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Supporting Information

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The first example of a 3rd generation liquid crystalline carbosilane dendrimer with peripheral bent-core mesogenic units – understanding of “dark conglomerate phases”

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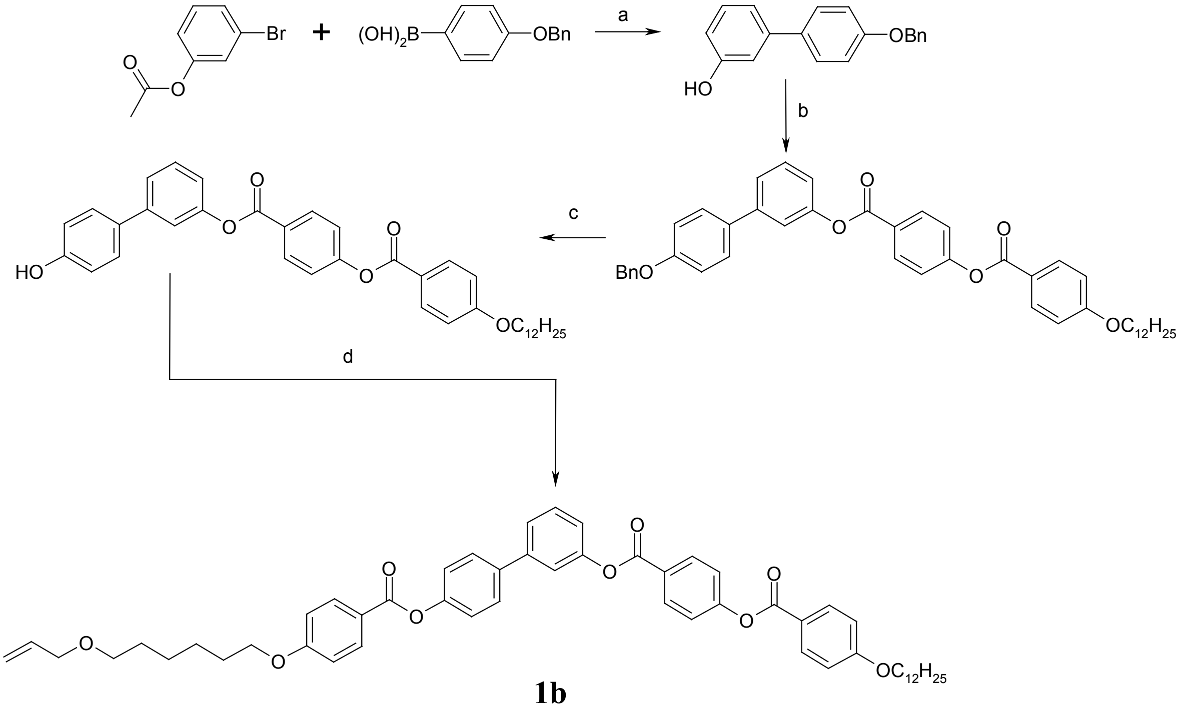
Supporting Information

1. Synthesis and analytical data

1.1. Synthesis of the bent core units



1b

Scheme S1 Synthesis of the bent core units. *Reagents and conditions*: a) Pd(PPh$_3$)$_4$, NaHCO$_3$, glyme, reflux, 8 h; b) 4-(4-dodecyloxybenzoyloxy)benzoic acid, DCC, DMAP, CH$_2$Cl$_2$, r.t., 24h; c) Pd/C, H$_2$, THF, 40°C; d) 4-[6-(2-propenyloxy)hexyloxy]benzoic acid, DCC, DMAP, CH$_2$Cl$_2$, r.t., 24h.

6-(2-Propenyloxy)-1-hexanol

Hexane-1,6-diol (30.0 g, 0.25 mol) and KOH (14.2 g, 0.25 mol) were stirred in 100 ml of anhydrous THF and heated to reflux. Then allyl bromide (30.0g, 0.25 mol) is added dropwise within one hour with stirring. The mixture is heated at reflux for additional 30 minutes. When cooled to room temperature the liquids were filtered off and the residue was washed several times with diethyl ether. After evaporation of the excess of allyl bromide and the solvents the crude product was dissolved in n-pentane and extracted with water. The aqueous phases were extracted with $CHCl_3$ (3 x 100 mL), the combined organic solutions were washed with water and brine and dried with anhydrous Na_2SO_4. After evaporation of the solvent the product was obtained as a colourless liquid, yield 13.0 g (36 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.95-5.85 (m, 1H, C*H*=CH_2), 5.28-5.13 (m, 2H, CH=C*H*$_2$), 3.94 (m, 2H, OCH_2), 3.69 (m, 2H, $HOCH_2$), 3.47 (m, 2H, OCH_2), 1.59 (m, 4H, CH_2), 1.38 (m, 4H, CH_2).

6-(2-Propenyloxy)hexyl 4-toluenesulfonate

6-(2-Propenyloxy)-1-hexanol (7.4 g, 47 mmol) was dissolved in anhydrous pyridine (60 mL) and cooled to 0 °C. 4-Toluenesulfonyl chloride (17.85 g, 94 mmol) was added in small portions with stirring. The mixture was stirred for additional 2 hours and then poured into a water/ice-mixture and extracted with diethyl ether. The combined organic layers are washed with 2 M HCl, $NaHCO_3$, water and brine. After drying over anhydrous Na_2SO_4 the solvent was evaporated to yield 14.4 g (97 %) 6-(2-propenyloxy)hexyl 4-toluenesulfonate as a colourless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.1 Hz, 2H, Ar-H), 7.32 (d, J = 8.5 Hz, 2H, Ar-H), 5.88 (m, 1H, C*H*=CH_2), 5.21 (m, 2H, CH=C*H*$_2$), 4.00 (t, J = 6.4 Hz, 2H, OCH_2), 3.93 (m, 2H, OCH_2), 3.36 (t, J = 6.5 Hz, 2H, OCH_2), 2.43 (s, 3H, CH_3), 1.51 (m, 2H, CH_2), 1.27 (m, 4H, CH_2).

Ethyl 4-[6-(2-propenyloxy)hexyloxy]benzoate

A mixture of 6-(2-propenyloxy)hexyl 4-toluenesulfonate (14.3g, 46 mmol), ethyl 4-hydroxybenzoate 7.0 g (42.5 mmol), K_2CO_3 (11.73 g, 85 mmol) and tetrabutylammonium iodide (0.05 g) was stirred in 2-butanone (200 mL) and heated to reflux temperature for 10 hours. Then the mixture was cooled to room temperature and water and diethyl ether was added. After extraction with diethyl ether the organic layers were washed with water and brine. The solvent was evaporated after drying over anhydrous Na_2SO_4 to yield 13.0 g (99 %) ethyl 4-[6-(2-propenyloxy)hexyloxy]benzoate as a colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.9 Hz, 2H, Ar-H), 6.87 (d, J = 8.9 Hz, 2H, Ar-H), 5.89 (m, 1H, C*H*=CH_2), 5.23 (m, 2H, CH=C*H*$_2$), 4.29 (q, J = 7.1 Hz, 2H, OCH_2), 3.94 (m, 4H, OCH_2), 3.43 (t, J = 6.5 Hz, 2H, OCH_2), 1.79 (q, J = 6.9 Hz, 2H, CH_2), 1.61 (q, J = 6.9 Hz, 2H, CH_2), 1.45 (m, 4H, CH_2), 1.36 (t, J = 7.2 Hz, 3H, CH_3).

4-[6-(2-Propenyloxy)hexyloxy]benzoic acid

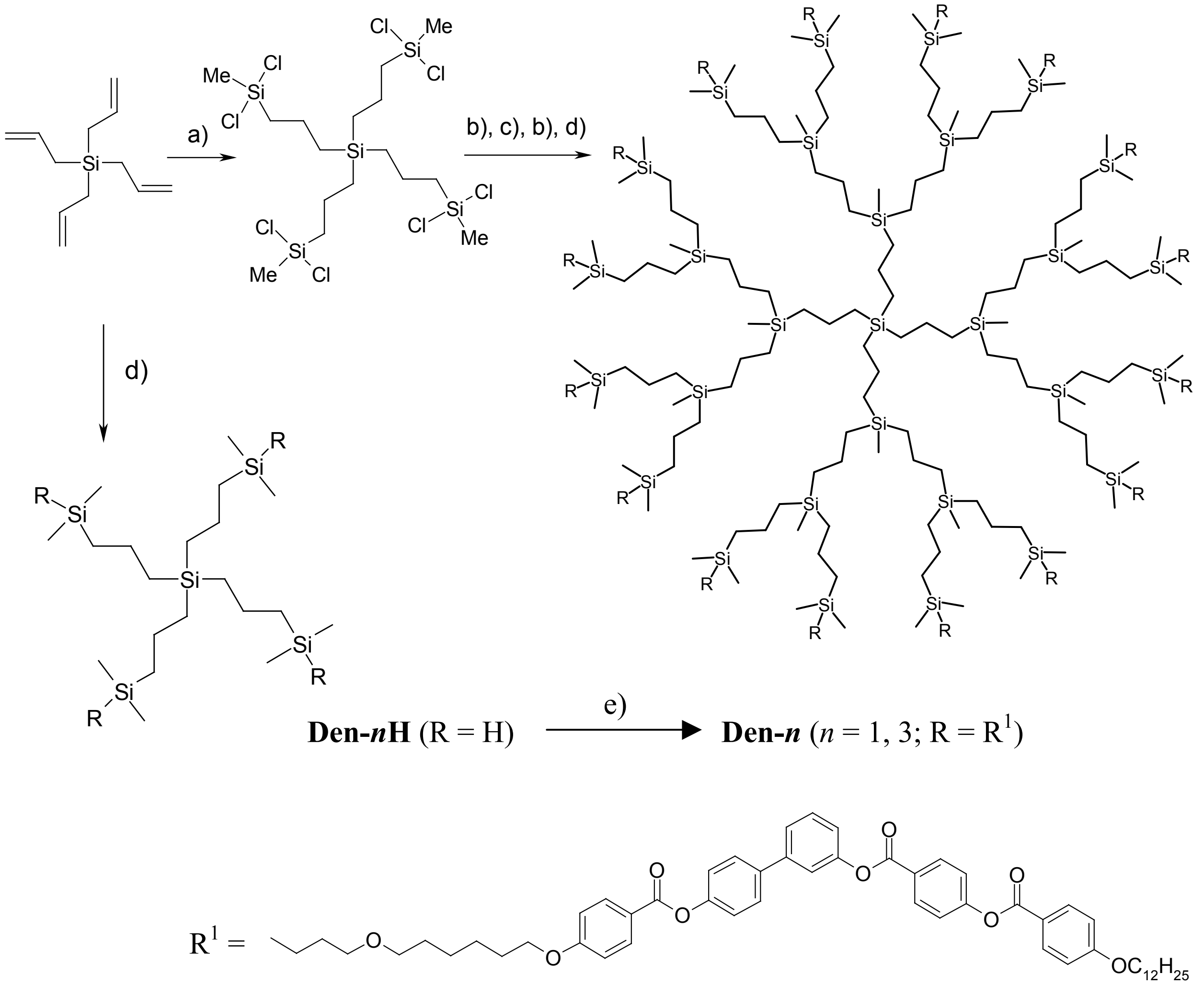
A mixture of ethyl 4-[6-(2-propenyloxy)hexyloxy]benzoate (12.9 g, 42 mmol), ethanol (150 mL) and NaOH (3.36 g, 84 mmol), dissolved in water (30 mL) was heated to reflux for 2 hours. After hydrolysis is completed (TLC, ca. 2 h) the mixture is cooled to room temperature and acidified with 2 M HCl. The crude product is filtered off, washed with water and crystallised from ethanol to yield 7.4 g (63 %) 4-[6-(2-propenyloxy)hexyloxy]benzoic acid as a colourless solid. Transition temperatures: Cr 67 SmA 84 N 105 Iso; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.7 Hz, 2H, Ar-H), 6.91 (d, J = 8.7 Hz, 2H, Ar-H), 5.89 (m, 1H, C*H*=CH_2), 5.16 (m, 2H, CH=C*H*$_2$), 3.99 (m, 4H, OCH_2), 3.96 (d, J = 5.6 Hz, 2H, OCH_2), 3.43 (t, J = 6.5 Hz, 2H, OCH_2), 1.81 (q, J = 6.8 Hz, 2H, CH_2), 1.62 (q, J = 6.9 Hz, 2H, CH_2), 1.46 (m, 4H, CH_2).

3'-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-4-(7-oxodec-9-enyloxy)benzoyloxybiphenyl (1b)

4'-Hydroxy-3-[4-(dodecyloxybenzoyloxy)benzoyloxy]biphenyl [1] (8.0 g,13.5 mmol), 4-(7-oxodec-9-enyloxy)benzoic acid (4.5 g,16.2 mmol), DCC (3.3 g,16.2 mmol) and DMAP (0.05

g, 0.2 mmol) were dissolved in anhydrous CH_2Cl_2 (150 mL) and stirred at room temperature for 24 h. After evaporation of the solvent the crude product was purified by column chromatography (silica gel, eluent $CHCl_3$) followed by crystallisation from ethyl acetate to give 7.6 g (66 %) of **1b**. Transition temperatures: Cr 92 ($SmCP_A$ 74) Iso; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.9 Hz, 2H, Ar-H), 8.13 (d, J = 8.9 Hz, 4H, Ar-H), 7.63 (d, ^3J = 8.5 Hz, 2H, Ar-H), 7.49 (d, ^3J = 5.2 Hz, 2H, Ar-H), 7.43 (s, 1H, Ar-H), 7.36 (d, ^3J = 8.7 Hz, 2H, Ar-H), 7.26 (d, J = 8.8 Hz, 2H, Ar-H), 7.21 (m, 1H, Ar-H), 6.97 (d, J = 8.9 Hz, 2H, Ar-H), 6.96 (d, J = 8.9 Hz, 2H, Ar-H), 5.89 (m, 1H, C*H*=CH_2), 5.24 (m, 2H, CH=CH_2), 4.04 (t, J = 5.6 Hz, 4 H, OCH_2), 3.95 (d, ^3J = 5.6 Hz, 2H, OCH_2), 3.43 (t, J = 6.4 Hz, 2H, OCH_2), 1.81 (m, 4H, CH_2), 1.62 (q, J = 6.9 Hz, 2H, CH_2), 1.46 (q, J = 6.0 Hz, 2H, CH_2), 1.25 (m, 18 H, CH_2), 0.87 (t, J = 6.8 Hz, 3H, CH_3);^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.82, 164.39, 164.24, 163.81, 163.52, 155.42, 151.34, 150.87, 142.15, 137.73, 135.05, 132.38, 132.27, 131.78, 129.79, 128.20, 127.89, 124.63, 122.14, 122.07, 121.56, 121.02, 120.51, 120.39, 116.63, 114.44, 114.33, 68.43, 68.24, 31.94, 29.74, 29.68, 29.66, 29.61, 29.58, 29.38, 29.37, 29.13, 29.11, 26.03,25.92, 22.71, 14.12.

1.2 Synthesis of the carbosilane dendrimers Den-1 and Den-3



Scheme S2 Synthesis of **Den-3**, reagents and conditions: a) $HSiMeCl_2$, Speier's cat. b) CH_2=CH-CH_2-MgBr, Et_2O, c) $HSiMeCl_2$, Speier's cat.; d) 1. $HSiMe_2Cl$, Speier's cat., 2. $LiAlH_4$, Et_2O;[2] e) **1b**, Karstedt's cat., toluene, 20 °C, 72 h.[3]

Den-1H

^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.87 (m, 4H, Si-H), 1.40 (m, 8H, CH_2), 1.33 (m, 8H, CH_2), 0.66 (m, 8H, $SiCH_2$), 0.58 (m, 8H, $SiCH_2$), 0.57 (m, 16H, $SiCH_2$), 0.07 (d, 24H, $SiMe_2$-H); –0.04 (s, 24H, $SiMe_2$); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ 20.6, 19.8, 19.1, 18.9, 18.8, 17.8, –3.0, –4.2; ^{29}Si-NMR (49.7 MHz, $CDCl_3$): δ 1.0 ($SiMe_2$), 0.6, –14.0 (Si-H).

Den-3H

^{1}H-NMR (250 MHz, $CDCl_3$): δ 3.87 (m, 16H, Si-H), 1.39 (m, 24H,, CH_2), 1.33 (m, 32H, CH_2), 0.66 (m, 32H, $SiMe_2$), 0.57 (m, 80H, $SiMe_2$), 0.07 (d, 96H, $SiMe_2H$), – 0.06 (s, 36H, $SiMe_2$); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ 19.5, 19.19, 19.16, 19.11, 19.06, 18.8, 18.7, 18.4, 18.0, –4.1, –4.8; ^{29}Si-NMR (49.7 MHz, $CDCl_3$): δ 1.2, 1.0,–14.1 (Si-H).

Den-1

Under an argon atmosphere **1b** (400 mg, 0.47 mmol) was dissolved in anhydrous toluene (3 mL). **Den-1H** (34 mg, 0.08 mmol) and one drop of Karstedt's catalyst (platinum-divinyltetramethylsiloxane complex in xylene) were added to this solution. The mixture was stirred at room temperature. After reaction was completed (detection by TLC, ca 72 hours) the solvent was evaporated and the crude product was purified by repeated column chromatography with silica gel using $CHCl_3$ as eluent to give 100 mg (32 %) of **Den-1**. Transition temperatures: Cr 68 $\mathrm{SmCP_A}^{[*]}$ 113 Iso; calcd. for $C_{236}H_{300}O_{36}Si_5$: C, 73.56; H, 7.85, found: C, 73.47; H, 8.38; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 8.5 Hz, 8H, Ar-H), 8.14 (m, 16H, Ar-H), 7.61 (m, 8H, Ar-H), 7.48 (m, 8H, Ar-H), 7.43 (s, 4H, Ar-H), 7.35 (d, J = 8.9 Hz, 8H, Ar-H), 7.27 (m, 4H, Ar-H), 6.98 (m, 8H, Ar-H), 6.95 (d, J = 8.5 Hz, 16H, Ar-H), 4.03 (m, 16H, OCH_2), 3.35 (m, 16H, CH_2), 1.81 (m, 16H, CH_2), 1.53-1.26 (m, 104H, CH_2), 0.87 (t, J = 6.3 Hz, 12H, CH_3), 0.54 (m, 12H, $SiCH_2$), 0.44 (m, 6H, $SiCH_2$), -0.05 [s, 24H, Si-$(CH_3)_2$]; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.79, 164.38, 164.22, 163.76, 163.48, 155.37, 151.28, 142.09, 137.69, 132.36, 132.25, 131.76, 129.78, 128.17, 126.83, 124.62, 122.12, 122.06, 121.49, 120.95, 120.49, 120.36, 114.28, 74.02, 70.74, 68.40, 68.23, 31.93, 29.79, 29.67, 29.65, 29.60, 29.57, 29.36, 29.11, 26.07, 26.00, 25.95, 24.22, 22.71, 20.25, 18.60, 17.61, 14.13, 11.39, –3.28.

Den-3

Synthesized in an analogous way as described for **Den-1** from **1b** (0.40 g , 0.47 mmol) and **Den-3H** (0.062 g, 0.0158 mmol), yield 100 mg (39 %). Transition temperatures: Cr 73 $\mathrm{SmCP_A}^{[*]}$ 111 Iso; MS (Maldi-TOF (matrix: HABA): M = 15527.45 g mol^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.5 Hz, 30H, Ar-H), 8.12 (m, 60H, Ar-H), 7.60 (d, ^3J = 8.1 Hz, 30H, Ar-H), 7.48 (d, J = 4.8 Hz, 30H, Ar-H), 7.41 (s, 15H, Ar-H), 7.34 (d, J = 8.9 Hz, 30H, Ar-H), 7.25 (m, 30H, Ar-H), 7.18 (m, 15H, Ar-H), 6.94 (m, 60H, Ar-H), 4.01 (m, 60H, OCH_2), 3.39 (t, J = 6.5 Hz, 33H, OCH_2, Si-OCH_3), 3.34 (t, J = 7.1 Hz, 30H, OCH_2), 1.79 (m, 60H, CH_2), 1.58 (m, 30H, CH_2), 1.46 (m, 146H, CH_2), 0.87 (t, J = 6.9 Hz, 45H, CH_3), 0.55 (m, 112H, $SiCH_2$), 0.46 (m, 30H, $SiCH_2$), -0.05 [s, 96H, Si-$(CH_3)_2$], -0.09 (s, 36H, Si-CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.78, 164.38, 164.23, 163.78, 163.48, 155.38, 151.31, 150.82, 142.08, 137.68, 132.37, 132.26, 131.77, 129.78, 128.16, 126.85, 122.12, 122.06, 121.52, 120.98, 120.51, 120.35, 114.41, 114.28, 74.05, 70.80, 68.41, 68.24, 31.94, 29.83, 29.68, 29.66, 29.61, 29.58, 29.39, 29.37, 29.17, 29.13, 26.11, 26.01, 24.24, 22.71, 20.15, 18.90, 18.54, 14.13, 11.43, –3.21; ^{29}Si-NMR (99.3 MHz, $CDCl_3$): δ 2.18, 0.99.

2. Additional figures and data

2.1. Origin of suprastructural chirality in the smectic phases of bent core molecules

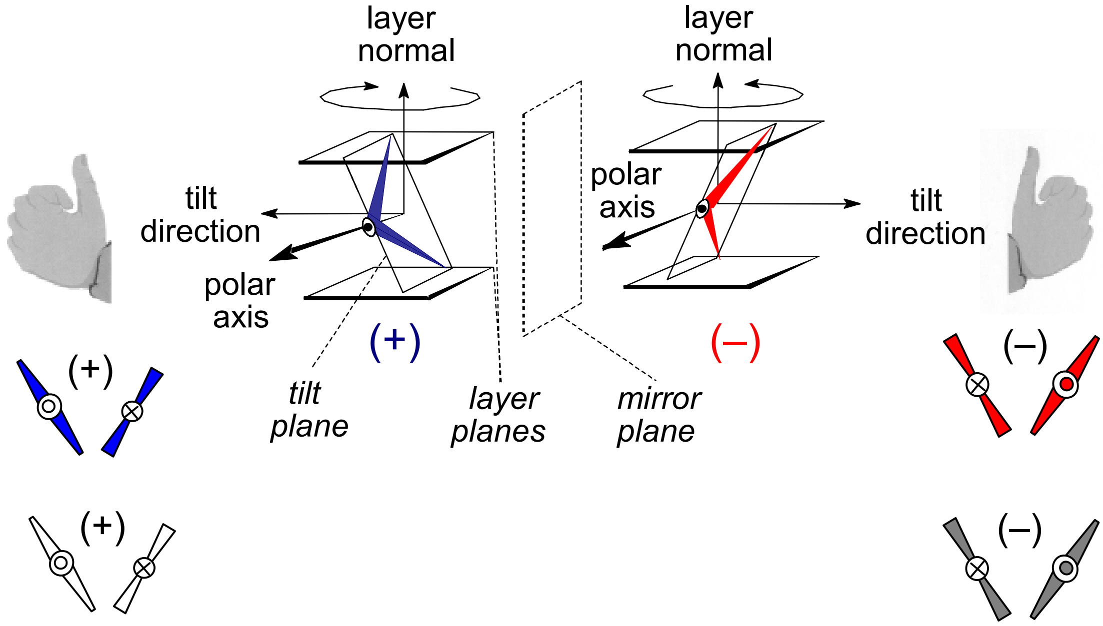


Figure S1. (a) Origin of the chirality within the smectic phases of bent-core molecules.[4] Owing to the bend shape each molecule possesses a dipole moment in the molecular plane and perpendicular to the long axis of the molecules. Layer normal, tilt direction and the polar axis define either a right handed coordinate system (+), whereas in the mirror image these vectors define a left handed system (–). Changing either polarisation direction or tilt direction changes the chirality sense of the layer (indicated by blue/red colour in Figure S3 and by white/gray colour in Figure 5 in the main text). Changing both, polarisation direction and tilt direction retains the chirality sense.

2.2 X-ray scattering

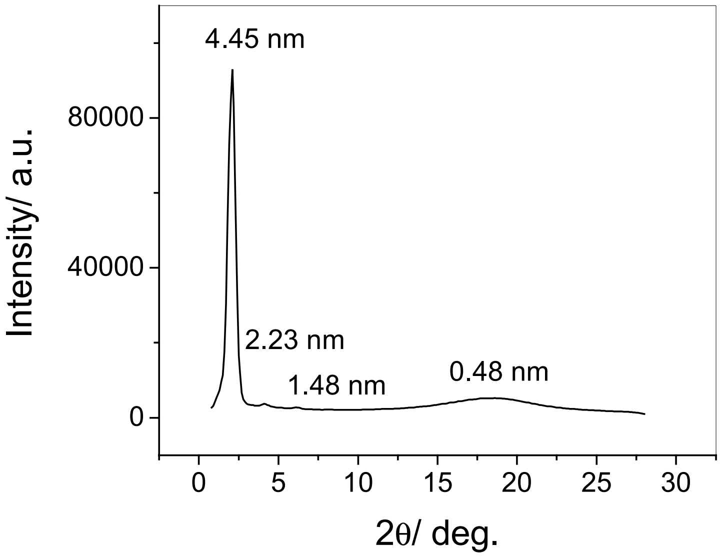


Figure S2 The X-ray angular intensity profile obtained in the SmCP$_A$$^{[*]}$ phase of compound **Den-3** at 96 °C.

2.3. Alternative models of the SmC_aP_A and (±)-SmC_aP_A phases

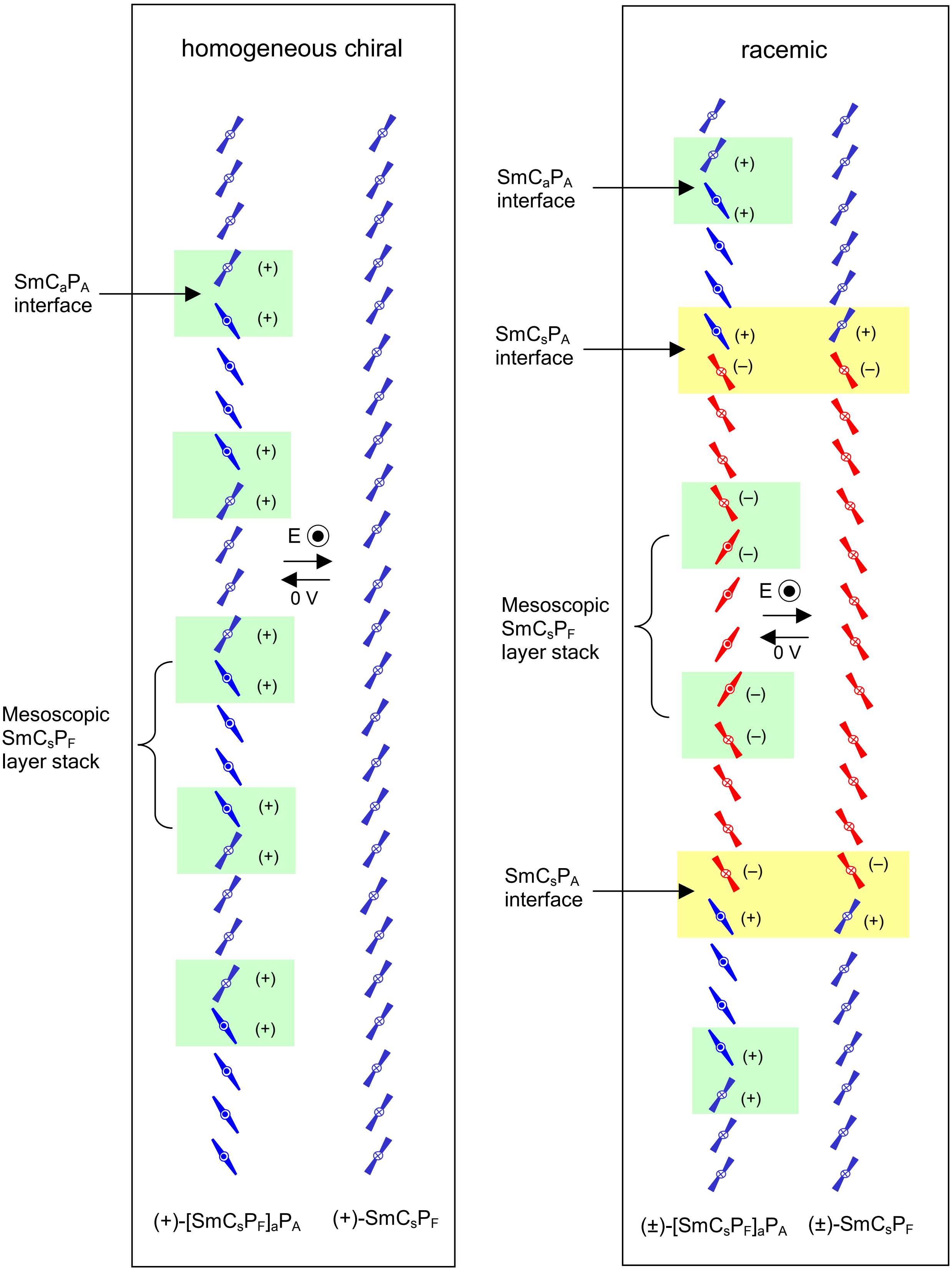


Figure S3: Models showing the organization of the molecules in the mesophases formed by SmC_sP_F layer stacks. The individual molecules in the anticlinic phases shown in Figure 5b,d are replaced by SmC_sP_F layer stacks which are separated by SmC_aP_A interfaces (green). The size of the layer stacks can be different, but on average the number of layers with opposite tilt direction is identical. The structure composed of SmC_sP_F layer stacks with exclusively SmC_aP_A interfaces assigned as $[SmC_sP_F]_aP_A$ would correspond to the homogeneous chiral domains ((+)- and (–)-$[SmC_sP_F]_aP_A$ domains, only (+)-$[SmC_sP_F]_aP_A$ is shown) and a phase with SmC_aP_A interfaces and occasional (racemic) SmC_sP_A interfaces, assigned as (±)-$[SmC_sP_F]_aP_A$, would correspond to the racemic domains in Figure 3.

2.4. Investigation of Den-3

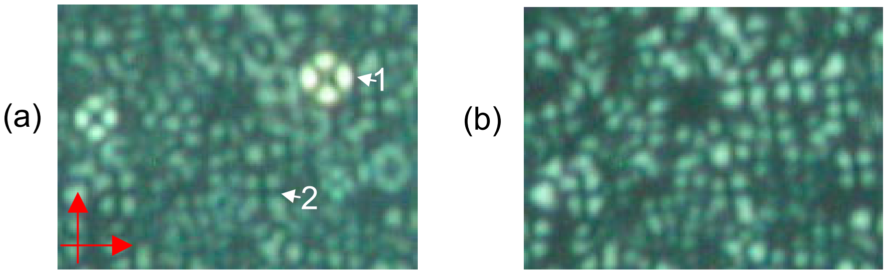


Figure S4: (a) Circular domains with chiral (1) and racemic (2) domains as obtained in the $SmCP_A$[*] phase of **Ban-3** on applying a triangular wave field (210 Vpp; 100 Hz; 6µm ITO-cell, EHC, Japan) at 90°C; the extinction crosses obtained are independent of the sign of the applied field; (b) same area after switching off the electric field.

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