/6** (10 K min^{-1})

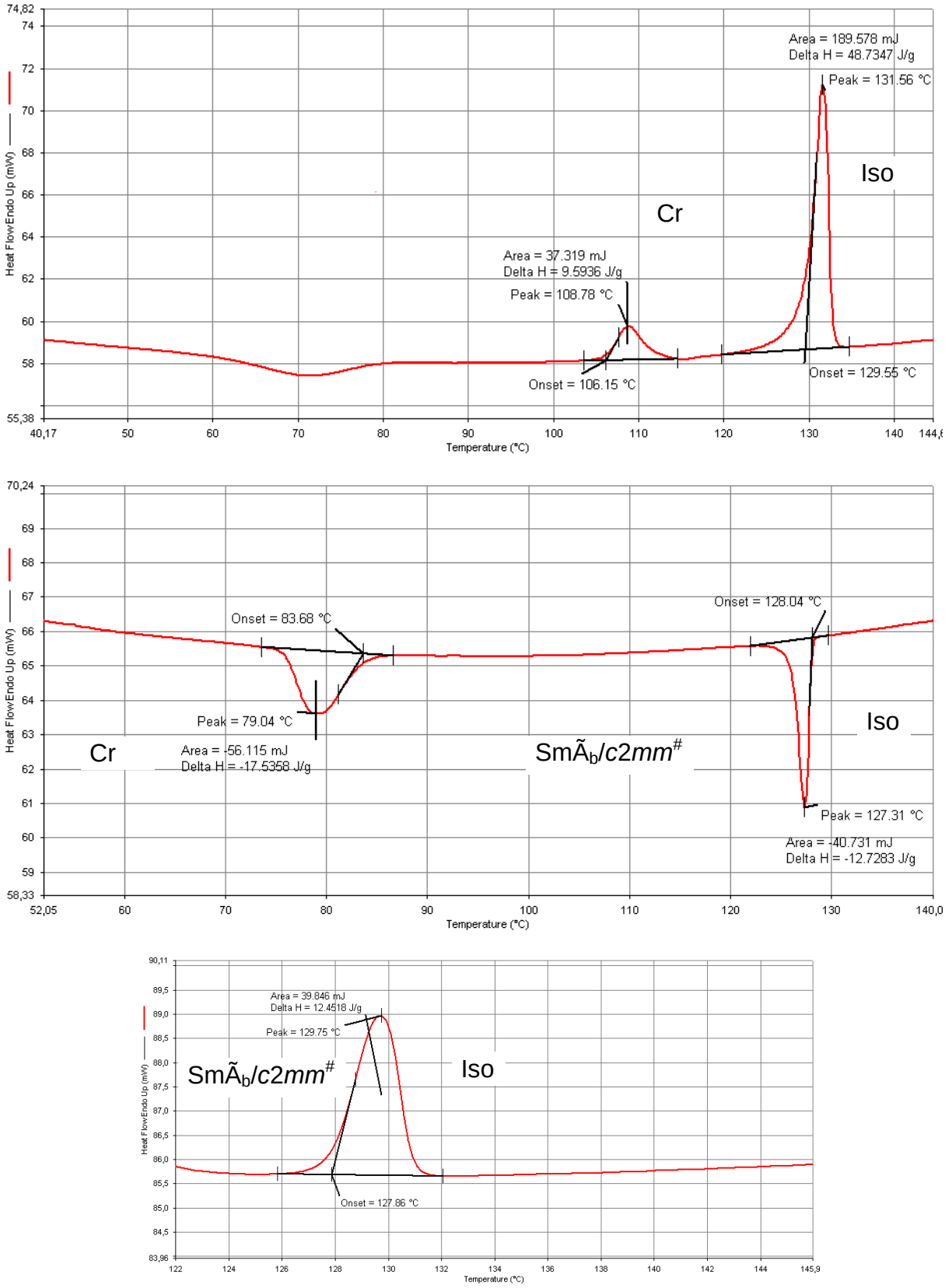


Fig. S2. DSC heating (top) and cooling scans (middle) of **1/18** and second heating immediately after cooling to T = 122 °C at 10 K min^{-1} (bottom).

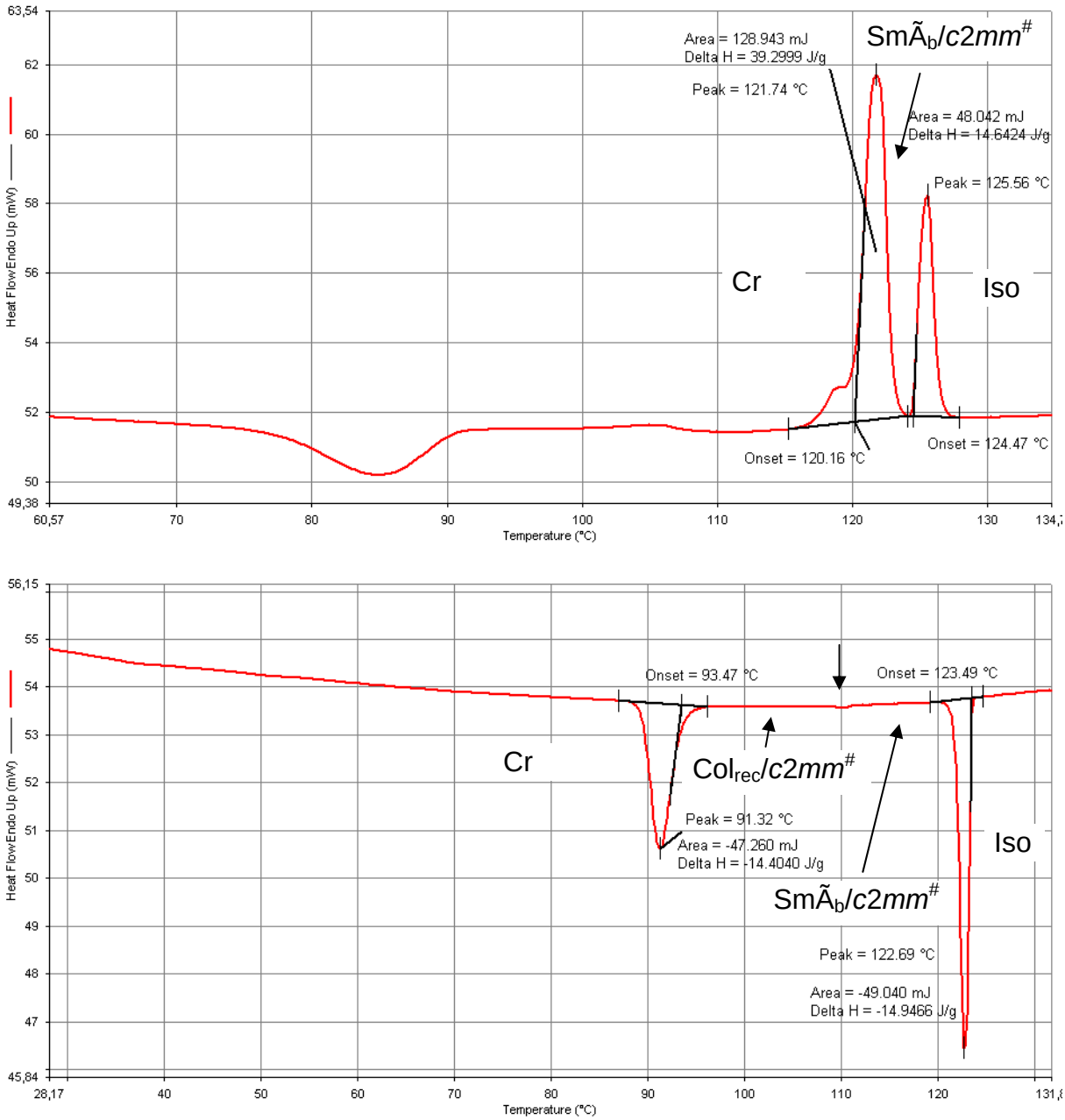


Fig. S3. DSC heating (top) and cooling scans (bottom) of **1F/22** (10 K min^{-1})

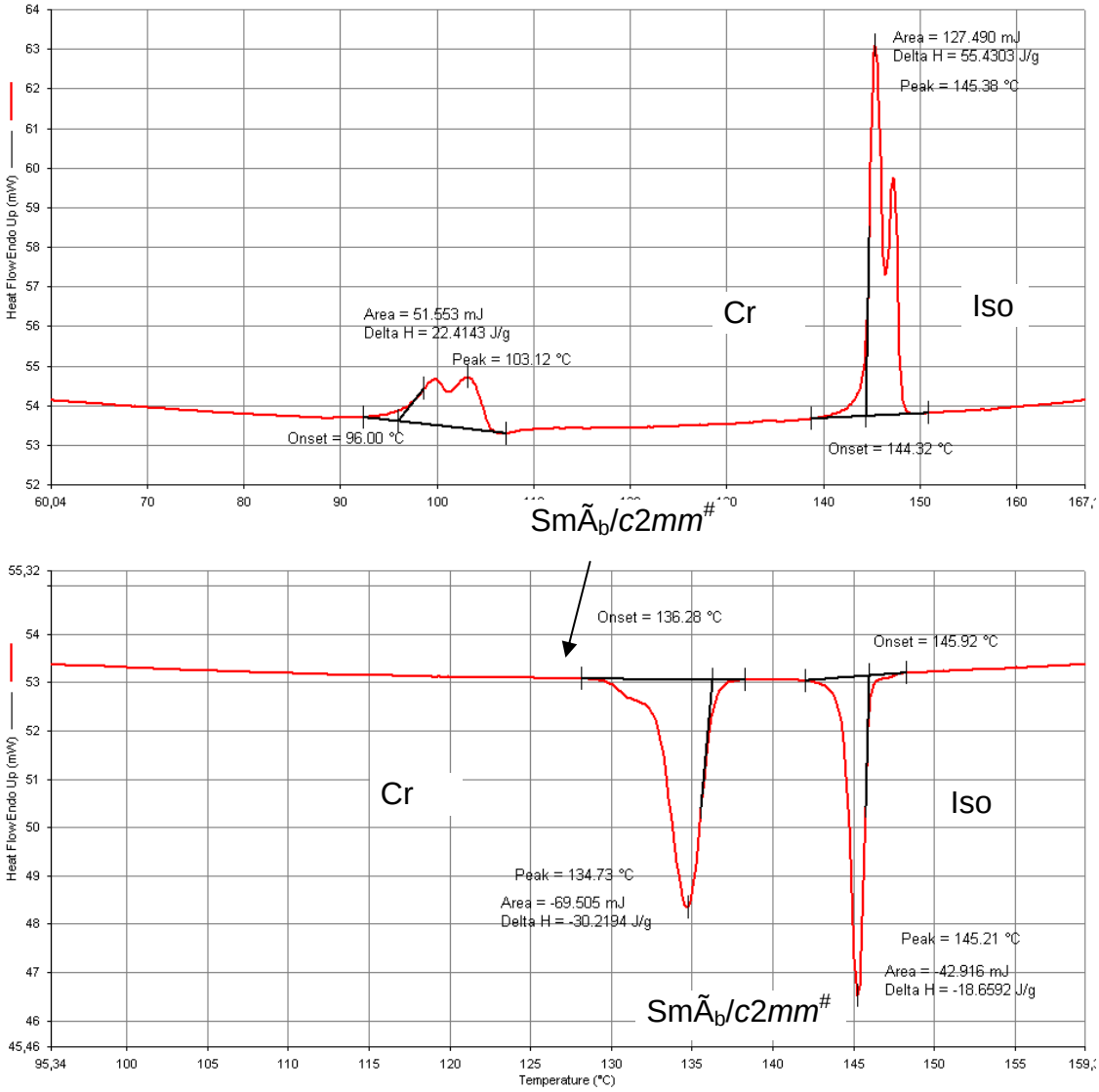


Fig. S4. DSC heating (top) and cooling scans (bottom) of **2/22** (10 K min^{-1})

3.2 Additional Textures

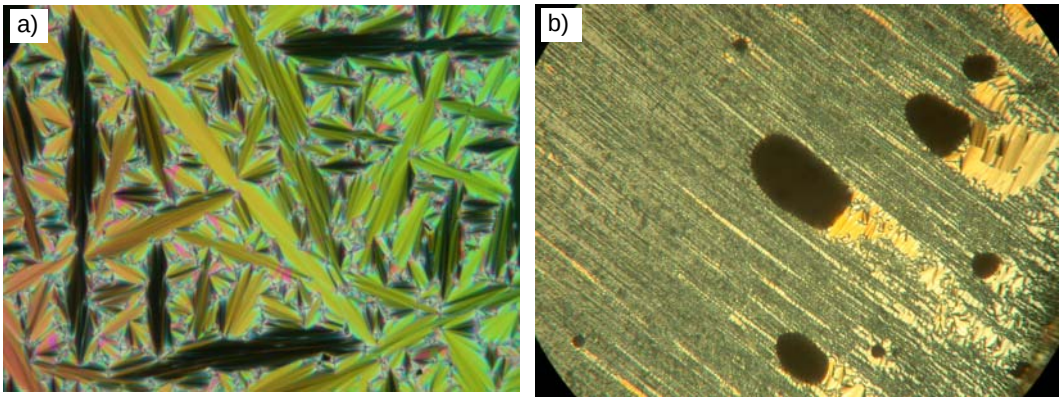


Fig. S5. Texture as observed between crossed polarizers for compound **1/6**, at T = 152 °C, a) planar alignment, b) after shearing.

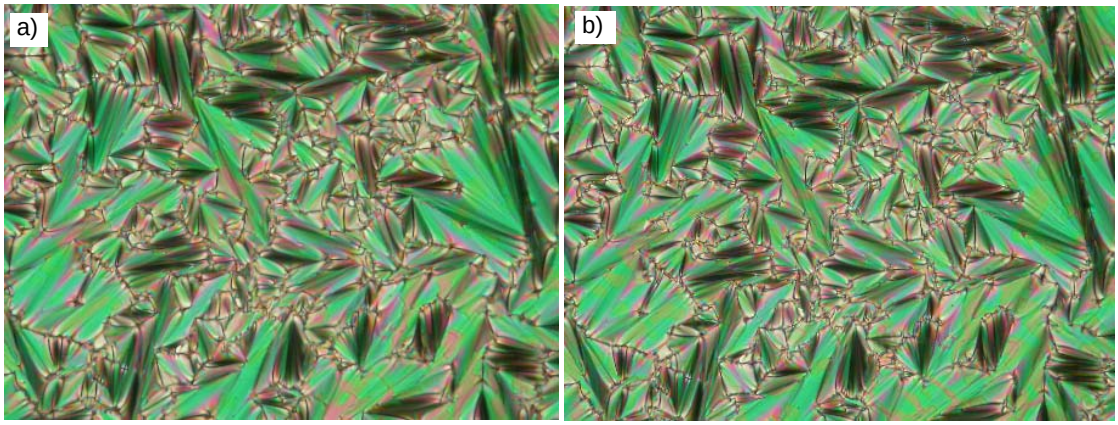


Fig. S6. Texture as observed between crossed polarizers for compound **1F/22** (planar alignment) a) at T = 108 °C in the $Col_{rec}/c2mm^{\#}$ phase and b) at T = 123 °C in the $SmÃ_b/c2mm^{\#}$ phase.

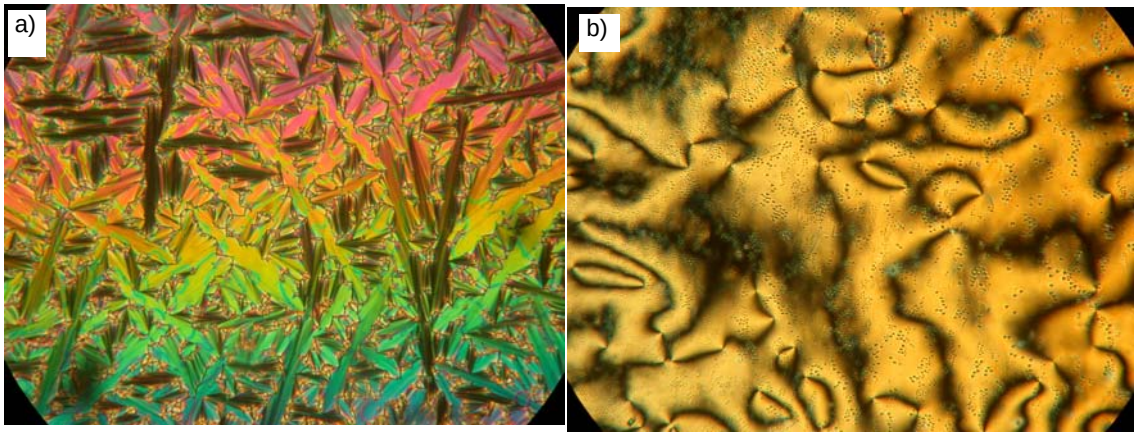


Fig. S7. Texture as observed between crossed polarizers for compound **2/22**, at T = 144 °C, a) planar alignment, b) homeotropic alignment after shearing.

3.3 Additional XRD Data

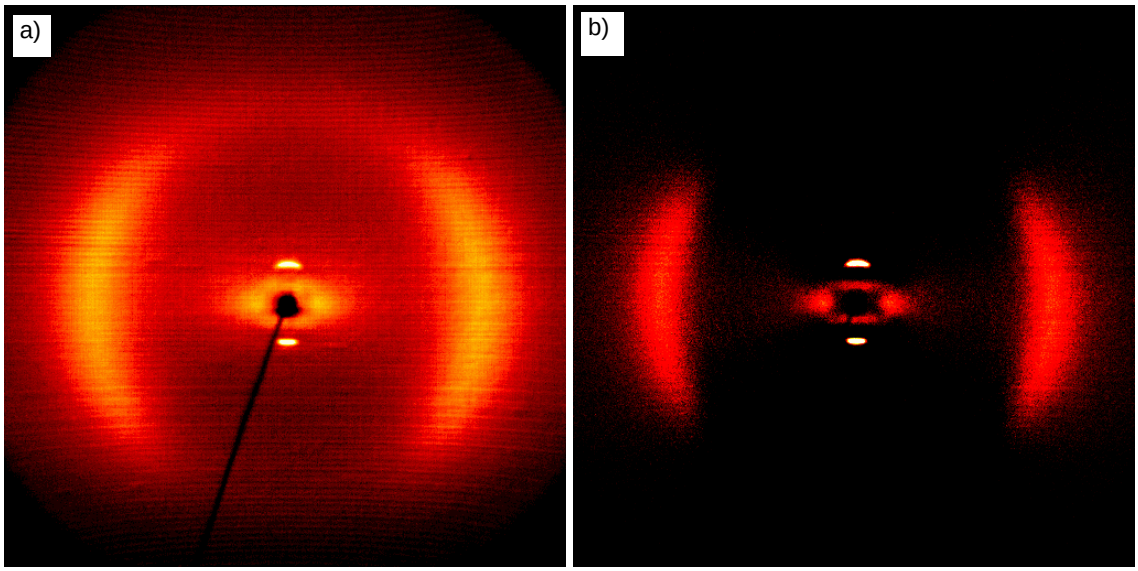


Fig S8. XRD pattern of a surface aligned sample of the mesophases of compounds **2/22** at T = 145 °C, a) original pattern and b) pattern after subtraction of the isotropic phase at T = 150 °C.

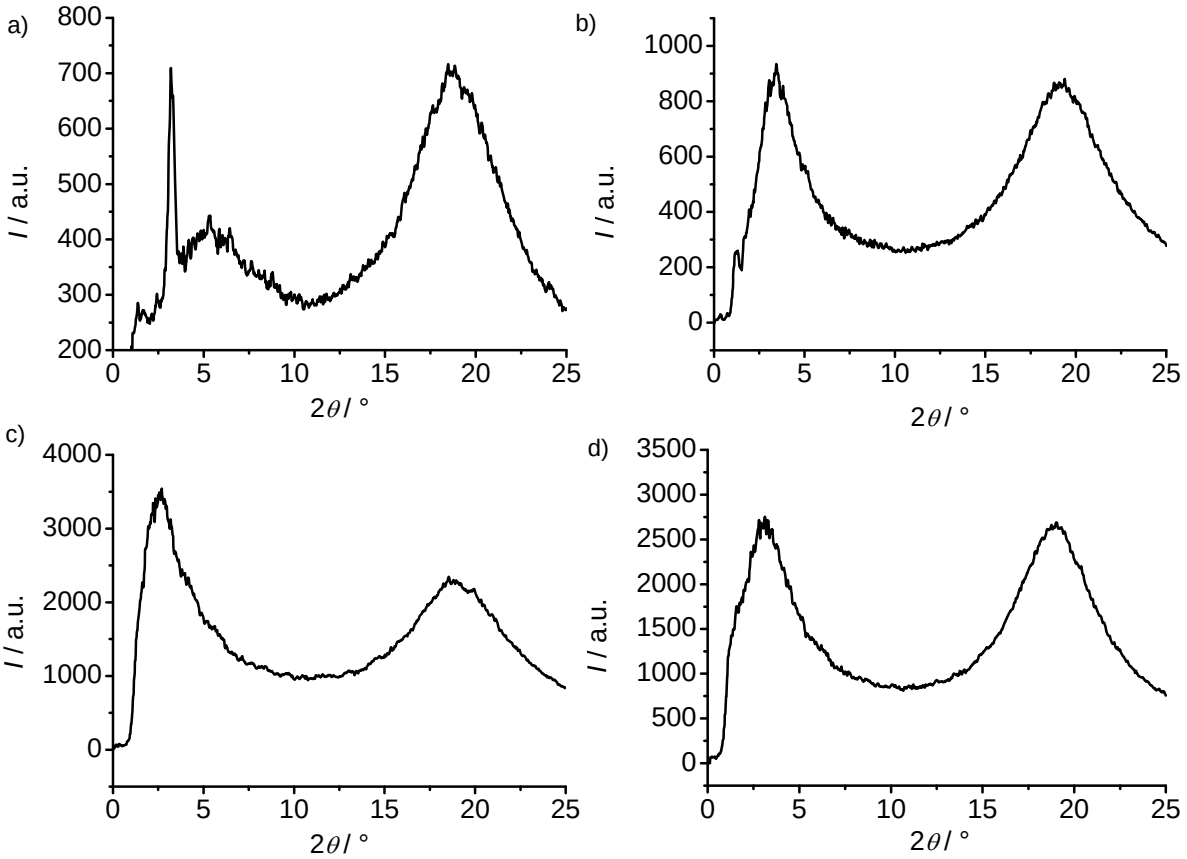


Figure S9. Diffraction intensity profiles as functions of 2θ along the meridian of the diffraction pattern: a) $SmÃ_b^{\#}$ phase of **1/6** at 120 °C (χ = 80 - 100°); b) $SmÃ_b/c2mm^{\#}$ phase of **1/18** at 125 °C (χ = 85 - 105°); c) $SmÃ_b/c2mm^{\#}$ phase of **1F/22** at 123 °C (χ = 80 - 100°); d) $SmÃ_b/c2mm^{\#}$ phase of **2/22** at 145 °C (χ = 80 - 100°).

Table S1. Crystallographic data of compounds **1/*n*, 1F/22 and 2/22**. [a]

Comp.	Phase (T/°C)	θ / °	d_{obs}/nm	hk,d_1,d_2	*lattice parameters*/nm
1/6	$SmÃ_b^{\#}$ (120)	1.586	2.79	d_1	d = 2.79
		3.025	1.46	d_2	
		9.597	0.46	diff	
1/18	$SmÃ_b/c2mm^{\#}$ (125)	1.433	3.08	11	a = 3.84
		1.708	2.59	02	b = 5.17
		1.746	2.53	d_2	
		9.661	0.46	diff	
1F/22	$SmÃ_b/c2mm^{\#}$ (123)	1.181	3.74	11	a = 5.54
		1.385	3.19	d_2	b = 5.07
		1.743	2.53	02	
		9.535	0.47	diff	
	$Col_{rec}/c2mm^{\#}$ (110)	1.161	3.80	11	a = 5.75
		1.367	3.23	d_2	b = 5.07
		1.741	2.54	02	
		9.605	0.46	diff	
2/22	$SmÃ_b/c2mm^{\#}$ (145)	1.209	3.65	11	a = 6.32
		1.595	2.77	d_2	b = 4.48
		1.973	2.24	02	
		9.520	0.47	diff	

[a] (θ_{obs}: experimental scattering angle; d_{obs}: experimental d spacing; *hk*: assigned indices for 2D phases ($SmÃ_b/c2mm^{\#}$, $Col_{rec}/c2mm^{\#}$); d_1: layer distance, d_2: diffuse scattering in the small angle region perpendicular to the layer reflection; diff: diffuse scattering in the wide angle region.

Table S2. Full width at half maximum (FWHM) and estimated domain size (L, calculated with Scherrer equation[S10], $K = 1$) of the diffuse small angle scatterings (d_2) on the equator in the diffraction patterns of the $Sm\tilde{A}_b$ and $Sm\tilde{A}_b/c2mm^{\#}$ phases.

Comp.	Phase (T/°C)	FWHM/°	L/nm
1/6	$Sm\tilde{A}_b^{\#}$ (120)	4.6	3.8
1/18	$Sm\tilde{A}_b/c2mm^{\#}$ (125)	1.6	11.0
1F/22	$Sm\tilde{A}_b/c2mm^{\#}$ (123)	6.4	2.7
2/22	$Sm\tilde{A}_b/c2mm^{\#}$ (145)	2.6	6.7

Table S3. Calculation of the number of molecules in the patches (n_p) of the mesophases of compounds **1/18**, **1F/22** and **2/22** as calculated from the XRD data and molecular volumina.[a]

Comp.	V_p [nm^3]	V_{mol} [nm^3]	$n_{p,cr}$	$n_{p,liqu}$	n_p
1/18	24.8	1.75	14.2	11.1	12.6
1F/22 ($Sm\tilde{A}_b/c2mm^{\#}$)	44.9	1.86	24.1	19.9	21.5
1F/22 ($Col_{rec}/c2mm^{\#}$)	46.6	1.86	25.0	19.7	22.3
2/22	39.6	1.47	26.9	21.1	24.0

[a] V_P = volume of the patch defined by (a x b x d_2)/2; V_{mol} = molecular volume as calculated using crystal volume increments;[S9] $n_{p,cr}$ number of molecules in the patch, calculated according $n_{p,cr} = V_p/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$; $n_{p,liqu}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{liqu} = 0.55/0.7$ x $n_{p,cr}$; n_p (average) = number of molecules in the patch of the columnar phase estimated as the average of that in the $n_{p,cryst}$ and $n_{p,liqu}$.

5. References

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