

Supporting Information

Silylated bent-core molecules: The influence of the direction of the carboxyl connecting groups on the mesophase behaviour

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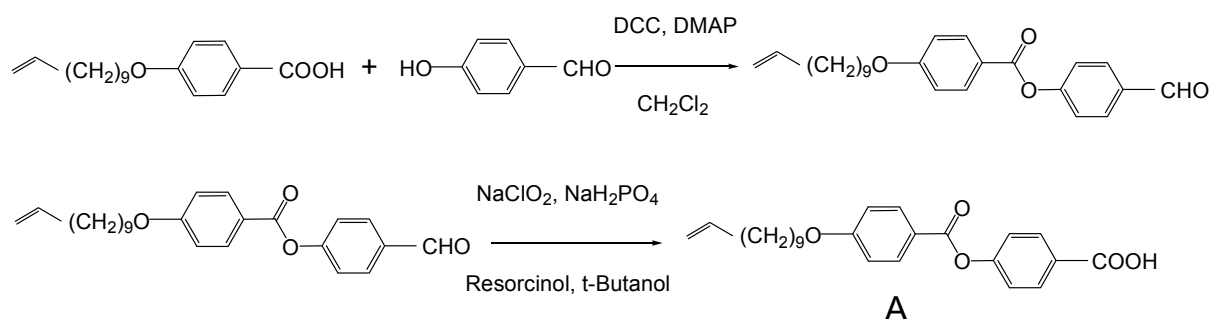
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1. Synthesis and Analytical data

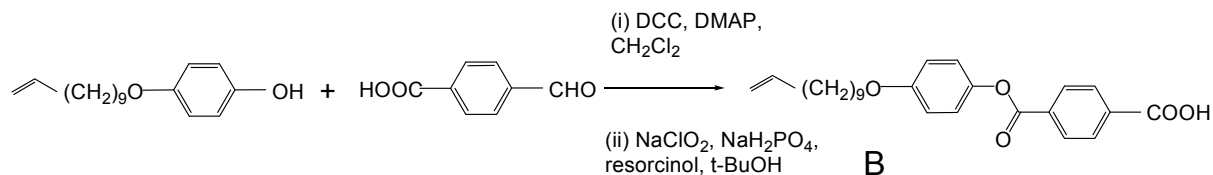
1.1 Synthesis of the intermediates

1.1.1 4-[4-(10-Undecen-1-yloxy)benzoyloxy] benzoic acid (A). - Synthesized as described in ref.^{S1}



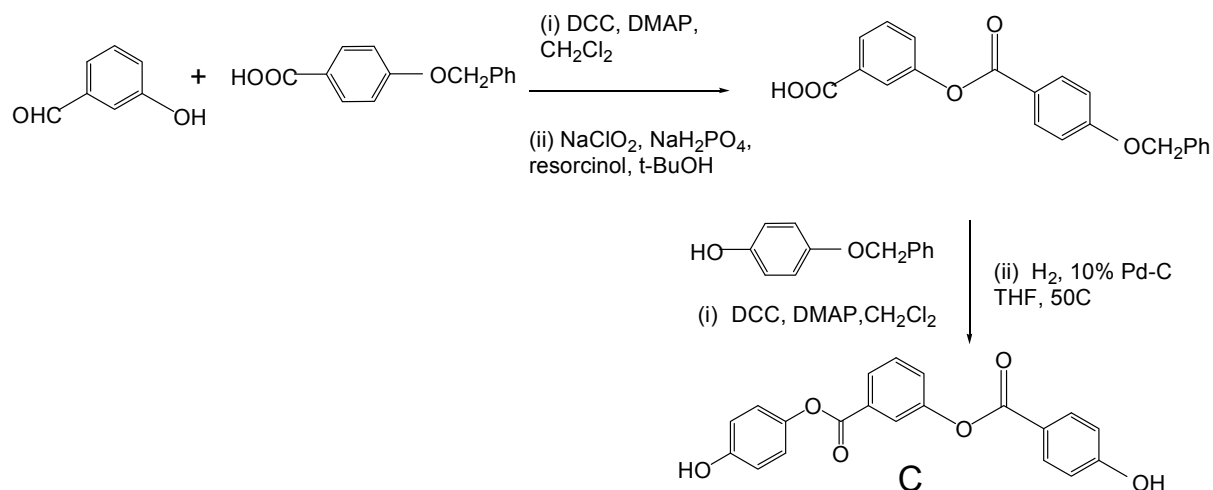
Scheme S1: Synthetic scheme for the preparation of compound A.

1.1.2 4-[4-(10-Undecen-1-yloxy)phenoxy]benzoic acid (B). - Synthesized as described in ref. ^{S2}



Scheme S2: Synthetic scheme for the preparation of compound B.

1.1.3 4-Hydroxyphenyl 3-(4'-hydroxybenzoyloxy)benzoate (C)



Scheme S3: Synthetic scheme for the preparation of compound C.

a) 3-Formylphenyl 4-benzyloxybenzoate. - A mixture of 3-hydroxybenzaldehyde (2.24 g, 20 mmol), 4-benzyloxybenzoic acid (4.56 g, 20 mmol), 4-(*N,N*-dimethylamino)pyridine (DMAP) (0.24 g, 2 mmol) and dry dichloromethane (100 ml) was stirred for 10 minutes under argon flow. To this mixture, *N,N'*-dicyclohexylcarbodiimide (DCC) (4.5 g, 22 mmol) was added and the stirring continued for 10 hours at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was washed with 5% aqueous acetic acid (2 × 50ml), cold 5% aqueous sodium hydroxide (2 × 50 ml) and finally washed with water (3 × 50 ml) and dried over anhydrous sodium sulphate. The solvent was removed and the solid material so obtained was purified by column chromatography on silica gel using 1% ethyl acetate in chloroform as an eluent. Removal of solvent from the eluate afforded a white solid. This was crystallized from acetonitrile and few drops of chloroform. Yield: 76 %; M.P. 131°C; ¹H-NMR (400 MHz, CDCl₃): δ 10.01 (s, 1H, Ar-CHO), 8.16-8.13 (m, 2H, Ar-H), 7.78-7.76 (m, 1H, Ar-H), 7.73-7.72 (m, 1H, Ar-H), 7.60-7.56 (t, ³J=8.4Hz, 1H, Ar-H), 7.49-7.32 (m, 6H, Ar-H), 7.08-7.04 (m, 2H, Ar-H), 5.15 (s, 2H, Ar-OCH₂).

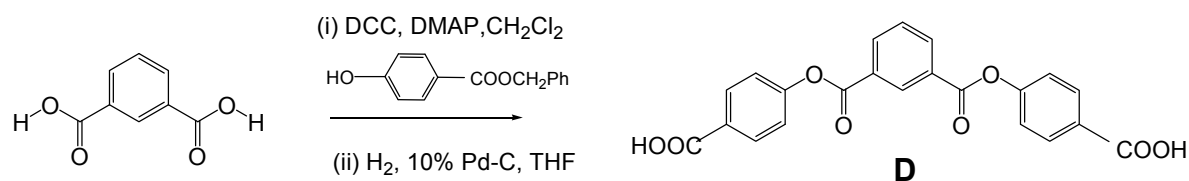
b) 3-(4-Benzyloxybenzoyloxy)benzoic acid. - 3-Formylphenyl 4-benzyloxybenzoate (2.6 g, 6.63 mmol) and resorcinol (0.95 g, 8.62 mmol) were dissolved in 130 ml of tetra butyl alcohol. To this solution was added drop wise, over 30 min, a solution of sodium chlorite (NaClO_2 , 3.6 g, 39.8 mmol) and sodium dihydrogen phosphate monohydrate (2.74 g, 19.9 mmol) in 40 ml water. The resulting pale yellow reaction mixture was then stirred overnight at room temperature. Volatile components were removed in vacuum and the residue dissolved in excess of water. The resulting aqueous solution was then acidified to p_{H} 2 by adding 1M HCl. The white precipitate so obtained was filtered, washed several times with water, and dried. The white powder was crystallized from ethanol; Yield: 62%; M.P. 196°C ; $^1\text{H-NMR}$ (400 MHz, acetone- d_6): δ 7.99-7.96 (m, 2H, Ar-H), 7.80-7.78 (m, 1H, Ar-H), 7.71-7.70 (m, 1H, Ar-H), 7.36-7.16 (m, 7H, Ar-H), 6.93-6.90 (m, 2H, Ar-H), 5.01 (s, 2H, Ar- OCH_2).

c) 4-Benzyloxyphenyl 3-(4-benzyloxybenzoyloxy)benzoate. - Synthesized following the procedure described 1.1.3a, using 3-(4-benzyloxybenzoyloxy)benzoic acid and 4-benzyloxy phenol as the starting materials. Yield: 68%; M.P. 190°C ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.16-8.00 (m, 4H, Ar-H), 7.57-6.98 (m, 18H, Ar-H), 5.15 (s, 2H, Ar- OCH_2), 5.06 (s, 2H, Ar- OCH_2).

d) 4-Hydroxyphenyl 3-(4-hydroxybenzoyloxy)benzoate (C). - 4-Benzyloxyphenyl 3-(4-benzyloxybenzoyloxy)benzoate was dissolved in THF and 5% Pd-C catalyst was added to it. The mixture was stirred at 50°C in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The resultant mixture was filtered in hot and the solvent removed under reduced pressure. The solid material obtained was dissolved in 1,4-dioxane and precipitated with petroleum-ether (b.p. $60\text{-}80^\circ\text{C}$). The precipitate obtained was filtered and dried. Yield: 87 %; M.P. 220°C ; $^1\text{H-NMR}$ (400 MHz, acetone- d_6): δ 9.32 (s, 1H, Ar-OH), 8.39 (s, 1H, Ar-OH), 8.10-8.00 (m, 4H, Ar-H), 7.70-7.59 (m, 2H, Ar-H), 7.14-7.08 (m, 2H, Ar-H), 7.06-6.97 (m, 2H, Ar-H), 6.95-6.83 (m, 2H, Ar-H).

1.1.4 Benzene-1,3-dicarbonyloxy-4-dibenzoic acid (D)

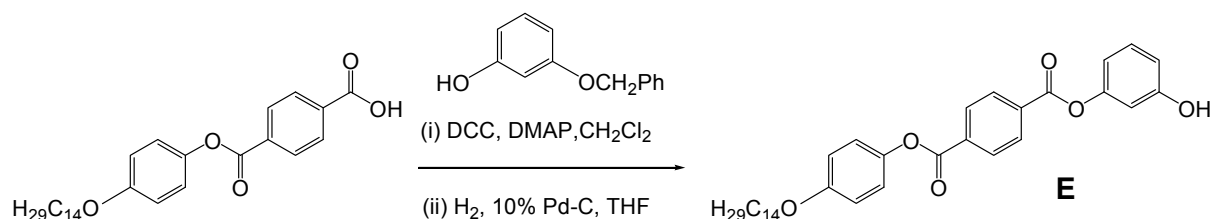
Synthesized as described in ref. ^{S3}



Scheme S4: Synthetic scheme for the preparation of **D**.

1.1.5 Resorcinol 4-(4-tetradecyloxyphenoxy)benzoate (E)

Synthesized as described in ref. ^{S4}



Scheme S5: Synthetic scheme for the preparation of phenol **E**.

1.2 Olefins En-1 to En-6

Synthesized by esterification reaction following the procedure described in 1.1.3a.

En-1: Synthesized from resorcinol (0.25 g, 2.27 mmol) and **A** (2.05 g, 5 mmol). Yield: 70 %; M.P. 101 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.27-8.25 (dd, $^3J=6.4\text{Hz}$, $^4J=2.0\text{Hz}$, 4H, Ar-H), 8.15-8.12 (d, $^3J=8.8\text{Hz}$, 4H, Ar-H), 7.5-7.46 (t, $^3J=8.4\text{Hz}$, 1H, Ar-H), 7.37-7.35 (dd, $^3J=6.4\text{Hz}$, $^4J=2.0\text{Hz}$, 4H, Ar-H), 7.19-7.15 (m, 3H, Ar-H), 6.98-6.96 (d, $^3J=8.8\text{Hz}$, 4H, Ar-H), 5.83-5.75 (m, 2H, 2 \times -CH=C), 5.00-4.90 (m, 4H, 2 \times -C=CH₂), 4.05-4.02 (t, $^3J=6.4\text{Hz}$, 4H, 2 \times Ar-OCH₂), 2.06-2.01 (q, $^3J=6.8\text{Hz}$, 4H, 2 \times -CH₂), 1.85-1.81 (q, $^3J=6.8\text{Hz}$, 4H, 2 \times -CH₂), 1.53-1.29 (m, 24H, 12 \times -CH₂). $\text{C}_{56}\text{H}_{62}\text{O}_{10}$ requires C, 75.14; H, 6.98; found: C, 74.89; H, 7.21%.

En-2: Synthesized from **C** (1.0 g, 2.85 mmol) and 4-(10-undecen-1-yloxy)benzoic acid (1.82 g, 6.28 mmol). Yield: 65 %; M.P. 107 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.30-8.27 (d, $^3J=8.8\text{Hz}$, 2H, Ar-H), 8.15-8.11 (m, 5H, Ar-H), 8.08-8.05 (m, 1H, Ar-H), 7.61-7.50 (m, 2H, Ar-H), 7.39-7.36 (d, $^3J=8.8\text{Hz}$, 2H, Ar-H), 7.28-7.21 (m, 4H, Ar-H), 6.98-6.94 (m, 4H, Ar-H), 5.85-5.75 (m, 2H, 2 \times -CH=C), 5.00-4.91 (m, 4H, 2 \times -C=CH₂), 4.06-4.01 (m, 4H, 2 \times Ar-OCH₂), 2.06-2.01 (q, $^3J=6.4\text{Hz}$, 4H, 2 \times -CH₂), 1.85-1.77 (q, $^3J=6.4\text{Hz}$, 4H, 2 \times -CH₂), 1.50-1.3 (m, 24H, 12 \times -CH₂). $\text{C}_{56}\text{H}_{62}\text{O}_{10}$ requires C, 75.14; H, 6.98; found: C, 75.01; H, 7.10%.

En-3: Synthesized from resorcinol (0.25 g, 2.27 mmol) and **B** (2.05 g, 5 mmol). Yield: 72 %; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.31 (s, 8H, Ar-H), 7.51-7.52 (m, 1H, Ar-H), 7.25-7.20 (m, 3H, Ar-H), 7.14-7.12 (d, $^3J=9.2\text{Hz}$, 4H, Ar-H), 6.94-6.92 (d, $^3J=9.2\text{Hz}$, 4H, Ar-H), 5.81-5.79 (m, 2H, 2 \times -CH=C), 5.00-4.90 (m, 4H, 2 \times -C=CH₂), 3.97-3.94 (t, $^3J=6.4\text{Hz}$, 4H, 2 \times Ar-OCH₂), 2.06-2.01 (q, $^3J=6.4\text{Hz}$, 4H, 2 \times -CH₂), 1.80-1.76 (q, $^3J=6.4\text{Hz}$, 4H, 2 \times -CH₂), 1.45-1.29 (m, 24H, 12 \times -CH₂). $\text{C}_{56}\text{H}_{62}\text{O}_{10}$ requires C, 75.14; H, 6.98; found: C, 74.83; H, 7.26%.

En-4: Synthesized from 4-(10-undecen-1-yloxy)phenol (1.26 g, 5.42 mmol) and **D** (1.0 g, 2.46 mmol). Yield: 62 %; M.P. 182 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 9.10-9.02 (t, $^4J=1.2\text{Hz}$, 1H, Ar-H), 8.50-8.48 (dd, $^3J=6.0\text{Hz}$, $^4J=1.6\text{Hz}$, 2H, Ar-H), 8.30-8.28 (m, 4H, Ar-H), 7.74-7.70 (t, $^3J=8.0\text{Hz}$, 1H, Ar-H), 7.41-7.38 (m, 4H, Ar-H), 7.19-7.09 (m, 4H, Ar-H), 6.94-6.91 (m, 4H, Ar-H), 5.84-5.75 (m, 2H, 2 \times -CH=C), 5.00-4.90 (m, 4H, 2 \times -C=CH₂), 3.97-3.93 (t, $^3J=6.4\text{Hz}$, 4H, 2 \times Ar-OCH₂), 2.06-2.01 (q, $^3J=6.4\text{Hz}$, 4H, 2 \times -CH₂), 1.81-1.74 (q, $^3J=6.4\text{Hz}$, 4H, 2 \times -CH₂), 1.45-1.29 (m, 24H, 12 \times -CH₂). $\text{C}_{56}\text{H}_{62}\text{O}_{10}$ requires C, 75.14; H, 6.98; found: C, 74.74; H, 7.06%.

En-5: Synthesized from **E** (1.0 g, 1.83 mmol) and **B** (0.82 g, 2.01 mmol). Yield: 75 %; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.31 (s, 8H, Ar-H), 7.54-7.49 (t, $^3J=8.4\text{Hz}$, 1H, Ar-H), 7.26-7.20 (m, 3H, Ar-H), 7.15-7.11 (m, 4H, Ar-H), 6.95-6.91 (m, 4H, Ar-H), 5.84-5.77 (m, 1H, -

CH=C), 5.01-4.90 (m, 2H, -C=CH₂), 3.97-3.94 (t, ³J=6.4Hz, 4H, 2 × Ar-OCH₂), 2.06-2.01 (q, ³J=6.8Hz, 2H, 1 × -CH₂), 1.81-1.74 (q, ³J=6.8Hz, 4H, 2 × -CH₂), 1.54-1.25 (m, 34H, 17 × -CH₂), 0.88-0.85 (t, ³J=6.8Hz, 3H, 1 × -CH₃). C₅₉H₇₀O₁₀ requires C, 75.45; H, 7.51; found: C, 75.91; H, 7.89%.

En-6: Synthesized from **E** (1.0 g, 1.83 mmol) and **A** (0.82 g, 2.01 mmol). Yield: 78 %; ¹H-NMR (400 MHz, CDCl₃): δ 8.29-8.25 (m, 4H, Ar-H), 8.15-8.07 (m, 4H, Ar-H), 7.62-7.52 (m, 2H, Ar-H), 7.39-7.35 (m, 4H, Ar-H), 7.11-7.09 (dd, ³J=7.0Hz, ⁴J=1.6Hz, 4H, Ar-H), 6.98-6.90 (m, 4H, Ar-H), 5.83-5.77 (m, 1H, -CH=C), 5.0-4.91 (m, 2H, -C=CH₂), 4.06-4.02 (t, ³J=6.8Hz, 2H, 1 × Ar-OCH₂), 3.96-3.93 (t, ³J=6.4Hz, 2H, 1 × Ar-OCH₂), 2.06-2.01 (q, ³J=6.8Hz, 2H, 1 × -CH₂), 1.85-1.74 (q, ³J=6.8Hz, 4H, 2 × -CH₂), 1.50-1.20 (m, 34H, 17 × -CH₂), 0.88-0.85 (t, ³J=6.4Hz, 3H, 1 × -CH₃). C₅₉H₇₀O₁₀ requires C, 75.45; H, 7.51; found: C, 75.88; H, 7.73%.

1.3.1 Siloxanes Si-1 to Si-4

Hydrosilylation reaction.^{S5} - Compound **En-n** (0.30 g, 0.335 mmol) was dissolved in anhydrous toluene (5 ml) under an argon atmosphere. To this solution, was added 1,1,3,3,5,5,5-heptamethyltrisiloxane (0.164 g, 0.74 mmol) and a drop of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene). The resultant reaction mixture was stirred continuously at room temperature under argon till completion of the reaction, which was determined by TLC. The solvent was evaporated and the crude product was purified by chromatography on silica gel using CHCl₃ as an eluent.

Si-1: Yield: 54 %; ¹H-NMR (500 MHz, CDCl₃): δ 8.27-8.25 (dd, ³J=8.5Hz, ⁴J=2.0Hz, 4H, Ar-H), 8.15-8.12 (dd, ³J=9.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 7.5-7.46 (t, ³J=8.0Hz, 1H, Ar-H), 7.37-7.35 (dd, ³J=9.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 7.20-7.16 (m, 3H, Ar-H), 6.98-6.96 (dd, ³J=9.0Hz, ⁴J=2.0Hz, 4H, Ar-H), 4.05-4.02 (t, ³J=6.5Hz, 4H, 2 × Ar-OCH₂), 1.84-1.78 (q, ³J=7.5Hz, 4H, 2 × OCH₂CH₂), 1.51-1.43 (q, ³J=7.5Hz, 4H, 2 × OCH₂CH₂CH₂), 1.35-1.27 (m, 28H, 14×CH₂), 0.53-0.5 (m, 4H, 2 × SiCH₂), 0.073-0.066 [s, 18H, 2 × Si-(CH₃)₃], 0.046-0.040 [s, 12H, 2 × Si-(CH₃)₂], 0.013-0.006 [s, 12H, 2 × Si-(CH₃)₂]. ¹³C-NMR (125 MHz, CDCl₃): δ 164.29, 164.091, 163.84, 155.50, 151.43, 132.42, 131.85, 129.87, 126.62, 122.13, 120.95, 119.28, 115.81, 114.42, 68.40, 33.43, 29.62, 29.57, 29.55, 29.38, 29.37, 29.09, 25.98, 23.22, 18.29, 1.81, 1.27, 0.20. ²⁹Si-NMR (99.3 MHz, CDCl₃): δ 7.47, 7.03, -21.07. C₇₀H₁₀₆O₁₄Si₆ requires C, 62.74; H, 7.97; found: C, 63.21; H, 8.36%.

Si-2: Yield 55 %; ¹H-NMR (500 MHz, CDCl₃): δ 8.30-8.28 (d, ³J=9.0Hz, 2H, Ar-H), 8.15-8.11 (m, 5H, Ar-H), 8.06-8.05 (m, 1H, Ar-H), 7.60-7.57 (t, ³J=8.0Hz, 1H, Ar-H), 7.53-7.51 (m, 1H, Ar-H), 7.39-7.37 (d, ³J=9.0Hz, 2H, Ar-H), 7.27-7.26 (m, 4H, Ar-H), 6.98-6.95 (m, 4H, Ar-H), 4.05-4.02 (m, 4H, 2 × Ar-OCH₂), 1.83-1.79 (m, 4H, OCH₂CH₂), 1.48-1.45 (m, 4H, OCH₂CH₂CH₂), 1.36-1.27 (m, 28H, 14×CH₂), 0.53-0.5 (m, 4H, SiCH₂), 0.072-0.052 [s, 18H, 2 × Si-(CH₃)₃], 0.046-0.029 [s, 12H, 2 × Si-(CH₃)₂], 0.013-0.006 [s, 12H, 2 × Si-(CH₃)₂]. ¹³C-NMR (125 MHz, CDCl₃): δ 164.78, 164.28, 164.16, 163.86, 163.62, 155.62, 151.02, 148.67, 148.10, 132.43, 132.3, 131.89, 131.08, 129.77, 127.76, 127.22, 126.41, 123.55, 122.77, 122.49, 122.20, 121.35, 120.91, 114.44, 114.33, 68.41, 68.35, 33.43, 32.56, 29.62, 29.57, 29.55, 29.38, 29.30, 29.09, 25.98, 23.22, 18.29, 17.91, 1.81, 1.27, 0.20. ²⁹Si-NMR (99.3 MHz, CDCl₃): δ 7.47, 7.02, -21.07. C₇₀H₁₀₆O₁₄Si₆ requires C, 62.74; H, 7.97; found: C, 63.14; H, 8.03%.

Si-3: Yield: 58 %; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.31 (s, 8H, Ar-H), 7.54-7.50 (t, $^3J=8.5\text{Hz}$, 1H, Ar-H), 7.26-7.20 (m, 3H, Ar-H), 7.14-7.12 (m, 4H, Ar-H), 6.95-6.92 (m, 4H, Ar-H), 3.96-3.94 (t, $^3J=6.5\text{Hz}$, 4H, $2 \times \text{Ar-OCH}_2$), 1.81-1.75 (q, $^3J=7.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2$), 1.53-1.42 (q, $^3J=7.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2\text{CH}_2$), 1.34-1.24 (m, 28H, $14 \times \text{CH}_2$), 0.53-0.5 (m, 4H, $2 \times \text{SiCH}_2$), 0.079-0.066 [s, 18H, $2 \times \text{Si-(CH}_3)_3$], 0.057-0.034 [s, 12H, $2 \times \text{Si-(CH}_3)_2$], 0.013-0.006 [s, 12H, $2 \times \text{Si-(CH}_3)_2$]. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.58, 163.92, 157.13, 151.27, 144.01, 134.27, 133.45, 130.29, 130.08, 122.21, 119.37, 115.65, 115.18, 68.45, 33.45, 29.64, 29.58, 29.41, 29.39, 29.28, 26.05, 23.23, 18.3, 1.81, 1.27, 0.21. $^{29}\text{Si-NMR}$ (99.3 MHz, CDCl_3): δ 7.48, 7.03, -21.07. $\text{C}_{70}\text{H}_{106}\text{O}_{14}\text{Si}_6$ requires C, 62.74; H, 7.97; found: C, 63.24; H, 8.31%.

Si-4: Yield: 51 %; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 9.04-9.03 (t, $^4J=2.0\text{Hz}$, 1H, Ar-H), 8.50-8.48 (dd, $^3J=6.0\text{Hz}$, $^4J=2.0\text{Hz}$, 2H, Ar-H), 8.31-8.28 (m, 4H, Ar-H), 7.74-7.71 (t, $^3J=8.0\text{Hz}$, 1H, Ar-H), 7.41-7.39 (m, 4H, Ar-H), 7.13-7.10 (m, 4H, Ar-H), 6.94-6.91 (m, 4H, Ar-H), 3.97-3.94 (t, $^3J=6.5\text{Hz}$, 4H, $2 \times \text{Ar-OCH}_2$), 1.79-1.76 (q, $^3J=7.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2$), 1.54-1.42 (q, $^3J=7.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2\text{CH}_2$), 1.38-1.27 (m, 28H, $14 \times \text{CH}_2$), 0.88-0.50 (m, 4H, $2 \times \text{SiCH}_2$), 0.084-0.063 [s, 18H, $2 \times \text{Si-(CH}_3)_3$], 0.057-0.035 [s, 12H, $2 \times \text{Si-(CH}_3)_2$], 0.018-0.003 [s, 12H, $2 \times \text{Si-(CH}_3)_2$]. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.69, 163.59, 157.03, 154.74, 144.14, 135.31, 131.97, 131.9, 131.62, 129.97, 129.35, 127.64, 124.58, 122.32, 121.88, 115.15, 68.47, 33.44, 32.57, 32.52, 31.9, 29.64, 29.58, 29.41, 29.39, 29.33, 29.28, 29.06, 26.05, 23.22, 18.29, 1.81, 1.27, 0.20. $^{29}\text{Si-NMR}$ (99.3 MHz, CDCl_3): δ 7.49, 7.03, -21.06. $\text{C}_{70}\text{H}_{106}\text{O}_{14}\text{Si}_6$ requires C, 62.74; H, 7.97; found: C, 63.09; H, 8.21%.

1.3.2 Siloxanes Si-5 and Si-6

Synthesized according to the hydrosilylation procedure described for the compounds **Si-1** to **Si-4** (1.3.1) except that 1.2 molar equivalents of 1,1,3,3,5,5,5-heptamethyltrisiloxane were used.

Si-5: Yield: 62 %; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.31 (s, 8H, Ar-H), 7.53-7.50 (t, $^3J=8.0\text{Hz}$, 1H, Ar-H), 7.26-7.20 (m, 3H, Ar-H), 7.14-7.11 (m, 4H, Ar-H), 6.95-6.92 (m, 4H, Ar-H), 3.96-3.94 (t, $^3J=6.5\text{Hz}$, 4H, $2 \times \text{Ar-OCH}_2$), 1.80-1.75 (q, $^3J=6.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2$), 1.46-1.42 (q, $^3J=7.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2\text{CH}_2$), 1.36-1.25 (m, 34H, $17 \times \text{CH}_2$), 0.88-0.85 (t, $^3J=6.5\text{Hz}$, 3H, $1 \times \text{CH}_3$), 0.53-0.5 (m, 2H, $1 \times \text{SiCH}_2$), 0.078-0.065 [s, 9H, $1 \times \text{Si-(CH}_3)_3$], 0.051-0.038 [s, 6H, $1 \times \text{Si-(CH}_3)_2$], 0.012-(-0.003) [s, 6H, $1 \times \text{Si-(CH}_3)_2$]. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.58, 163.92, 157.13, 151.27, 144.01, 134.27, 133.45, 130.29, 130.08, 122.21, 119.37, 115.64, 115.19, 68.48, 33.44, 31.92, 29.68, 29.67, 29.65, 29.58, 29.39, 29.35, 29.26, 26.03, 23.22, 22.68, 18.29, 14.10, 1.80, 1.26, 0.20. $^{29}\text{Si-NMR}$ (99.3 MHz, CDCl_3): δ 7.48, 7.03, -21.06. $\text{C}_{66}\text{H}_{92}\text{O}_{12}\text{Si}_3$ requires C, 68.24; H, 7.98; found: C, 68.68; H, 8.38%.

Si-6: Yield: 65 %; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.29-8.26 (m, 4H, Ar-H), 8.15-8.07 (m, 4H, Ar-H), 7.62-7.52 (m, 2H, Ar-H), 7.39-7.35 (m, 4H, Ar-H), 7.24-7.09 (dd, $^3J=9.0\text{Hz}$, $^4J=2.5\text{Hz}$, 4H, Ar-H), 6.98-6.92 (m, 4H, Ar-H), 4.05-4.03 (t, $^3J=6.5\text{Hz}$, 2H, $1 \times \text{Ar-OCH}_2$), 3.96-3.93 (t, $^3J=6.5\text{Hz}$, 2H, $1 \times \text{Ar-OCH}_2$), 1.83-1.76 (q, $^3J=7.0\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2$), 1.46-1.42 (q, $^3J=7.0\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2\text{CH}_2$), 1.36-1.25 (m, 34H, $17 \times \text{CH}_2$), 0.88-0.85 (t, $^3J=7.0\text{Hz}$, 3H, $1 \times \text{CH}_3$), 0.53-0.5 (m, 2H, $1 \times \text{SiCH}_2$), 0.079-0.066 [s, 9H, $1 \times \text{Si-(CH}_3)_3$], 0.052-0.039 [s, 6H, $1 \times \text{Si-(CH}_3)_2$], 0.013-(-0.001) [s, 6H, $1 \times \text{Si-(CH}_3)_2$]. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.74, 164.28, 163.88, 163.7, 156.97, 155.66, 154.88, 151.08, 144.17, 132.43, 131.89, 131.84, 130.68, 129.88, 127.47, 126.34, 123.65, 122.33, 122.23, 121.90, 120.88, 115.14, 114.44, 68.46, 68.41, 33.43, 31.92, 29.69, 29.67, 29.65, 29.62, 29.60, 29.57,

29.55, 29.38, 29.37, 29.35, 29.27, 29.09, 26.04, 25.98, 23.22, 22.68, 18.29, 14.10, 1.81, 1.27, 0.20. ^{29}Si -NMR (99.3 MHz, CDCl_3): δ 7.48, 7.03, -21.06. $\text{C}_{66}\text{H}_{92}\text{O}_{12}\text{Si}_3$ requires C, 68.24; H, 7.98; found: C, 68.64; H, 8.35%.

2. Additional XRD data

2.1 Diffraction patterns and scans

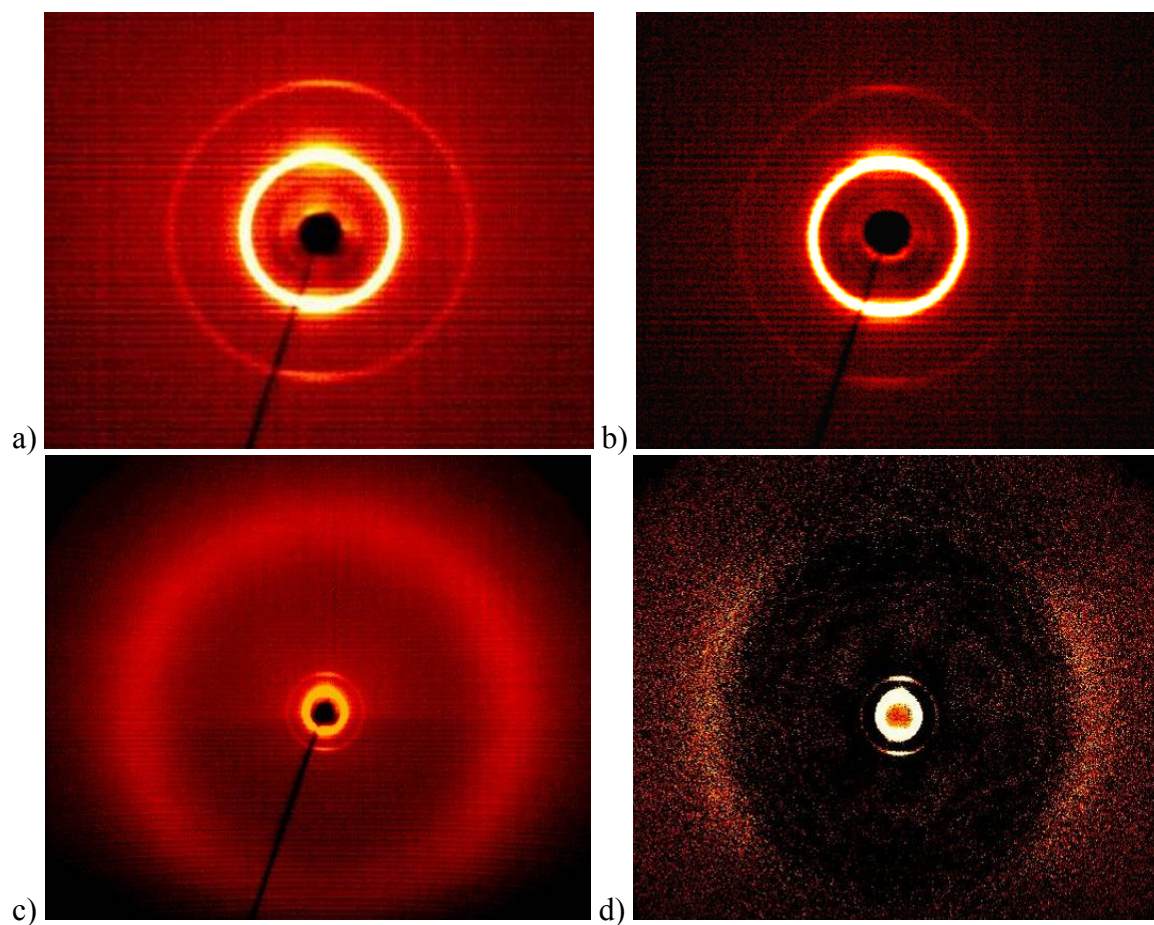


Figure S1. XRD patterns of partially surface aligned samples on cooling: a) SAXD patterns of **En-3** at 142 °C; b) **En-5** at 151 °C; c) WAXD pattern of **En-3** at 140 °C, original and d) scattering of the isotropic liquid at 153 °C subtracted.

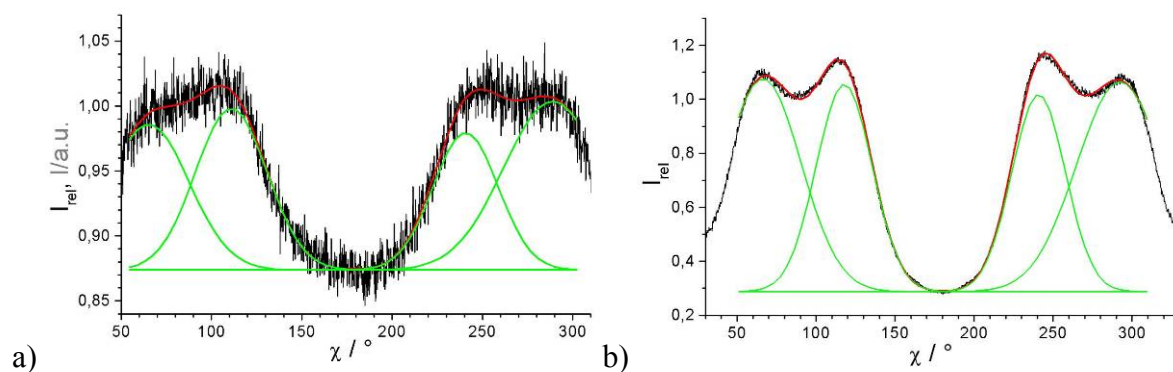


Figure S2. χ -scans for the outer diffuse scattering in the WAXD patterns of surface aligned samples a) of **En-3** at 140 °C and b) **En-6** at 100 °C with maxima at $\chi = 65, 111, 241,$ and 289° (**En-3**) and $\chi = 66, 118, 241,$ and 292° (**En-6**) determined by fitting 4 Gaussian curves to the experimental relative intensity $I_{rel} = I(T)/I(\text{isotropic liquid})$ yielding an average tilt of 24° (**En-3**) and 26° (**En-6**) for the molecular long axes with respect to the layer normal.

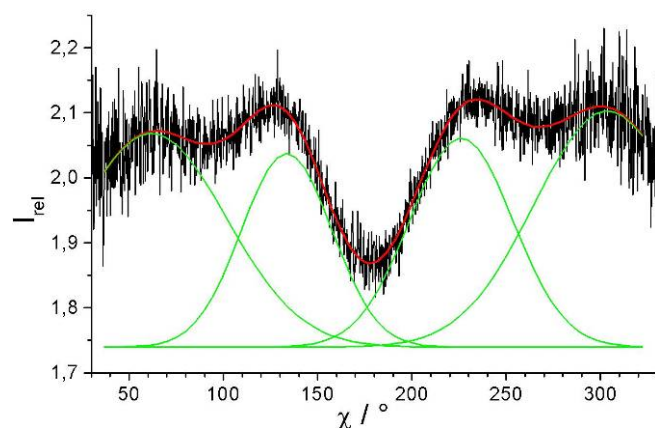


Figure S3. χ -scan for the outer diffuse scattering in the WAXD pattern of a surface aligned sample of **Si-2** at 110 °C with maxima at $\chi = 62, 134, 226,$ and 304° determined by fitting 4 Gaussian curves to the experimental relative intensity $I_{rel} = I(110 \text{ }^\circ\text{C})/I(115 \text{ }^\circ\text{C}, \text{isotropic liquid})$ yielding an average tilt of 44° for the molecular long axes with respect to the layer normal.

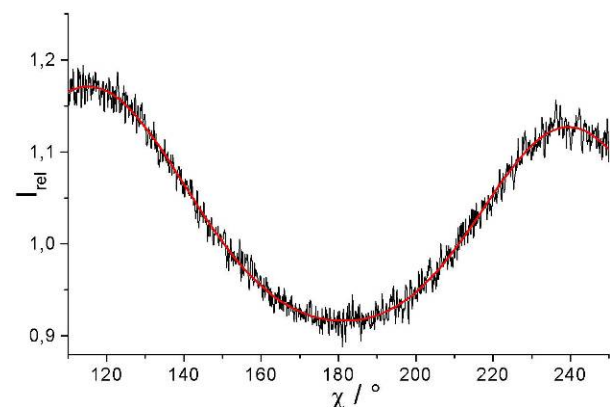


Figure S4. χ -scan for the outer diffuse scattering in the WAXD pattern of a surface aligned sample of **Si-3** at 125 °C with maxima at $\chi = 115$ and 239° determined by fitting 2 Gaussian

curves to the experimental relative intensity $I_{\text{rel}} = I(125 \text{ }^\circ\text{C})/I(140 \text{ }^\circ\text{C, isotropic liquid})$ yielding an average tilt of 28° for the molecular long axes with respect to the layer normal.

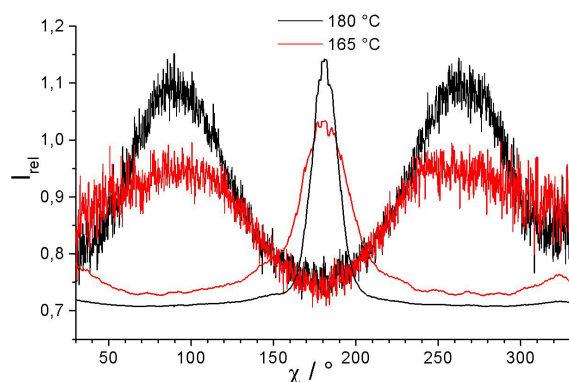


Figure S5. χ -scans for the outer diffuse scattering in the WAXD patterns for a surface aligned sample of **Si-4** on heating at 180 °C with maxima at $\chi = 91^\circ, 264^\circ$ and at 165 °C at 66, 117, 249, 289°, determined by fitting 2 and 4 Gaussian curves, respectively, to the experimental relative intensity $I_{\text{rel}} = I(T)/I(185 \text{ }^\circ\text{C, isotropic liquid})$ yielding an average tilt of 23° for the molecular long axes with respect to the layer normal in the low temperature smectic phase at 165 °C and a non-tilted arrangement in the high temperature phase at 180 °C (curves with maxima at $\chi = 180^\circ$ for the corresponding scans of the first-order layer reflections for comparison).

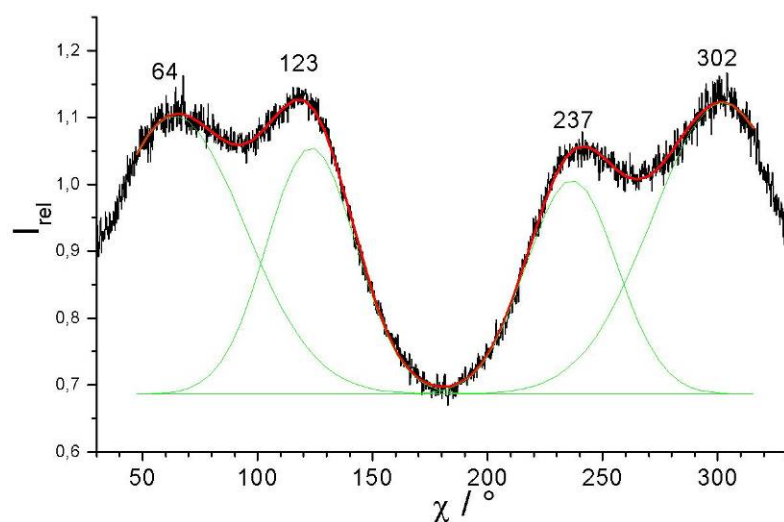


Figure S6. χ -scan for the outer diffuse scattering in the WAXD pattern of a surface aligned sample of **Si-6** at 130 °C with maxima at $\chi = 64, 123, 237,$ and 302° determined by fitting 4 Gaussian curves to the experimental relative intensity $I_{\text{rel}} = I(130 \text{ }^\circ\text{C})/I(137 \text{ }^\circ\text{C, isotropic liquid})$ yielding an average tilt of 31° for the molecular long axes with respect to the normal to the modulated layers.

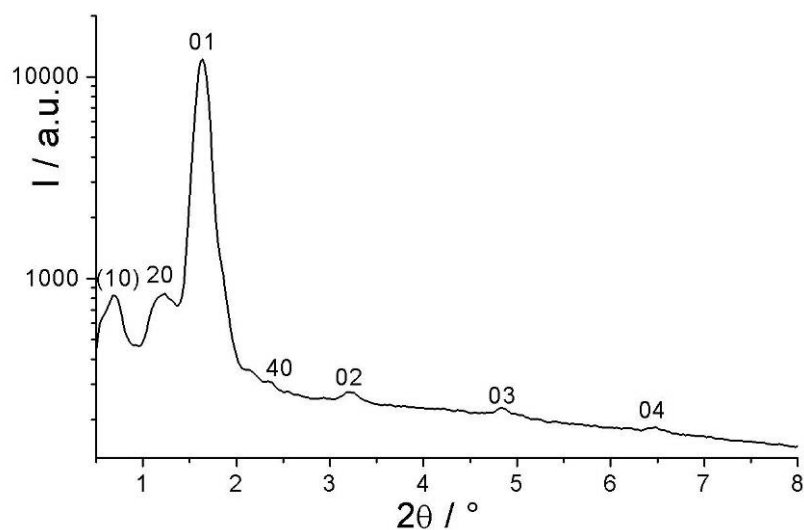


Figure S7. SAXD pattern of **Si-5** at 130 °C on cooling showing the tentative indexing analogous to **Si-6** (The 10 reflection is partly shadowed by the beam stop).

2.2 Additional tabular XRD data

Table S1. Observed d values (Å) for the reflections in the XRD patterns (T ... temperature in °C, n ... order of the reflections, hk ... Miller indices)

Compound	T	Kind of reflection	n/hk	d
En-3	145	inner		90.4
		layer	1	44.8
		layer	2	22.5
En-5	151	inner		89.0
		layer	1	48.6
		layer	2	24.4
		layer	3	16.3
Si-3	125	layer	1	51.9
		layer	2	25.7
Si-4	165	layer	1	52.1
		layer	2	26.4
		layer	3	17.6
		diffuse		7.5
		diffuse		4.7
	180		1	52.5
		diffuse		7.3
		diffuse		4.8
Si-5	130		20	74.8
			01	54.0
			40	37.3
			02	27.4
			03	18.2
			04	13.6

Table S2. Indexing for the small angle reflections of **En-6** on an oblique 2D lattice with parameters a) $a = 156 \text{ \AA}$, $b = 48.1 \text{ \AA}$, and $\gamma = 103^\circ$ ($T = 110 \text{ }^\circ\text{C}$) and b) $a = 139 \text{ \AA}$, $b = 48.2 \text{ \AA}$, and $\gamma = 102^\circ$ ($T = 120 \text{ }^\circ\text{C}$); $h, k \dots$ Miller indices, $2\theta \dots$ Bragg angle (in $^\circ$), $d_{\text{obs}} \dots$ observed d value (\AA), $d_{\text{calc}} \dots$ d value calculated from the lattice parameters (\AA)

a)

h	k	2θ	d_{obs}	d_{calc}	$d_{\text{obs}}-d_{\text{calc}}$
2	0	1.160	76.2	76.0	0.2
-1	1	1.830	48.3	47.9	0.4
0	1	1.883	46.9	46.9	0
-2	1	1.955	45.2	44.6	0.6
-3	1	2.257	39.1	39.1	0
2	1	2.418	36.5	36.4	0.1
-2	2	3.664	24.1	24.0	0.1
-1	2	3.684	24.0	24.0	0
0	2	3.772	23.4	23.4	0
0	3	5.641	15.7	15.6	0.1

b)

h	k	2θ	d_{obs}	d_{calc}	$d_{\text{obs}}-d_{\text{calc}}$
2	0	1.316	67.1	68.0	-0.9
3	0	1.910	46.2	45.3	0.9
0	1	1.875	47.1	47.1	0
-1	1	1.847	47.8	47.7	0.1
-2	1	2.050	43.1	43.2	-0.1
2	1	2.475	35.7	35.4	0.3
0	2	3.753	23.5	23.6	-0.1
-1	2	3.627	24.4	24.1	0.3
-2	2	3.675	24.0	23.9	0.1
0	3	5.608	15.8	15.7	0.1
-1	3	5.504	16.1	16.0	0.1

Table S3. Indexing for the small angle reflections of **Si-3** on an oblique 2D lattice with parameters $a = 78.7 \text{ \AA}$, $b = 54.5 \text{ \AA}$, and $\gamma = 112^\circ$ ($T = 86 \text{ }^\circ\text{C}$); $h, k \dots$ Miller indices, $2\theta \dots$ Bragg angle (in $^\circ$), $d_{\text{obs}} \dots$ observed d value (\AA), $d_{\text{calc}} \dots$ d value calculated from the lattice parameters (\AA).

h	k	2θ	d_{obs}	d_{calc}	$d_{\text{obs}}-d_{\text{calc}}$
1	0	1.207	73.2	73.0	0.2
-1	1	1.715	51.5	51.6	-0.1
0	1	1.742	50.7	50.5	0.2
2	0	2.414	36.6	36.5	0.1
-2	1	2.414	36.6	36.8	-0.2
0	2	3.492	25.3	25.3	0
0	3	5.292	16.7	16.8	-0.1
0	4	7.071	12.5	12.6	-0.1

Table S4. Indexing for the small angle reflections of **Si-6** on an oblique 2D lattice with parameters $a = 179 \text{ \AA}$, $b = 53 \text{ \AA}$, and $\gamma = 100^\circ$ ($T = 130 \text{ }^\circ\text{C}$); $h, k \dots$ Miller indices, $2\theta \dots$ Bragg angle (in $^\circ$), $d_{\text{obs}} \dots$ observed d value (\AA), $d_{\text{calc}} \dots$ d value calculated from the lattice parameters (\AA).

h	k	2θ	d_{obs}	d_{calc}	$d_{\text{obs}}-d_{\text{calc}}$
2	0	1.004	88.0	88.1	-0.1
3	0	1.500	58.9	58.5	0.4
-1	1	1.683	52.5	52.6	-0.1
0	1	1.683	52.5	52.2	0.3
4	0	2.008	44.0	44.1	-0.1
-3	1	2.103	42.0	42.9	-0.9
2	1	2.103	42.0	41.8	0.2
0	2	3.334	26.5	26.1	0.4
0	3	5.021	17.6	17.4	0.2
0	4	6.799	13.0	13.0	0

Table S5. An estimate of the number of molecules in the cross section of the ribbons within the Col_{ob} phases of compounds **En-6**, **Si-3** and **Si-6**.^a

Compound	$V_{\text{mol,cr}}$	$V_{\text{mol,is}}$	T	V_{cell}	$n_{\text{cell,cr}}$	$n_{\text{cell,is}}$	$n_{\text{cell,LC}}$
En-6	1307.0	1663.5	110	38018.7	29.1	22.9	26
			120	34077.6	26.1	20.5	23
Si-3	1802.2	2293.7	86	20679.5	11.5	9.0	10
Si-6	1595.2	2030.3	130	48582.9	30.5	23.9	27

^a $V_{\text{mol,cr}}$... molecular volume in the crystal calculated using crystal volume increments^{S6}, average packing coefficient in the crystal $k = 0.7$ according to Kitaigorodski,⁷ T ... measuring temperature, $V_{\text{mol,is}}$... molecular volume in the isotropic liquid, average packing coefficient $k = 0.55$, V_{cell} ... unit cell volume obtained from the lattice parameters and assuming a height of $h = 0.52$ nm (assuming a stacking in bend direction of molecules with a bend angle of 120°), n_{cell} ... number of molecules in a unit cell with crystal-like density (cr) according to $n_{\text{cell,cr}} = V_{\text{cell}}/V_{\text{mol,cr}}$, with liquid-like density (is) according to $n_{\text{cell,is}} = n_{\text{cell,cr}} \cdot 0.55/0.7$, and in the LC phase ($n_{\text{cell,LC}}$) estimated as the intermediate between that in the crystalline and the liquid phase (V in \AA^3 , T in $^\circ\text{C}$); for **Si-1** $n_{\text{cell,LC}} = 2$.^{S8}

3. Additional Figures

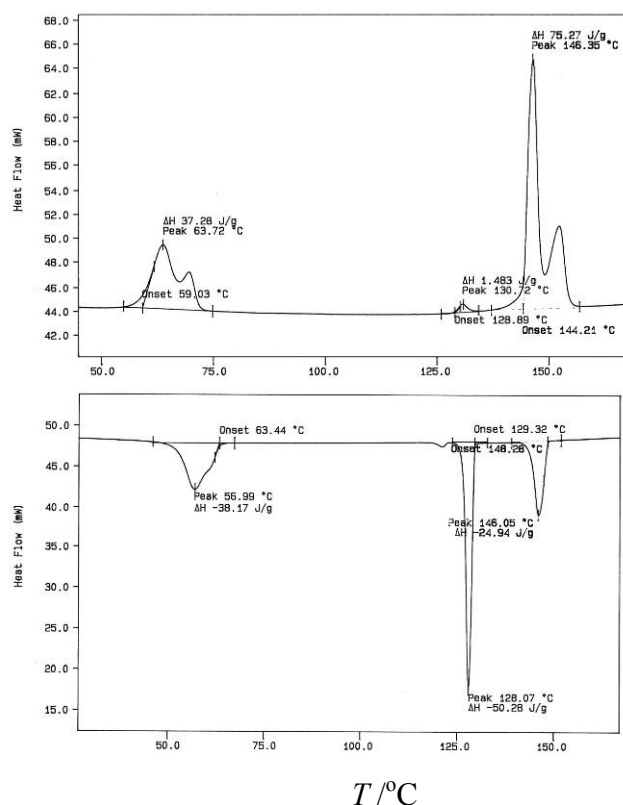


Figure S8. DSC heating and cooling curves (10 K min^{-1}) of compound **En-3**.

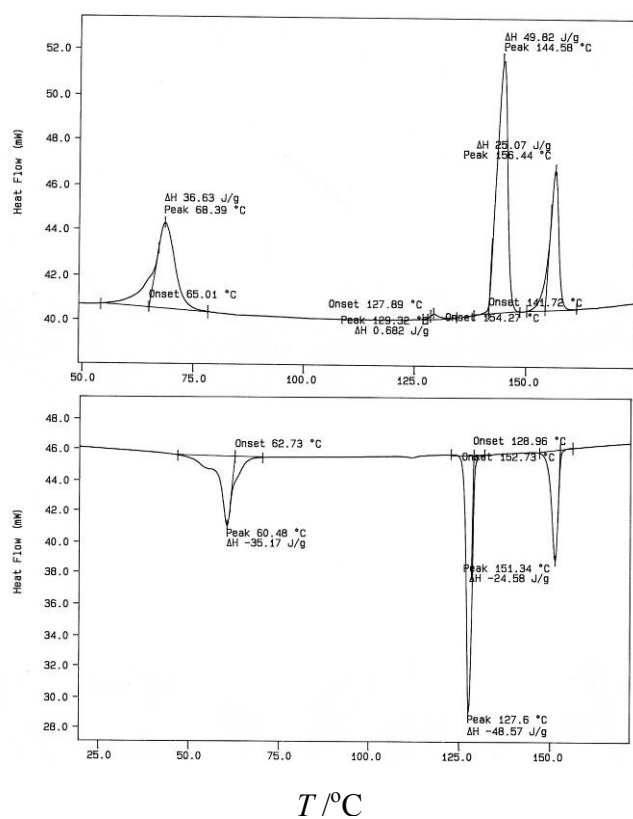


Figure S9. DSC heating and cooling scans (10 K min^{-1}) of compound **En-5**.

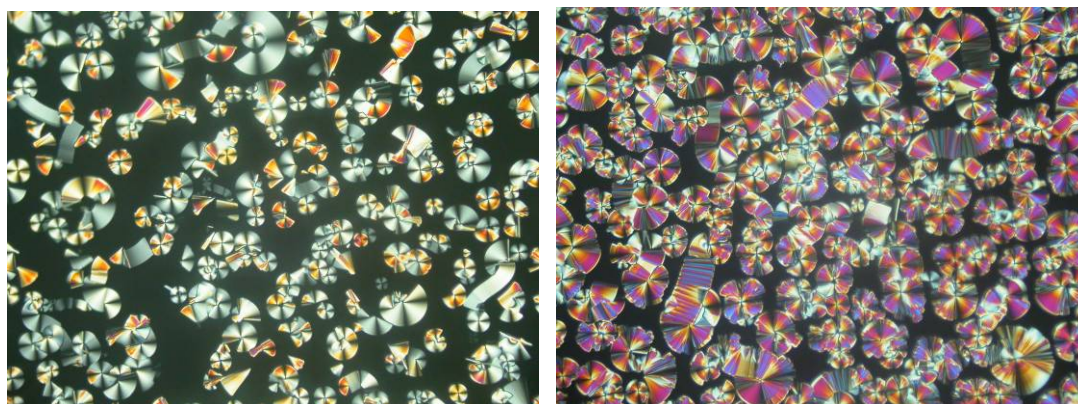


Figure S10. Textures of compound **En-5** (crossed polarizers): a) at $T = 156 \text{ }^\circ\text{C}$ and b) at $T = 155 \text{ }^\circ\text{C}$.

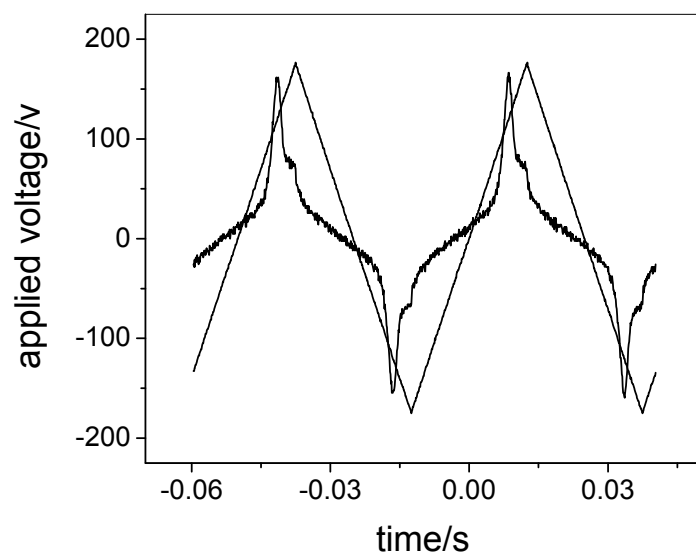


Figure S11. FE switching current response obtained for **En-5** under a triangular wave field ($350 V_{pp}$, 20 Hz, $5 \mu m$, $P_s = 240 nC cm^{-2}$) at $T = 145 ^\circ C$.

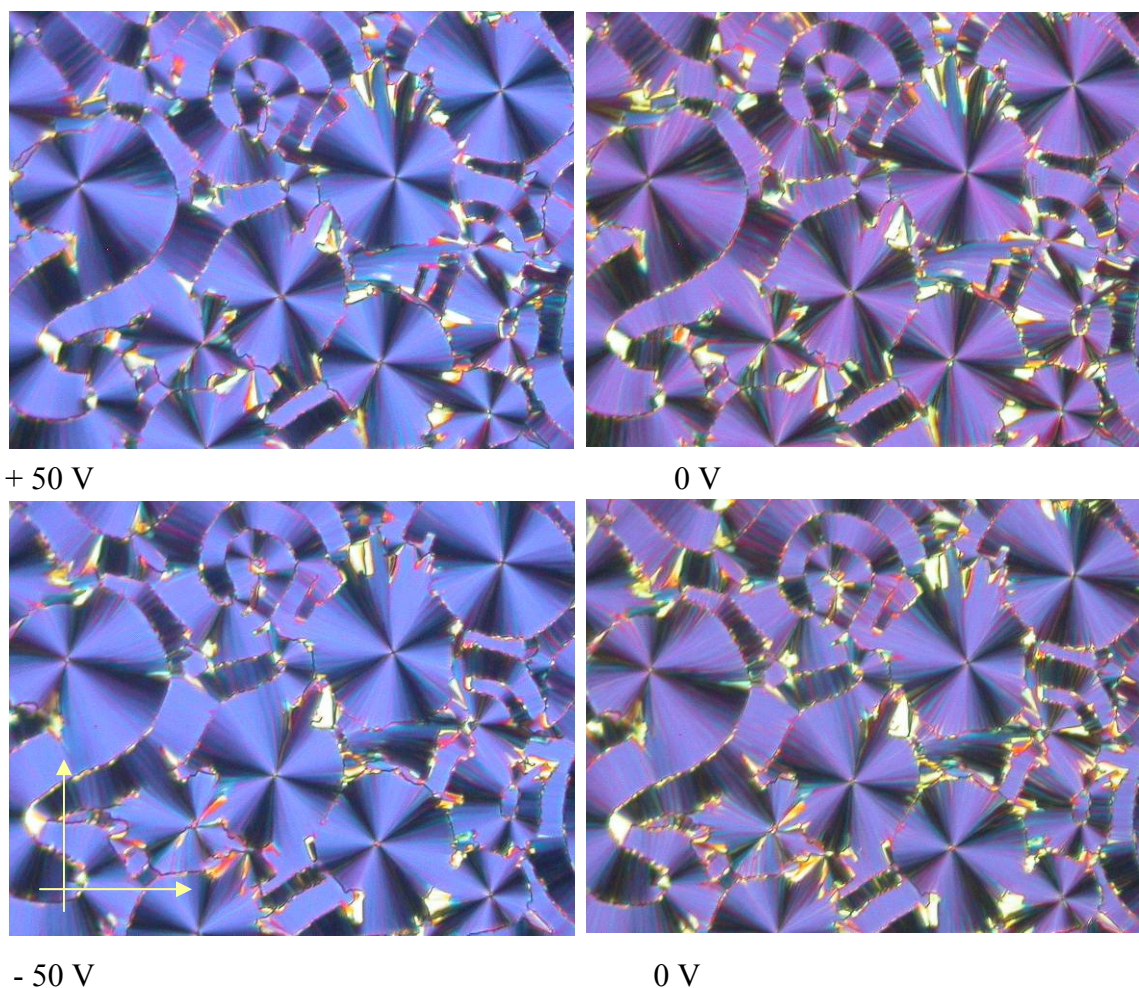


Figure S12. Bistable switching of **En-5** as seen under a DC electric field at $142 ^\circ C$ (circular domains generated with a triangular wave field: $350 V_{pp}$; 30 Hz; $5 \mu m$); arrows indicate the direction of polarizer and analyzer.

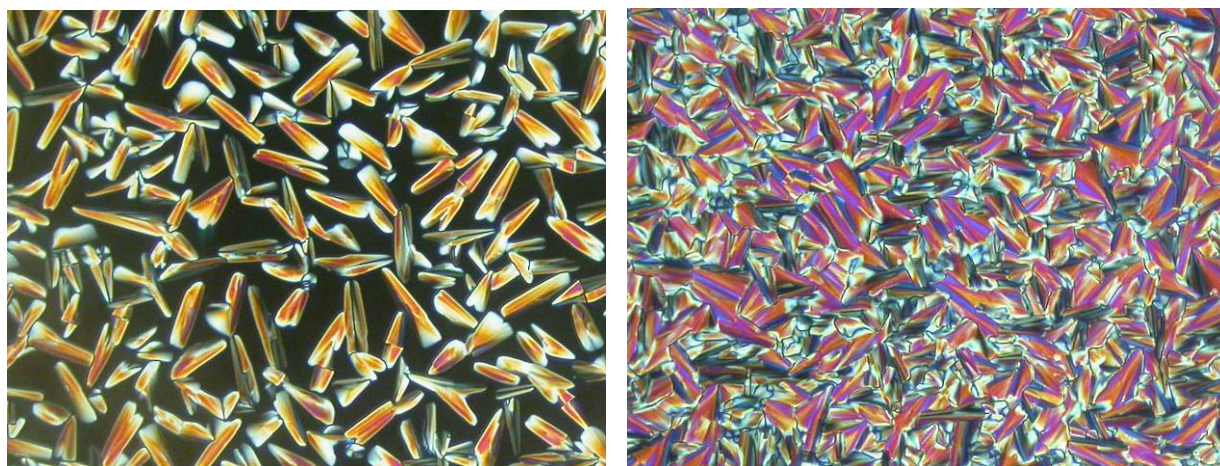


Figure S13. Textures of compound **En-6** (crossed polarizers): a) at $T = 123\text{ }^{\circ}\text{C}$ and b) at $122\text{ }^{\circ}\text{C}$.

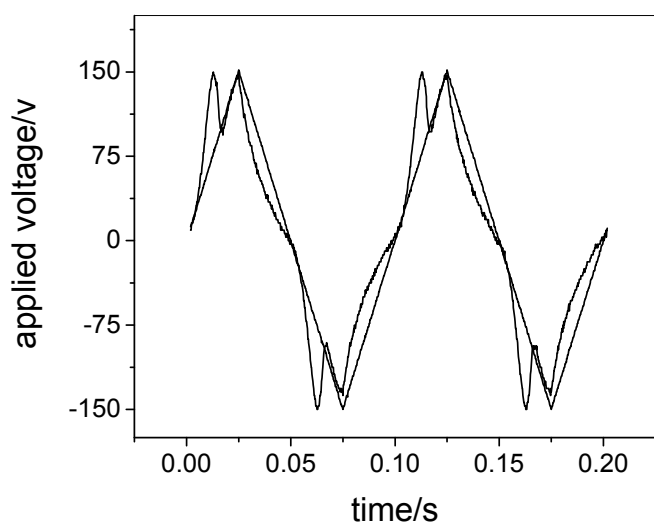
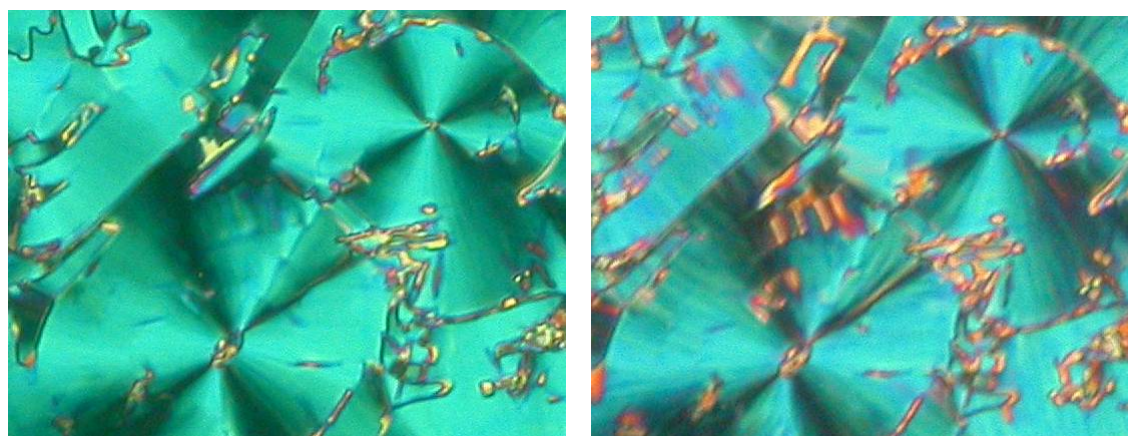


Figure S14. FE switching current response obtained for **En-6** under a triangular wave field (300 V_{pp} , 10 Hz , $5\text{ }\mu\text{m}$, $P_s = 800\text{ nC cm}^{-2}$) at $T = 105\text{ }^{\circ}\text{C}$.



+50 V

0V

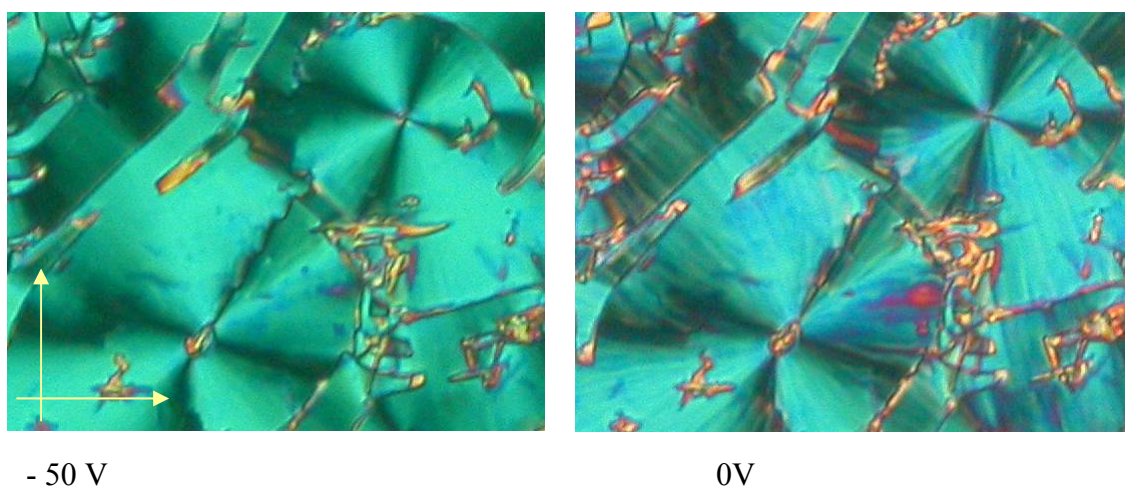


Figure S15. Bistable switching of **En-6** as seen under a DC electric field (300 Vpp; 30 Hz; 5 μm) at 105 $^{\circ}\text{C}$; arrows indicate the direction of polarizer and analyzer.

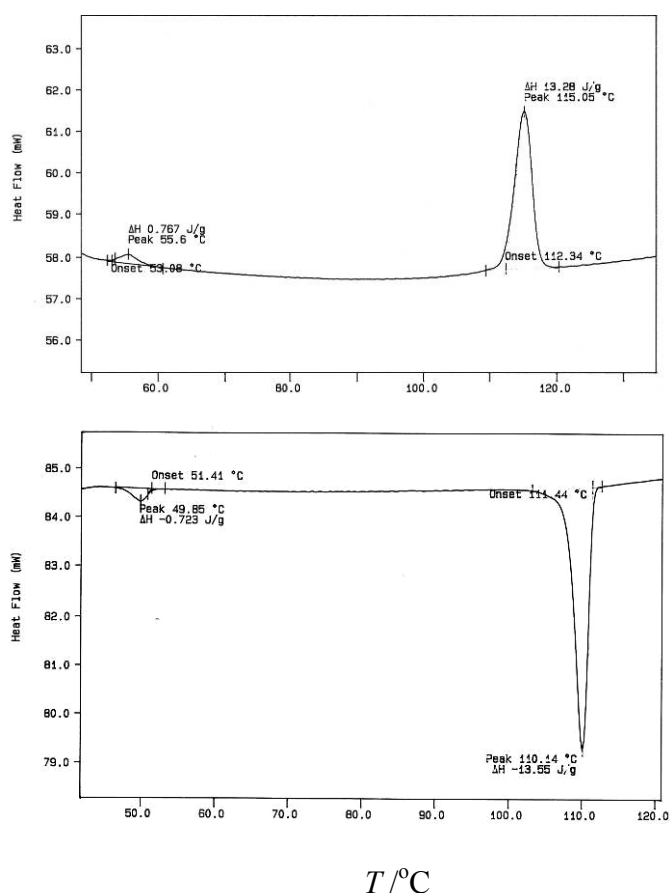


Figure S16. DSC heating and cooling scans (10 K min^{-1}) of compound **Si-2**.

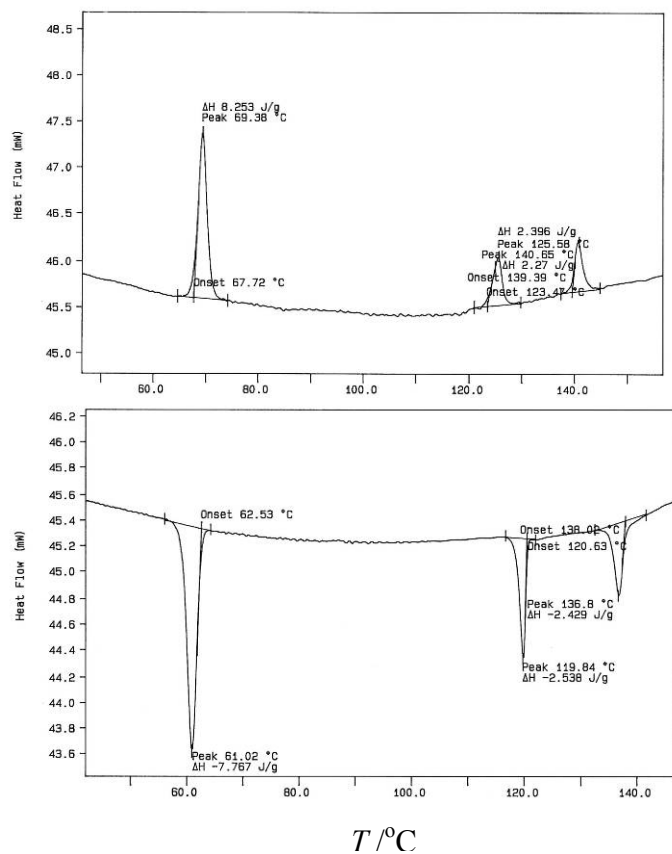


Figure S17. DSC heating and cooling scans (10 K min⁻¹) of compound Si-3.

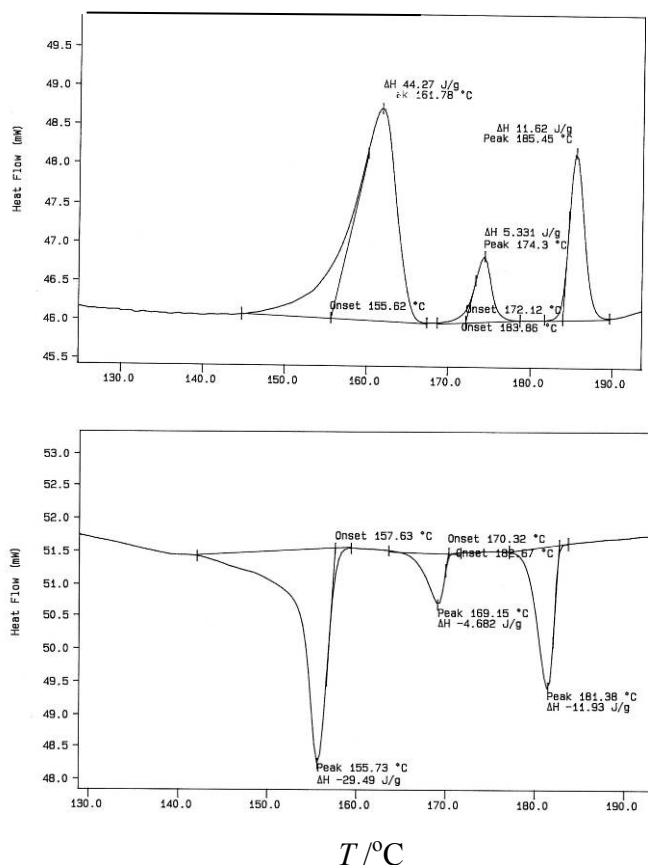


Figure S18. DSC heating and cooling scans (10 K min⁻¹) of compound Si-4.

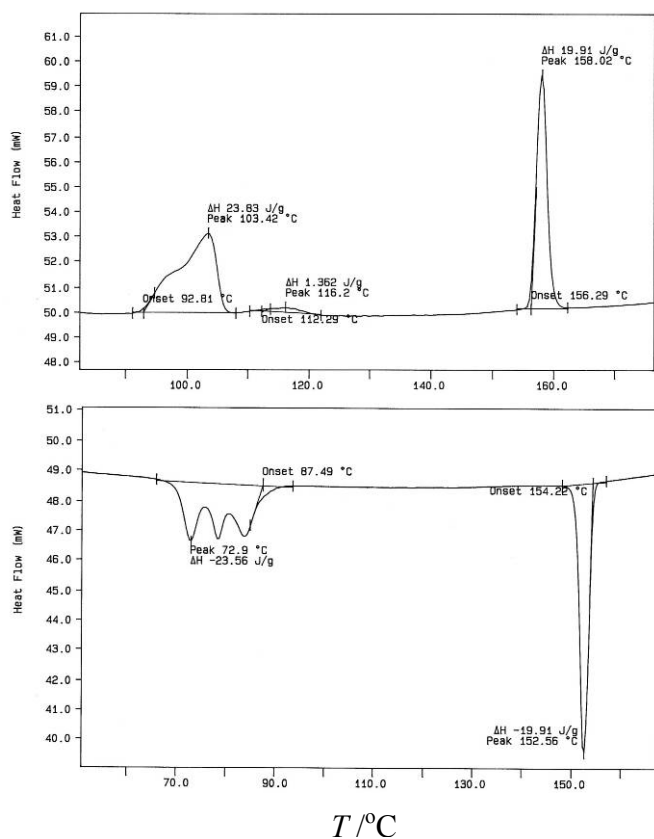


Figure S19. DSC heating and cooling scans (10 K min^{-1}) of compound Si-5.

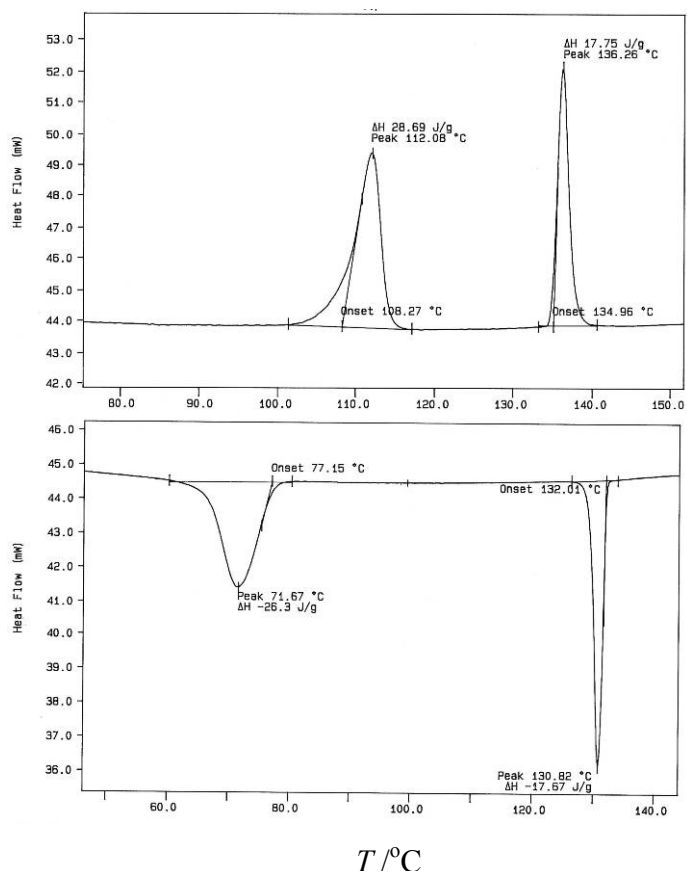


Figure S20. DSC heating and cooling scans (10 K min^{-1}) of compound Si-6.



$L = 6.1$ nm



$L = 5.6$ nm



$L = 6.7$ nm



$L = 7.1$ nm

Figure S21. Molecular models and molecular lengths (L) of compounds: a) **En-5**; b) **En-3**; c) **Si-5** and d) **Si-3** assuming a 120° angle of the bent aromatic core with the terminal chains in the most stretched conformation.

5. References

- S1 C. Keith, R. Amaranatha Reddy, A. Hauser, U. Baumeister and C. Tschierske, *J. Am. Chem. Soc.*, 2006, **16**, 3051; R. Achten, A. Koudijs, M. Giesbers, A. T. M. Marcelis and E. J. Sudhölter, *Liq. Cryst.*, 2005, **32**, 277.
S2 R. Amaranatha Reddy, U. Baumeister and C. Tschierske, *Chem. Commun.*, 2009, 4236.
S3 S. Umadevi, S. Radhika and B. K. Sadashiva, *Liq. Cryst.*, 2006, **33**, 139.
S4 H. N. Shreenivasa. Murthy and B. K. Sadashiva, *Liq. Cryst.*, 2004, **31**, 1347.

- S5 G. Mehl and J. W. Goodby, *Chem. Ber.*, 1996, **129**, 3051.
S6 A. Immirzi and B. Perini, *Acta Cryst. Sect., A* 1977, **33**, 216.
S7 A. I. Kitaigorodski, “Molekülkristalle”, Akademie-Verlag Berlin, 1979.
S8 R. Amaranatha Reddy, U. Baumeister, H. Hahn, H. Lang and C. Tschierske, *Soft Matter*, 2007, **3**, 558.