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# Electronic Supporting Information

## 4-Methylresorcinol based bent-core liquid crystals with azobenzene wings - A new class of compounds with dark conglomerate phases

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**Contents**

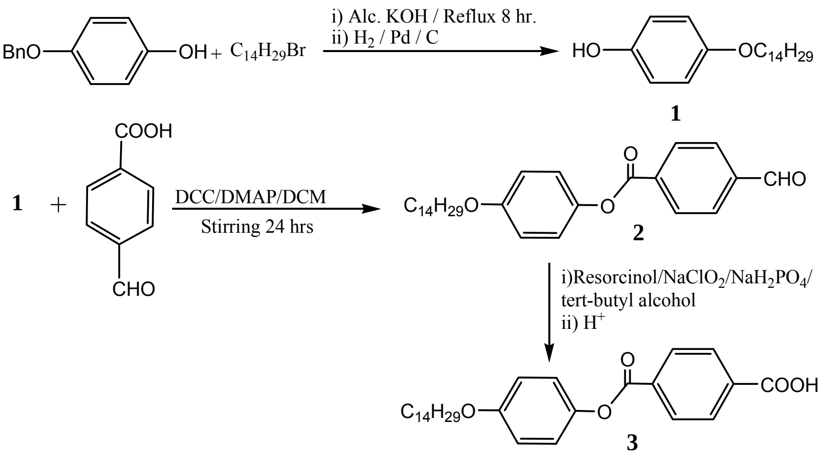
## 1. Characterization methods

Thin layer chromatography (TLC) was performed on aluminium sheet precoated with silica gel. Starting materials were obtained from commercial sources and used without further purification. The solvents were dried using the standard methods when required. The purity and the chemical structures of all synthesized compounds were confirmed by the spectral data. The structure characterization of the synthesized bent-core compounds is based on $^1$H-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard). Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

## 2. Syntheses and analytical data

### *2.1. Synthesis of 4-(4'-n-tetradecyloxyphenoxycarbonyl)benzoic acid*

The synthesis of 4-(4'-*n*-tetradecyloxyphenoxycarbonyl)benzoic acid is shown in Scheme S1.



**Scheme S1**

4-*n*-Tetradecyloxyphenol **1** was prepared by the alkylation of 4-benzyloxyphenol with 4-*n*-tetradecylbromide followed by deprotection with hydrogen in the presence of 5% Pd–C. Compound **1** was then esterificated with 4-formylbenzoic acid in the presence of DCC to give the intermediate **2**. The aldehyde **2** was oxidized to the acid **3** using the method reported in Ref. [S1] as following: (4-Tetradecyloxyphenyl)-4-formylbenzoate, **2** (3.89 g, 8.88 mmol) and resorcinol (1.04 g, 9.50 mmol) were dissolved in *tert*-butyl alcohol (140 mL). Independently, sodium chlorite (3.80 g, 34.57 mmol) and sodium dihydrogenphosphate (3.04 g, 21.41 mmol) were dissolved in water (30 mL). The aqueous solution was added in a dropwise manner into the *tert*-butyl alcohol solution over a 10-min period. The pale yellow reaction mixture was then stirred at room temperature overnight. Volatile components were removed under vacuum and the residue was dissolved in water (100 mL). The aqueous solution was acidified to pH 3 by adding 1 N aqueous HCl. The liberated white precipitate was isolated, washed successively with water and hexane, and dried in air, and it was used for the next step without any further purification.

### *1.1.1. 4-n-Tetradecyloxybenzyloxybenzene*

Yield 84%, m.p. 84-86 °C. $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.73–7.32 (m, 5H, Ar-H), 6.85 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.6 Hz, 2H, Ar-H), 3.85 (t, *J* = 6.6 Hz, 2H, $-OCH_2$), 1.70–1.64 (m, 2H, $-OCH_2\underline{CH_2}$), 1.50–1.17 (m, 22H, $CH_2$), 0.82 (t, *J* = 6.9 Hz, 3H, $CH_3$).

### *2.1.2. 4-n-Tetradecyloxyphenol* **1**

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

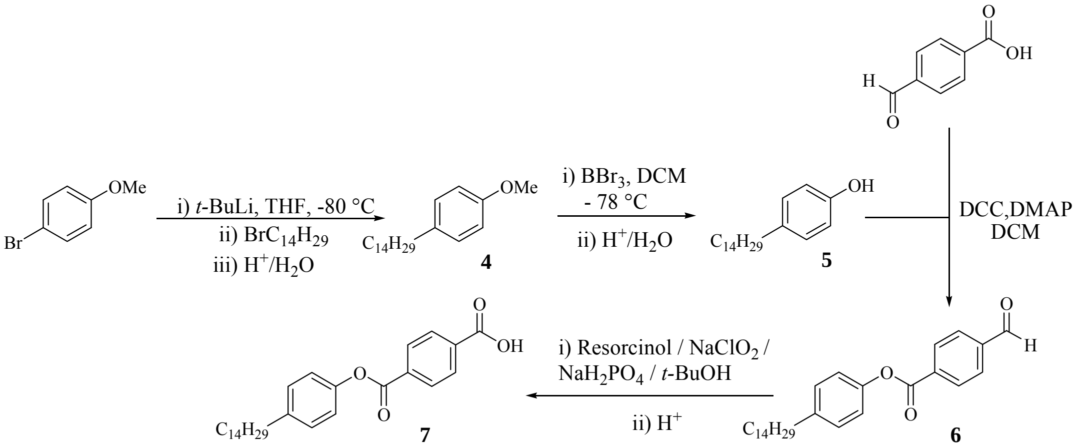
### *1.1.3. 4-Tetradecyloxyphenyl 4'-formylbenzoate* **2**

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

### *2.1.4. 4-(4-n-Tetradecyloxyphenoxycarbonyl)benzoic acid* **3**

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

## ***2.2. Synthesis of 4-(4-n-tetradecylphenoxycarbonyl)benzoic acid***



**Scheme S2**

The synthesis of 4-(4-*n*-tetradecylphenoxycarbonyl)benzoic acid is shown in Scheme S2. The synthesis of this compound was done using similar methods to that reported in reference [S2].

### *2.2.1. Synthesis of 4-n-tetradecylanisole* **4**

Under an inert atmosphere, a solution of *tert*-butyllithium in hexane (26.4 mL, 44.9 mmol) was introduced drop wise to a solution of 4-bromoanisole (4.0 g, 21.4 mmol) in THF (150 mL) at -78 °C and the mixture was stirred for two hours then a solution of *n*-bromotetradecane (5.9 mL, 21.4 mmol) in THF (40 mL) was added at -78 °C. The mixture was stirred for one hour, then gradually warmed to room temperature, then further stirred for two days, quenched with water and the organic layer was separated. The aqueous layer was extracted with diethyl ether (50 mL × 3). The combined organic layer was washed with saturated NaCl (100 mL × 2), dried over $MgSO_4$, filtered and evaporated in vacuo. The resulting residue was chromatographed using *n*-hexane as an eluent. Yield, 52%, m.p. 32 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.6 Hz, 2H, Ar-H), 6.82 (d, J = 8.6 Hz, 2H, Ar-H), 3.79 (s, 3H, $-OCH_3$), 2.54 (t, J = 6.7 Hz, 2H, Ar-$CH_2$-), 1.62 - 1.53 (m, 2H, $-CH_2\underline{CH_2}$), 1.36 – 1.21 (m, 22H, $CH_2$), 0.88 (t, *J* = 6.8 Hz, 3H, $-CH_3$).

### *2.2.2. Synthesis of 4-n-tetradecylphenol* **5**

Under inert atmosphere a solution of 4-*n*-tetradecylanisole (3.3 g, 1 10.86 mmol) in 50 mL of $CH_2Cl_2$ is added at -78 °C to a solution of $BBr_3$ (2.4 mL, 24.96 mmol) and the reaction mixture was stirred overnight. The mixture is then shaken with water to hydrolyse excess reagent and boron complexes and the organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (50 mL × 3). The combined organic layer was washed with saturated NaCl (100 mL × 2), dried ($MgSO_4$), filtered and evaporated in vacuo. The resulting residue was chromatographed using $CH_2Cl_2$ as an eluent. Yield, 84%, m.p. 69 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.4 Hz, 2H, Ar-H), 6.74 (d, J = 8.4 Hz, 2H, Ar-H), 4.49 (s, 1H, -OH), 2.52 (t, J = 6.7 Hz, 2H, Ar-$CH_2$-), 1.61 - 1.50 (m, 2H, $-CH_2\underline{CH_2}$), 1.36 – 1.20 (m, 22H, $-CH_2-$), 0.88 (t, *J* = 6.8 Hz, 3H, $-CH_3$).

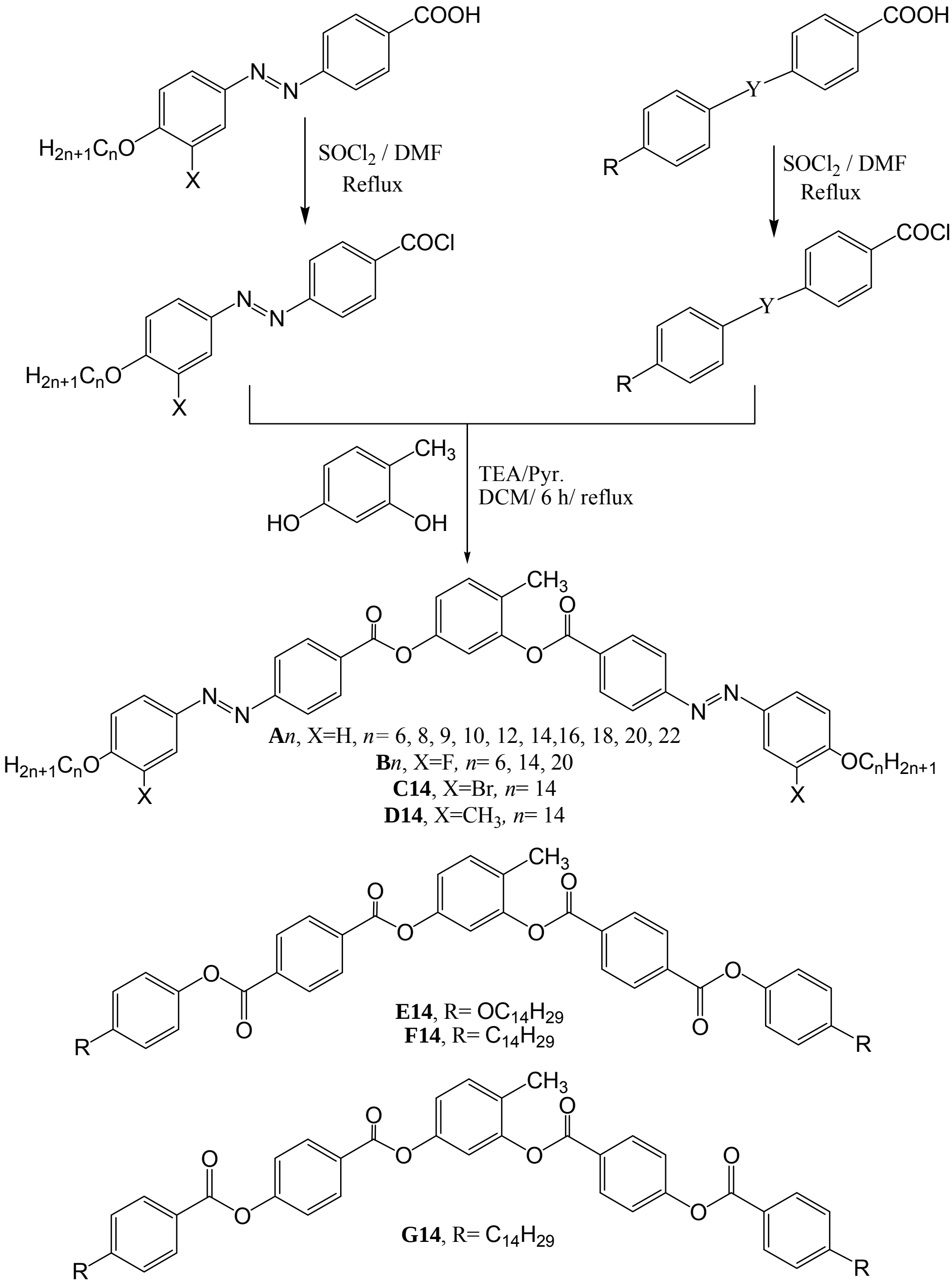
### *2.2.3. Synthesis of 4-(4-n-tetradecylphenoxycarbonyl)benzaldehyde* **6**

Prepared using the same method described for compound **2**. Yield, 93%, m.p. 89 °C. $^1$H-NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H, -CHO), 8.23 (d, J = 8.5 Hz, 2H, Ar-H), 7.89 (d, J = 8.5 Hz, 2H, Ar-H), 7.11 (d, J = 8.4 Hz, 2H, Ar-H), 7.00 (d, J = 8.4 Hz, 2H, Ar-H), 2.50 (t, J = 6.7 Hz, 2H, Ar-$CH_2$-), 1.55 - 1.46 (m, 2H, $-CH_2\underline{CH_2}$), 1.31 – 1.04 (m, 22H, $-CH_2-$), 0.75 (t, *J* = 6.8 Hz, 3H, $-CH_3$).

### *2.2.4. Synthesis of 4-(4-n-tetradecylphenoxycarbonyl)benzoic acid* **7**

Prepared using the same method described for compound **3**. Yield, 85%, m.p. 220 °C. $^1$H-NMR (400 MHz, DMSO-$d_6$) δ 8.20 (d, J = 8.0 Hz, 2H, Ar-H), 8.11 (d, J = 8.0 Hz, 2H, Ar-H), 7.26 (d, J = 7.3 Hz, 2H, Ar-H), 7.18 (d, J = 7.3 Hz, 2H, Ar-H), 2.58 (t, J = 6.7 Hz, 2H, Ar-$CH_2$-), 1.66 - 1.47 (m, 2H, $-CH_2\underline{CH_2}$), 1.38 – 1.04 (m, 22H, $-CH_2-$), 0.82 (t, *J* = 6.8 Hz, 3H, $-CH_3$).

## *2.3. Synthesis of the final bent-core molecules An-Gn*



**Scheme S3**

The synthesis of the final bent-core mesogens is shown in Scheme 1. The general procedure is as follows: 2.4 mmol of the correspondence acid was heated under reflux with thionyl chloride (3 ml) and a catalytic amount of *N,N*-dimethylformamide (DMF) for one hour. The excess of thionyl chloride was removed by distillation under reduced pressure. The acid chloride was then dissolved in dry dichloromethane (DCM, 20 ml). To this solution, 4-methylresorcinol (1.2 mmol) previously dissolved in DCM (10 ml) was added, followed by addition of triethylamine (TEA, 2.8 mmol) and a catalytic amount of pyridine. The solution was then refluxed for 6 hours under an argon atmosphere. After cooling the reaction mixture to the room temperature, it was washed with 10% HCl (2 × 50 mL) and several times with cold water then extracted with dichloromethane (3 × 50 mL) and finally dried over anhydrous sodium sulphate. The crude residue obtained after removal of solvent was chromatographed on silica gel using chloroform as eluent. The obtained material was then recrystallized twice from chloroform/ethanol mixture to give the final bent core compounds.

### *2.3.1. 4-Methyl-1,3-phenylene bis-[4-(4-n-hexyloxyphenylazo)benzoate]* **A6**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 8.30-8.36 (m, 4H, Ar-H), 8.03 – 7.87 (m, 8H, Ar-H), 7.36 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.18 (d, *J* = 2.3 Hz, 1H, Ar-H), 7.13 (dd, *J* = 8.3, *J* = 2.3 Hz, 1H, Ar-H), 7.02 (d, *J* = 8.7 Hz, 4H, Ar-H), 4.06 (t, *J* = 6.4 Hz, 4H, $-O\underline{CH_2}CH_2$), 2.28 (s, 3H, $CH_3$), 1.90 – 1.78 (m, 4H, $-OCH_2\underline{CH_2}$), 1.60 – 1.30 (m, 12H, $CH_2$), 0.92 (t, *J* = 7.0 Hz, 6H, $CH_3$). Elemental Analysis: Calc. for $\mathbf{C_{45}H_{48}N_4O_6}$ C, 72.95; H, 6.53; N, 7.56. Found C, 72.95; H, 6.70; N, 7.52 %.

### *2.3.2. 4-Methyl-1,3-phenylene bis-[4-(4-n-octyloxyphenylazo)benzoate]* **A8**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 8.30 - 8.35 (m, 4H, Ar-H), 8.04 – 7.90 (m, 8H, Ar-H), 7.36 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.18 (d, *J* = 2.3 Hz, 1H, Ar-H), 7.13 (dd, *J* = 8.2, 2.3 Hz, 1H, Ar-H), 7.02 (d, *J* = 8.3 Hz, 4H, Ar-H), 4.06 (t, *J* = 6.5 Hz, 4H, $-O\underline{CH_2}CH_2$), 2.29 (s, 3H, $CH_3$), 1.90 – 1.76 (m, 4H, $-OCH_2\underline{CH_2}$), 1.58 – 1.23 (m, 20 H, $CH_2$), 0.90 (t, *J* = 6.8 Hz, 6H, $CH_3$). Elemental Analysis: Calc. for $\mathbf{C_{49}H_{56}N_4O_6}$ C, 73.84; H, 7.08; N, 7.03. Found C, 73.83; H, 7.20; N, 7.00 %.

### *2.3.3. 4-Methyl-1,3-phenylene bis-[4-(4-n-nonyloxyphenylazo)benzoate]* **A9**

$^1$H-NMR (500 MHz, $CDCl_3$) δ 8.40 - 8.27 (m, 4H, Ar-H), 8.01 – 7.91 (m, 8H, Ar-H), 7.36 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.18 (d, *J* = 2.3 Hz, 1H, Ar-H), 7.13 (dd, *J* = 8.3, 2.4 Hz, 1H, Ar-H), 7.02 (d, *J* = 7.8 Hz, 4H, Ar-H), 4.06 (t, *J* = 6.5 Hz, 4H, $-O\underline{CH_2}CH_2$), 2.29 (s, 3H, $CH_3$), 1.90 – 1.77 (m, 4H, $-OCH_2\underline{CH_2}$), 1.60 – 1.19 (m, 24 H, $CH_2$), 0.89 (t, *J* = 6.9 Hz, 6H, $CH_3$). Elemental Analysis: Calc. for $\mathbf{C_{51}H_{60}N_4O_6}$ C, 74.24; H, 7.33; N, 6.79. Found C, 74.27; H, 7.30; N, 6.77 %.

### *2.3.4. 4-Methyl-1,3-phenylene bis-[4-(4-n-decyloxyphenylazo)benzoate]* **A10**

$^1$H-NMR (400 MHz, $CDCl_3$) δ 8.40 - 8.27 (m, 4H, Ar-H), 8.03 – 7.92 (m, 8H, Ar-H), 7.36 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.18 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.14 (dd, *J* = 8.4, 2.2 Hz, 1H, Ar-H), 7.01 (d, *J* = 7.8 Hz, 4H, Ar-H), 4.06 (t, *J* = 6.5 Hz, 4H, $-O\underline{CH_2}CH_2$), 2.30 (s, 3H, $CH_3$), 1.91 – 1.76 (m, 4H, $-OCH_2\underline{CH_2}$), 1.61 – 1.20 (m, 28 H, $CH_2$), 0.89 (t, *J* = 6.7 Hz, 6H, $CH_3$). Elemental Analysis: Calc. for $\mathbf{C_{53}H_{64}N_4O_6}$ C, 74.62; H, 7.56; N, 6.57. Found C, 74.58; H, 7.60; N, 6.66 %.

### *2.3.5. 4-Methyl-1,3-phenylene bis-[4-(4-n-dodecyloxyphenylazo)benzoate]* **A12**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.39 - 8.28 (m, 4H, Ar-H), 8.03 – 7.91 (m, 8H, Ar-H), 7.35 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.18 (d, $J$ = 2.2 Hz, 1H, Ar-H), 7.13 (dd, $J$ = 8.4, 2.2 Hz, 1H, Ar-H), 7.02 (d, $J$ = 7.8 Hz, 4H, Ar-H), 4.06 (t, $J$ = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.31 (s, 3H, CH$_3$), 1.90 – 1.75 (m, 4H, -OCH$_2\underline{CH_2}$), 1.58 – 1.21 (m, 36 H, CH$_2$), 0.89 (t, $J$ = 6.7 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{57}H_{72}N_4O_6$** C, 75.30; H, 7.98; N, 6.16. Found C, 75.28; H, 8.02; N, 6.23 %.

### *2.3.6. 4-Methyl-1,3-phenylene bis-[4-(4-n-tetradecyloxyphenylazo)benzoate]* **A14**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.40 - 8.28 (m, 4H, Ar-H), 8.02 – 7.92 (m, 8H, Ar-H), 7.35 (d, $J$ = 8.5 Hz, 1H, Ar-H), 7.18 (d, $J$ = 2.2 Hz, 1H, Ar-H), 7.13 (dd, $J$ = 8.2, 2.3 Hz, 1H, Ar-H), 7.02 (d, $J$ = 7.8 Hz, 4H, Ar-H), 4.06 (t, $J$ = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.29 (s, 3H, CH$_3$), 1.89 – 1.77 (m, 4H, -OCH$_2\underline{CH_2}$), 1.55 – 1.19 (m, 44 H, CH$_2$), 0.88 (t, $J$ = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{61}H_{80}N_4O_6$** C, 75.90; H, 8.35; N, 5.80. Found C, 75.85; H, 8.40; N, 5.78 %.

### *2.3.7. 4-Methyl-1,3-phenylene bis-[4-(4-n-hexadecyloxyphenylazo)benzoate]* **A16**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.45 - 8.21 (m, 4H, Ar-H), 8.08 – 7.85 (m, 8H, Ar-H), 7.36 (d, $J$ = 8.5 Hz, 1H, Ar-H), 7.18 (d, $J$ = 2.2 Hz, 1H, Ar-H), 7.13 (dd, $J$ = 8.3, 2.3 Hz, 1H, Ar-H), 7.02 (d, $J$ = 7.8 Hz, 4H, Ar-H), 4.06 (t, $J$ = 6.3 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.27 (s, 3H, CH$_3$), 1.96 – 1.68 (m, 4H, -OCH$_2\underline{CH_2}$), 1.65 – 1.08 (m, 52 H, CH$_2$), 0.88 (t, $J$ = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{65}H_{88}N_4O_6$** C, 76.43; H, 8.68; N, 5.49. Found C, 76.50; H, 8.76; N, 5.44 %.

### *2.3.8. 4-Methyl-1,3-phenylene bis-[4-(4-n-octadecyloxyphenylazo)benzoate]* **A18**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.44 - 8.25 (m, 4H, Ar-H), 8.07 – 7.87 (m, 8H, Ar-H), 7.36 (d, $J$ = 8.5 Hz, 1H, Ar-H), 7.19 (d, $J$ = 2.2 Hz, 1H, Ar-H), 7.13 (dd, $J$ = 8.2, 2.3 Hz, 1H, Ar-H), 7.02 (d, $J$ = 7.8 Hz, 4H, Ar-H), 4.06 (t, $J$ = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.27 (s, 3H, CH$_3$), 1.95 – 1.73 (m, 4H, -OCH$_2\underline{CH_2}$), 1.63 – 1.13 (m, 60 H, CH$_2$), 0.88 (t, $J$ = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{69}H_{96}N_4O_6$** C, 76.91; H, 8.98; N, 5.20. Found C, 76.84; H, 8.99; N, 5.29 %.

### *2.3.9. 4-Methyl-1,3-phenylene bis-[4-(4-n-eicosyloxyphenylazo)benzoate]* **A20**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.39 - 8.28 (m, 4H, Ar-H), 8.02 – 7.92 (m, 8H, Ar-H), 7.36 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.18 (d, $J$ = 2.2 Hz, 1H, Ar-H), 7.14 (dd, $J$ = 8.3, 2.3 Hz, 1H, Ar-H), 7.02 (d, $J$ = 7.6 Hz, 4H, Ar-H), 4.06 (t, $J$ = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.29 (s, 3H, CH$_3$), 1.92 – 1.76 (m, 4H, -OCH$_2\underline{CH_2}$), 1.58 – 1.18 (m, 68 H, CH$_2$), 0.88 (t, $J$ = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for **$C_{73}H_{104}N_4O_6$** C, 77.34; H, 9.25; N, 4.94. Found C, 77.37; H, 9.21; N, 4.92 %.

### *2.3.10. 4-Methyl-1,3-phenylene bis-[4-(4-n-docosyloxyphenylazo)benzoate]* **A22**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.40 - 8.27 (m, 4H, Ar-H), 8.08 – 7.91 (m, 8H, Ar-H), 7.36 (d, $J$ = 8.4 Hz, 1H, Ar-H), 7.18 (d, $J$ = 2.2 Hz, 1H, Ar-H), 7.13 (dd, $J$ = 8.3, 2.3 Hz, 1H, Ar-H), 7.02 (d, *J* = 7.6 Hz, 4H, Ar-H), 4.06 (t, *J* = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.3 (s, 3H, CH$_3$), 1.97 – 1.79 (m, 4H, -OCH$_2$$\underline{CH_2}$), 1.59 – 1.20 (m, 76 H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{77}H_{112}N_4O_6}$ C, 77.73; H, 9.49; N, 4.71. Found C, 77.43; H, 9.44; N, 4.68 %.

### *2.3.11. 4-Methyl-1,3-phenylene bis-[4-(3-fluoro-4-n-hexyloxyphenylazo)benzoate]* **B6**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.40 - 8.28 (m, 4H, Ar-H), 8.04 – 7.92 (m, 4H, Ar-H), 7.82 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.74 (dd, *J* = 12.0 Hz, 2.3 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.3, 1H, Ar-H), 7.19 (d, *J* = 2.3 Hz, 1H, Ar-H), 7.16 – 7.06 (m, 3H, Ar-H), 4.14 (t, *J* = 6.6 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.30 (s, 3H, CH$_3$), 1.94 – 1.82 (m, 4H, -OCH$_2$$\underline{CH_2}$), 1.59 – 1.29 (m, 12 H, CH$_2$), 0.92 (t, *J* = 7.0 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{45}H_{46}F_2N_4O_6}$ C, 69.57; H, 5.97; N, 7.21. Found C, 69.55; H, 5.98; N, 7.17 %.

### *2.3.12. 4-Methyl-1,3-phenylene bis-[4-(3-fluoro-4-n-tetradecyloxyphenylazo)-benzoate]* **B14**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.40 - 8.28 (m, 4H, Ar-H), 8.04 – 7.93 (m, 4H, Ar-H), 7.82 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.74 (dd, *J* = 11.9 Hz, 2.5 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.5, 1H, Ar-H), 7.18 (d, *J* = 2.3, 1H, Ar-H), 7.16 – 7.04 (m, 3H, Ar-H), 4.14 (t, *J* = 6.4 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.29 (s, 3H, CH$_3$), 1.95 – 1.80 (m, 4H, -OCH$_2$$\underline{CH_2}$), 1.59 – 1.19 (m, 44 H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{61}H_{78}F_2N_4O_6}$ C, 73.17; H, 7.85; N, 5.60. Found C, 73.10; H, 7.84; N, 5.61 %.

### *2.3.13. 4-Methyl-1,3-phenylene bis-[4-(3-fluoro-4-n-eicosyloxyphenylazo)benzoate]* **B20**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.40 - 8.28 (m, 4H, Ar-H), 8.04 – 7.93 (m, 4H, Ar-H), 7.82 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.73 (dd, *J* = 11.9 Hz, 2.5 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.5, 1H, Ar-H), 7.18 (d, *J* = 2.2, 1H, Ar-H), 7.16 – 7.05 (m, 3H, Ar-H), 4.14 (t, *J* = 6.5 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.30 (s, 3H, CH$_3$), 1.95 – 1.81 (m, 4H, -OCH$_2$$\underline{CH_2}$), 1.61 – 1.17 (m, 44 H, CH$_2$), 0.88 (t, *J* = 6.8 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{73}H_{102}F_2N_4O_6}$ C, 74.96; H, 8.79; N, 4.79. Found C, 74.98; H, 8.77; N, 4.80 %.

### *2.3.14. 4-Methyl-1,3-phenylene bis-[4-(3-bromo-4-n-tetradecyloxyphenylazo)-benzoate]* **C14**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.41 - 8.29 (m, 4H, Ar-H), 8.23 (s, 2H), 8.03 – 7.90 (m, 6H, Ar-H), 7.36 (d, *J* = 8.3 Hz, 1H, Ar-H), 7.18 (s, 1H, Ar-H), 7.13 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.02 (d, *J* = 8.7, 2H, Ar-H), 4.13 (t, *J* = 6.3 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.28 (s, 3H, CH$_3$), 1.97 – 1.82 (m, 4H, -OCH$_2$$\underline{CH_2}$), 1.62 – 1.18 (m, 44 H, CH$_2$), 0.88 (t, *J* = 6.6 Hz, 6H, CH$_3$). Elemental Analysis: Calc. for $\mathbf{C_{61}H_{78}Br_2N_4O_6}$ C, 65.23; H, 7.00; N, 4.99. Found C, 65.20; H, 6.97; N, 5.03 %.

### *2.3.15. 4-Methyl-1,3-phenylene bis-[4-(3-methyl-4-n-tetradecyloxyphenylazo)-benzoate]* **D14**

$^1$H-NMR (400 MHz, CDCl$_3$) δ 8.39 - 8.27 (m, 4H, Ar-H), 8.01- 7.91 (m, 4H, Ar-H), 7.88 – 7.78 (m, 4H, Ar-H), 7.35 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.18 (s, 1H, Ar-H), 7.13 (d, *J* = 8.3 Hz, 1H, Ar-H), 6.94 (d, *J* = 7.8, 2H, Ar-H), 4.07 (t, *J* = 6.1 Hz, 4H, -O$\underline{CH_2}$CH$_2$), 2.37- 2.25 (m, 9H, CH$_3$), 1.91 – 1.77 (m, 4H, -OCH$_2$$\underline{CH_2}$), 1.60 – 1.17 (m, 44 H, CH$_2$), 0.88 (t, *J* = 6.6 Hz, 6H, CH$_3$).

Elemental Analysis: Calc. for $\mathbf{C_{63}H_{84}N_4O_6}$ C, 76.17; H, 8.52; N, 5.64. Found C, 76.20; H, 8.60; N, 5.61 %.

*2.3.16. 4-Methyl-1,3-phenylene bis-[4-(4'-n-tetradecyloxyphenoxy)carbonyl benzoate]* **E14**

$^1$H-NMR (400 MHz, $\mathrm{CDCl_3}$) δ 8.40 - 8.25 (m, 8H, Ar-H), 7.37 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.20 (d, *J* = 2.3 Hz, 1H, Ar-H), 7.18 – 7.10 (m, 5H, Ar-H), 6.99 – 6.89 (m, 4H, Ar-H), 3.97 (t, *J* = 6.5 Hz, 4H, $\text{-O}\underline{\text{CH}_2}\text{CH}_2$), 2.29 (s, 3H, $\mathrm{CH_3}$), 1.87 – 1.72 (m, 4H, $\text{-OCH}_2\underline{\text{CH}_2}$), 1.58 – 1.14 (m, 44 H, $\mathrm{CH_2}$), 0.88 (t, *J* = 6.8 Hz, 6H, $\mathrm{CH_3}$). Elemental Analysis: Calc. for $\mathbf{C_{63}H_{80}O_{10}}$ C, 75.87; H, 8.09. Found C, 75.85; H, 8.11 %.

*2.3.17. 4-Methyl-1,3-phenylene bis-[4-(4'-n-tetradecylphenoxy)carbonyl benzoate]* **F14**

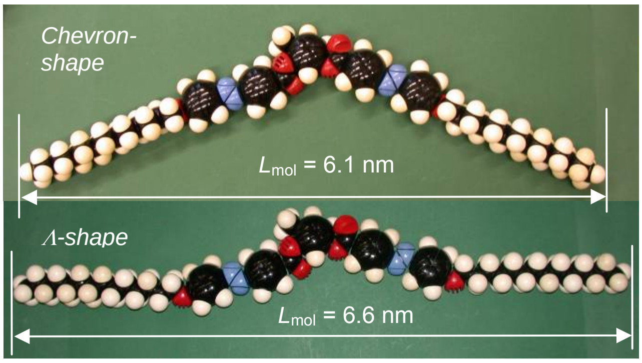
$^1$H-NMR (400 MHz, $\mathrm{CDCl_3}$) δ 8.46 - 8.11 (m, 8H, Ar-H), 7.38 (d, *J* = 8.6, 1H, Ar-H), 7.24 – 7.06 (m, 10H, Ar-H), 2.63 (t, *J* = 7.8 Hz, 4H, $\text{-}\underline{\text{CH}_2}\text{CH}_2$), 2.29 (s, 3H, $\mathrm{CH_3}$), 1.75 – 1.13 (m, 48H, $\mathrm{CH_2}$), 0.88 (t, *J* = 6.8 Hz, 6H, $\mathrm{CH_3}$). Elemental Analysis: Calc. for $\mathbf{C_{63}H_{80}O_8}$ C, 78.39; H, 8.35. Found C, 78.43; H, 8.37 %.

*2.3.18. 4-Methyl-1,3-phenylene bis-[4-(4'-n-tetradecylbenzoyloxy)benzoyl benzoate]* **G14**

$^1$H-NMR (400 MHz, $\mathrm{CDCl_3}$) δ 8.34 - 8.24 (m, 4H, Ar-H), 8.12 (dd, *J* = 8.2, 2.5 Hz, 4H, Ar-H), 7.42 – 7.30 (m, 9H, Ar-H), 7.16 – 7.08 (m, 2H, Ar-H), 2.71 (t, *J* = 7.6 Hz, 4H, $\text{-}\underline{\text{CH}_2}\text{CH}_2$), 2.27 (s, 3H, $\mathrm{CH_3}$), 1.73 – 1.58 (m, 4H, $\text{CH}_2\underline{\text{CH}_2}$), 1.42 – 1.18 (m, 44 H, $\mathrm{CH_2}$), 0.88 (t, *J* = 6.8 Hz, 6H, $\mathrm{CH_3}$). Elemental Analysis: Calc. for $\mathbf{C_{63}H_{80}O_8}$ C, 78.39; H, 8.35. Found C, 78.44; H, 8.35 %.

## 3. Supporting data

### 3.1. Determination of the molecular length



| Comp. | $L_{\mathrm{mol}}$(<) | $L_{\mathrm{mol}}$(Λ) |
|---|---|---|
| **A6** | 4.3 | 4.5 |
| **A8** | 4.7 | 5.1 |
| **A10** | 5.1 | 5.7 |
| **A12** | 5.6 | 6.2 |
| **A14** | 6.1 | 6.6 |
| **A16** | 6.5 | 7.0 |
| **A18** | 6.9 | 7.6 |
| **A20** | 7.2 | 8.2 |

**Fig. S1**. CPK-models showing the chevron shaped (top) and Λ-shaped (bottom) conformers used for determination of the molecular lengths for compound **A14** as an example; the values for the other compounds **A*n*** are collated in the table at the right.

### *3.2. Additional textures*

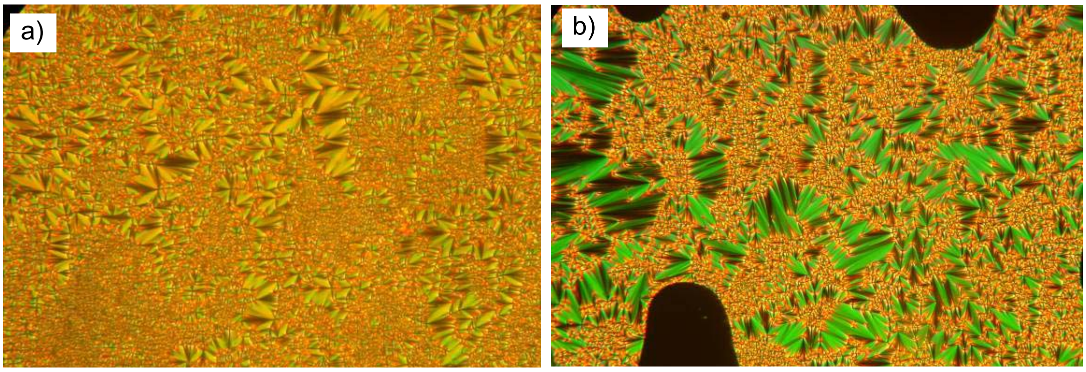


**Fig. S2.** Textures as observed immediately after shearing the $B_6$ phase of **A6** (the texture before mechanical shearing is shown in Figure 1a) at *T* = 120 °C.

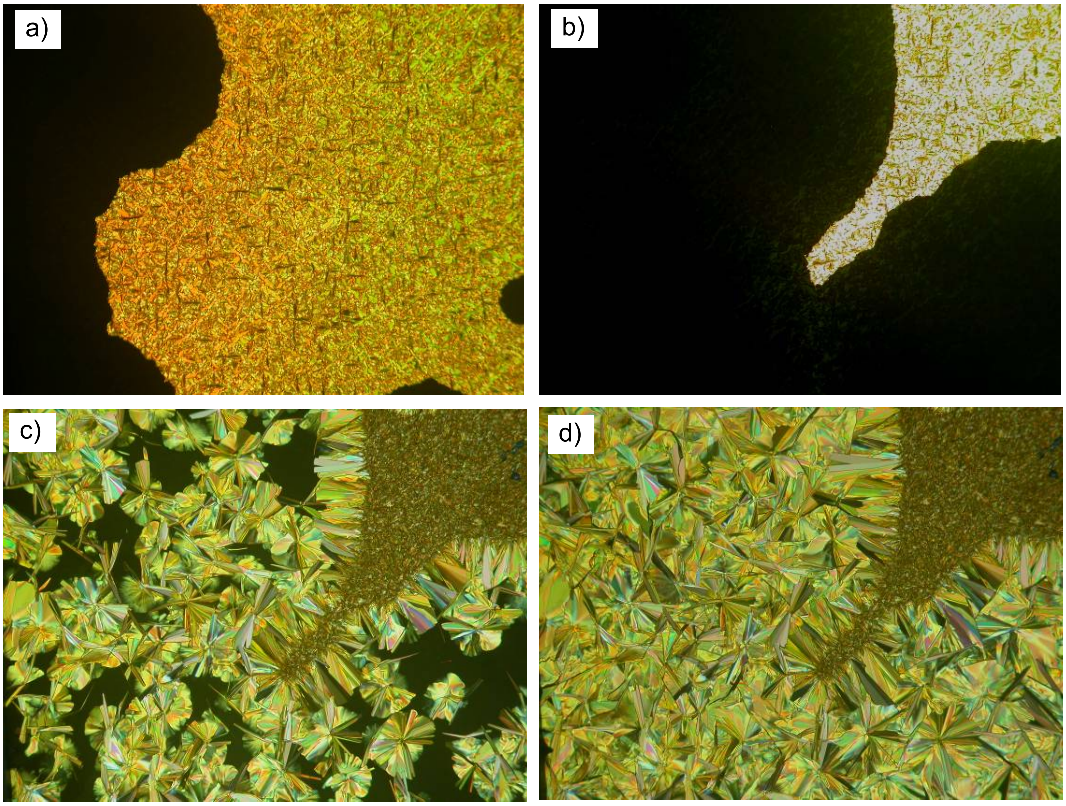


**Fig. S3.** Textures as observed on cooling **A9** between crossed polarizers. a) $B_6$-DC transition at *T* = 84 °C, b) at *T* = 83 °C; c) slow crystallization of the DC phase at *T* = 67 °C and d) fully crystallized sample at *T* = 59 °C (see also Fig. 3).

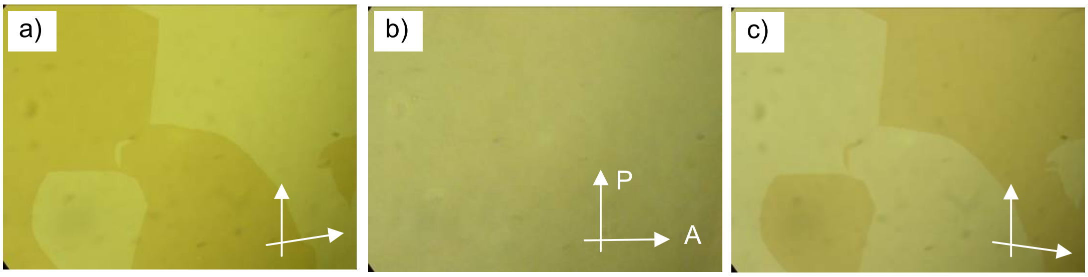


**Fig. S4.** Textures of the DC phase of compound **A**14 at *T* = 70 °C: b) between crossed polarizers and a) after rotating one polarizer by 8° from the crossed position in clockwise direction and c) in anticlockwise direction, indicating a conglomerate of dark and bright domains with opposite chirality sense.

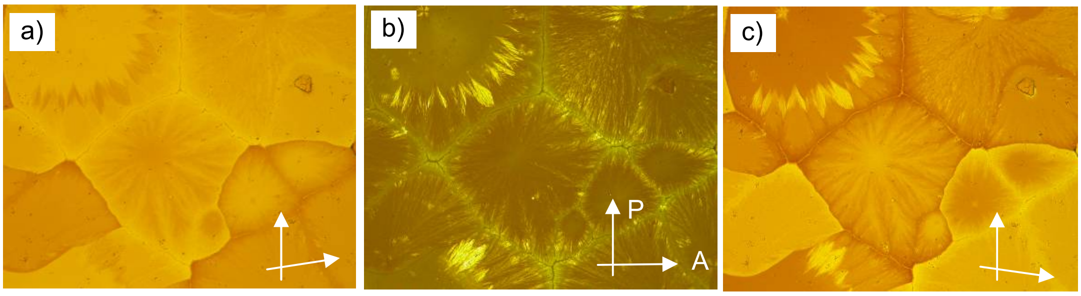


**Fig. S5.** Textures of the crystalline phase of compound **A22** at *T* = 88 °C, b) between crossed polarizers and a) after rotating one polarizer by 8° from the crossed position in anticlockwise direction and c) in clockwise direction, indicating the chirality of the crystalline phase.

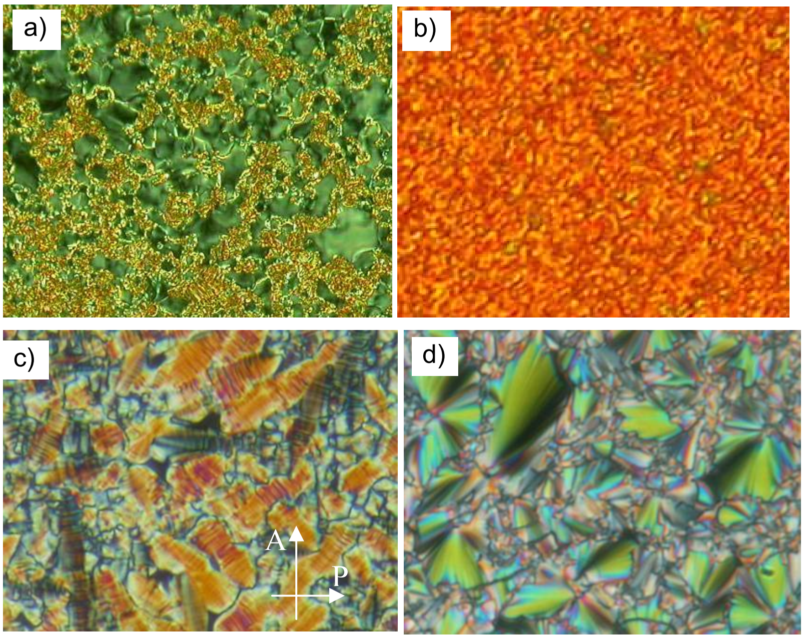


**Fig. S6**. a) Textures a) of the SmC$_a$P$_A$ phase of compound **B14** on cooling at *T* = 80°C, b) of the SmC phase of compound **D14** on cooling at *T* = 25 °C and of the modulated smectic phases of c) compound **E14** at *T* = 120 °C and d) compound **G14** at *T* = 79 °C.

### *3.3. Additional DSC traces*

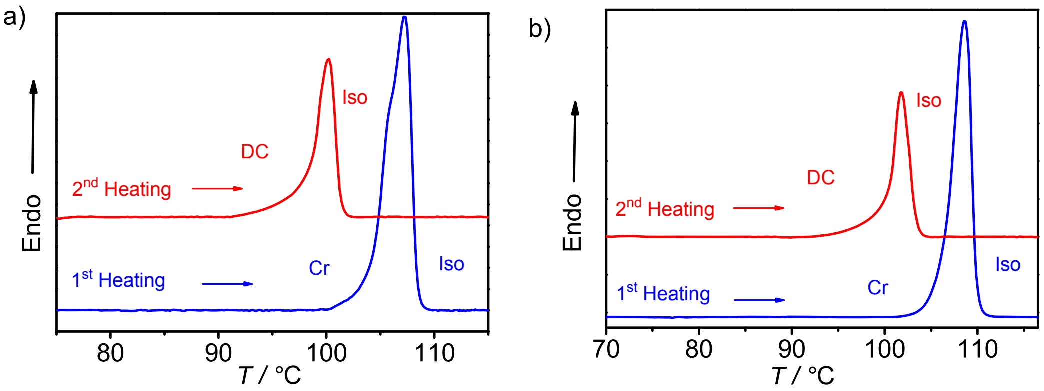


**Fig. S7.** First and second DSC heating traces of compounds a) **A10** and b) **A12** at 10 K min$^{-1}$.

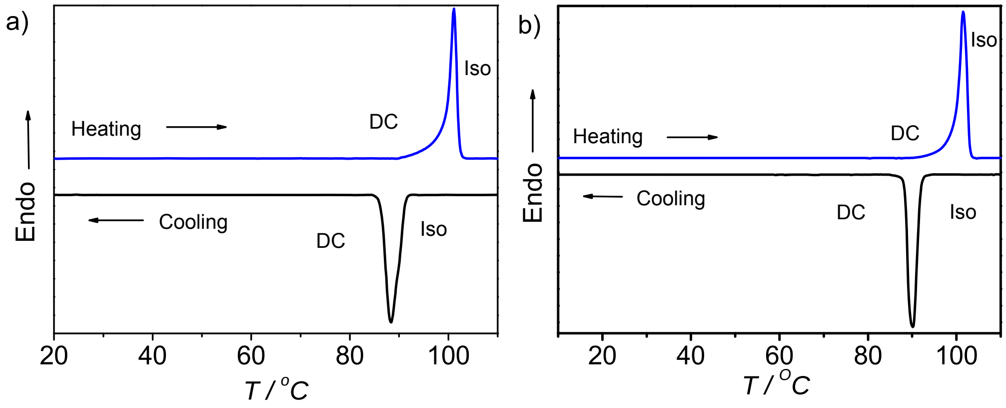


**Fig. S8.** DSC heating and cooling curves of compounds a) **A14** and b) **A16** at10 K min$^{-1}$.

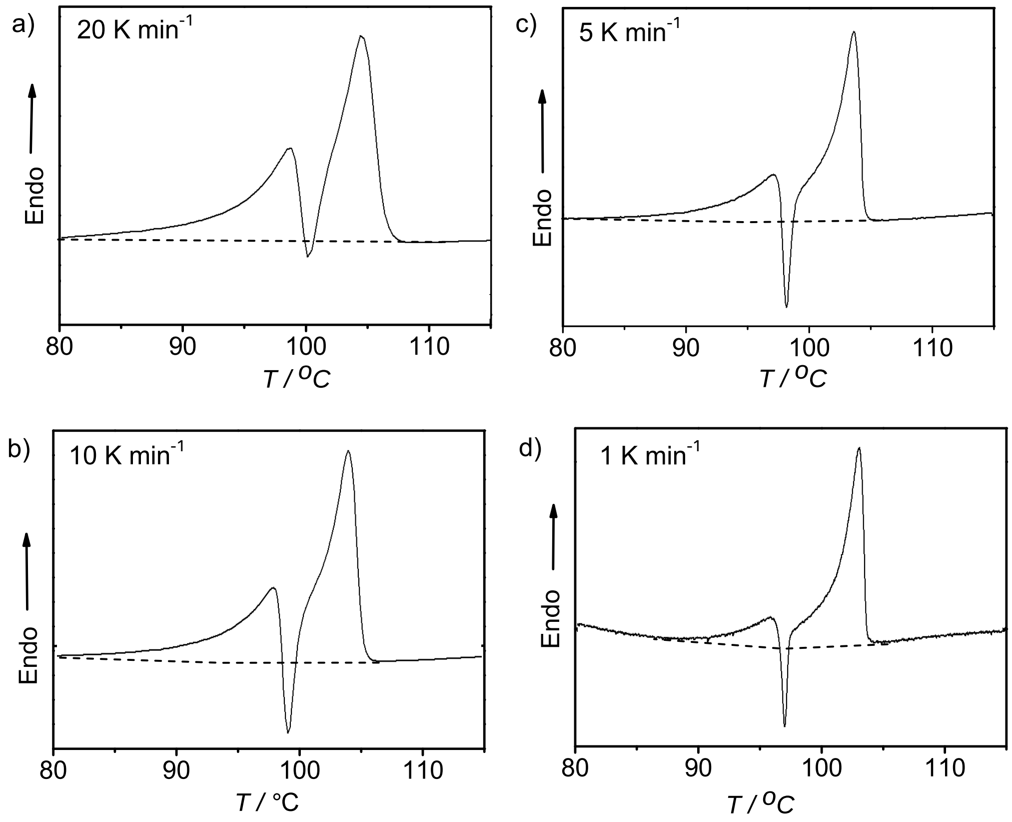


**Fig. S9.** DSC heating curves of compound **A20** at different heating rates, all curves were recorded after cooling with 10 K min$^{-1}$.

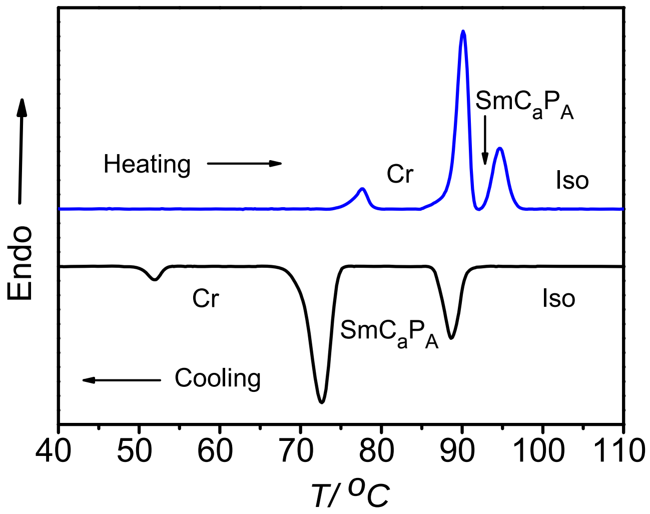


**Fig. S10.** DSC Heating and cooling traces of compound **B14** at 10 K min$^{-1}$.

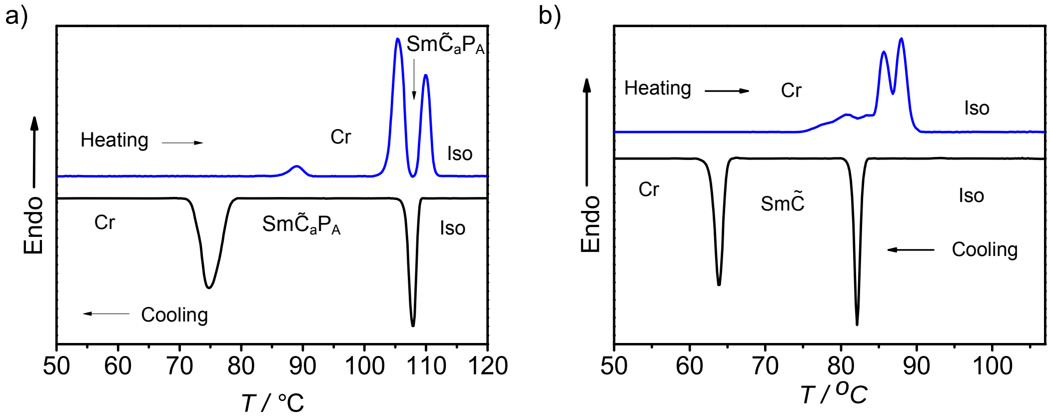
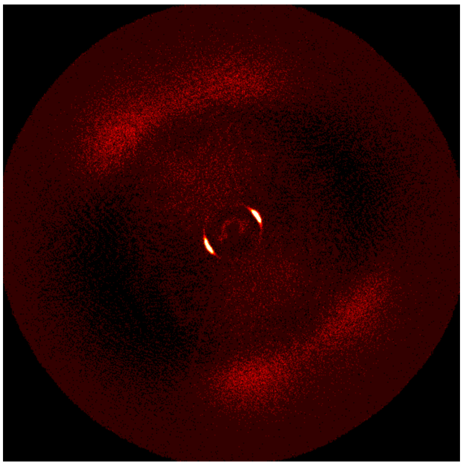


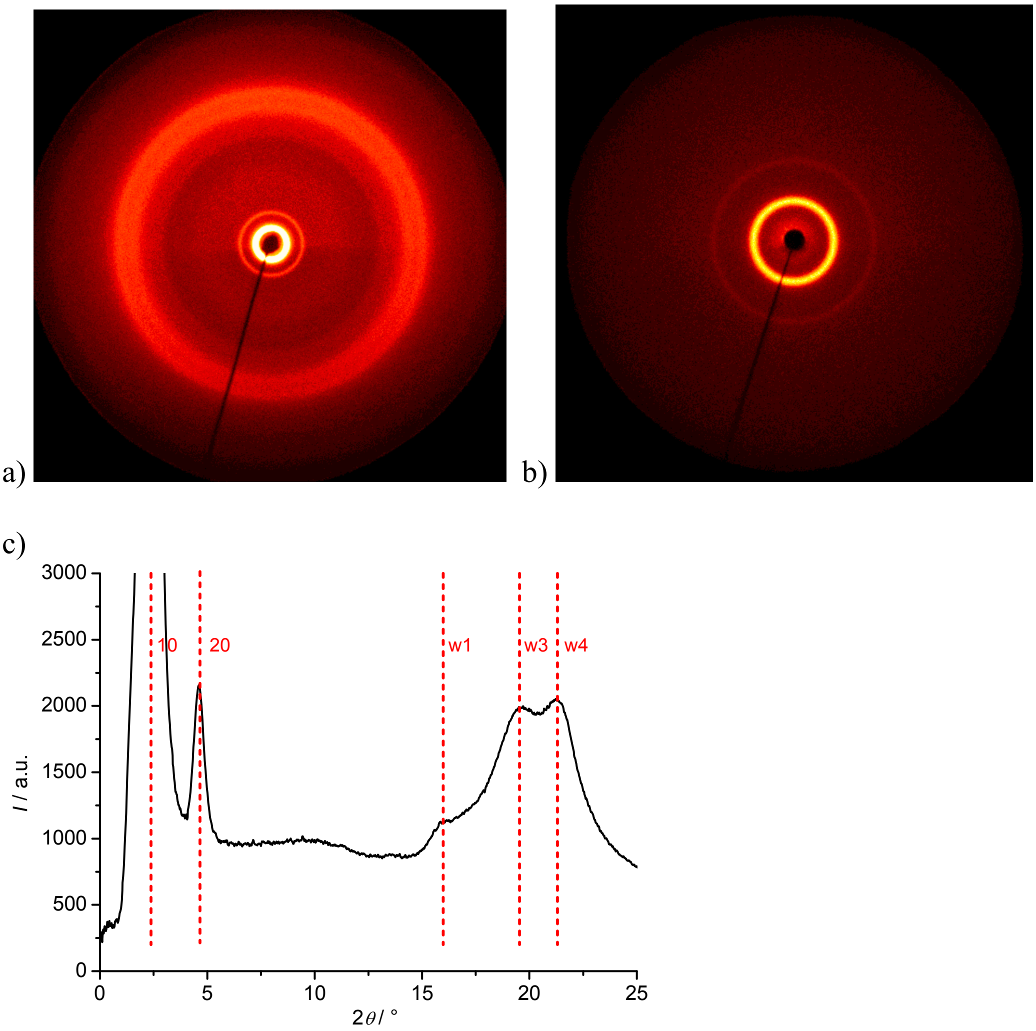
**Fig. S11**. DSC Heating and cooling traces of compounds a) **F14** and b) **G14** at 10 K min$^{-1}$.

## *3.4. Additional XRD Data*



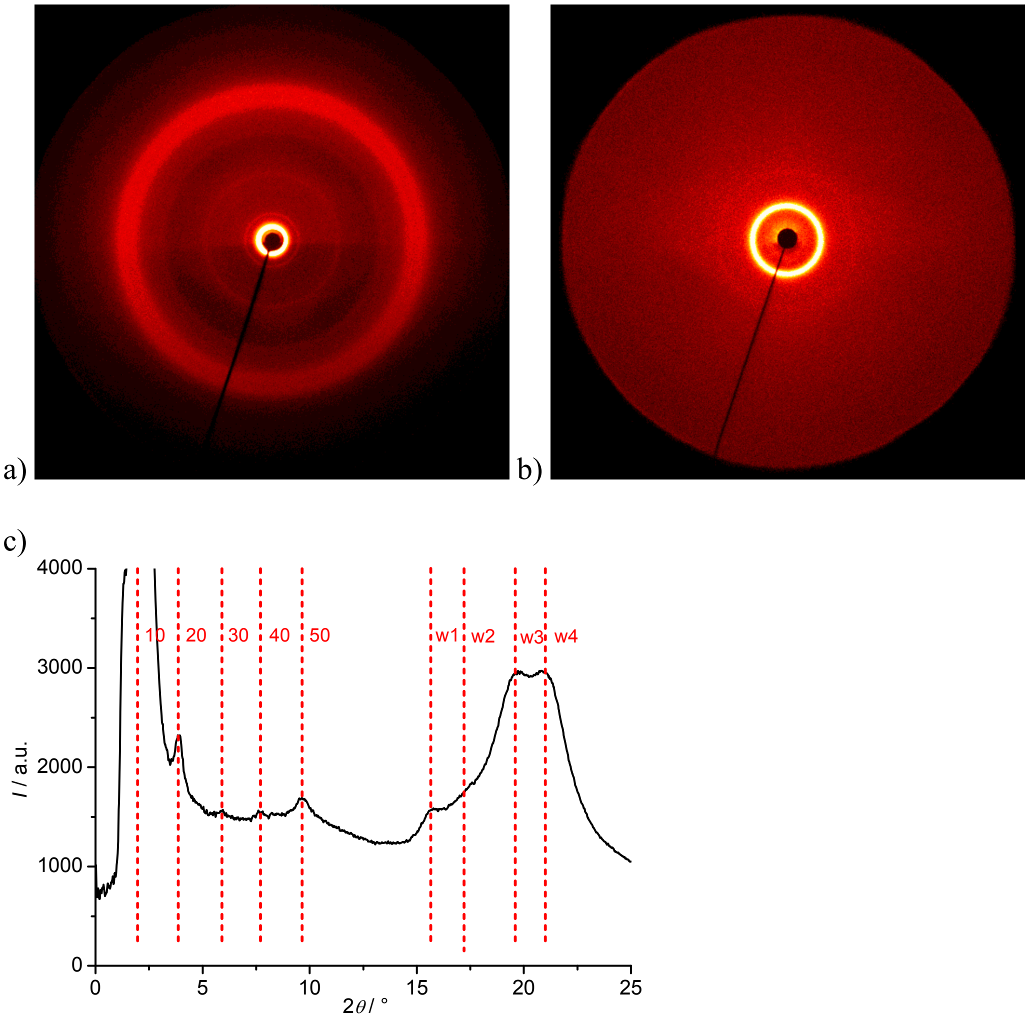
a)

**Fig. S12.** XRD investigations of the LC phase of **A6** at 80 °C: diffraction pattern after subtraction of the scattering in the isotropic liquid phase at 140 °C.



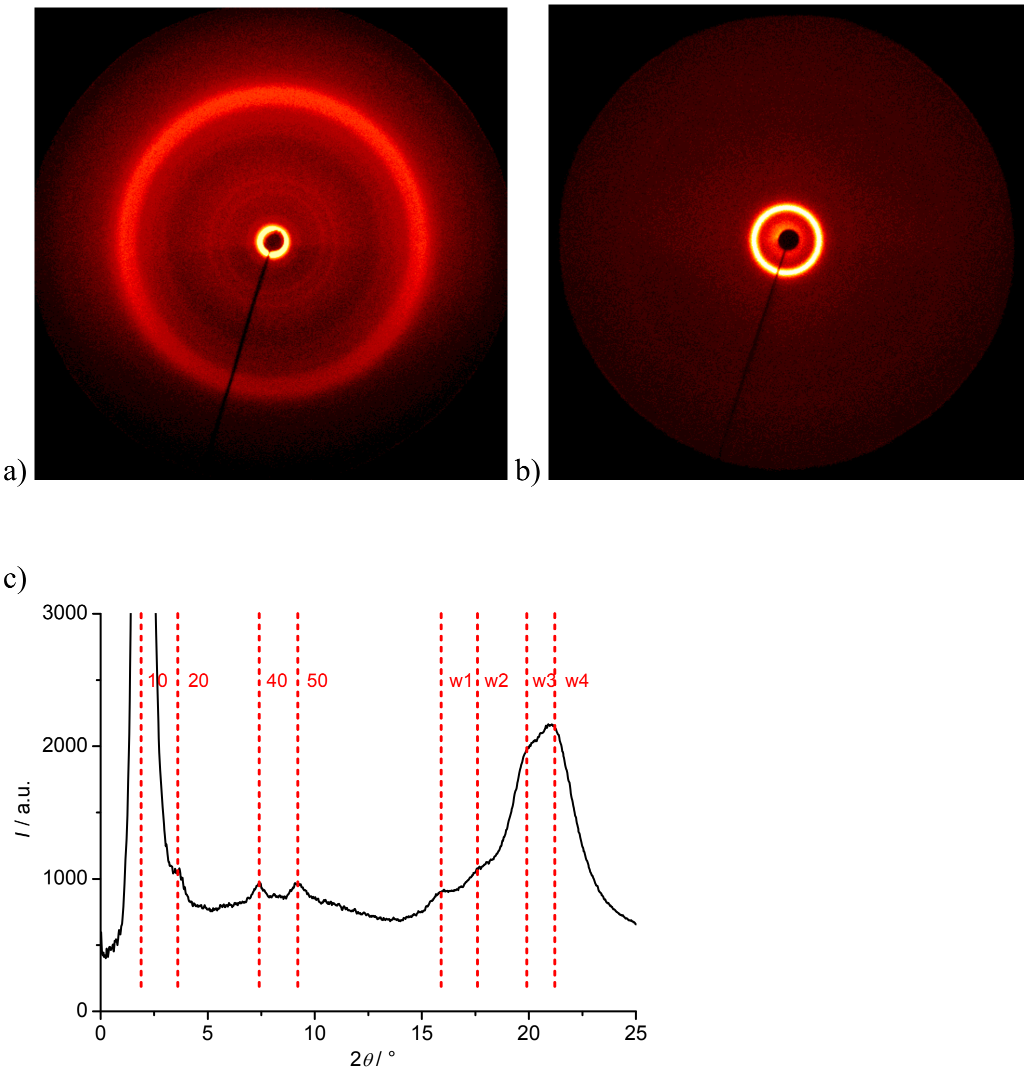
| reflex | 2$\theta$/° | $d$/nm | $d_{calc}$ | $d_{obs}$-$d_{calc}$ |
|---|---|---|---|---|
| 10 | 2.29 | 3.85 | | |
| 20 | 4.56 | 1.94 | 1.93 | 0.01 |
| w1 | 16.21 | 0.55 | | |
| w3 | 19.46 | 0.46 | | |
| w4 | 21.45 | 0.41 | | |

**Fig. S13.** XRD investigations of the DC phase of **A10** at 85 °C: a) wide angle, b) small angle scattering and c) diffraction intensity profile as a function of 2$\theta$ with the visible reflections.



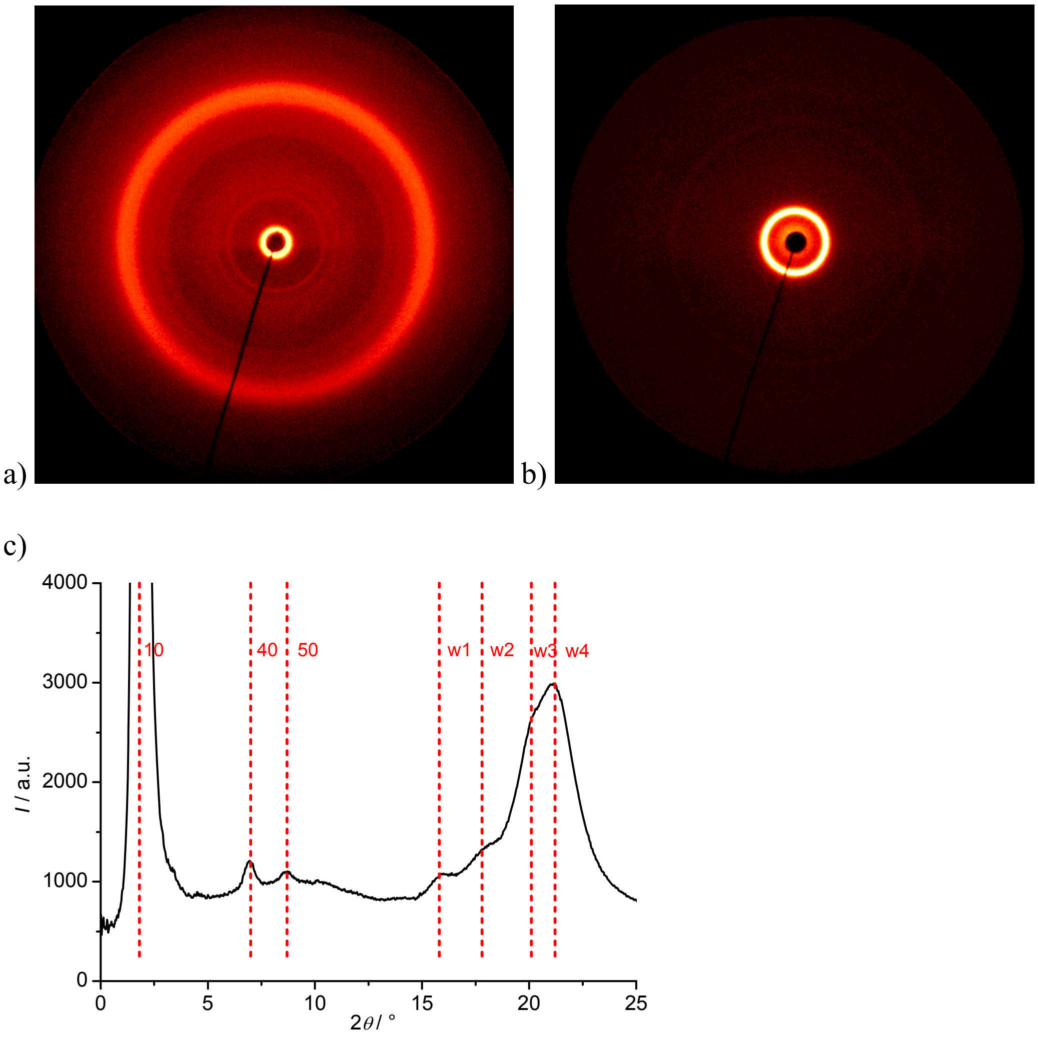
| reflex | $2\theta$/° | $d$/nm | $d_{calc}$ | $d_{obs}$-$d_{calc}$ |
|---|---|---|---|---|
| 10 | 1.96 | 4.51 | | |
| 20 | 3.85 | 2.29 | 2.26 | 0.03 |
| 30 | 5.87 | 1.51 | 1.50 | 0.01 |
| 40 | 7.70 | 1.15 | 1.13 | 0.02 |
| 50 | 9.65 | 0.92 | 0.90 | 0.02 |
| w1 | 15.65 | 0.57 | | |
| w2 | 17.17 | 0.52 | | |
| w3 | 19.50 | 0.46 | | |
| w4 | 21.17 | 0.42 | | |

**Fig. S14.** XRD investigations of the DC phase of **A14** at 90 °C: a) wide angle, b) small angle scattering and c) diffraction intensity profile as a function of $2\theta$ with the visible reflections.



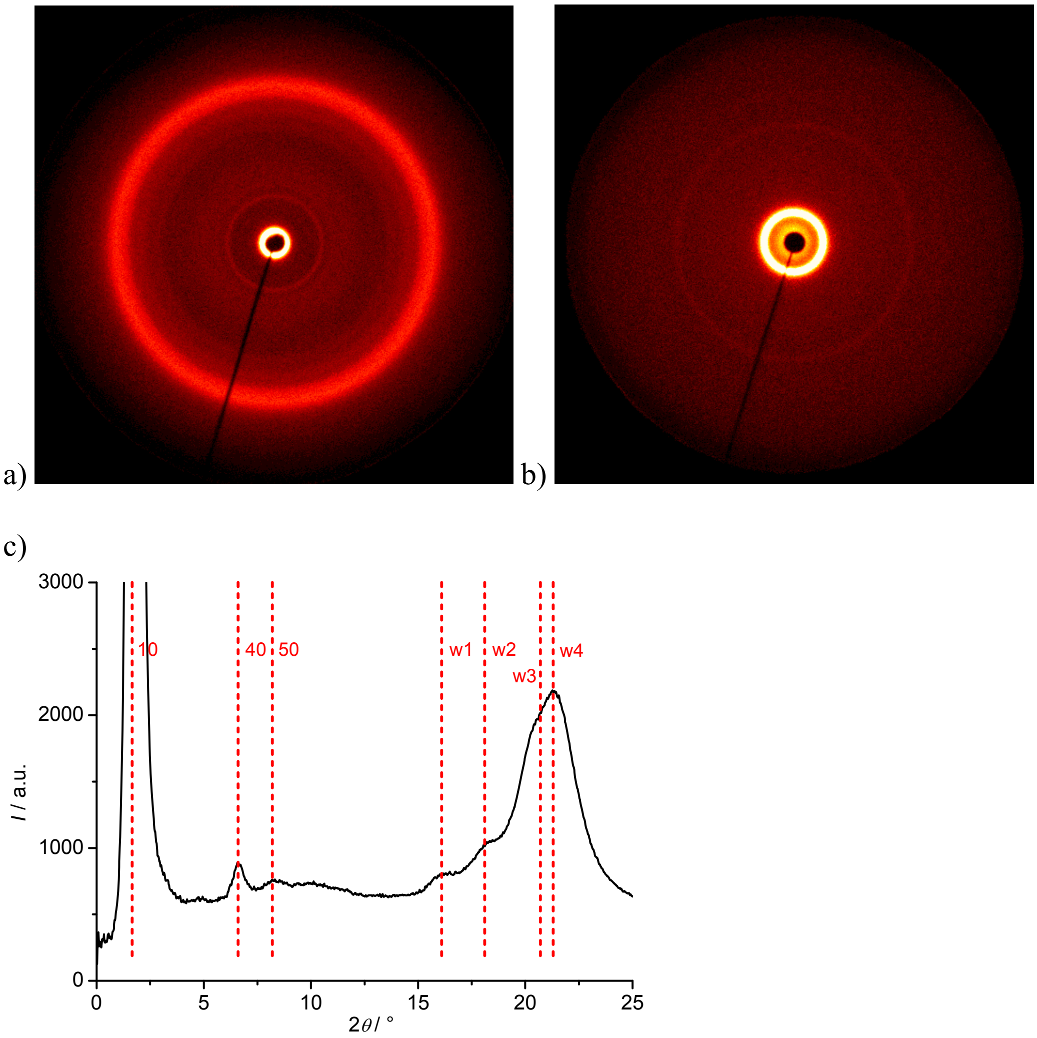
| reflex | $2\theta$/° | $d$/nm | $d_{calc}$ | $d_{obs}$-$d_{calc}$ |
|---|---|---|---|---|
| 10 | 1.86 | 4.74 | | |
| 20 | 3.60 | 2.46 | 2.37 | 0.09 |
| 40 | 7.39 | 1.20 | 1.18 | 0.02 |
| 50 | 9.21 | 0.96 | 0.95 | 0.01 |
| w1 | 15.90 | 0.56 | | |
| w2 | 17.65 | 0.50 | | |
| w3 | 19.81 | 0.45 | | |
| w4 | 21.22 | 0.42 | | |

**Fig. S15.** XRD investigations of the DC phase of **A16** at 85 °C: a) wide angle, b) small angle scattering and c) diffraction intensity profile as a function of $2\theta$ with the visible reflections.



| reflex | $2\theta$/° | $d$/nm | $d_{calc}$ | $d_{obs}$-$d_{calc}$ |
|---|---|---|---|---|
| 10 | 1.75 | 5.05 | | |
| 40 | 6.97 | 1.27 | 1.26 | 0.01 |
| 50 | 8.68 | 1.02 | 1.01 | 0.01 |
| w1 | 15.87 | 0.56 | | |
| w2 | 17.82 | 0.50 | | |
| w3 | 20.03 | 0.44 | | |
| w4 | 21.28 | 0.42 | | |

**Fig. S16.** XRD investigations of the DC phase of **A18** at 85 °C: a) wide angle, b) small angle scattering and c) diffraction intensity profile as a function of $2\theta$ with the visible reflections.



| reflex | $2\theta$/° | $d$/nm | $d_{calc}$ | $d_{obs}$-$d_{calc}$ |
|---|---|---|---|---|
| 10 | 1.66 | 5.32 | | |
| 40 | 6.53 | 1.35 | 1.33 | 0.02 |
| 50 | 8.15 | 1.09 | 1.06 | 0.03 |
| w1 | 16.10 | 0.55 | | |
| w2 | 18.17 | 0.49 | | |
| w3 | 20.70 | 0.43 | | |
| w4 | 21.15 | 0.42 | | |

**Fig. S17.** XRD investigations of the DC phase of **A20**: a) wide angle, b) small angle scattering and c) diffraction intensity profile as a function of $2\theta$ with the visible reflections for the DC phase at 90 °C after cooling with 1 K $\mathrm{min}^{-1}$.

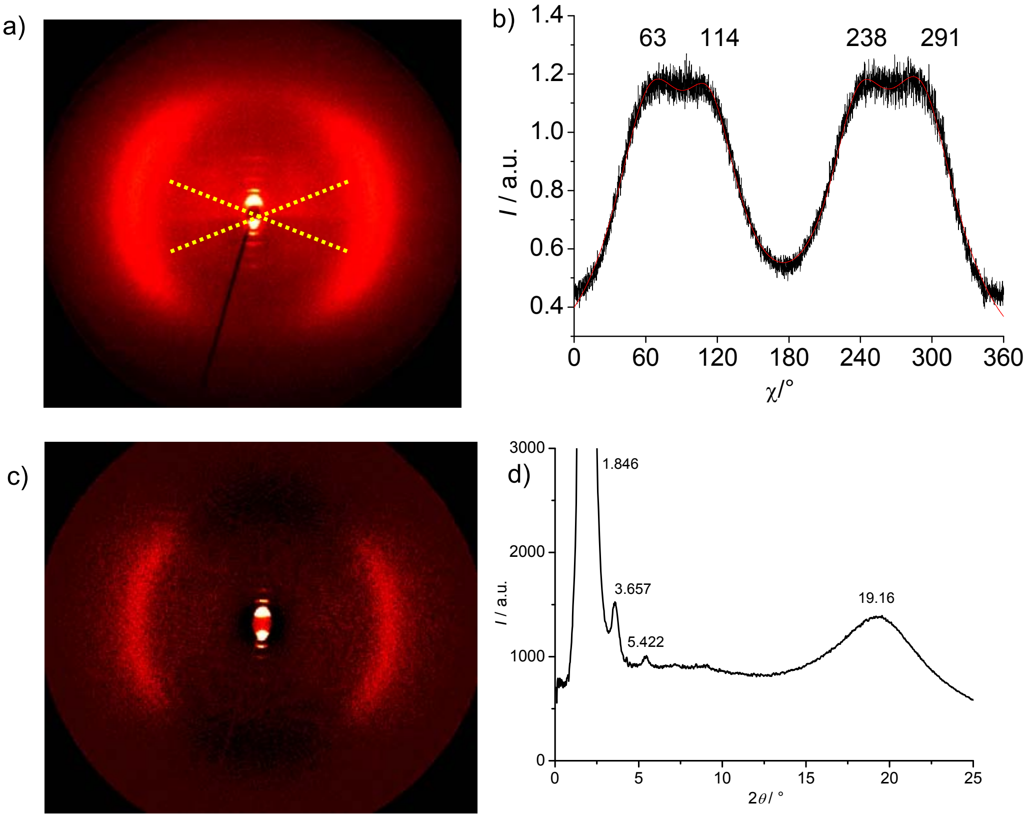


**Fig. S18.** XRD investigations of the LC phase of **E14**: a) complete diffraction pattern at 80 °C and b) χ-scan of the wide angle scattering ($2\theta$=15-25°); c) diffraction pattern at 120 °C after subtraction of the scattering in the isotropic liquid phase at 140 °C and d) diffraction intensity profile as a function of $2\theta$ with the visible reflections.

### *3.5. Investigation of binary mixtures*

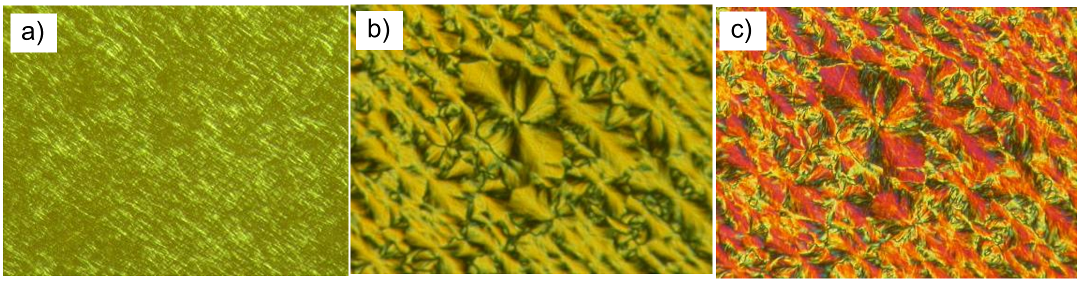


**Fig. S19**. Textures observed for a 1:1 mixture of **A14** with 5-CB on cooling. a) nematic phase at $T$ = 53 °C, b) crystalline phase at $T$ = 39 °C and c) at $T$ = 25 °C

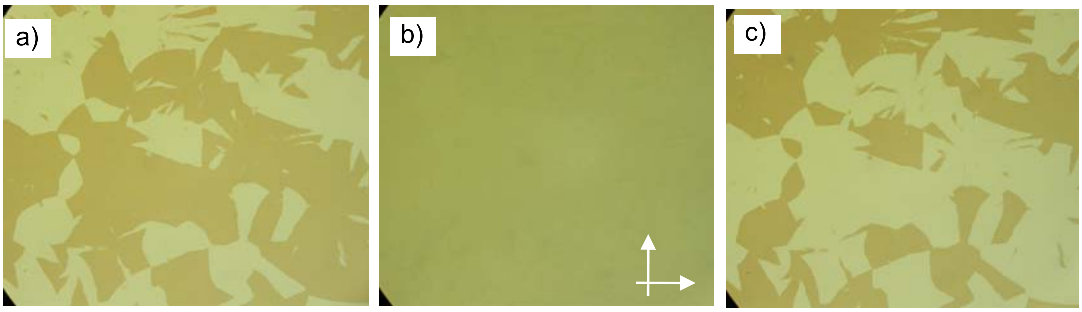


**Fig. S20**. Textures of the induced DC phases observed for a 1:1 mixture of **A20** with 5-CB at $T$ = 59 °C; a, c) decrossed polarizers, b) crossed polarizers.

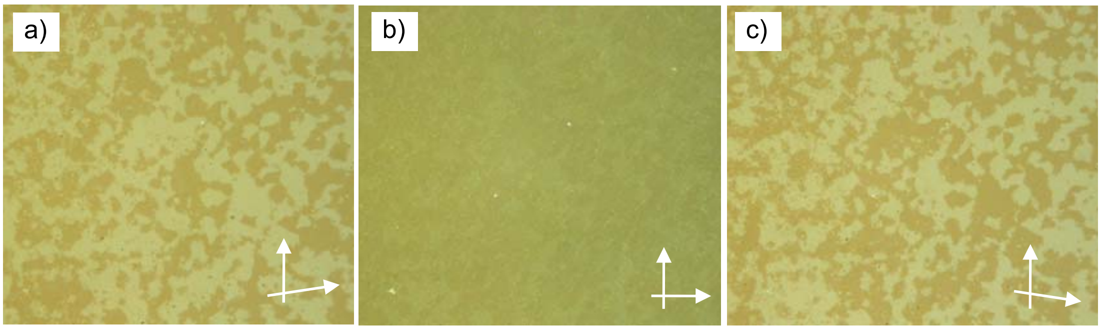


**Fig. S21**. Textures of the induced DC phases observed for a 1:1 mixture of **A22** with 5-CB at $T$ = 59 °C; a, c) decrossed polarizers, b) crossed polarizers.

### *3.6. Electrooptical investigations*

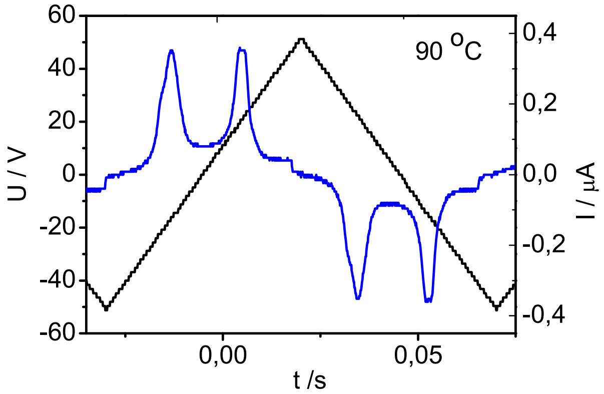


**Fig. S22.** Switching current response curve of compound **E14** recorded by applying a triangular wave voltage (160 $V_{pp}$, 10 Hz, 5 kΩ) to a 6 µm coated ITO cell with homogeneous alignment layer at the indicated temperatures in the $\mathrm{Sm}\tilde{\mathrm{C}}_{a}\mathrm{P}_{A}$ phase.

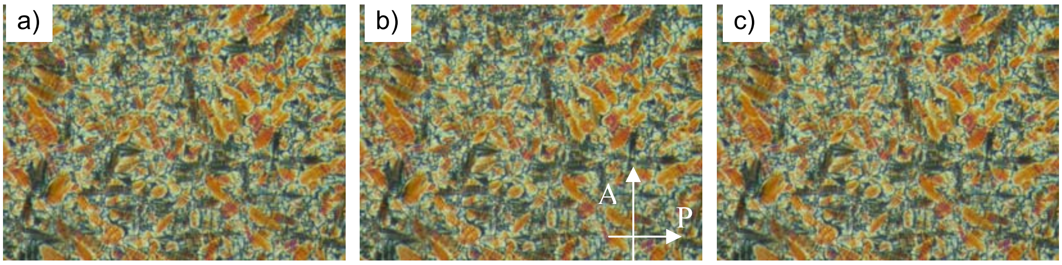


**Fig. S23.** Optical textures of compound **E14** under an applied DC voltage between crossed polarizers (parallel rubbing, rubbing direction parallel to polarizer, direction of the polarizers is shown in b); in the $\mathrm{Sm}\tilde{C}_a\mathrm{P}_A$ phase at $T$ = 120 °C; a) at +10 V, b) after switching off the field (0 V) and c) at -10 V.

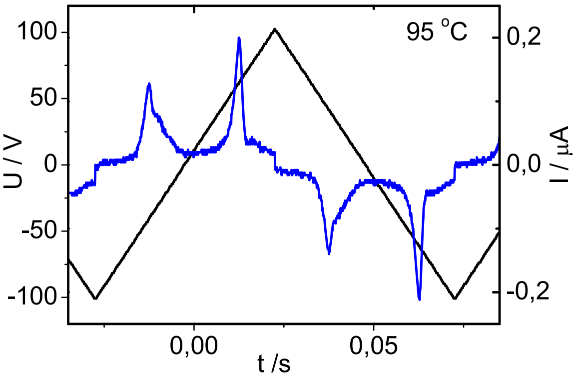


**Fig. S24.** Switching current response curve of compound **F14** recorded by applying a triangular wave voltage (160 $V_{pp}$, 10 Hz, 5 kΩ) to a 6 µm coated ITO cell with homogeneous alignment layer at the indicated temperatures in the $\mathrm{Sm}\tilde{C}_a\mathrm{P}_A$ phase.

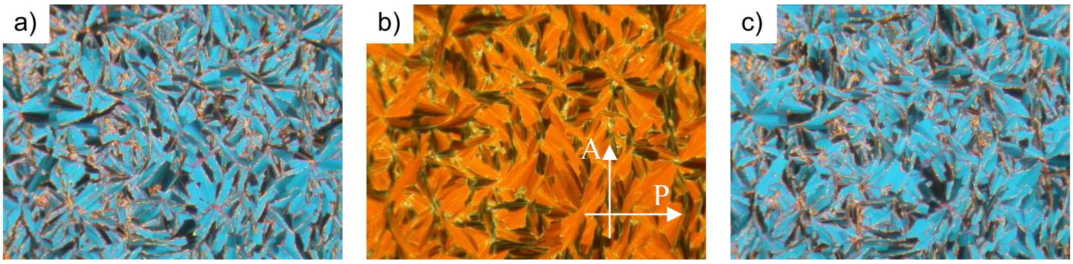


**Fig. S25.** Optical textures of compound **F14** under an applied DC voltage between crossed polarizers (parallel rubbing, rubbing direction parallel to polarizer, direction of the polarizers is shown in b); in the $\mathrm{Sm}\tilde{C}_a\mathrm{P}_A$ phase at $T$ = 100 °C; a) at +10 V, b) after switching off the field (0 V) and c) at -10 V.

## 4. References

S1. G. S. Lee, Y. J. Lee, S. Y. Choi, Y. S. Park, K. B. Yoon, *J. Am. Chem. Soc.* **2000**, *122*, 12151.

S2. a) H.-C. Lin, W.-Y. Lin, H.-T. Bai, J.-H. Chen, B.-Y. Jin, T.-Y. Luh, *Angew. Chem.* **2007**, *119*, 915; b) J. F. W. Mcomie, M. L. Watis, D. E. West, *Tetrahedron* **1968**, *24*, 2289; c) A. Lehmann, *Ph.D. Dissertation, Martin-Luther University Halle-Wittenberg*, **2014**.