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Supplementary Information

Controlling the formation of heliconical smectic phases by molecular design of achiral bent-core molecules

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Contents

1. Experimental Methods

Polarizing microscopy

The particular textures of the liquid crystalline phases were recorded by polarization microscopy. Therefore the samples were placed in a heating stage (Mettler FP82 HT) which was inserted into the polarization microscope (DMRXP, Leica Microsystems). The textures were recorded with a camera (Nikon Coolpix E 4500, Leica MC120HD).

DSC

The DSC investigations were carried out on a DSC 7 (Perkin-Elmer) with a constant heating and ccoling rate of 10 K/min. The transition temperatures are characterized by the peak temperatures.

XRD

X-ray investigations on powderlike samples were carried out at Cu-Kα line (λ = 1.54 Å) using standard Coolidge tube source with a Ni-filter. Samples were prepared in the isotropic state on a glass plate. The sample was cooled (rate: 5 K min−1) to the measuring temperature. The samples were held on a temperature-controlled heating stage and the diffraction patterns were recorded with a 2D detector (Vantec 500, Bruker); exposure time was 15-30 min. For the WAXS measurement the distance between the sample and the detector defined to be 9.0 cm; for SAXS measurement the distance is 26.8 cm. As result a XRD pattern is obtained which is transformed in a 1D plot by using GADDS over the full Chi-range.

Electrooptical and switching experiments

For the switching experiments the compounds were filled in commercially available cells (EHC Japan) which consist of two glass plates with a constant distance of usually 6 µm. Afterwards the cell was placed in a heating stage (Mettler FP 82 HT) and the appropriate electric field was applied. The electric field was generated by an AC/DC generator (3322 A, AGILENT). The switching response was guided through an resistance cascade (type 1435, FLC ELECTRONICS) and tracked by an oscilloscope (TDS 2014, TEKTRONIX).

a) AC field
The AC field experiments were carried out at a constant frequency of 10 Hz and a resistance of 5 kΩ. Characteristic for antiferroelectric switching are 2 switching peaks, for ferroelectric switching only one switching peak is characteristic.

b) DC field
The DC field experiments were carried out at a constant frequency of 20 MHz of the applied field and a resistance of 5 kΩ.

c) Determination of the spontanous polarization
To determine the spontanous polarization the area of the switching peak, the cell area and the resistance are needed. The determination also depends on the type of the switching response (antiferroelectric or ferroelectric case).

$$P_s = \frac{A_{peak}}{A_{cell}\, R}$$

- for antiferroelectric switching:

$$A_{\text{peak}} = \frac{\Sigma A_{\text{i,peak}}}{2}$$

- for ferroelectric switching:

$$A_{\text{peak}} = \frac{A_{\text{i,peak}}}{2}$$

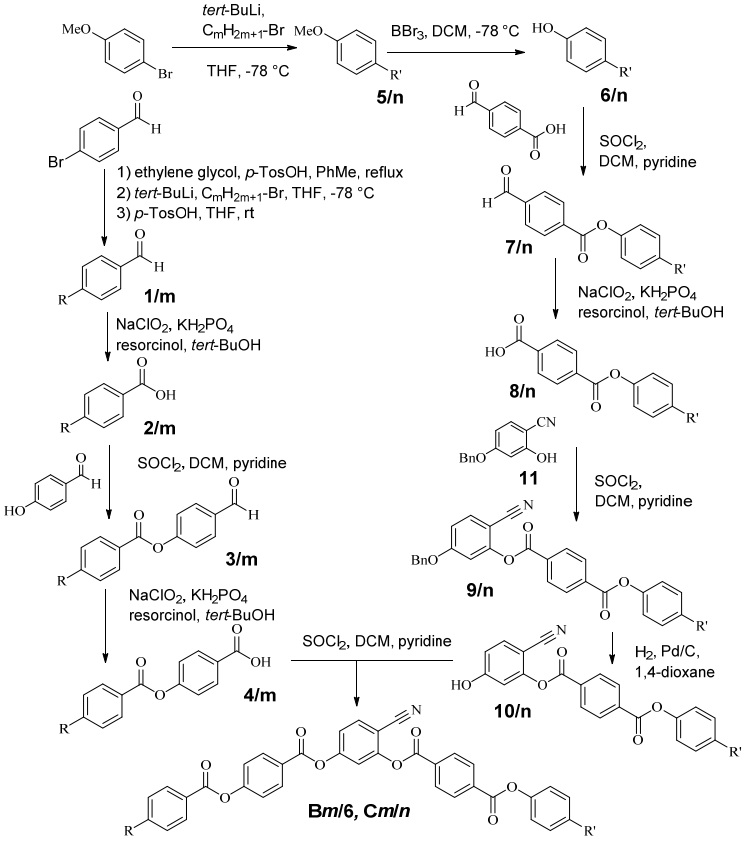
Dielectric investigations

Dielectric spectroscopy was carried out on a 10 μm planar aligned device having indium tin oxide electrodes. The alignment was obtained by coating the substrates with RN1175 (Nissan Chemicals Japan) polymer alignment layer. Experiments were done on cooling the sample from the isotropic phase from 145 ^{o}C to 25 ^{o}C, and in a frequency range between 1 Hz and 10 MHz.

SHG

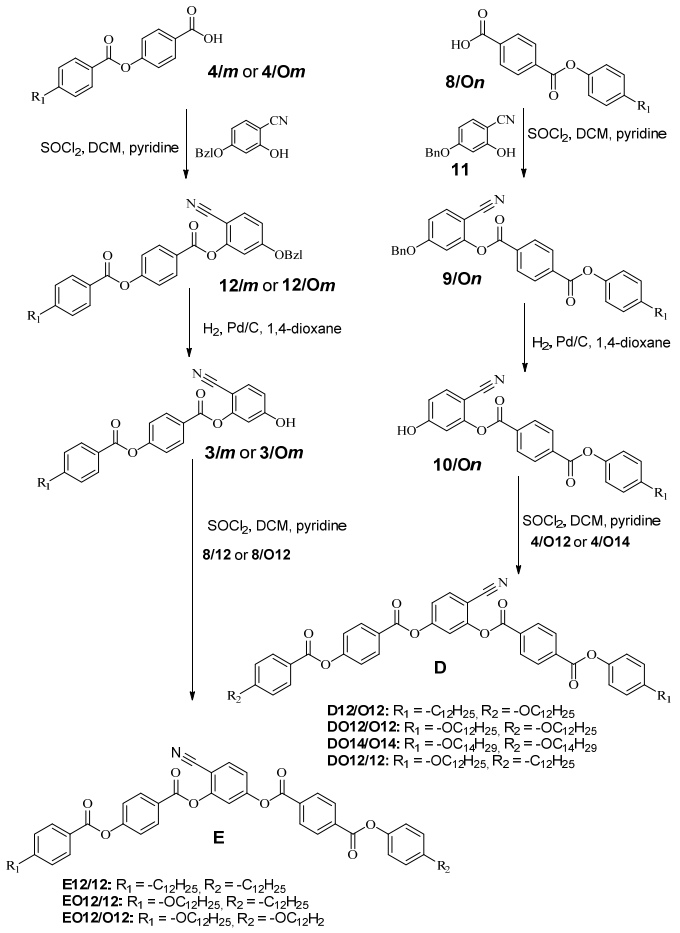
Measurements of the optical second harmonic generation (SHG) were performed using a Nd:YAG laser operating at λ = 1064 nm (11 mJ pulse energy 10 ns pulse width and 10 Hz repetition rate). The primary beam was incident at an angle of 30° to the cell normal. The SHG signal was acquired in transmission by a photomultiplier tube (Hamamatsu). The acquired signal was calibrated using a 50 mm reference quartz plate.

2. Synthesis and Analytical data



Scheme S1. Synthesis of compounds **B*m*/6 and C*m/n***.

General. The starting materials 4-(4-tetradecyloxyphenoxycarbonyl)benzoic acid **(8/O14)**,[S1] 4-(4-tetradecyloxybenzoyloxy)benzoic acid **(4/O14)**,[S1] 4-(4-n-dodecyloxyphenoxycarbonyl)benzoic acid **(8/O12)**,[S2] 4-(4-n-dodecyloxybenzoyloxy)benzoic acid **(15/O12)**,[S3] the intermediates compounds 2-cyano-5-benzyloxyphenyl-4-[(4-tetradecyloxyphenoxy)carbonyl]benzoate (**9/O14**),[S1] 2-cyano-5-hydroxyphenyl-4-[(4-tetradecyloxyphenoxy)carbonyl]benzoate (**10/O14**),[S1] 2-cyano-5-benzyloxyphenyl-4-(4-tetradecyloxybenzoyloxy)benzoate (**12/O14**)[S1] and 2-cyano-5-hydroxyphenyl-4-(4-tetradecyloxybenzoyloxy)benzoate (**3/O14**)[S1] were prepared according to the procedures described in the literature. The other intermediates with alkyl terminal chains (**17/*m*** and **17/*m***) instead of alkoxy terminal chains were prepared in a similar manner to that described in ref. S1 and to those used for the intermediates **9/*n*** and **10/*n*** (see Scheme S1). The final bent-core molecules were synthesized using method **P4** described above for compounds **B*m*/*n***. The detailed analytical data for the final compounds **D** and **E** are given below.



Scheme S2. Synthesis of compounds **D** and compounds **E**.

2.1 Analytical methods

The purity was checked by thin-layer chromatography (TLC, silica gel 60 F254, Merck). Column chromatography was performed with silica gel 60 (0.063-0.2, Merck), flash-chromatography with silica gel 60 (0.040-0.063, Merck). DCM was dried over P_2O_5 and stored over molecular sieve. ^{1}H-, ^{13}C-NMR spectra (Varian Unity 500 and Varian Unity 400 spectrometers) were recorded in CDCl3 or pyridine-d5 solutions, with tetramethylsilane as internal standard). All measurements were operated at 27 °C. Elemental analyses were performed using a Leco CHNS-932 elemental analyzer.

2.2 Synthesis Procedures

Starting materials. - 4-Benzyloxy-2-hydroxybenzonitrile[S4], 2-(4-bromophenyl)-1,3-dioxolane[S5], 4-octylbenzoic acid (**2/18**)[S6,S7], 4-hexyloxyphenol (**2/O6**)[S8,S9,S10], 4-dodecylbenzoic acid (**2/12**)[S6,S7] and 4-dodecyloxybenzoic acid (**2/O12**)[S6,S7 were prepared according to the procedures given in the literature.
tert-butyl lithium (1.7 M in *n*-heptane), *n*-bromo tetradecane, 1-bromo *n*-hexadecane and 1-bromo *n*-eicosane were used as obtained from Sigma-Aldrich. 1-Bromo *n*-hexadecane and terephthal aldehydic acid were used as obtained by Merck. 4-bromo benzaldehyde, 4-hydroxy benzaldehyde and 1-bromo *n*-octadecane were used as obtained from Acros. 4-bromo anisole was used as obtained from Lancaster.

P1: Alkylation of aryl bromides. - The reaction was performed under an argon atmosphere. The appropriate aryl bromide (1 equ) was dissolved in dry THF (1 ml per mmol) and cooled to – 80 °C. *tert*-Butyl lithium (2.3 equ) was slowly added und the mixture was stirred for additional 2 hours at – 80 °C. After addition of the appropriate *n*-alkyl bromide the cooling bath was removed. The mixture was stirred for 2 days at room temperature. After quenching with water the solvent was removed under reduced pressure. The obtained residue was solved in ethanol and *p*-TosOH was added. The reaction mixture was stirred for 2 hours at room temperature and the reaction was monitored by TLC. The solvent was removed under reduced pressure and diethylether and water were added to the residue. The phases were seperated and the organic layer was washed with water and brine. After drying over Na_2SO_4 the solvent was removed and the obtained crude product was purified by column chromatography.

P2: Deprotection of aryl methyl ethers with boron tribromide[S10]. - The appropriate aryl methyl ether **5** (1 equ) was dissolved in dry DCM (1 ml per mmol). The reaction mixture was cooled to – 80 °C. Boron tribromide (2.3 equ) was dissolved in DCM and added slowly to the mixture. The reaction mixture was stirred for 12 hours at room temperature and quenched carefully with water. The phases were seperated and the aqueous layer was extracted with DCM. The combined organic layers were washed with water and brine and dried over Na_2SO_4. The solvent was removed under removed pressure and the obtained residue was purified by column chromatography.

P3: Oxidation of benzaldehydes with sodium chlorite[S6]. **-** The appropriate benzaldehyde **1**/***m***, **3**/***m*** or **7**/***n*** (1 equ) and resorcin (1.3 equ) were dissolved in *t*-butanole (1 ml per mmol). An aquous solution of sodium chlorite (5.8 equ) and potassium dihydrogenphosphate (1.3 equ) was added slowly to the reaction mixture und stirred for 1 hour at room temperature. The solvent was removed under reduced pressure und the obtained residue was suspended in water. Hydrochloric acid (10%) was added up to a pH value of 2-3. The benzoic acid **2**/***m***, **4**/***m*** or **8**/***n*** was filtered off washed with water and *n*-hexane und recrystallised from ethanol.

P4: Esterification of benzoyl chlorides[S7]. - To the appropriate benzoic acid **2**/***m***, **4**/***m*** or **8**/***n*** (1 equ) thionyl chloride (5 equ) is added and the mixture is refluxed for 2 hours. The unreacted thionyl chloride is removed under reduced pressure and the residue is dissolved in dry DCM (1 ml per mmol). After addition of the appropriate phenol (4-hydroxybenzaldehyde, 4-benzyloxy-2-hydroxybenzonitrile or **6/n**) (1.3 equ) and pyridine (1 mL) the reaction mixture was refluxed for additional 2 hours. The reaction was monitored by TLC. The mixture was cooled to room temperature quenched with water and the resulting phases were seperated. The organic layer was washed with aqu. HCl (10%), aqu. $NaHCO_3$ and brine. The organic layer

was dried over Na_2SO_4 and the solvent was removed under removed pressure. The obtained crude products **3**/***m***, **7**/***n*** or **B*m*/*n*** were purified by column chromatography.

P5: STEGLICH-Esterification[S11]. - The appropriate benzoic acid **2**/***m*** or 4-formyl benzoic acid (1 equ) and the phenol **6**/***n*** or 4-hydroxybenzaldehyde (1.3 equ) were dissolved in dry DCM (^ml per mmol). After the addition of DCC (1.3 equ) and DMAP the mixture was stirred for 24 hours at room temperature. The reaction was tracked by TLC. After finishing the reaction the solvent was removed under reduced pressure and the obtained crude product (compounds **3**/***m***, **7**/***n***) was purified by column chromatography.

P6: WILLIAMSON-Etherification[S12]**.** - The appropriate phenol (1 equ) and the alkyl bromide (1.1 equ) were dissolved in 2-butanone (5 mL per mmol). Potassium carbonate (2 equ) and tetrabutylammoniumiodide (tip of spatula) were added and the reaction mixture was refluxed for 6 h. The reaction was monitored by TLC. The solvent was removed under reduced pressure. Water and DCM were added to the obtained residue. The phases were seperated and the organic layer was washed with water and brine. The solvent was removed under reduced pressure and the obtained crude product was purified by column chromatography.

P7: Removal of the benzyl-group by hydrogenation[S13]**.** - The appropriate benzyl ether **9**/***n*** (1 equ) was dissolved in THF (5 ml per mmol) and Pd/C (10%, 50 mg) was added. The mixture was stirred under a hydrogen atmosphere for 24 hours. The solvent was removed by column chromatography and the obtained crude phenols **10**/***n*** were purified by column chromatography.

2.3 Analytical data of intermediates

2.3.1 4-(4-Alkylbenzoyloxy)benzoic acids 3/*n*

4-(4-Octylbenzoyloxy)benzoic acid (4/8)

4-(4-Octylbenzoyloxy)benzaldehyde (3/8): Synthesized according to **P4** from **2/8** (2.00g, 9.0 mmol), thionyl chloride (5 mL), 4-hydroxybenzaldehyde (1.35 g, 11.0 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 1.80 g (60%), $C_{22}H_{26}O_3$, M = 338.44 g/mol, mp. 83 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H, –C*H*O), 8.11 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 7.97 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.40 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.73 - 2.69 (m, 2H, Ar–CH_2–), 1.69 - 1.62 (m, 2H, –CH_2–), 1.32 - 1.28 (m, –CH_2–), 0.89 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octylbenzoyloxy)benzoic acid (4/8): Synthesized according to **P3** from **3/8** (1.80 g, 5.3 mmol), resorcinol (0.76 g, 6.9 mmol), sodium chlorite (3.50 g, 31.0 mmol) and potassium dihydrogenphosphate (2.16 g, 15.9 mmol) in *tert*-BuOH (100 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 0.66 g (35%), $C_{22}H_{26}O_4$, M = 326.4 g/mol, mp. 230 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 7.35 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.73 - 2.69 (m, 2H, Ar–CH_2–), 1.68 - 1.63 (m, 2H, –CH_2–), 1.33 - 1.28 (m, 10H, –CH_2–), 0.89 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Tetradecylbenzoyloxy)benzoic acid (4/14)

4-Tetradecylbenzaldehyde (1/14): Synthesized according to **P1** from 2-(4-bromophenyl)-1,3-dioxolane (3.00 g, 13.0 mmol), *n*-bromo tetradecane (3.30 g, 16.9 mmol) an *tert*-butyl lithium (1.7 M in *n*-heptane, 18.0 mL 30.6 mmol) in THF (50 mL). Afterwards the crude product was solved in ethanol (150 mL) and 4-toluene sulfonic acid (0.1 g) was added. Purification by column chromatography (eluent: DCM). Colourless liquid, yield: 1.03 g (92%), $C_{21}H_{34}O$, M = 302.49 g/mol. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H, –C*H*O), 7.79 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.74 - 2.62 (m, 2H, Ar–CH_2–), 1.73 - 1.57 (m, 2H, –CH_2–), 1.41 - 1.17 (m, 22H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Tetradecylbenzoic acid (2/14): Synthesized according to **P3** from **1/14** (1.03 g, 3.4 mmol), resorcinol (0.48 g, 4.4 mmol), sodium chlorite (1.76 g, 19.7 mmol) and potassium dihydrogenphosphate (1.36 g, 10.2 mmol) in *tert*-BuOH (120 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 0.97 g (90%), $C_{21}H_{34}O_2$, M = 318.49 g/mol, mp. 95 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.28 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.69 - 2.65 (m, 2H, Ar–CH_2–), 1.65 - 1.60 (m, 2H, –CH_2–), 1.32 - 1.25 (m, 22H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Tetradecylbenzoyloxy)benzaldehyde (3/14): Synthesized according to **P4** from **2/14** (386 mg, 1.2 mmol), thionyl chloride (5 mL), 4-hydroxybenzaldehyde (188 mg, 1.6 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 300 mg (59%), $C_{28}H_{38}O_3$, M = 422.60 g/mol, mp. 86 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 10.00 (s, 1H, –C*H*O), 8.08 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.95 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 7.39 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.70 - 2.67 (m, 2H, Ar–CH_2–), 1.67 - 1.61 (m, 2H, –CH_2–), 1.33 - 1.24 (m, 22H, –CH_2–), 0.86 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm.

4-(4-Tetradecylbenzoyloxy)benzoic acid (4/14): Synthesized according to **P3** from **3/14** (300 mg, 0.7 mmol), resorcinol (100 mg, 0.9 mmol), sodium chlorite (460 mg, 5.2 mmol) and potassium dihydrogenphosphate (300 mg, 2.1 mmol) in *tert*-BuOH (120 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 250 mg (81%), $C_{28}H_{38}O_4$, M = 438.60 g/mol, mp. 209 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.09 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.32 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.71 - 2.66 (m, 2H, Ar–CH_2–), 1.68 - 1.62 (m, 2H, –CH_2–), 1.38 - 1.20 (m, 22H, –CH_2–), 0.86 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm.

4-(4-Hexadecylbenzoyloxy)benzoic acid (4/16)

4-Hexadecylbenzaldehyde (1/16): Synthesized according to **P1** from 2-(4-bromophenyl)-1,3-dioxolane (5.00 g, 21.8 mmol), *n*-bromo hexadecane (6.6 g, 21.8 mmol) and *tert*-butyl lithium (1.7 M in *n*-heptane, 18.6 mL. 31.6 mmol) in THF (150 mL). Afterwards the crude product was solved in ethanol (150 mL) and 4-toluene sulfonic acid (0.2 g) was added. Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.25 g (95%), $C_{23}H_8O$, M = 302.49 g/mol, mp. 34 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.97 (s, 1H, –C*H*O), 7.80 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.34 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.71 - 2.66 (m, 2H, Ar–CH_2 –), 1.68 - 1.60 (m, 2H, –CH_2–), 1.37 - 1.21 (m, 26H, –CH_2–), 0.88 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm.

4-Hexadecylbenzoic acid (2/16): Synthesized according to **P3** from **1/16** (2.25 g, 6.8 mmol), resorcinol (0.98 g, 8.86 mmol), sodium chlorite (4.50 g, 39.5 mmol) and potassium dihydrogenphosphate (2.80 g, 20.5 mmol) in *tert*-BuOH (150 mL). Purification by

crystallisation from ethanol. Colourless solid, yield: 2.12 g (90%), $C_{23}H_{38}O_1$, M = 346.55 g/mol, mp. 97 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.82 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.28 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 2.67 - 2.57 (m, 2H, Ar–CH_2–), 1.65 - 1.56 (m, 2H, –CH_2–), 1.32 - 1.14 (m, 26H, –CH_2–), 0.83 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Hexadecylbenzoyloxy)benzaldehyde (3/16): Synthesized according to **P4** from **2/16** (1.00g, 2.9 mmol), thionyl chloride (5 mL), 4-hydroxybenzaldehyde (463 mg, 3.8 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 1.08 g (83%), $C_{30}H_{42}O_3$, M = 450.65 g/mol, mp. 87 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H, –C*H*O), 8.09 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 7.95 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.39 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.71 - 2.67 (m, 2H, Ar–CH_2–), 1.68 - 1.61 (m, 2H, –CH_2–), 1.37 - 1.20 (m, 26H, –CH_2–), 0.86 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Hexadecylbenzoyloxy)benzoic acid (4/16): Synthesized according to **P3** from **3/16** (1.08 g, 3.1 mmol), resorcinol (343 mg, 3.1 mmol), sodium chlorite (1.26 g, 13.9 mmol) and potassium dihydrogenphosphate (1.00 g, 7.2 mmol) in *tert*-BuOH (150 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 1.02 g (91%), $C_{30}H_{42}O_4$, M = 466.65 g/mol, mp. 260 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.09 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.32 (d, ^3J = 9.2 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.71 - 2.66 (m, 2H, Ar–CH_2–), 1.68 - 1.60 (m, 2H, –CH_2–), 1.38 - 1.19 (m, 26H, –CH_2–), 0.86 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecylbenzoyloxy)benzoic acid (4/18)

4-Octadecylbenzaldehyde (1/18): Synthesized according to **P1** from 2-(4-bromophenyl)-1,3-dioxolane (5.00 g, 21.8 mmol), *n*-bromo octadecane (7.30 g, 21.8 mmol) an *tert*-butyl lithium (1.7 M in *n*-heptane, 13.6 mL. 23.1 mmol) in THF (150 mL). Afterwards the crude product was solved in ethanol (150 mL) and 4-toluene sulfonic acid (0.2 g) was added. Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.80 g (95%), $C_{25}H_{42}O$, M = 358.60 g/mol, mp. 34 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H, –C*H*O), 7.76 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.68 - 2.63 (m, 2H, Ar–CH_2–), 1.67 - 1.59 (m, 2H, –CH_2–), 1.37 - 1.20 (m, 30H, –CH_2–), 0.86 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Octadecylbenzoic acid (2/18): Synthesized according to **P3** from **1/18** (2.80 g, 7.8 mmol), resorcinol (1.07 g, 9.7 mmol), sodium chlorite (4.86 g, 43.0 mmol) and potassium dihydrogenphosphate (3.10 g, 22.5 mmol) in *tert*-BuOH (150 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 2.85 g (95%), $C_{25}H_{42}O_2$, M = 374.60 g/mol, mp. 98 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.27 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.70 - 2.64 (m, 2H, Ar–CH_2–), 1.67 - 1.59 (m, 2H, –CH_2–), 1.36 - 1.21 (m, 30H, –CH_2–), 0.88 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm.

4-(4-Octadecylbenzoyloxy)benzaldehyde (3/18): Synthesized according to **P4** from **2/18** (1.00g, 2.7 mmol), thionyl chloride (5 mL), 4-hydroxybenzaldehyde (0.48 g, 3.5 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 1.20 g (92%), $C_{32}H_{46}O_3$, M = 478.71 g/mol, mp. 90 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H, –C*H*O), 8.09 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.95 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.38 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.71 - 2.66 (m, 2H, Ar–CH_2–), 1.68 - 1.61 (m, 2H, –CH_2–), 1.38 - 1.22 (m, 30H, –CH_2–), 0.86 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecylbenzoyloxy)benzoic acid (4-18): Synthesized according to **P3** from **3/18** (1.20 g, 2.5 mmol), resorcinol (368 mg, 3.3 mmol), sodium chlorite (1.64 g, 14.5 mmol) and potassium dihydrogenphosphate (1.02 g, 7.5 mmol) in *tert*-BuOH (150 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 1.20 g (95%), $C_{32}H_{46}O_4$, M = 494.71.4 g/mol, mp. 276 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 8.09 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.31 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.70 - 2.67 (m, 2H, Ar–CH_2–), 1.69 - 1.59 (m, 2H, –CH_2–), 1.37 - 1.18 (m, 30H, –CH_2–), 0.86 (t, ^3J = 6.75 Hz, 3H, –CH_3) ppm.

4-(4-Eicosylbenzoyloxy)benzoic acid (4/20)

4-n-Eicosylbenzaldehyde (1/20): Synthesized according to **P1** from 2-(4-bromophenyl)-1,3-dioxolane (8.60 g, 37.6 mmol), *n*-bromo eicosane (13.60 g, 37.6 mmol) an *tert*-butyl lithium in *n*-heptane (1.7 M, 50.0 mL, 85.0 mmol) in THF (250 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 7.30 g (50%), $C_{27}H_{46}O$, M = 386.65 g/mol, mp. 57 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.97 (s, 1H, –C*H*O), 7.79 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.34 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 2.71 - 2.65 (m, 2H, Ar–CH_2–), 1.68 - 1.59 (m, 2H, –CH_2–), 1.37 - 1.21 (m, 34H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Eicosylbenzoic acid (2/20): Synthesized according to **P3** from **1/20** (7.00 g, 18.1 mmol), resorcinol (2.60 g, 23.5 mmol), sodium chlorite (9.00 g, 100.0 mmol) and potassium dihydrogenphosphate (7.40 g, 54.3 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 5.66 g (78%), $C_{27}H_{46}O_2$, M = 402.65 g/mol, mp. 97 °C. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 7.82 (d, ^3J = 7.7 Hz, 2H, Ar–*H*), 7.28 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 2.63 - 2.56 (m, 2H, Ar–CH_2–), 1.61 - 1.50 (m, 2H, –CH_2–), 1.31 - 1.14 (m, 34H, –CH_2–), 0.82 (d, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Eicosylbenzoyloxy)benzaldehyde (3/20): Synthesized according to **P4** from **2/20** (3.00g, 7.4 mmol), thionyl chloride (5 mL), ? (1.20 g, 9.7 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 3.50 g (93%), $C_{34}H_{31}NO_5$, M = 506.76 g/mol, mp. 70 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.03 (s, 1H, –C*H*O), 8.11 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.97 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.41 (d, J = 8.5 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 2.74 - 2.68 (m, 2H, Ar–CH_2–), 1.70 - 1.61 (m, 2H, –CH_2–), 1.38 - 1.22 (m, 34H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Eicosylbenzoyloxy)benzoic acid (4/20): Synthesized according to **P3** from **3/20** (3.28 g, 6.5 mmol), resorcinol (0.93 g, 8.4 mmol), sodium chlorite (3.40 g, 37.6 mmol) and potassium dihydrogenphosphate (2.64 g, 19.4 mmol) in *tert*-BuOH (150 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 1.95 g (58%), $C_{34}H_{50}O_4$, M = 522.76 g/mol, mp. 200 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 8.11 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 2.76 - 2.65 (m, 2H, Ar–CH_2–), 1.72 - 1.60 (m, 2H, –CH_2–), 1.40 - 1.18 (m, 34H, –CH_2–), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

4-(4-Docosylbenzoyloxy)benzoic acid (4/22)

4-Docosylbenzaldehyde (1/22): Synthesized according to **P1** from 2-(4-bromophenyl)-1,3-dioxolane (5.00 g, 21.9 mmol), *n*-bromo docosane (8.50 g, 21.9 mmol) an *tert*-butyl lithium in *n*-heptane (1.7 M, 25.8 mL. 44.0 mmol) in THF (150 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 4.00 g (40%), $C_{29}H_{50}O$, M =

414.71 g/mol, mp. 52 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.97 (s, 1H, –C*H*O), 7.79 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.72 - 2.64 (m, 2H, Ar–CH_2–), 1.70 - 1.58 (m, 2H, –CH_2–), 1.41 - 1.15 (m, 38H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Docosylbenzoic acid (2/22): Synthesized according to **P3** from **1/22** (3.50 g, 8.5 mmol), resorcinol (1.20 g, 11.0 mmol), sodium chlorite (4.40 g, 49.0 mmol) and potassium dihydrogenphosphate (3.50 g, 33.9 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 5.79 g (93%), $C_{29}H_{50}O_2$, M = 430.71 g/mol, mp. 104 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.04 - 7.95 (m, 2H, Ar–*H*), 7.27 (d, 2H, Ar–*H*), 2.74 - 2.61 (m, 2H, Ar–CH_2–), 1.71 - 1.57 (m, 2H, –CH_2–), 1.39 - 1.15 (m, 38H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Docosylbenzoyloxy)benzaldehyde (3/22): Synthesized according to **P5** from **2/22** (2.50 g, 5.8 mmol), 4-hydroxy benzaldehyde (0.92g, 7.6 mmol), DCC (1.56 g, 7.6 mmol) and DMAP (tip of spatula) in abs. DCM (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.30 g (74%), $C_{36}H_{54}O_3$, M = 534.41 g/mol, mp = 78 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.03 (s, 1H, –C*H*O), 8.11 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.97 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.41 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 2.75 - 2.66 (m, 2H, Ar–CH_2–), 1.72 - 1.59 (m, 2H, –CH_2–), 1.41 - 1.17 (m, 38H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Docosylbenzoyloxy)benzoic acid (4/22): Synthesized according to **P3** from **3/22** (2.00 g, 3.7 mmol), resorcinol (0.54 g, 4.9 mmol), sodium chlorite (1.96 g, 21.7 mmol) and potassium dihydrogenphosphate (1.52 g, 11.2 mmol) in *tert*-BuOH (300 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 2.00 g (98%), $C_{36}H_{54}O_4$, M = 550.40 g/mol, mp. 213 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.11 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.34 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.74 - 2.67 (m, 2H, Ar–CH_2–), 1.70 - 1.61 (m, 2H, –CH_2–), 1.38 - 1.19 (m, 38H, –CH_2–), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

4-(4-Dodecyloxybenzoyloxy)benzoic acid (4/O12)

4-(4-Dodecyloxybenzoyloxy)benzaldehyde (3/O12): Synthesized according to **P5** from **2/O12** (3.00 g, 9.8 mmol), 4-hydroxy benzaldehyde (1.20 g, 9.8 mmol), DCC (2.60 g, 12.7 mmol) and DMAP (tip of spatula) in DCM (120 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 4.10 g (98%), $C_{26}H_{34}O_4$, M = 410.55 g/mol, mp. 91 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.00 (s, 1H, –C*H*O), 8.12 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 7.94 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.38 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 6.96 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 4.03 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 1.86 - 1.75 (m, 2H, –CH_2–), 1.51 - 1.40 (m, 2H, –CH_2–), 1.40 - 1.07 (m, 16H, –CH_2–), 0.86 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

4-(4-Dodecyloxybenzoyloxy)benzoic acid (4/O12): Synthesized according to **P3** from **3/O12** (4.30 g, 10.5 mmol), resorcinol (1.50 g, 13.8 mmol), sodium chlorite (80%, 5.50 g, 61.0 mmol) and potassium dihydrogenphosphate (4.30 g, 32.0 mmol) in *tert*-BuOH (100 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 3.35 g (76%), $C_{26}H_{34}O_5$, M = 426.55 g/mol, mp. 245 °C. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 8.07 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 8.01 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.37 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.10 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.08 (t, ^3J = 6.5 Hz, 2H, Ar–O–CH_2–), 1.81 - 1.64 (m, 2H, –CH_2–), 1.50 - 1.36 (m, 2H, –CH_2–), 1.35 - 1.14 (m, 16H, –CH_2–), 0.84 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecyloxybenzoyloxy)benzoic acid (4/O18)

4-Octadecyloxybenzaldehyde (1/O18): Synthesized according to **P6** From 4-hydroxybenzaldehyde (3.00 g, 24.6 mmol), *n*-bromo octadecane (9.00 g, 27.1 mmol), Potassium carbonate (6.80 g, 49.2 mmol) and tetrabutylammoniumiodide (tip of spatula) in 2-butanone (200 mL). Purification by column chromatography (eluent: DCM) and crystallization from ethanol. Colourless solid, yield: 5.70 g (65%), $C_{25}H_{42}O_2$, M = 374.60 g/mol, mp. 51 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.87 (s, 1H, –C*H*O), 7.82 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 6.98 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 4.03 (t, ^3J = 6.6 Hz, 2H, Ar–CH_2–), 1.85 - 1.76 (m, 2H, –CH_2–), 1.52 - 1.41 (m, 2H, –CH_2–), 1.41 - 1.16 (m, 28H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Octadecyloxybenzoic acid (2/O18): Synthesized according to **P3** from **1/O18** (4.00 g, 10.7 mmol), resorcinol (1.53 g, 13.9 mmol), sodium chlorite (4.84 g, 53.5 mmol) and potassium dihydrogenphosphate (4.37 g, 32.1 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 3.56 g (85%), $C_{25}H_{42}O_3$, M = 522.76 g/mol, mp. 174 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 6.93 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 4.02 (t, J = 6.5 Hz, 2H, Ar–CH_2–), 1.85 - 1.74 (m, 2H, –CH_2–), 1.51 - 1.40 (m, 2H, –CH_2–), 1.40 - 1.15 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecyloxybenzoyloxy)benzaldehyde (3/O18): Synthesized according to **P4** from **2/O18** (3.00 g, 7.7 mmol), thionyl chloride (10 mL), 4-hydroxy benzaldehyde (1.22 g, 10.0 mmol) and pyridine (1 mL) in DCM (25 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 3.10 g (78%), $C_{32}H_{46}O_4$, M = 494.34 g/mol, mp. 82 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.90 (s, 1H, –C*H*O), 8.01 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.84 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.27 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 6.86 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 3.92 (t, ^3J = 6.6 Hz, 2H, Ar–CH_2–), 1.76 - 1.63 (m, 2H, –CH_2–), 1.40 - 1.29 (m, 2H, –CH_2–), 1.29 - 1.07 (m, 28H, –CH_2–), 0.75 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecyloxybenzoyloxy)benzoic acid (4/O18): Synthesized according to **P3** from **3/O18** (3.00 g, 5.8 mmol), resorcinol (0.83 g, 7.5 mmol), sodium chlorite (3.04 g, 33.6 mmol) and potassium dihydrogenphosphate (2.37 g, 17.4 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 2.80 g (95%), $C_{32}H_{46}O_5$, M = 510.33 g/mol, mp. 234 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.14 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.33 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 6.98 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.05 (t, ^3J = 6.5 Hz, 2H, Ar–CH_2–), 1.89 - 1.76 (m, 2H, –CH_2–), 1.54 - 1.42 (m, 2H, –CH_2–), 1.42 - 1.19 (m, 28H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Docosyloxybenzoyloxy)benzoic acid (4/O22)

4-Docosyloxybenzaldehyde (1/O22): Synthesized according to **P6** From 4-hydroxybenzaldehyde (2.30 g, 18.8 mmol), *n*-bromo docosane (7.00 g, 18.0 mmol), Potassium carbonate (4.60 g, 32.8 mmol) and tetrabutylammoniumiodide (tip of spatula) in acetonitrile (200 mL). Purification by column chromatography (eluent: DCM) and crystallization from ethanol. Colourless solid, yield: 7.20 g (93%), $C_{29}H_{50}O_2$, M = 430.71 g/mol, mp. 59 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.88 (s, 1H, –C*H*O), 7.82 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 6.99 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 4.04 (t, ^3J = 6.5 Hz, 2H, Ar–O–CH_2–), 1.86 - 1.76 (m, 2H, –CH_2–), 1.51 - 1.41 (m, 2H, –CH_2–), 1.40 - 1.21 (m, 36H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Docosyloxybenzoic acid (2/O22): Synthesized according to **P3** from **1/O22** (6.00 g, 14.5 mmol), resorcinol (2.10 g, 18.8 mmol), sodium chlorite (80%, 6.70 g, 84.0 mmol) and potassium dihydrogenphosphate (5.90 g, 43.5 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 5.79 g (93%), $C_{29}H_{50}O_3$, M = 446.71 g/mol, mp. 155 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 6.93 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.02 (t, ^3J = 6.6 Hz, 2H, Ar–O–C*H*$_2$–), 1.85 - 1.75 (m, 2H, –C*H*$_2$–), 1.51 - 1.41 (m, ^3J = 15.3, 7.3 Hz, 2H, –C*H*$_2$–), 1.40 - 1.17 (m, 36H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Docosyloxybenzoyloxy)benzaldehyde (3/O22): Synthesized according to **P4** from **2/O22** (3.50 g, 8.1 mmol), thionyl chloride (10 mL), 4-hydroxy benzaldehyde (1.30 g, 10.6 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 1.40 g (31%), $C_{36}H_{54}O_4$, M = 550.40 g/mol, mp. 78 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.02 (s, 1H, –C*H*O), 8.14 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.96 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.40 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 6.98 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.05 (t, ^3J = 6.6 Hz, 2H, Ar–O–C*H*$_2$–), 1.91 - 1.74 (m, 2H, –C*H*$_2$–), 1.52 - 1.41 (m, 2H, –C*H*$_2$–), 1.42 - 1.18 (m, 36H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Docosyloxybenzoyloxy)benzoic acid (4/O22): Synthesized according to **P3** from **3/O22** (1.40 g, 2.55 mmol), resorcinol (0.36 g, 3.31 mmol), sodium chlorite (80%, 1.34 g, 14.8 mmol) and potassium dihydrogenphosphate (1.28 g, 7.6 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 1.30 g (90%), $C_{36}H_{54}O_5$, M = 566.40 g/mol, mp. 225 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.62 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.81 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.46 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.53 (t, ^3J = 6.6 Hz, 2H, Ar–C*H*$_2$–), 2.36 - 2.25 (m, 2H, –C*H*$_2$–), 2.00 - 1.90 (m, 2H, –C*H*$_2$–), 1.89 - 1.53 (m, 36H, –C*H*$_2$–), 1.36 (t, ^3J = 7.0 Hz, 3H, –C*H*$_3$) ppm.

2.3.2 4-(4-Alkylphenoxycarbonyl)benzoic acids 8/*n*

4-(4-Hexylphenoxycarbonyl)benzoic acid (8/6)

4-(4-Hexylphenoxycarbonyl)benzaldehyde (7/6): Synthesized according to **P5** from 4-hexylphenol (3.10g, 17.3 mmol), terephthalaldehydic acid (2.00 g, 17.3 mmol), DCC (3.60 g, 17.3 mmol) and DMAP (tip of spatula) in abs. DCM (150 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 3.50 g (65%), $C_{20}H_{22}O_3$, M = 310.39 g/mol, mp. 73 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.15 (s, 1H, –C*H*O), 8.36 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 8.02 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.24 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.13 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.68 - 2.60 (m, 2H, Ar–C*H*$_2$–), 1.69 - 1.58 (m, 2H, –C*H*$_2$–), 1.41 - 1.24 (m, 6H, –C*H*$_2$–), 0.89 (t, ^3J = 6.9 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Hexylphenoxycarbonyl)benzoic acid (8/6): Synthesized according to **P3** from **7/6** (3.50 g, 11.3 mmol), resorcinol (1.30 g, 14.7 mmol), sodium chlorite (5.90 g, 65.5 mmol) and potassium dihydrogenphosphate (4.60 g, 33.9 mmol) in *tert*-BuOH (150 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 3.00 g (81%), $C_{20}H_{22}O_4$, M = 326.4 g/mol, mp. 235 °C. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 8.21 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 8.11 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.27 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.18 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.59 (t, ^3J = 7.6 Hz, 2H, Ar–C*H*$_2$–), 1.64 - 1.50 (m, 2H, –C*H*$_2$–), 1.35 - 1.20 (m, 6H, –C*H*$_2$–), 0.85 (t, ^3J = 6.6 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Dodecylphenoxycarbonyl)benzoic acid (8/12)

4-Dodecylanisole (5/12): Synthesized according to **P1** from 4-bromo anisole (5.00 g, 26.8 mmol), *n*-bromo dodecane (6.50 g, 26.8 mmol) an *tert*-butyl lithium in *tert*-heptane (1.7 M, 31.8 mL. 54.0 mmol) in THF (150 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless liquid, yield: 7.00 g (94%), $C_{19}H_{32}O$, M = 276.46 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 6.97 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 6.70 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 3.66 (s, 2H, Ar–O–C*H*$_3$), 2.49 - 2.34 (m, 2H, Ar–C*H*$_2$–), 1.54 - 1.38 (m, 2H, –C*H*$_2$–), 1.27 - 1.03 (m, 18H, –C*H*$_2$–), 0.76 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-Dodecylphenol (6/12): Synthesized according to **P2** from **5/12** (7.02 g, 25.4 mmol) and boron tribromide (14.55 g, 58.5 mmol) in absolute DCM (60 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 5.40 g (81%), $C_{18}H_{33}O$, M = 262.23 g/mol, mp. 60 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 6.75 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 5.54 (s, 1H, Ar–O*H*), 2.59 - 2.43 (m, 2H, Ar–C*H*$_2$–), 1.61 - 1.48 (m, 2H, –C*H*$_2$–), 1.36 - 1.17 (m, 18H, –C*H*$_2$–), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH$_3$) ppm.

4-(4-Dodecylphenoxycarbonyl)benzaldehyde (7/12): Synthesized according to **P5** from **6/12** (5.00g, 19.1 mmol), terephthalaldehydic acid (2.90 g, 19.1 mmol), DCC (5.10 g, 24.8 mmol) and DMAP (tip of spatula) in abs. DCM (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 4.10 g (55%), $C_{26}H_{34}O_3$, M = 394.25 g/mol, mp = 80 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.14 (s, 1H, –C*H*O), 8.36 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 8.02 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.24 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.13 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.68 - 2.57 (m, 2H, Ar–C*H*$_2$–), 1.69 - 1.55 (m, 2H, –C*H*$_2$–), 1.41 - 1.18 (m, 18H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Dodecylphenoxycarbonyl)benzoic acid (8/12): Synthesized according to **P3** from **7/12** (4.00 g, 10.2 mmol), resorcinol (1.45 g, 13.2 mmol), sodium chlorite (5.30 g, 58.9 mmol) and potassium dihydrogenphosphate (4.15 g, 30.5 mmol) in *tert*-BuOH (200 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 3.80 g (91%), $C_{26}H_{34}O_4$, M = 410.25 g/mol, mp. 255 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 8.22 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.24 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.13 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.68 - 2.58 (m, 2H, Ar–C*H*$_2$–), 1.70 - 1.56 (m, 2H, –C*H*$_2$–), 1.40 - 1.18 (m, 18H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Tetradecylphenoxycarbonyl)benzoic acid (8/14)

4-Tetradecylanisole (5/14): Synthesized according to **P1** from 4-bromo anisole (4.00 g, 21.4 mmol), *n*-bromo tetradecane (5.90 g, 21.4 mmol) and *tert*-butyl lithium (1.7 M in *n*-heptane, 26.4 mL. 44.9 mmol) in THF (150 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 3.40 g (52%), $C_{21}H_{36}O$, M = 304.51 g/mol, mp. 34 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 6.82 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 3.79 (s, 3H, –O–C*H*$_3$), 2.57 - 2.51 (m, 2H, Ar–C*H*$_2$–), 1.62 - 1.53 (m, 2H, –C*H*$_2$–), 1.36 - 1.21 (m, 22H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-Tetradecylphenol (6/14): Synthesized according to **P2** from **5/14** (3.30 g, 10.9 mmol) and boron tribromide (6.34 g, 25.0 mmol) in absolute DCM (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.63 g (84%), $C_{20}H_{34}O$, M = 290.48 g/mol, mp. 69 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 6.74 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 4.49 (s, 1H, –O*H*), 2.56 - 2.48 (m, 2H, Ar–C*H*$_2$–), 1.61 - 1.50 (m, 2H, –C*H*$_2$–), 1.36 - 1.20 (m, 22H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 3H, –C*H*$_3$) ppm.

4-(4-Tetradecylphenoxycarbonyl)benzaldehyde (7/14): Synthesized according to **P5** from **6/14** (2.50g, 8.6 mmol), terephthalaldehydic acid (1.70 g, 11.2 mmol), DCC (1.70 g, 11.2 mmol) and DMAP (tip of spatula) in abs. DCM (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 3.37 g (93%), $C_{28}H_{38}O_3$, M = 422.28 g/mol, mp = 89 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.02 (s, 1H, –C*H*O), 8.23 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.89 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.11 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 7.00 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.54 - 2.46 (m, 2H, Ar–CH_2–), 1.55 - 1.46 (m, 2H, –CH_2–), 1.31 - 1.04 (m, 22H, –CH_2–), 0.75 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Tetradecylphenoxycarbonyl)benzoic acid (8/14): Synthesized according to **P3** from **7/14** (3.30 g, 7.8 mmol), resorcinol (1.12 g, 10.2 mmol), sodium chlorite (4.10 g, 45.4 mmol) and potassium dihydrogenphosphate (3.20 g, 23.5 mmol) in *tert*-BuOH (250 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 2.90 g (85%), $C_{28}H_{38}O_4$, M = 438.28 g/mol, mp. 252 °C. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 8.20 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 8.11 (d, ^3J = 7.9 Hz, 2H, Ar–*H*), 7.26 (d, ^3J = 7.3 Hz, 2H, Ar–*H*), 7.18 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 2.58 (t, ^3J = 5.8 Hz, 2H, Ar–CH_2–), 1.66 - 1.47 (m, 2H, –CH_2–), 1.38 - 1.04 (m, 22H, –CH_2–), 0.82 (t, ^3J = 6.7 Hz, 3H, –CH_3) ppm.

4-(4-Octadecylphenoxycarbonyl)benzoic acid (8/18)

4-Octadecylanisole (5/18): Synthesized according to **P1** from 4-bromo anisole (5.00 g, 26.8 mmol), *n*-bromo octadecane (8.90 g, 26.8 mmol) and *tert*-butyl lithium (1.7 M in *n*-heptane, 31.8 mL. 54.1 mmol) in THF (150 mL). Purification by column chromatography (eluent: *n*-hexane). Colourless solid, yield: 6.00 g (60%), $C_{25}H_{44}O$, M = 360.34 g/mol, mp. 38 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 6.82 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 3.79 (s, 3H, Ar–O–CH_3), 2.58 - 2.50 (m, 2H, Ar–CH_2–), 1.63 - 1.53 (m, 2H, –CH_2–), 1.37 - 1.18 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Octadecylphenol (6/18): Synthesized according to **P2** from **5/18** (6.00 g, 16.6 mmol) and boron tribromide (9.24 g, 38.3 mmol) in absolute DCM (100 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 5.00 g (87%), $C_{24}H_{42}O$, M = 346.32 g/mol, mp. 79 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.04 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 6.74 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 4.50 (s, 1H, Ar–O*H*), 2.56 - 2.48 (m, 2H, Ar–CH_2–), 1.62 - 1.51 (m, 2H, –CH_2–), 1.37 - 1.18 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecylphenoxycarbonyl)benzaldehyde (7/18): Synthesized according to **P4** from **6/18** (5.00g, 14.5 mmol), terephthalaldehydic acid (2.18 g, 14.5 mmol), DCC (3.80 g, 18.8 mmol) and DMAP (tip of spatula) in abs. DCM (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 6.00 g (87%), $C_{32}H_{46}O_3$, M = 478.34 g/mol, mp = 96 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.15 (s, 1H, –C*H*O), 8.36 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 8.02 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.24 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.13 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.66 - 2.60 (m, 2H, Ar–CH_2–), 1.67 - 1.58 (m, 2H, –CH_2–), 1.39 - 1.21 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-(4-Octadecylphenoxycarbonyl)benzoic acid (8/18): Synthesized according to **P3** from **7/18** (5.00 g, 10.5 mmol), resorcinol (1.50 g, 13.6 mmol), sodium chlorite (5.50 g, 60.7 mmol) and potassium dihydrogenphosphate (4.30 g, 31.4 mmol) in *tert*-BuOH (300 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 5.00 g (95%), $C_{32}H_{46}O_4$, M = 494.34 g/mol, mp. 243 °C. **^{1}H-NMR (**400 MHz, $CDCl_3$) δ 8.29 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 8.21 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.24 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.12 (d, ^3J = 8.5 Hz, 2H, Ar–*H*),

2.70 - 2.57 (m, 2H, Ar–CH_2–), 1.71 - 1.57 (m, 2H, –CH_2–), 1.42 - 1.13 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

4-(4-Hexyloxyphenoxycarbonyl)benzoic acid (8/O6)

4-(4-Hexyloxyphenoxycarbonyl)benzaldehyde (7/O6): Synthesized according to **P5** from 4-hexyloxyphenol (2.60g, 13.3 mmol), terephthalaldehydic acid (2.00 g, 13.3 mmol), DCC (3.60 g, 17.3 mmol) and DMAP (tip of spatula) in abs. DCM (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.90 g (67%), $C_{20}H_{22}O_4$, M = 326.39 g/mol, mp. 102 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.12 (s, 1H, –C*H*O), 8.34 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 8.00 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.11 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 6.92 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 4.04 - 3.86 (m, 2H, Ar–CH_2–), 1.88 - 1.69 (m, 2H, –CH_2–), 1.51 - 1.39 (m, 2H, –CH_2–), 1.39 - 1.27 (m, 4H, –CH_2–), 0.90 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm.

4-(4-Hexyloxyphenoxycarbonyl)benzoic acid (8/O6): Synthesized according to **P3** from **7/O6** (2.90 g, 11.6 mmol), resorcinol (1.30 g, 11.6 mmol), sodium chlorite (4.70 g, 51.6 mmol) and potassium dihydrogenphosphate (3.60 g, 26.7 mmol) in *tert*-BuOH (150 mL). Purification by crystallisation from ethanol. Colourless solid, yield: 2.80 g (92%), $C_{20}H_{22}O_5$, M = 342.39 g/mol, mp. 305 °C. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ 8.09 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 8.03 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.18 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 6.98 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 3.97 (t, ^3J = 6.5 Hz, 2H, Ar–CH_2–), 1.75 - 1.66 (m, 2H, –CH_2–), 1.47 - 1.37 (m, 2H, –CH_2–), 1.35 - 1.25 (m, 4H, –CH_2–), 0.87 (t, ^3J = 7.1 Hz, 3H, –CH_3) ppm.

2.3.3 4-Cyano-3-[4-(4-alkylphenoxycarbonyl)benzoyloxy]phenols

4-Benzyloxy-2-[4-(4-hexylphenoxycarbonyl)benzoyloxy]benzonitrile (9/6): Synthesized according to **P4** from **8/6** (2.00g, 6.1 mmol), thionyl chloride (5 mL), **11** (1.40 g, 6.1 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 2.72 g (84%), $C_{34}H_{31}NO_5$, M = 533.6 g/mol, mp. 90 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.30 (m, 4H, Ar–*H*), 7.64 (d, ^3J = 8.7 Hz, 1H, Ar–*H*), 7.47 - 7.33 (m, 5H, Ar–*H*), 7.25 (d, ^3J = 7.9 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.13 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 6.97 (dd, ^3J = 8.7 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.14 (s, 2H, Ar–CH_2–Ar), 2.68 - 2.60 (m, 2H, –CH_2–), 1.70 - 1.58 (m, 2H, –CH_2–), 1.41 - 1.22 (m, 6H, –CH_2–), 0.90 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

4-Cyano-3-[4-(4-hexylphenoxycarbonyl)benzoyloxy]phenol (10/6): Synthesized according to **P7** from **9/6** (2.50 g, 4.7 mmol) and Pd/C (10%, 50 mg) in 1,4-dioxane (10 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 900 mg (43%), $C_{27}H_{25}NO_5$, M = 443.49 g/mol, mp. 134 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.40 - 8.31 (m, 4H, Ar–*H*), 7.59 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.25 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.00 (d, ^3J = 2.3 Hz, 1H, Ar–*H*), 6.81 (dd, ^3J = 8.6 Hz, ^4J = 2.3 Hz, 1H, Ar–*H*), 6.04 (br, 1H, Ar–O*H*), 2.67 - 2.60 (m, 2H, Ar–CH_2–), 1.67 - 1.59 (m, 2H, –CH_2–), 1.41 - 1.27 (m, 6H, –CH_2–), 0.90 (t, J = 6.9 Hz, 3H, –CH_3) ppm.

4-Benzyloxy-2-[4-(4-dodecylphenoxycarbonyl)benzoyloxy]benzonitrile (9/12): Synthesized according to **P4** from **8/12** (2.50g, 6.1 mmol), thionyl chloride (5 mL), **11** (1.40 g, 6.1 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 2.65 g (70%), $C_{40}H_{43}NO_5$, M = 617.77 g/mol, mp. 87 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.40 - 8.31 (m, 4H, Ar–*H*), 7.64 (d, ^3J = 8.7 Hz, 1H, Ar–*H*), 7.45 - 7.32 (m, 5H, Ar–*H*), 7.25 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.14 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.13 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 6.97 (dd, ^3J = 8.7

Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.15 (s, 2H, Ar–O–CH_2–Ar), 2.68 - 2.58 (m, 2H, Ar–CH_2–), 1.70 - 1.57 (m, 2H, –CH_2–), 1.41 - 1.20 (m, 18H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Cyano-3-[4-(4-dodecylphenoxycarbonyl)benzoyloxy]phenol (10/12): Synthesized according to **P7** from **9/12** (2.50 g, 4.0 mmol) and Pd/C (10%, 100 mg) in THF (20 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 1.70 g (81%), $C_{33}H_{37}NO_5$, *M* = 527.27 g/mol, mp. 127 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.39 - 8.31 (m, 4H, Ar–*H*), 7.60 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.24 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.14 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.01 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 6.83 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.76 (br, 1H, Ar–O*H*), 2.67 - 2.59 (m, 2H, Ar–CH_2–), 1.69 - 1.58 (m, 2H, –CH_2–), 1.42 - 1.19 (m, 18H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Benzyloxy-2-[4-(4-tetradecylphenoxycarbonyl)benzoyloxy]benzonitrile (9/14): Synthesized according to **P4** from **8/14** (2.50g, 5.7 mmol), thionyl chloride (5 mL), **11** (1.30 g, 5.7 mmol) and pyridine (1 mL) in DCM (25 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 3.28 g (89%), $C_{42}H_{47}NO_5$, *M* = 645.35 g/mol, mp. 67 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.40 - 8.32 (m, 4H, Ar–*H*), 7.64 (d, ^3J = 8.7 Hz, 1H, Ar–*H*), 7.45 - 7.34 (m, 5H, Ar–*H*), 7.25 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.13 (d,^4J = 2.4 Hz, 1H, Ar–*H*), 6.97 (dd, ^3J = 8.7, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.15 (s, 2H, Ar–O–CH_2–Ar), 2.68 – 2.59 (m, 2H, , Ar–CH_2–), 1.71 - 1.58 (m, 2H, –CH_2–), 1.42 - 1.19 (m, 22H, –CH_2–), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

4-Cyano-3-[4-(4-tetradecylphenoxycarbonyl)benzoyloxy]phenol (10/14): Synthesized according to **P7** from **9/14** (3.00 g, 4.6 mmol) and Pd/C (10%, 200 mg) in THF (20 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.30 g (90%), $C_{35}H_{41}NO_5$, *M* = 555.30 g/mol, mp. 124 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.39 - 8.32 (m, 4H, Ar–*H*), 7.61 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.25 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.14 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.02 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 6.83 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.68 (br, 1H, Ar–O*H*), 2.67 - 2.60 (m, 2H, Ar–CH_2–), 1.68 - 1.59 (m, 2H, –CH_2–), 1.42 - 1.17 (m, 22H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Benzyloxy-2-[4-(4-octadecylphenoxycarbonyl)benzoyloxy]benzonitril (9/18): Synthesized according to **P4** from **8/18** (4.00g, 8.1 mmol), thionyl chloride (10 mL), **11** (1.80 g, 8.1 mmol) and pyridine (1 mL) in DCM (25 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 4.40 g (77%), $C_{46}H_{55}NO_5$, *M* = 701.41 g/mol, mp. 82 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.39 - 8.31 (m, 4H, Ar–*H*), 7.64 (d, ^3J = 8.7 Hz, 1H, Ar–*H*), 7.45 – 7.34 (m, 5H, Ar–*H*), 7.28 - 7.21 (m, 2H, Ar–*H*), 7.14 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.13 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 6.97 (dd, ^3J = 8.7 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.14 (s, 2H, Ar–CH_2–O–Ar), 2.69 - 2.57 (m, 2H, Ar–CH_2–), 1.71 - 1.56 (m, 2H, –CH_2–), 1.43 - 1.16 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Cyano-3-[4-(4-octadecylphenoxycarbonyl)benzoyloxy]phenol (10/18): Synthesized according to **P7** from **9/18** (4.00 g, 5.7 mmol) and Pd/C (10%, 100 mg) in THF (50 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 2.90 g (83%), $C_{39}H_{49}NO_5$, *M* = 611.36 g/mol, mp. 125 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.39 - 8.31 (m, 4H, Ar–*H*), 7.61 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.28 - 7.22 (m, 2H, Ar–*H*), 7.14 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.02 (d, ^4J = 2.3 Hz, 1H, Ar–*H*), 6.84 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.70 (br, 1H, Ar–O*H*), 2.67 - 2.59 (m, 2H, Ar–CH_2–), 1.69 - 1.58 (m, 2H, –CH_2–), 1.41 - 1.19 (m, 30H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm.

4-Benzyloxy-2-[4-(4-hexyloxyphenoxycarbonyl)benzoyloxy]benzonitrile (9/O6): Synthesized according to **P4** from **8/O6** (1.35 g, 3.9 mmol), thionyl chloride (5 mL), **11** (0.87 g, 3.9 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol. Colourless solid, yield: 1.22 g (57%), $C_{34}H_{31}NO_6$, M = 549.61 g/mol, mp. 92 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.40 - 8.32 (m, 4H, Ar–*H*), 7.64 (d, ^3J = 8.7 Hz, 1H, Ar–*H*), 7.48 - 7.30 (m, 5H, Ar–*H*), 7.15 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 7.13 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 7.00 - 6.91 (m, 3H, Ar–*H*), 5.15 (s, 2H, Ar–CH_2–O–Ar), 3.98 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 1.86 - 1.74 (m, 2H, –CH_2–), 1.52 - 1.43 (m, 2H, –CH_2–), 1.41 - 1.31 (m, 4H, –CH_2–), 0.92 (t, J = 7.1 Hz, 3H, –CH_3) ppm.

4-Cyano-3-[4-(4‘-n-hexyloxyphenoxycarbonyl)benzoyloxy]phenol (10/O6): Synthesized according to **P7** from **9/O6** (1.22 g, 2.2 mmol) and Pd/C (10%, 30 mg) in 1,4-dioxane (10 mL). Purification by column chromatography (eluent: DCM). Colourless solid, yield: 0.44 g (55%), $C_{27}H_{25}NO_6$, M = 359.49 g/mol, mp. 143 °C. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.37 - 8.29 (m, 4H, Ar–*H*), 7.58 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.13 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 7.00 (d, ^4J = 2.4 Hz, 1H, Ar–*H*), 6.93 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 6.81 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 5.71 (br, 1H, –O*H*), 3.95 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 1.81 - 1.74 (m, 2H, –CH_2–), 1.50 - 1.41 (m, 2H, –CH_2–), 1.38 - 1.29 (m, 4H, –CH_2–), 0.90 (t, ^3J = 7.1 Hz, 3H, –CH_3) ppm.

2.4. Compounds B*m*/6

2-[‘-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-octylbenzoyloxy)benzoyloxy]benzonitrile (B8/6): Synthesized according to **P4** from **4/8** (318 mg, 0.72 mmol), thionyl chloride (2 mL), **10/6** (192 mg, 0.55 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 182 mg (37%), $C_{49}H_{49}NO_8$, M = 779.79 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.45 - 8.32 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 8.13 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 7.36 (dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.25 (d, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.78 - 2.68 (m, 2H, Ar–CH_2–), 2.68 - 2.60 (m, 2H, Ar–CH_2–), 1.75 - 1.58 (m, 4H, –CH_2–), 1.43 - 1.19 (m, 16H, –CH_2–), 1.00 - 0.80 (m, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.69 (–*C*OOR), 164.38 (–*C*OOR), 163.39 (–*C*OOR), 162.98 (–*C*OOR), 156.03, 155.00, 153.37, 150.15, 148.75, 141.08, 135.00, 134.20, 132.39, 132.19, 130.80, 130.63, 130.52, 129.57, 128.97, 126.42, 125.91, 122.51, 121.29, 120.42, 117.50, 114.80 (–*C*N), 104.41 (C_{Ar}–CN), 36.28 (C_{Ar}–*C*H$_2$–), 35.55 (C_{Ar}–*C*H$_2$–), 32.00, 31.87, 31.58, 31.26, 29.57, 29.40, 29.37, 29.10, 22.80, 22.76, 14.24 (–*C*H$_3$) ppm. **EA**: calc. for $C_{49}H_{49}NO_8$: C 75.46, H 6.33, N 1.80; found C 75.10, H 6.26, N 1.79.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-decylbenzoyloxy)benzoyloxy]benzonitrile (B10/6): Synthesized according to **P4** from **4/10** (112 mg, 0.32 mmol), thionyl chloride (2 mL), **10/6** (138 mg, 0.32 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 160 mg (62%), $C_{51}H_{53}NO_8$, M = 807.07 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.28 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.75 - 2.68 (m, 2H, Ar–CH_2–), 2.67 - 2.60 (m, 2H, Ar–CH_2–), 1.72 - 1.59 (m, 4H, –CH_2–), 1.41 – 1.20 (m, 20H, –CH_2–), 0.90 (t, ^3J = 6.9 Hz, 3H, –CH_3), 0.89 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.70 (–*C*OOR), 164.40 (–*C*OOR), 163.40 (–*C*OOR), 162.99 (–*C*OOR), 156.04, 155.00, 153.38, 150.17, 148.75, 141.09, 135.00, 134.21, 132.39, 132.20, 130.80, 130.64, 130.53, 129.58, 128.97, 126.42, 125.92, 122.51, 121.29, 120.43, 117.51, 114.81 (–*C*N), 104.42 (C_{Ar}–CN), 36.29 (C_{Ar}–*C*H_2–), 35.56 (C_{Ar}–*C*H_2–), 32.05, 31.87, 31.58, 31.26, 29.75, 29.71, 29.61, 29.47, 29.40, 29.11, 22.84, 22.77, 14.26 (–*C*H_3), 14.25 (–*C*H_3) ppm. **EA**: calc. for $C_{51}H_{53}NO_8$: C 75.81, H 6.61, N 1.73; found C 75.65, H 6.35, N 1.76.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecylbenzoyloxy)benzoyloxy]benzonitrile (B12/6): Synthesized according to **P4** from **4/12** (113 mg, 0.28 mmol), thionyl chloride (25 mL), **10/6** (117 mg, 0.26 mmol) and pyridine (1 mL) in DCM (30 mL). Purification by column chromatography (eluent: $CHCl_3$:petrolether 95:5) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 154 mg (71%), $C_{53}H_{57}NO_8$, *M* = 836.02 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.47-8.31 (m, 8H, Ar–*H*), 7.87 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.64 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.28 (d, ^3J = 8.2 Hz, 4H, Ar–*H*), 7.18 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 7.17 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.73-2.61 (m, 4H, Ar–CH_2–), 1.73-1.60 (m, 4H, –CH_2–), 1.44-1.23 (m, 24H, –CH_2–), 0.91 (t, ^3J = 7.4 Hz, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.12, 163.17, 162.80, 154.55, 153.21, 148.56, 140.93, 134.93, 134.76, 134.06, 132.49, 132.12, 130.63, 130.47, 130.42, 130.41, 129.43, 129.41, 121.10, 121.06, 120.14, 117.25, 114.53, 104.50, 35.38, 31.90, 31.69, 31.44, 31.40, 29.65, 29.64, 29.62, 29.57, 29.48, 29.33, 29.27, 28.93, 22.67, 22.59, 14.09, 14.07 ppm. **EA**: calc. for $C_{53}H_{57}NO_8$: C 76.14, H 6.87, N 1.68; found C 76.02, H 6.74, N 1.64.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-tetradecylbenzoyloxy)benzoyloxy]benzonitrile (B14/6): Synthesized according to **P4** from **4/14** (175 mg, 0.40 mmol), thionyl chloride (2 mL), **10/6** (178 mg, 0.40 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 228 mg (65%), $C_{55}H_{61}NO_8$, *M* = 864.07 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.35 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.27 - 7.23 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.74 - 2.68 (m, 2H, Ar–CH_2–), 2.67 - 2.61 (m, 2H, Ar–CH_2–), 1.71 - 1.58 (m, 2H, –CH_2–), 1.42 - 1.20 (m, 28H, –CH_2–), 0.94 - 0.85 (m, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.22 (–*C*OOR), 163.22 (–*C*OOR), 162.81 (–*C*OOR), 155.86, 154.82, 153.20, 149.99, 148.57, 140.91, 134.82, 134.03, 132.21, 132.02, 130.62, 130.46, 130.35, 129.40, 128.79, 126.24, 125.73, 122.33, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.24 (C_{Ar}–CN), 36.11 (C_{Ar}–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.90, 31.69, 31.40, 31.09, 29.67, 29.65, 29.63, 29.61, 29.53, 29.43, 29.33, 29.23, 28.93, 22.67, 22.59, 14.09 (–*C*H_3), 14.07 (– *C*H_3) ppm. **EA**: calc. for $C_{55}H_{61}NO_8$: C 76.45, H 7.12, N 1.62; found C 76.32, H 6.88, N 1.59.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-hexadecylbenzoyloxy)benzoyloxy]benzonitrile (B16/6): Synthesized according to **P4** from **4/16** (163 mg, 0.35 mmol), thionyl chloride (2 mL), **10/6** (155 mg, 0.35 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 175 mg (56%), $C_{57}H_{65}NO_8$, *M* = 892.13 g/mol. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.27 - 7.23 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.75 - 2.68 (m, 2H, Ar–CH_2–), 2.68 - 2.60 (m, 2H, Ar–CH_2–), 1.72 - 1.58 (m, 4H, –CH_2–),

1.41 - 1.19 (m, 32H, –CH_2–), 0.94 - 0.84 (m, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.22 (–*C*OOR), 163.22 (–*C*OOR), 162.81 (–*C*OOR), 155.86, 154.82, 153.20, 149.99, 148.57, 140.91, 134.82, 134.03, 132.21, 132.02, 130.62, 130.46, 130.35, 129.40, 128.79, 126.24, 125.73, 122.33, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.24 (C_{Ar}–CN), 36.11 (C_{Ar}–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.90, 31.69, 31.40, 31.09, 29.67, 29.65, 29.63, 29.61, 29.53, 29.43, 29.33, 29.23, 28.93, 22.67, 22.59, 14.09 (–*C*H_3), 14.07 (–*C*H_3) ppm. **EA**: calc. for $C_{57}H_{65}NO_8$: C 76.74, H 7.34, N 1.57; found C 76.75, H 7.33, N 1.57.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-octadecylbenzoyloxy)benzoyloxy]benzonitrile (B18/6): Synthesized according to **P4** from **4/18** (212 mg, 0.43 mmol), thionyl chloride (2 mL), **10/6** (190 mg, 0.43 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 350 mg (88%), $C_{59}H_{69}NO_8$, *M* = 920.18 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.36 (dd, ^3J = 8.5, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.27 - 7.24 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.76 - 2.68 (m, 2H, Ar–CH_2–), 2.68 - 2.60 (m, 2H, Ar–CH_2–), 1.72 - 1.59 (m, ^3J = 15.4, 7.6 Hz, 4H, –CH_2–), 1.41 - 1.22 (m, 36H, –CH_2–), 0.90 (t, ^3J = 7.0 Hz, 3H, –CH_3), 0.88 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.55 (–*C*OOR), 164.25 (–*C*OOR), 163.25 (–*C*OOR), 162.84 (–*C*OOR), 155.89, 154.85, 153.23, 150.02, 148.60, 140.94, 134.85, 134.06, 132.24, 132.05, 130.66, 130.49, 130.38, 129.43, 128.82, 126.27, 125.77, 122.36, 121.14, 120.28, 117.36, 114.66 (–*C*N), 104.27 (C_{Ar}–CN), 36.14 (C_{Ar}–*C*H_2–), 35.41 (C_{Ar}–*C*H_2–), 31.93, 31.72, 31.44, 31.12, 29.71, 29.68, 29.66, 29.64, 29.56, 29.46, 29.36, 29.26, 28.96, 22.70, 22.62, 14.12 (–*C*H_3), 14.10 (–*C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_8$: C 77.01, H 7.56, N 1.52; found C 76.71, H 7.78, N 1.37.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-eicosylbenzoyloxy)benzoyloxy]benzonitrile (B20/6): Synthesized according to **P4** from **4/20** (200 mg, 0.38 mmol), thionyl chloride (2 mL), **10/6** (170 mg, 0.38 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 140 mg (40%), $C_{61}H_{73}NO_8$, *M* = 947.53 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.29 - 7.21 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.76 - 2.68 (m, 2H, Ar–CH_2–), 2.68 - 2.60 (m, 2H, Ar–CH_2–), 1.73 - 1.58 (m, 4H, –CH_2–), 1.44 - 1.19 (m, 40H, –CH_2–), 0.94 - 0.84 (m, 6H, –CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.22 (–*C*OOR), 163.23 (–*C*OOR), 162.81 (–*C*OOR), 155.87, 154.83, 153.20, 149.99, 148.58, 140.92, 134.83, 134.03, 132.22, 132.02, 130.63, 130.46, 130.35, 129.41, 128.80, 126.25, 125.74, 122.34, 121.12, 120.25, 117.33, 114.63 (–*C*N), 104.25 (C_{Ar}–CN), 36.12 (C_{Ar}–*C*H_2–), 35.39 (C_{Ar}–*C*H_2–), 31.91, 31.70, 31.41, 31.09, 29.68, 29.64, 29.62, 29.54, 29.44, 29.34, 29.24, 28.94, 22.67, 22.59, 14.10 (–*C*H_3), 14.07 (–*C*H_3) ppm. **EA**: calc. for $C_{61}H_{73}NO_8$: C 77.26, H 7.76, N 1.48; found C 77.25, H 7.46, N 1.39.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-docosylbenzoyloxy)benzoyloxy]benzonitrile (B22/6): Synthesized according to **P4** from **4/22** (202 mg, 0.37 mmol), thionyl chloride (2 mL), **10/6** (162 mg, 0.37 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 265 mg (74%), $C_{63}H_{77}NO_8$, *M* = 975.56 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.44 - 8.32 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.7 Hz, 2H,

Ar–*H*), 8.12 (d, ^{3}J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^{3}J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^{4}J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^{3}J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^{3}J = 8.2 Hz, 2H, Ar–*H*), 7.29 - 7.21 (m, 2H, Ar–*H*), 7.15 (d, ^{3}J = 8.5 Hz, 2H, Ar–*H*), 2.77 - 2.67 (m, 2H, Ar–CH_2–), 2.67 – 2.58 (m, 2H, Ar–CH_2–), 1.72 - 1.58 (m, 4H, –CH_2–), 1.45 - 1.15 (m, 44H, –CH_2–), 0.95 - 0.83 (m, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.21 (–*C*OOR), 163.22 (–*C*OOR), 162.80 (–*C*OOR), 155.86, 154.82, 153.20, 149.98, 148.57, 140.91, 134.82, 134.02, 132.21, 132.02, 130.62, 130.45, 130.35, 129.40, 128.79, 126.24, 125.74, 122.33, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.24 (C_{Ar}–CN), 36.11 (C_{Ar}–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.90, 31.69, 31.40, 31.09, 29.67, 29.66, 29.63, 29.62, 29.54, 29.43, 29.33, 29.24, 28.93, 22.66, 22.59, 14.09 (–*C*H_3), 14.07 (–*C*H_3) ppm. **EA**: calc. for $C_{63}H_{77}NO_8$: C 77.51, H 7.95, N 1.43; found C 77.27, H 7.93, N 1.62.

2.5 Compound C*m*/*n*

2-[4-(4-Dodecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecylbenzoyloxy)benzoyloxy]benzonitrile (C12/12): Synthesized according to **P4** from **4/12** (191 mg, 0.47 mmol), thionyl chloride (2 mL), **10/12** (240 mg, 0.47 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 146 mg (34%), $C_{59}H_{69}NO_8$, *M* = 919.50 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.43 - 8.33 (m, 4H, Ar–*H*), 8.28 (d, ^{3}J = 8.8 Hz, 2H, Ar–*H*), 8.12 (d, ^{3}J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^{3}J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^{4}J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^{3}J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^{3}J = 8.5, ^{4}J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^{3}J = 8.3 Hz, 2H, Ar–*H*), 7.26 - 7.23 (m, 2H, Ar–*H*), 7.15 (d, ^{3}J = 8.5 Hz, 2H, Ar–*H*), 2.75 - 2.68 (m, 2H, Ar–CH_2–), 2.67 - 2.59 (m, 2H, Ar–CH_2–), 1.72 - 1.58 (m, 4H, –CH_2–), 1.42 - 1.17 (m, 36H, –CH_2–), 0.88 (t, ^{3}J = 6.8 Hz, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.21 (–*C*OOR), 163.22 (–*C*OOR), 162.81 (–*C*OOR), 155.86, 154.82, 153.20, 149.98, 148.57, 140.92, 134.83, 134.03, 132.21, 132.02, 130.62, 130.45, 130.35, 129.40, 128.79, 126.24, 125.74, 122.33, 121.11, 120.25, 117.33 (–*C*N), 114.63 (C_{Ar}–CN), 104.24, 36.11 (C_{Ar}–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.90, 31.89, 31.44, 31.08, 29.65, 29.64, 29.63, 29.62, 29.61, 29.57, 29.53, 29.48, 29.43, 29.33, 29.32, 29.27, 29.22, 22.67, 14.09 (–*C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_8$: C 77.01, H 7.56, N 1.52; found C 76.63, H 7.13, N 1.44.

2-[4-(4-Dodecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-docosylbenzoyloxy)benzoyloxy]benzonitril (C22/12): Synthesized according to **P4** from **4/22** (185 mg, 0.34 mmol), thionyl chloride (2 mL), **10/12** (178 mg, 0.34 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 187 mg (52%), $C_{69}H_{89}NO_8$, *M* = 1059.66 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^{3}J = 8.5 Hz, 2H, Ar–*H*), 8.12 (d, ^{3}J = 8.1 Hz, 2H, Ar–*H*), 7.82 (d, ^{3}J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^{4}J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^{3}J = 8.6 Hz, 2H, Ar–*H*), 7.35 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^{3}J = 8.3 Hz, 2H, Ar–*H*), 7.28 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^{3}J = 8.4 Hz, 2H, Ar–*H*), 2.75 - 2.68 (m, 2H, Ar–CH_2–), 2.67 - 2.60 (m, 2H, Ar–CH_2–), 1.72 - 1.58 (m, 4H, –CH_2–), 1.42 - 1.18 (m, 56H, –CH_2–), 0.88 (t, ^{3}J = 6.8 Hz, 3H, –CH_3), 0.88 (t, ^{3}J = 6.9 Hz, 3H, –CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.22 (–*C*OOR), 163.23 (–*C*OOR), 162.81 (–*C*OOR), 155.87, 154.83, 153.20, 149.99, 148.57, 140.92, 134.83, 134.03, 132.22, 132.02, 130.63, 130.46, 130.35, 129.41, 128.80, 126.25, 125.74, 122.34, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.25 (C_{Ar}–CN), 36.12 (C_{Ar}–*C*H_2–), 35.39 (C_{Ar}–*C*H_2–), 31.91, 31.45, 31.10, 29.68, 29.66, 29.64, 29.62, 29.58, 29.54, 29.49, 29.44, 29.34, 29.27, 29.24, 22.67, 14.10 (–*C*H_3) ppm. **EA**: calc. for $C_{69}H_{89}NO_8$: C 78.15, H 8.46, N 1.32; found C 77.70, H 8.35, N 1.33.

2-[4-(4-Tetradecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecylbenzoyloxy)-benzoyloxy]benzonitrile (C12/14): Synthesized according to **P4** from **4/12** (108 mg, 0.26 mmol), thionyl chloride (2 mL), **10/14** (150 mg, 0.26 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 153 mg (62%), $C_{61}H_{73}NO_8$, M = 948.23 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.33 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.4 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.28 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.76 - 2.68 (m, 2H, Ar–CH_2–), 2.67 - 2.59 (m, 2H, Ar–CH_2–), 1.72 - 1.58 (m, 4H, –CH_2–), 1.40 - 1.08 (m, 40H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 6H, –CH_3) ppm. **^{13}C-**NMR (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.21 (–*C*OOR), 163.22 (–*C*OOR), 162.81 (–*C*OOR), 155.86, 154.82, 153.20, 149.98, 148.57, 140.92, 134.82, 134.03, 132.21, 132.02, 130.62, 130.45, 130.35, 129.40, 128.79, 126.24, 125.74, 122.33, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.24 (C_{Ar}–CN), 36.11 (C_{Ar}–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.91, 31.90, 31.45, 31.08, 29.68, 29.66, 29.65, 29.64, 29.61, 29.58, 29.53, 29.49, 29.43, 29.34, 29.32, 29.27, 29.23, 22.67, 14.09 (–*C*H_3) ppm. **EA**: calc. for $C_{61}H_{73}NO_8$: C 77.26, H 7.76, N 1.48; found C 77.35, H 7.83, N 1.58.

2-[4-(4-Tetradecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-tetradecylbenzoyloxy)-benzoyloxy]benzonitrile (C14/14): Synthesized according to **P4** from **4/14** (160 mg, 0.37 mmol), thionyl chloride (2 mL), **10/14** (203 mg, 0.37 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 174 mg (48%), $C_{63}H_{77}NO_8$, M = 976.29 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.45 - 8.32 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.6 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.1 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.4 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.0 Hz, 2H, Ar–*H*), 7.25 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.78 - 2.67 (m, 2H, Ar–CH_2–), 2.67 - 2.58 (m, 2H, Ar–CH_2–), 1.74 - 1.58 (m, 4H, –CH_2–), 1.45 - 1.06 (m, 44H, –CH_2–), 0.88 (t, ^3J = 6.8 Hz, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.21 (–*C*OOR), 163.22 (–*C*OOR), 162.81 (–*C*OOR), 155.86, 154.82, 153.20, 149.99, 148.57, 140.92, 134.83, 134.03, 132.21, 132.02, 130.63, 130.46, 130.35, 129.40, 128.79, 126.24, 125.74, 122.33, 121.11, 120.25, 117.33, 114.65 (–*C*N), 104.24 (C_{Ar}–CN), 36.11 (C_{Ar}–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.90, 31.45, 31.08, 29.67, 29.67, 29.66, 29.65, 29.63, 29.61, 29.57, 29.53, 29.48, 29.43, 29.33, 29.27, 29.23, 22.67, 14.09 (–*C*H_3) ppm. **EA**: calc. for $C_{63}H_{77}NO_8$: C 77.51, H 7.95, N 1.43; found C 77.34, H 7.86, N 1.40.

2-[4-(4-Tetradecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-hexadecylbenzoyloxy)-benzoyloxy]benzonitrile (C16/14): Synthesized according to **P4** from **4/16** (198 mg, 0.36 mmol), thionyl chloride (2 mL), **10/14** (166 mg, 0.46 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 175 mg (49%), $C_{65}H_{81}NO_8$, M = 1003.60 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.29 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.77 - 2.68 (m, 2H, Ar–CH_2–), 2.67 - 2.59 (m, 2H, –CH_2–), 1.73 - 1.58 (m, 4H, –CH_2–), 1.45 - 1.06 (m, 38H, –CH_2–), 0.88 (t, 3H, –CH_3), 0.88 (t, 3H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.21 (–*C*OOR), 163.22 (–*C*OOR), 162.81 (–*C*OOR), 155.86,

154.82, 153.20, 149.99, 148.57, 140.92, 134.83, 134.03, 132.21, 132.02, 130.62, 130.45, 130.35, 129.40, 128.79, 126.24, 125.74, 122.33, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.24 (*C*$_{Ar}$–CN) , 36.11 (C$_{Ar}$–*C*H$_2$–), 35.38 (C$_{Ar}$–*C*H$_2$–), 31.90, 31.45, 31.09, 29.67, 29.67, 29.65, 29.63, 29.61, 29.57, 29.53, 29.49, 29.43, 29.34, 29.27, 29.23, 22.67, 14.09 (–*C*H$_3$) ppm. **EA**: calc. for $C_{65}H_{81}NO_8$: C 77.73, H 8.13, N 1.39; found C 77.58, H 7.82, N 1.35.

2-[4-(4-Tetradecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-octadecylbenzoyloxy)-benzoyloxy]benzonitrile (C18/14): Synthesized according to **P4** from **4/18** (171 mg, 0.35 mmol), thionyl chloride (2 mL), **10/14** (192 mg, 0.35 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 220 mg (61%), $C_{67}H_{85}NO_8$, *M* = 1031.63 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42 - 8.33 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.28 - 7.21 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.75 - 2.68 (m, 2H, Ar–C*H*$_2$–), 2.67 - 2.60 (m, 2H, Ar–C*H*$_2$–), 1.71 - 1.59 (m, 4H, –C*H*$_2$–), 1.45 - 1.17 (m, 52H, –C*H*$_2$–), 0.95 - 0.80 (m, 6H, –C*H*$_3$) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.22 (–*C*OOR), 163.23 (–*C*OOR), 162.81 (–*C*OOR), 155.87, 154.83, 153.20, 149.99, 148.57, 140.92, 134.83, 134.03, 132.22, 132.02, 130.63, 130.46, 130.35, 129.41, 128.80, 126.25, 125.74, 122.34, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.25 (*C*$_{Ar}$–CN), 36.12 (C$_{Ar}$–*C*H$_2$–), 35.39 (C$_{Ar}$–*C*H$_2$–), 31.91, 31.45, 31.09, 29.68, 29.66, 29.64, 29.62, 29.58, 29.54, 29.49, 29.44, 29.34, 29.28, 29.24, 22.67, 14.10 (–*C*H$_3$) ppm. **EA**: calc. for $C_{67}H_{85}NO_8$: C 77.95, H 8.30, N 1.36; found C 77.59, H 8.10, N 1.37.

2-[4-(4-Octadecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-octadecylbenzoyloxy)-benzoyloxy]benzonitrile (C18/18): Synthesized according to **P4** from **4/18** (162 mg, 0.33 mmol), thionyl chloride (2 mL), **10/18** (201 mg, 0.33 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 178 mg (50%), $C_{71}H_{93}NO_8$, *M* = 1087.69 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42 - 8.33 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.3, ^4J = 2.4 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.28 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.4 Hz, 2H, Ar–*H*), 2.76 - 2.67 (m, 2H, Ar–C*H*$_2$–), 2.67 - 2.59 (m, 2H, Ar–C*H*$_2$–), 1.72 - 1.58 (m, 4H, –C*H*$_2$–), 1.44 - 1.16 (m, 60H, –C*H*$_2$–), 0.88 (t, ^3J = 6.8 Hz, 6H, –C*H*$_3$) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.53 (–*C*OOR), 164.22 (–*C*OOR), 163.23 (–*C*OOR), 162.81 (–*C*OOR), 155.87, 154.83, 153.20, 149.99, 148.57, 140.93, 134.83, 134.03, 132.22, 132.02, 130.63, 130.46, 130.35, 129.41, 128.80, 126.25, 125.74, 122.34, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.25 (*C*$_{Ar}$–CN), 36.12 (C$_{Ar}$–*C*H$_2$–), 35.39 (C$_{Ar}$–*C*H$_2$–), 31.91, 31.46, 31.10, 29.69, 29.66, 29.64, 29.62, 29.58, 29.54, 29.49, 29.43, 29.34, 29.28, 29.24, 22.67, 14.10 (–*C*H$_3$) ppm. **EA**: calc. for $C_{71}H_{93}NO_8$: C 78.70, H 8.89, N 1.22; found C 78.45, H 8.69, N 1.26.

2-[4-(4-Octadecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-docosylbenzoyloxy)-benzoyloxy]benzonitrile (C22/18): Synthesized according to **P4** from **4/22** (172 mg, 0.31 mmol), thionyl chloride (2 mL), **10/18** (191 mg, 0.31 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 284 mg (80%), $C_{75}H_{101}NO_8$, *M* = 1143.75 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.37 - 7.32 (m, 3H, Ar–*H*), 7.28 - 7.22 (m, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 2.75 - 2.68 (m, 2H, Ar–C*H*$_2$–), 2.67 -

2.60 (m, 2H, Ar–CH_2–), 1.72 - 1.59 (m, 4H, –CH_2–), 1.41 - 1.08 (m, 68H, –CH_2–), 0.88 (t, ^3J = 6.9 Hz, 6H, –CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.52 (–*C*OOR), 164.22 (–*C*OOR), 163.23 (–*C*OOR), 162.81 (–*C*OOR), 155.87, 154.83, 153.20, 149.99, 148.57, 140.93, 134.83, 134.03, 132.22, 132.02, 130.63, 130.46, 130.35, 129.41, 128.79, 126.25, 125.74, 122.34, 121.11, 120.25, 117.33, 114.63 (–*C*N), 104.25 (C_{Ar}–CN), 36.12 (C_{Ar}–*C*H_2–), 35.39 (C_{Ar}–*C*H_2–), 31.91, 31.46, 31.10, 29.68, 29.66, 29.64, 29.58, 29.54, 29.49, 29.44, 29.34, 29.28, 29.24, 22.67, 14.10 (–*C*H_3) ppm. **EA**: calc. for $C_{75}H_{101}NO_8$: C 78.70, H 8.89, N 1.22; found C 78.45, H 8.69, N 1.26.

2.6 Compounds D

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-octadecyloxybenzoyloxy)benzoyloxy]benzonitrile (DO18/6): Synthesized according to **P4** from **4/O18** (191 mg, 0.38 mmol), thionyl chloride (2 mL), **10/6** (169 mg, 0.38 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 162 mg (46%), $C_{59}H_{69}NO_9$, *M* = 935.50 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42 - 8.34 (m, 4H, Ar–*H*), 8.27 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.15 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.40 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.6 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.25 (d, ^3J = 8.2 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 6.99 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 4.06 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 2.68 - 2.59 (m, 2H, Ar–CH_2–), 1.89 - 1.77 (m, 2H, –CH_2–), 1.69 - 1.59 (m, 2H, –CH_2–), 1.53 - 1.42 (m, 2H, –CH_2–), 1.43 - 1.19 (m, 34H, –CH_2–), 0.95 - 0.84 (m, 6H, –CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.20 (–*C*OOR), 164.17 (–*C*OOR), 163.90 (C_{Ar}–O–CH_2–), 163.23 (–*C*OOR), 162.79 (–*C*OOR), 155.95, 154.84, 153.20, 148.59, 140.89, 134.82, 134.01, 132.42, 132.23, 131.98, 130.62, 130.45, 129.40, 125.62, 122.35, 121.12, 120.76, 120.25, 117.32, 114.64, 114.45 (–*C*N), 104.21 (C_{Ar}–CN), 68.41 (C_{Ar}–O–*C*H_2–), 35.39 (C_{Ar}–*C*H_2–), 31.91, 31.70, 31.41, 29.69, 29.67, 29.65, 29.58, 29.54, 29.35, 29.07, 28.94, 25.97, 22.68, 22.60, 14.11 (–CH_3), 14.08 (–CH_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_9$: C 75.69, H 7.43, N 1.50; found C 75.74, H 7.15, N 1.44.

2-[4-(4-Hexyloxyphenoxycarbonyl)benzoyloxy]-4-[4-(4-octadecylbenzoyloxy)benzoyloxy]benzonitril (D18/O6): Synthesized according to **P4** from **4/18** (222 mg, 0.45 mmol), thionyl chloride (2 mL), **10/O6** (206 mg, 0.45 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 162 mg (38%), $C_{59}H_{69}NO_9$, *M* = 935.50 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.34 (m, 4H, Ar–*H*), 8.28 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.34 (d, ^3J = 8.3 Hz, 2H, Ar–*H*), 7.15 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 6.95 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 3.98 (t, ^3J = 6.6 Hz, 2H, Ar–CH_2–), 2.76 - 2.67 (m, 2H, Ar–CH_2–), 1.85 - 1.75 (m, 2H, –CH_2–), 1.71 - 1.60 (m, 2H, –CH_2–), 1.52 - 1.42 (m, 2H, –CH_2–), 1.42 - 1.18 (m, 34H, –CH_2–), 0.92 (t, ^3J = 7.1 Hz, 3H, –CH_3), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.69 (–*C*OO–),164.59 (–*C*OO–), 163.39 (–*C*OO–), 162.98 (–*C*OO–), 157.29, 156.04, 155.00, 153.38, 150.16, 144.15, 134.98, 134.20, 132.38, 132.20, 130.79, 130.61, 130.53, 128.97, 126.42, 125.91, 122.51, 122.37, 120.42, 117.50, 115.34, 114.81 (–*C*N), 104.42 (C_{Ar}–CN), 68.63 (C_{Ar}–O–*C*H_2–), 36.28 (C_{Ar}–*C*H_2–), 32.08, 31.74, 31.26, 29.85, 29.83, 29.81, 29.79, 29.71, 29.61, 29.51, 29.41, 29.39, 25.87, 22.84, 22.76, 14.27 (–*C*H_3), 14.19 (–*C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_9$: C 75.69, H 7.43, N 1.50; found C 75.21, H 6.93, N 1.41.

2-[4-(4-Hexyloxyphenoxycarbonyl)benzoyloxy]-4-[4-(4-octadecyloxybenzoyloxy)benzoyloxy]benzonitrile (DO18/O6): Synthesized according to **P4** from **4/O18** (191 mg,

0.38 mmol), thionyl chloride (2 mL), **10/O6** (172 mg, 0.38 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 175 mg (48%), $C_{59}H_{69}NO_{10}$, M = 951.49 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.44 - 8.37 (m, 4H, Ar–*H*), 8.30 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 8.18 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 7.85 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.60 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.44 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.39 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.19 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 7.02 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 6.98 (d, ^3J = 9.1 Hz, 2H, Ar–*H*), 4.09 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 4.01 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 1.90 - 1.80 (m, 4H, –CH_2–), 1.56 - 1.45 (m, 4H, –CH_2–), 1.45 - 1.22 (m, 32H, –CH_2–), 0.95 (t, ^3J = 7.1 Hz, 3H, –CH_3), 0.91 (t, ^3J = 7.0 Hz, 3H, –CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.42 (–*C*OOR), 164.20 (–*C*OOR), 163.91 (C_{Ar}–O–CH_2–), 163.25 (–*C*OOR), 162.81 (–*C*OOR), 157.12, 155.96, 154.84, 153.20, 143.98, 134.81, 134.03, 132.43, 132.21, 131.99, 130.62, 130.44, 125.62, 122.36, 122.20, 120.76, 120.26, 117.33, 115.17, 114.65, 114.45 (–*C*N), 104.23 (C_{Ar}–CN), 68.46 (C_{Ar}–O–*C*H_2–), 68.41 (C_{Ar}–O–*C*H_2–), 31.91, 31.57, 29.68, 29.66, 29.64, 29.57, 29.53, 29.34, 29.22, 29.06, 25.96, 25.70, 22.67, 22.59, 14.10 (–*C*H_3), 14.02 (–*C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_{10}$: C 74.42, H 7.30, N 1.47; found C 74.60, H 7.43, N 1.44.

2-[4-(4-Tetradecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzonitrile (DO12/14): Synthesized according to **P4** from **4/O12** (135 mg, 0.37 mmol), thionyl chloride (2 mL), **10/14** (205 mg, 0.37 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 275 mg (76%), $C_{61}H_{73}NO_9$, M = 963.53 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42 - 8.33 (m, 4H, Ar–*H*), 8.27 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.15 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.40 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.6 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.27 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 6.99 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.06 (t, ^3J = 6.5 Hz, 2H, Ar–O–CH_2–), 2.67 - 2.60 (m, 2H, Ar–CH_2–), 1.87 - 1.78 (m, 2H, –CH_2–), 1.69 - 1.58 (m, 2H, –CH_2–), 1.52 - 1.43 (m, 2H, –CH_2–), 1.42 - 1.20 (m, 38H, –CH_2–), 0.88 (t, ^3J = 6.7 Hz, 3H, –CH_3), 0.88 (t, ^3J = 6.9 Hz, 3H, –CH_3) ppm. **13C-NMR** (126 MHz, $CDCl_3$) δ 164.22 (–*C*OOR), 164.20 (–*C*OOR), 163.91 (C_{Ar}–O–CH_2–), 163.26 (–*C*OOR), 162.81 (–*C*OOR), 155.95, 154.84, 153.20, 148.57, 140.93, 134.83, 134.03, 132.43, 132.22, 132.00, 130.63, 130.46, 129.41, 125.62, 122.36, 121.11, 120.76, 120.26, 117.33, 114.45 (–*C*N), 104.23 (C_{Ar}–CN), 68.41 (C_{Ar}–O–*C*H_2–), 35.39 (C_{Ar}–*C*H_2–), 31.91, 31.90, 31.45, 29.69, 29.67, 29.66, 29.61, 29.58, 29.56, 29.53, 29.49, 29.35, 29.33, 29.27, 29.06, 25.96, 22.67, 14.10 (–*C*H_3) ppm. **EA:** calc. for $C_{61}H_{73}NO_9$: C 75.98, H 7.63, N 1.45; found C 75.76, H 7.43, N 1.47.

2-[4-(4-Dodecylphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzonitrile (DO12/12): Synthesized according to **P4** from **4/O12** (160 mg, 0.38 mmol), thionyl chloride (2 mL), **10/12** (200 mg, 0.38 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 205 mg (58%), $C_{59}H_{69}NO_9$, M = 935.50 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.41 - 8.33 (m, 4H, Ar–*H*), 8.26 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 8.15 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.81 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.40 (d, ^3J = 8.8 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.5 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.27 - 7.23 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 6.99 (d, ^3J = 9.0 Hz, 2H, Ar–*H*), 4.05 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 2.67 - 2.60 (m, 2H, Ar–CH_2–), 1.86 - 1.79 (m, 2H, –CH_2–), 1.67 - 1.60 (m, 2H, –CH_2–), 1.51 - 1.44 (m 2H, –CH_2–), 1.41 - 1.20 (m, 34H, –CH_2–), 0.88 (t, ^3J = 6.9 Hz, 6H, –CH_3) ppm. **13C-NMR** (126 MHz, $CDCl_3$) δ 164.21 (–*C*OOR), 164.19 (–*C*OOR), 163.91 (C_{Ar}–O–CH_2–), 163.25 (–*C*OOR), 162.81 (–*C*OOR), 155.96,

154.84, 153.20, 148.58, 140.92, 134.82, 134.02, 132.43, 132.23, 131.99, 130.63, 130.46, 129.41, 125.62, 122.36, 121.12, 120.76, 120.26, 117.33, 114.65, 114.45 (–*C*N), 104.22 (C_{Ar}–CN), 68.41 (C_{Ar}–O–*C*H_2–), 35.39 (C_{Ar}–*C*H_2–), 31.91, 31.91, 31.46, 29.67, 29.66, 29.64, 29.63, 29.62, 29.59, 29.57, 29.54, 29.50, 29.34, 29.33, 29.28, 29.07, 25.96, 22.68, 14.11 (–*C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_9$: C 75.69, H 7.43, N 1.50; found C 75.38, H 7.15, N 1.76.

2-[4-(4-Hexylphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzonitrile (DO12/6): Synthesized according to **P4** from **4/O12** (100 mg, 0.24 mmol), thionyl chloride (2 mL), **10/6** (101 mg, 0.24 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 128 mg (60%), $C_{53}H_{57}NO_9$, *M* = 852.02 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42 - 8.34 (m, 4H, Ar–*H*), 8.27 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 8.15 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar–*H*), 7.57 (d, ^4J = 2.1 Hz, 1H, Ar–*H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^3J = 8.6 Hz, ^4J = 2.2 Hz, 1H, Ar–*H*), 7.29 - 7.22 (m, 2H, Ar–*H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar–*H*), 6.99 (d, ^3J = 8.9 Hz, 2H, Ar–*H*), 4.06 (t, ^3J = 6.6 Hz, 2H, Ar–O–CH_2–), 2.68 - 2.60 (m, 2H, Ar–CH_2–), 1.88 - 1.78 (m, 2H, –CH_2–), 1.69 - 1.59 (m, 2H, –CH_2–), 1.52 - 1.42 (m, 2H, –CH_2–), 1.42 - 1.20 (m, 22H, –CH_2–), 0.90 (t, ^3J = 6.8 Hz , 3H, –CH_3), 0.89 (t, ^3J = 6.8 Hz, 3H, –CH_3) ppm. **13C-NMR** (101 MHz, $CDCl_3$) δ 164.22 (–*C*OOR), 164.19 (–*C*OOR), 163.90 (C_{Ar}–CH_2–), 163.25 (–*C*OOR), 162.81 (–*C*OOR), 155.95, 154.84, 153.20, 148.57, 140.91, 134.82, 134.02, 132.42, 132.22, 131.99, 130.62, 130.45, 129.40, 125.61, 122.36, 121.11, 120.75, 120.25, 117.33, 114.63, 114.45 (–*C*N), 104.22 (C_{Ar}–CN), 68.41 (C_{Ar}–O–*C*H_2–), 35.38 (C_{Ar}–*C*H_2–), 31.89, 31.69, 31.40, 29.63, 29.61, 29.56, 29.53, 29.32, 29.06, 28.93, 25.95, 22.67, 22.59, 14.09 (–*C*H_3), 14.07 (–*C*H_3) ppm. **EA:** calc. for $C_{53}H_{57}NO_9$: C 74.71, H 6.74, N 1.64; found C 74.39, H 6.50, N 1.66.

2-[4-(4-(4-Dodecylbenzoyloxy)benzoyloxy)]-4-[4-dodecyloxyphenoxycarbonyl)benzoyloxy]benzonitrile (D12/O12): Synthesized according to **P4** from **15/12** (Mw= 410.55, 120 mg, 0.29 mmol), thionyl chloride (2 mL), **14/O12** (Mw= 543.65, 159 mg, 0.29 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and recrystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 172 mg (63%), $C_{59}H_{69}NO_9$, *M* = 936.18 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.44 – 8.32 (m, 4H, Ar – *H*), 8.28 (d, ^3J = 8.7 Hz, 2H, Ar – *H*), 8.12 (d, ^3J = 8.3 Hz, 2H, Ar – *H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar – *H*), 7.57 (d, ^4J = 2.2 Hz, 1H, Ar – *H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar – *H*), 7.38-7.30 (m, 3H, Ar – *H*), 7.15 (d, ^3J = 7.6, 2H, Ar – *H*), 6.95 (d, ^3J = 8.7 Hz, 2H, Ar – *H*), 3.97 (t, ^3J = 6.6 Hz, 2H, Ar – O – CH_2 –), 2.71 (t, ^3J = 6.5 Hz, 2H, Ar – CH_2 –), 1.88 – 1.73 (m, 2H, – CH_2 –), 1.74 – 1.57 (m, 2H, – CH_2 –), 1.59 – 1.17 (m, 36H,– CH_2 –), 0.97-0.78 (m, 6H, – CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.52 (– *C*OOR), 164.42 (– *C*OOR), 163.22 (C_{Ar} – O – CH_2 –), 162.81 (– *C*OOR), 157.11, 155.86, 154.82, 153.20, 149.98, 143.97, 134.81, 134.03, 132.20, 132.02, 130.62, 130.44, 130.35, 128.79, 126.24, 125.73, 122.33, 122.19, 120.25, 117.33, 115.17, 114.63 (– *C*N), 104.24 (C_{Ar} – CN), 68.47 (C_{Ar} – O – *C*H_2 –), 36.11, 31.90, 31.08, 29.64, 29.61, 29.58, 29.56, 29.53, 29.43, 29.38, 29.32, 29.25, 29.23, 26.03, 22.67, 14.09 (– *C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_9$: C 75.69, H 7.43, N 1.50; found C 75.58, H 7.30, N 1.43.

2-[4-(4-Dodecyloxyphenoxycarbonyl)benzoyloxy]-4-[4-(4-dodecyloxybenzoyloxy)-benzoyloxy]benzonitrile (DO12/O12): Synthesized according to **P4** from **15/O12** (Mw= 426.55, 150 mg, 0.35 mmol), thionyl chloride (2 mL), **14/O12** (Mw= 543.65 191 mg, 0.35 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and recrystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 213 mg (65%), $C_{59}H_{69}NO_{10}$, *M* = 951.49 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.45 – 8.30 (m, 4H, Ar – *H*), 8.27 (d, ^3J = 8.7 Hz, 2H, Ar – *H*), 8.15 (d, ^3J = 8.9 Hz, 2H, Ar – *H*), 7.82 (d, ^3J =

8.6 Hz, 1H, Ar – *H*), 7.56 (d, ^{4}J = 2.1 Hz, 1H, Ar – *H*), 7.40 (d, ^{3}J = 8.7 Hz, 2H, Ar – *H*), 7.35 (dd, ^{3}J = 8.6, 2.1 Hz, 1H, Ar – *H*), 7.16 (d, ^{3}J = 7.3, 5.2 Hz, 2H, Ar – *H*), 7.05 – 6.83 (m, 4H, Ar – *H*), 4.06 (t, ^{3}J = 6.6 Hz, 2H, Ar – O – CH_2 –), 3.97 (t, ^{3}J = 6.5 Hz, 2H, Ar – O – CH_2 –), 1.92 – 1.69 (m, 4H, – CH_2 –), 1.60 – 1.14 (m, 34H,– CH_2 –), 0.88 (t, ^{3}J = 6.8 Hz, 6H, – CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.41 (– *C*OOR), 164.19 (– *C*OOR), 163.90 (C_{Ar} – O – CH_2 –), 163.24 (– *C*OOR), 162.80 (– *C*OOR), 157.11, 155.95, 154.84, 153.19, 143.98, 134.80, 134.02, 132.42, 132.20, 131.99, 130.62, 130.43, 125.61, 122.36, 122.19, 120.75, 120.25, 117.33, 115.17, 114.63, 114.44 (– *C*N), 104.23 (C_{Ar} – CN), 68.46 (C_{Ar} – O – *C*H_2 –), 68.40 (C_{Ar} – O – *C*H_2 –), 31.90, 29.64, 29.63, 29.62, 29.58, 29.56, 29.53, 29.38, 29.33, 29.25, 29.06, 26.03, 25.95, 22.67, 14.09 (– *C*H_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_{10}$: C 74.42, H 7.30, N 1.47; found C 74.35, H 7.28, N 1.45.

2- [4-(4-Tetradecyloxyphenoxycarbonyl)benzoyloxy]4-[4-(4-tetradecyloxybenzoyloxy)-benzoyloxy]-benzonitrile (DO14/O14): Synthesized according to **P4** from **15/O14** (Mw= 454.60, 120 mg, 0.22 mmol), thionyl chloride (2 mL), **14/O14** (Mw= 571.70, 151 mg, 0.22 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and recrystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 138 mg (52%), $C_{63}H_{77}NO_{10}$, *M* = 1008.29 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.43 – 8.33 (m, 4H, Ar – *H*), 8.27 (d, ^{3}J = 8.9 Hz, 2H, Ar – *H*), 8.15 (d, ^{3}J = 8.5 Hz, 2H, Ar – *H*), 7.82 (d, ^{3}J = 8.6 Hz, 1H, Ar – *H*), 7.56 (d, ^{3}J = 2.2 Hz, 1H, Ar – *H*), 7.41 (d, ^{3}J = 8.7 Hz, 2H, Ar – *H*), 7.35 (dd, ^{3}J = 8.5, 2.2 Hz, 1H, Ar – *H*), 7.15 (d, ^{3}J = 8.7 Hz, 2H, Ar – *H*), 7.02 – 6.89 (m, 4H, Ar – *H*), 4.06 (t, ^{3}J = 6.6 Hz, 2H, Ar – O – CH_2 –), 3.97 (t, ^{3}J = 6.6 Hz, 2H, Ar – O – CH_2 –), 1.88 – 1.71 (m, 4H, – CH_2 –), 1.60 – 1.17 (m, 42H, – CH_2 –), 0.88 (t, ^{3}J = 7.0 Hz, 6H, – CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.41 (– *C*OOR), 164.19 (– *C*OOR), 163.90 (C_{Ar} – O – CH_2 –), 163.25 (– *C*OOR), 162.81 (– *C*OOR), 157.11, 155.95, 153.19, 146.91, 134.80, 134.03, 132.42, 132.20, 131.99, 130.61, 130.43, 125.61, 122.35, 122.19, 120.25, 117.33, 115.17, 114.44 (– *C*N), 104.23 (C_{Ar} – CN), 68.46 (C_{Ar} – O – *C*H_2 –), 68.41 (C_{Ar} – O – *C*H_2 –), 31.90, 29.65, 29.63, 29.58, 29.56, 29.52, 29.37, 29.33, 29.25, 29.05, 26.02, 25.95, 22.66, 14.09 (– *C*H_3), 14.02 (– *C*H_3) ppm. **EA**: calc. for $C_{63}H_{77}NO_{10}$: C 75.05, H 7.70, N 1.39; found C 74.94, H 7.65, N 1.37.

2-[4-(4-Hexyloxyphenoxycarbonyl)benzoyloxy]-4-[4-(4-docosyloxybenzoyloxy)benzoyl-oxy]benzonitrile (DO22/O6): Synthesized according to **P4** from **4/O22** (200 mg, 0.35 mmol), thionyl chloride (2 mL), **10/O6** (163 mg, 0.35 mmol) and pyridine (1 mL) in DCM (10 mL). Purification by column chromatography (eluent: DCM) and crystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 140 mg (40%), $C_{63}H_{77}NO_{10}$, *M* = 1007.55 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.41 - 8.33 (m, 4H, Ar–*H*), 8.27 (d, ^{3}J = 8.7 Hz, 2H, Ar–*H*), 8.15 (d, ^{3}J = 8.8 Hz, 2H, Ar–*H*), 7.82 (d, ^{3}J = 8.5 Hz, 1H, Ar–*H*), 7.56 (d, ^{4}J = 2.1 Hz, 1H, Ar–*H*), 7.40 (d, ^{3}J = 8.7 Hz, 2H, Ar–*H*), 7.35 (dd, ^{3}J = 8.5 Hz, ^{4}J = 2.1 Hz, 1H, Ar–*H*), 7.15 (d, ^{3}J = 9.0 Hz, 2H, Ar–*H*), 6.99 (d, ^{3}J = 8.9 Hz, 2H, Ar–*H*), 6.95 (d, ^{3}J = 9.0 Hz, 2H, Ar–*H*), 4.06 (t, ^{3}J = 6.5 Hz, 2H, Ar–O–CH_2–), 3.97 (t, ^{3}J = 6.6 Hz, 2H, Ar–O–CH_2–), 1.88 - 1.74 (m, 4H, –CH_2–), 1.52 - 1.42 (m, 4H, –CH_2–), 1.42 - 1.19 (m, 40H, –CH_2–), 0.92 (t, ^{3}J = 7.0 Hz, 3H, –CH_3), 0.88 (t, ^{3}J = 6.8 Hz, 3H, –CH_3) ppm. **13C-NMR** (126 MHz, $CDCl_3$) δ 164.42 (–*C*OOR), 164.20 (–*C*OOR), 163.91 (C_{Ar}–O–CH_2–), 163.25 (–*C*OOR), 162.81 (–*C*OOR), 157.12, 155.96, 154.84, 153.20, 143.98, 134.81, 134.03, 132.43, 132.21, 131.99, 130.62, 130.44, 125.62, 122.36, 122.20, 120.76, 120.26, 117.33, 115.17, 114.45 (–*C*N), 104.23 (C_{Ar}–CN), 68.46 (C_{Ar}–O–*C*H_2–), 68.41 (C_{Ar}–O–*C*H_2–), 31.91, 31.57, 29.68, 29.67, 29.66, 29.64, 29.57, 29.54, 29.34, 29.22, 29.07, 25.96, 25.70, 22.67, 22.59, 14.10 (–*C*H_3), 14.01 (–*C*H_3) ppm. **EA**: calc. for $C_{63}H_{77}NO_{10}$: C 75.05, H 7.70, N 1.39; found C 74.75, H 7.42, N 1.46.

2.7 Compounds E

2-[4-(4-Dodecylbenzoyloxy)benzo-yloxy]-4-[4-(4-dodecylphenoxycarbonyl)benzoyloxy]-benzonitrile (E12/12): Synthesized according to **P4** from **8/12** (Mw= 410.55, 110 mg, 0.27 mmol), thionyl chloride (2 mL), **17/12** (Mw= 527.65, 141 mg, 0.27 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and recrystallisation from ethanol:chloroform 9:1. Colourless solid, yield 111 mg (45%), $C_{59}H_{69}NO_8$, M = 919.50 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.40 – 8.26 (m, 6H, Ar – *H*), 8.13 (d, ^3J = 8.3 Hz, 2H, Ar – *H*), 7.82 (d, ^3J = 8.7 Hz, 1H, Ar – *H*), 7.58 (d, ^4J = 2.1 Hz, 1H, Ar – *H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar – *H*), 7.38 – 7.30 (m, 3H, Ar – *H*), 7.26-7.23 (m, 2H, Ar – *H*), 7.15 (d, ^3J = 8.5 Hz, 2H, Ar – *H*), 2.75 – 2.68 (m, 2H, Ar – CH_2 –), 2.67 – 2.60 (m, 2H, Ar – CH_2 –), 1.74 – 1.58 (m, 4H,– CH_2 –), 1.41 – 1.14 (m, 36H, – CH_2 –), 0.88 (t, J = 7.0 Hz, 6H, CH_3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 164.47 (– *C*OOR), 164.20 (– *C*OOR), 163.14 (– *C*OOR), 162.84 (– *C*OOR), 156.00, 154.48, 153.48, 149.91, 148.54, 140.97, 134.70, 134.03, 132.61, 132.27, 130.40, 130.37, 129.42, 128.77, 126.29, 125.35, 122.38, 121.07, 119.88, 117.30, , 114.63 (– *C*N), 104.51 (C_{Ar} – CN), 36.10 (C_{Ar} – CH_2 –), 35.37 (C_{Ar} – CH_2 –), 31.90, 31.44, 31.08, 29.64, 29.61, 29.57, 29.53, 29.48, 29.43, 29.32, 29.27, 29.22, 22.66, 18.42, 14.09 (– CH_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_8$: C 77.01, H 7.56, N 1.52; found C 76.77, H 7.45, N 1.43.

2-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-4-[4-(4-dodecylphenoxycarbonyl)benzoyl-oxy]benzonitrile (EO12/12): Synthesized according to **P4** from **12/O12** (Mw= 426.55, 90 mg, 0.22 mmol), thionyl chloride (2 mL), **17/12** (Mw= 527.65, 117 mg, 0.22 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and recrystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 93 mg (44%), $C_{59}H_{69}NO_9$, M = 935.50 g/mol. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.39 – 8.28 (m, 6H, Ar – *H*), 8.20 – 8.10 (d, ^3J = 8.8 Hz, 2H, Ar – *H*), 7.82 (d, ^3J = 8.6 Hz, 1H, Ar – *H*), 7.58 (d, ^4J = 2.2 Hz, 1H, Ar – *H*), 7.41 (d, ^3J = 8.8 Hz, 2H, Ar – *H*), 7.36 (dd, ^3J = 8.5, 2.2 Hz, 1H, Ar – *H*), 7.28 – 7.21 (m, 2H, Ar – *H*), 7.14 (d, ^3J = 8.5 Hz, 2H, Ar – *H*), 6.99 (d, ^3J = 9.0 Hz, 2H, Ar – *H*), 4.06 (t, ^3J = 6.6 Hz, 2H, Ar – O – CH_2 –), 2.64 (t, ^3J = 6.4 Hz, 2H, Ar – CH_2 –), 1.88 – 1.75 (m, 2H, – CH_2 –), 1.71 – 1.58 (m, 2H, – CH_2 –), 1.56 – 1.11 (m, 34H, – CH_2 –), 0.94 – 0.82 (m, 6H,– CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.20 (– *C*OOR), 164.14 (– *C*OOR), 163.86 (C_{Ar} – O – CH_2 –), 163.14 (– *C*OOR), 162.87 (– *C*OOR), 156.09, 154.48, 153.49, 148.54, 140.97, 134.70, 134.02, 132.61, 132.44, 132.24, 130.40, 129.41, 125.23, 122.41, 121.07, 120.81, 119.87, 117.30, 114.64, 114.42 (– *C*N), 104.51 (C_{Ar} – CN), 68.39 (C_{Ar} – O – CH_2 –), 35.38 (C_{Ar} – CH_2 –), 31.89, 31.90, 31.44, 29.65, 29.64, 29.63, 29.62, 29.61, 29.57, 29.56, 29.53, 29.48, 29.33, 29.27, 29.06, 25.95, 22.66, 14.09 (– CH_3), 14.08 (– CH_3) ppm. **EA**: calc. for $C_{59}H_{69}NO_9$: C 75.69, H 7.43, N 1.50; found C 75.58, H 7.35, N 1.45.

2-[4-(4-Dodecyloxybenzoyloxy)-benzoyloxy] 4-(4-dodecyloxyphenoxycarbonyl)benzoyl-oxy]benzonitrile (EO12/O12): Synthesized according to **P4** from **12/O12** (Mw= 426.55, 100 mg, 0.23 mmol), thionyl chloride (2 mL), **17/O12** (Mw= 543.65 127 mg, 0.23 mmol) and pyridine (1 mL) in DCM (20 mL). Purification by column chromatography (eluent: DCM) and recrystallisation from ethanol:chloroform 9:1. Colourless solid, yield: 125 mg (56%), $C_{59}H_{69}NO_{10}$, M = 951.49 g/mol. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.40 – 8.28 (m, 6H, Ar – *H*), 8.16 (d, ^3J = 8.8 Hz, 2H, Ar – *H*), 7.82 (d, ^3J = 8.5 Hz, 1H, Ar – *H*), 7.58 (d, ^4J = 2.1 Hz, 1H, Ar – *H*), 7.41 (d, ^3J = 8.7 Hz, 2H, Ar – *H*), 7.35 (dd, ^3J = 8.6, 2.1 Hz, 1H, Ar – *H*), 7.15 (d, ^3J = 7.3, 2H, Ar – *H*), 7.04 – 6.89 (m, 4H, Ar – *H*), 4.06 (t, ^3J = 6.5 Hz, 2H, Ar – O – CH_2 –), 3.97 (t, ^3J = 6.5 Hz, 2H, Ar – O – CH_2 –), 1.93 – 1.69 (m, 4H, – CH_2 –), 1.63 – 1.12 (m, 34H, – CH_2 –), 0.88 (t, ^3J = 6.8 Hz, 6H, – CH_3) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 164.41 (– *C*OOR), 164.15 (– *C*OOR), 163.87 (C_{Ar} – O – CH_2 –), 163.14 (– *C*OOR), 162.87 (– *C*OOR),

157.14, 156.09, 154.48, 153.50, 143.94, 134.68, 134.02, 132.60, 132.44, 132.24, 130.40, 130.38, 125.23, 122.41, 122.16, 120.82, 119.87, 117.30, 115.18, 114.65, 114.43 (– *C*N), 104.51 (C_{Ar} – CN), 68.47 (C_{Ar} – O – CH_2 –), 68.39 (C_{Ar} – O – CH_2 –), 31.90, 29.63, 29.61, 29.58, 29.56, 29.53, 29.37, 29.32, 29.25, 29.06, 26.03, 25.96, 22.67, 14.09 (– CH_3). **EA**: calc. for $C_{59}H_{69}NO_{10}$: C 74.42, H 7.30, N 1.47; found C 74.38, H 7.25, N 1.43.

2.8 Representative NMR spectra

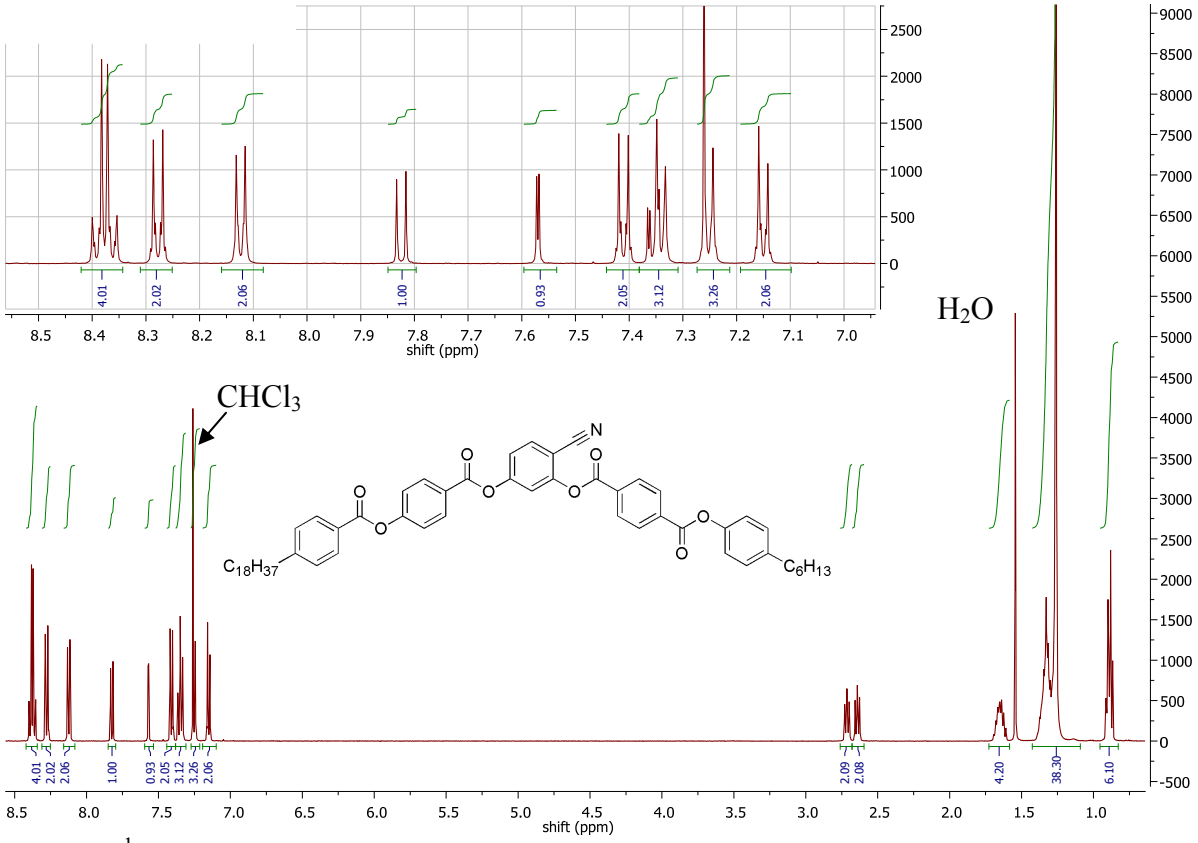


Fig. S1a: ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **B18/6**.

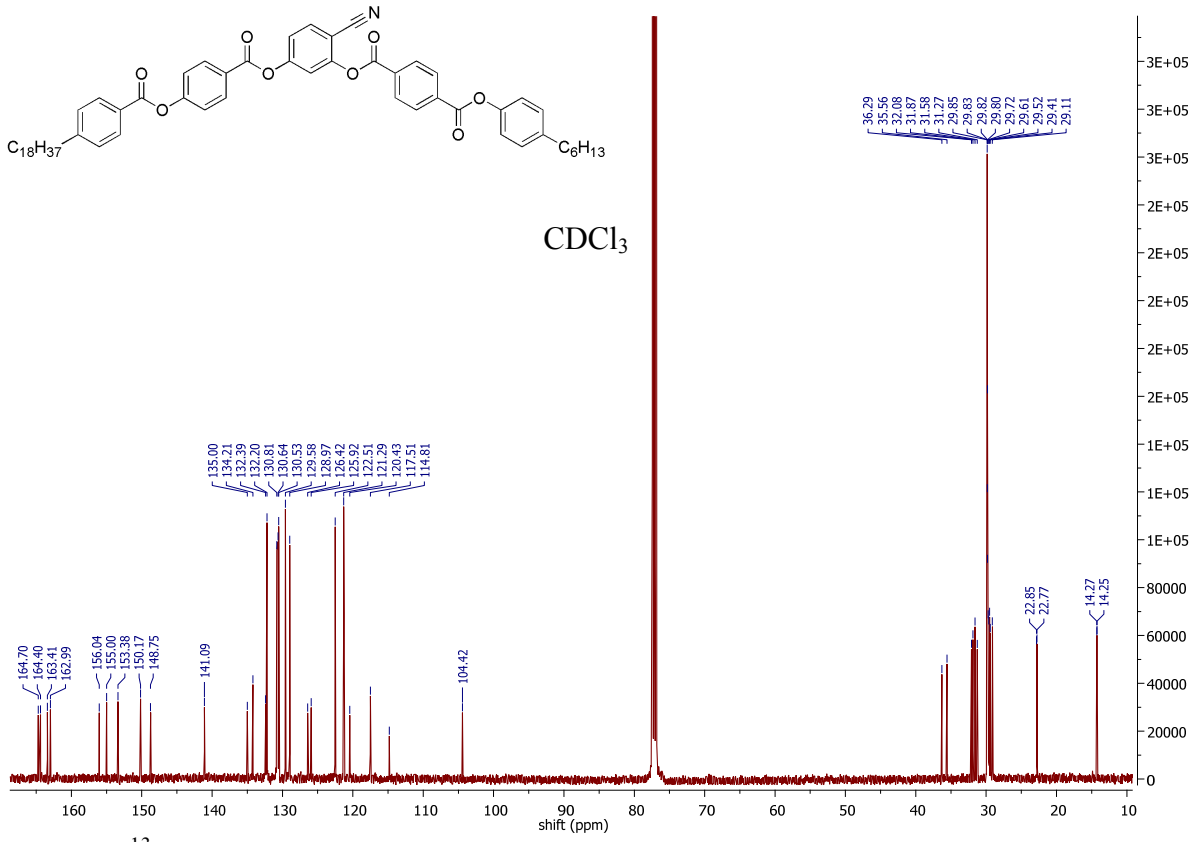


Fig. S1b: ^{13}C-NMR spectrum (126 MHz, $CDCl_3$) of **B18/6**.

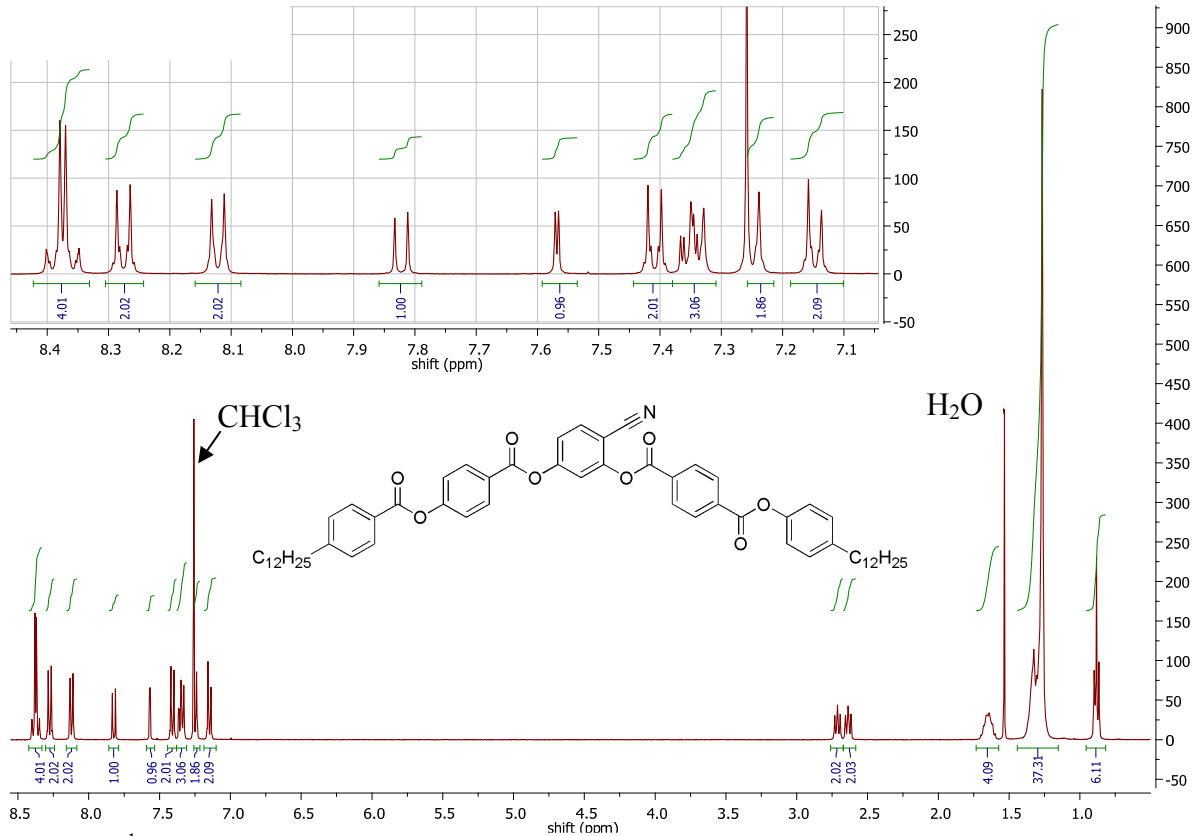


Fig. S1c: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **C12/12**.

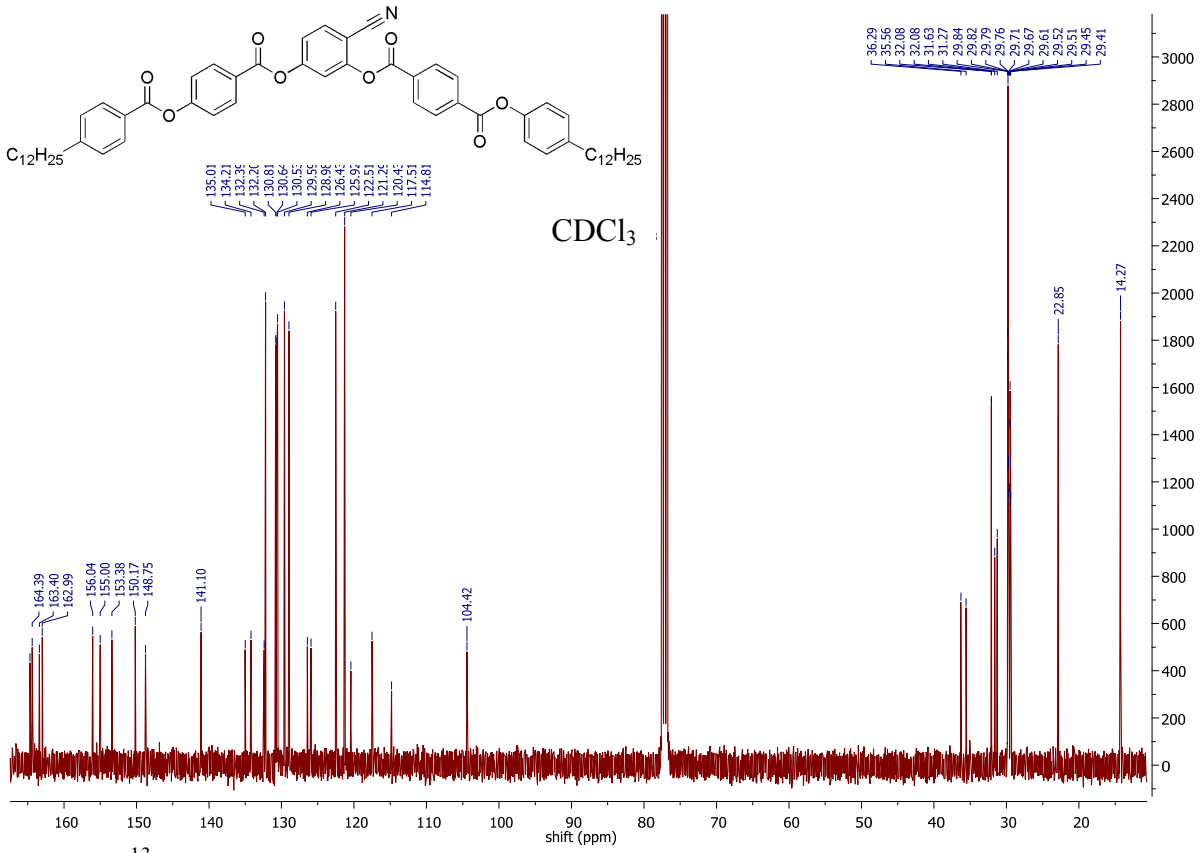


Fig. S1d: ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **C12/12**.

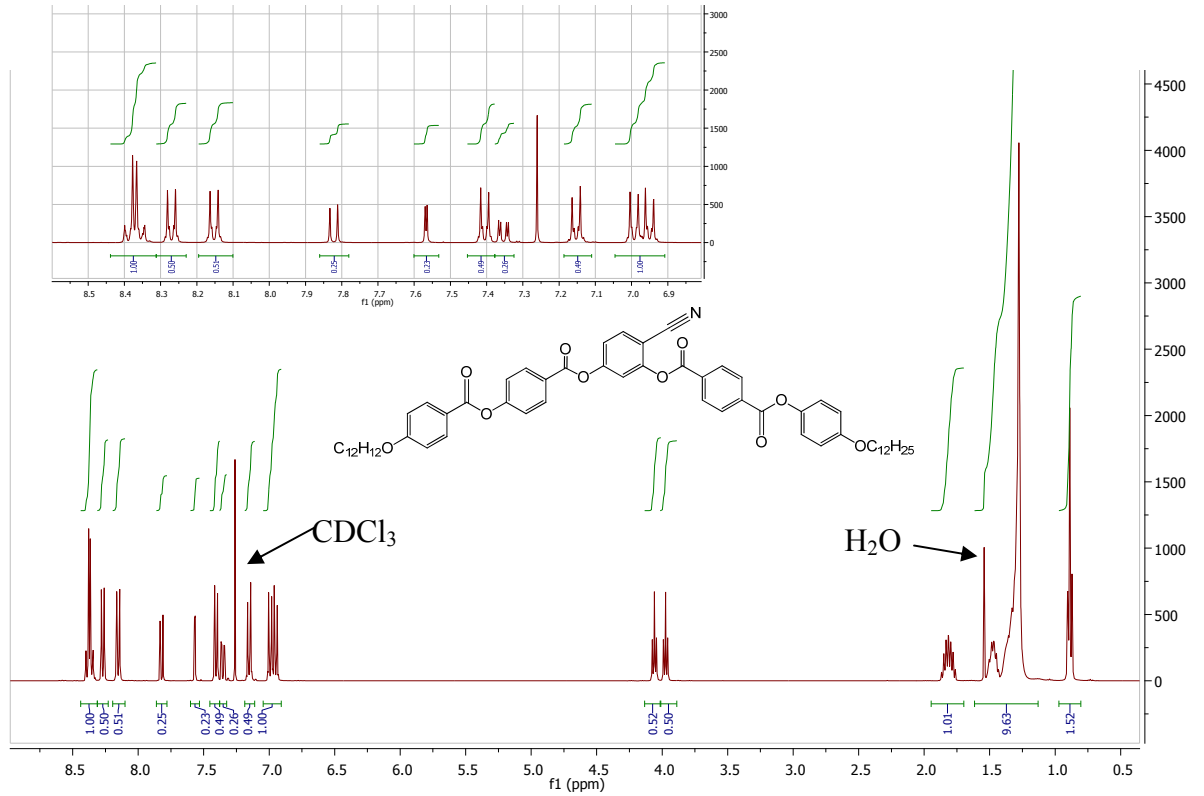


Figure S1e. ^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **DO12/12.**

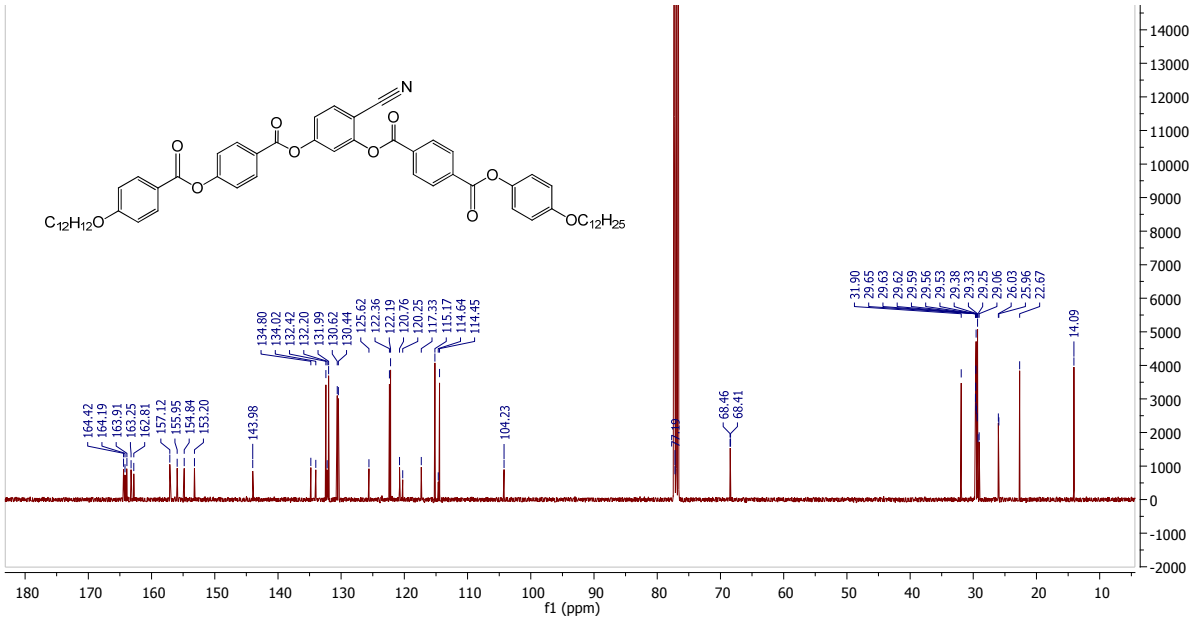


Figure S1f. ^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **DO12/12.**

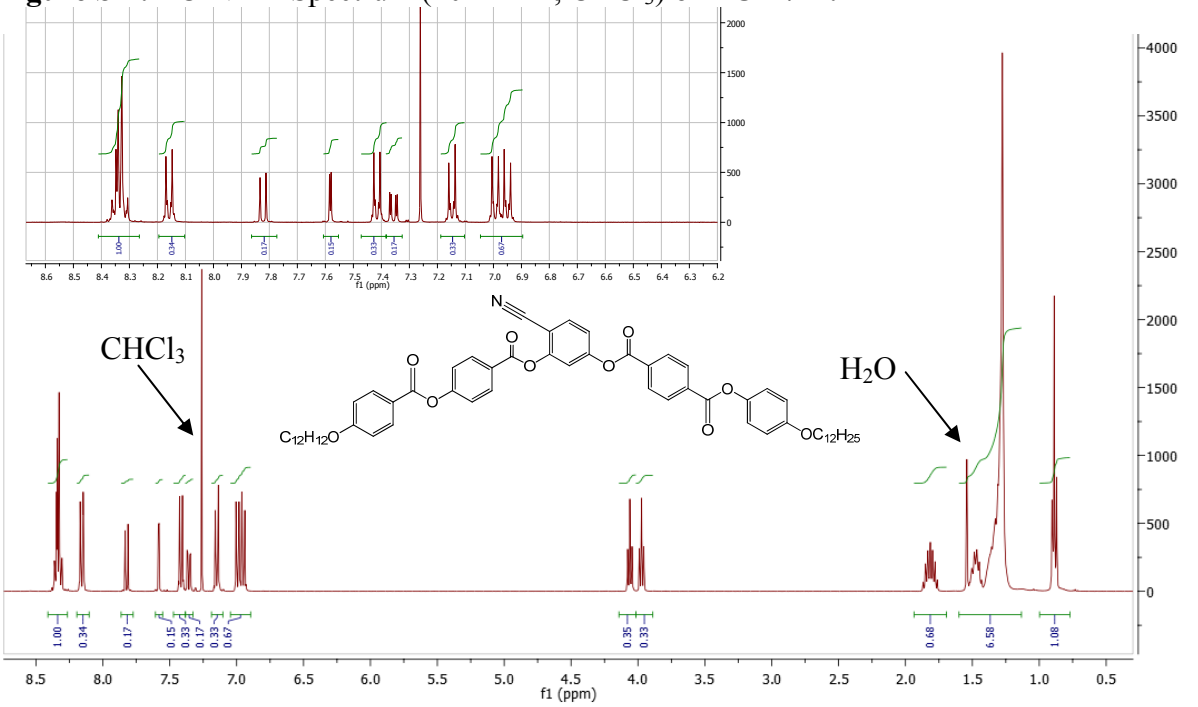


Figure S1g. ^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) of **EO12/12.**

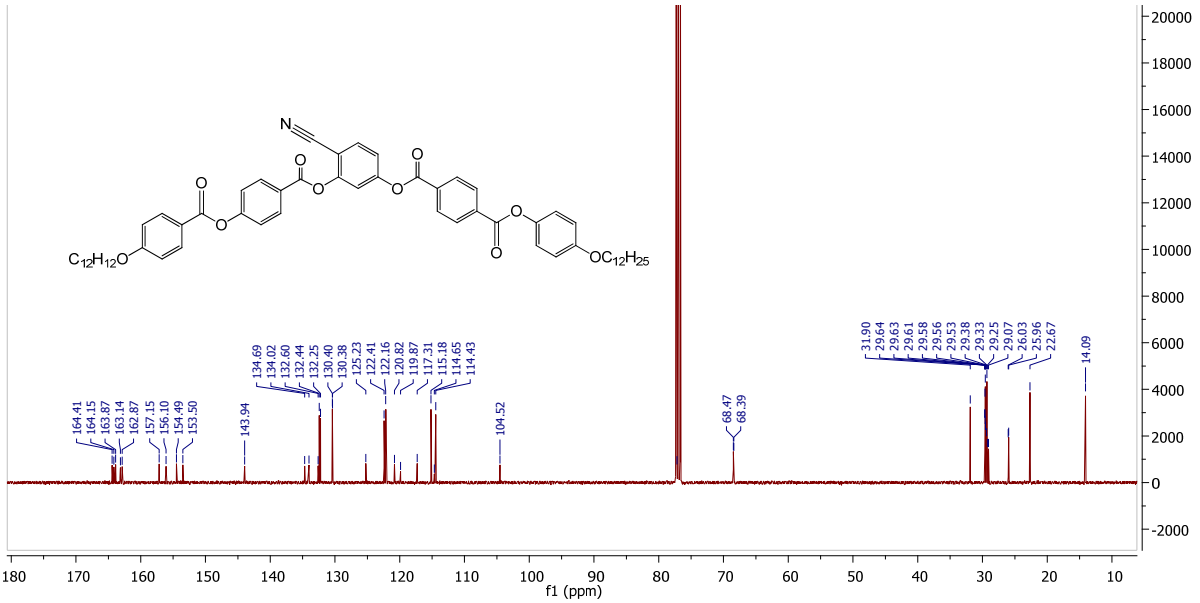


Figure S1h. ^{13}C-NMR Spectrum (101 MHz, $CDCl_3$) of **EO12/12.**

3. Additional Data:

3.1 Compound B8/6

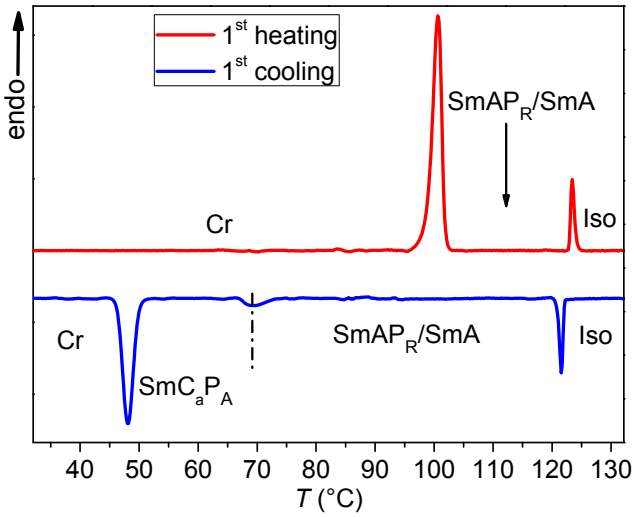


Figure S2. DSC heating and cooling traces of compound **B8/6** recorded at rates of 10 K min^{-1}.

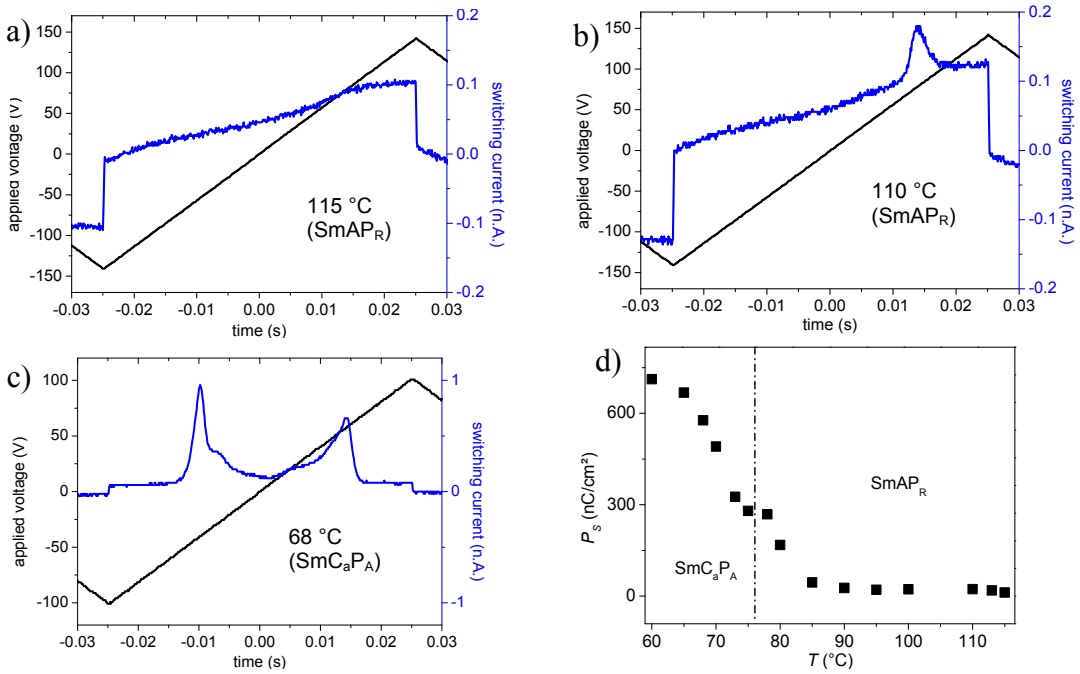


Figure S3. Polarization current response curves of **B8/6** at the indicated temperatures, measured in a ITO-coated cell (6 µm) under a triangular wave voltage of a,b) V_{PP} = 280 V ($SmAP_R$, a) T = 115 °C, b) T = 110 °C) and c) V_{PP} = 200 V (SmC_aP_A, T = 68 °C) and a frequency of 10 Hz; d) shows the development of the polarization values depending on T.

3.2 Compound B10/6

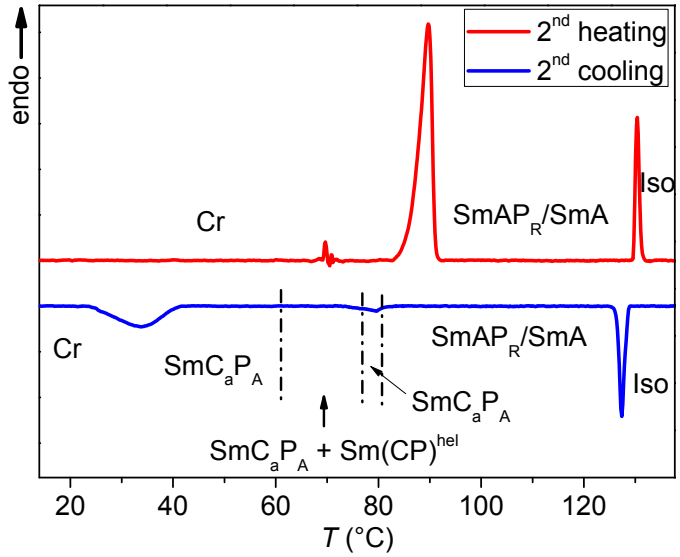


Figure S4. DSC heating and cooling traces of compound **B10/6** recorded at rates of 10 K min^{-1}.

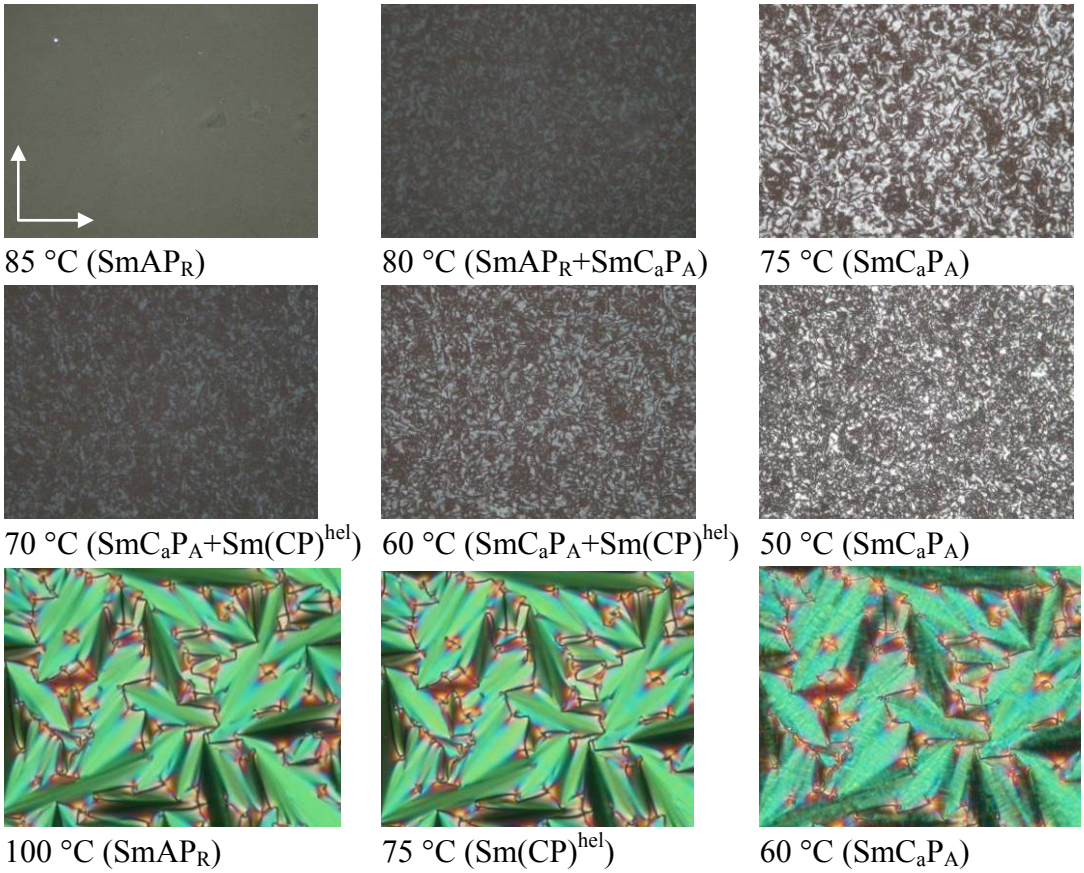


Figure S5. Textures as observed between crossed polarizers of compound **B10/6** depending on temperature; the upper two rows show the homeotropic textures and the bottom row the planar fan-like texture at the given temperatures in the indicated LC phases;

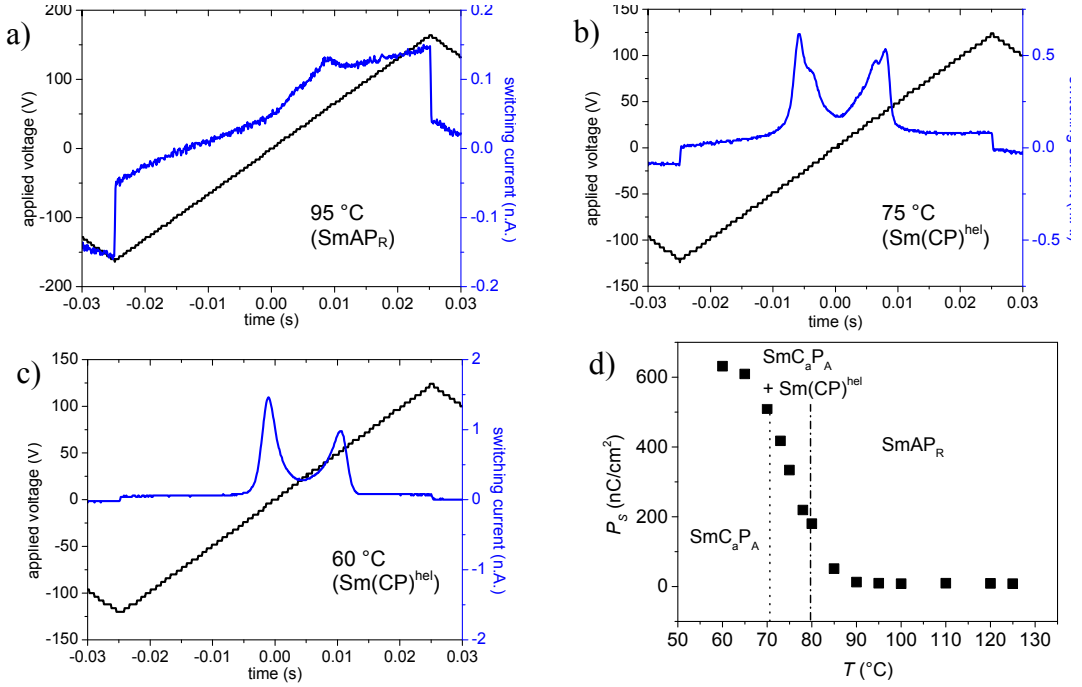
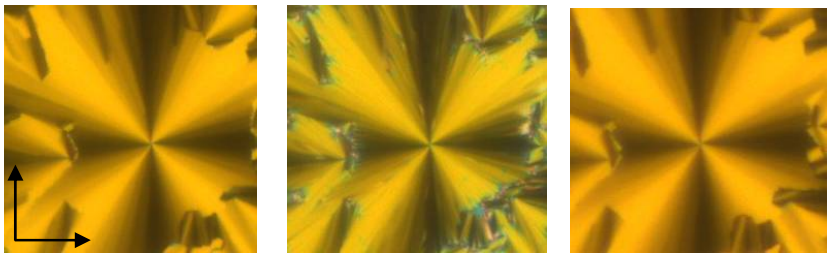


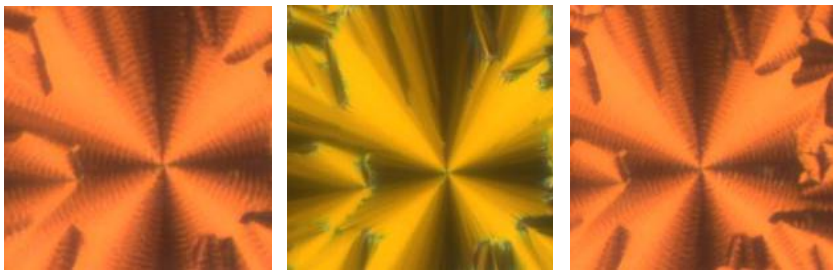
Figure S6. Polarization current response curves of **B10/6** at the indicated temperatures, measured in a ITO-coated cell (6 µm) under a triangular wave voltage of a) $SmAP_R$ at V_{pp} = 320 V (T = 95 °C) and b,c) $Sm(CP)^{hel}$ (T = 75 °C) and SmC_aP_A (T = 60 °C) at V_{pp} = 240 V and a frequency of 10 Hz; d) shows the development of the polarization values depending on T.

a) 110 °C ($SmAP_R$)



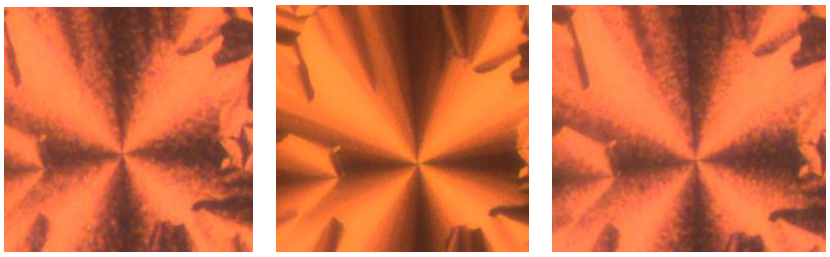
-32 V/µm 0 V/µm +32 V/µm

b) 75 °C (SmC_aP_A + $Sm(CP)^{hel}$, coexistence)



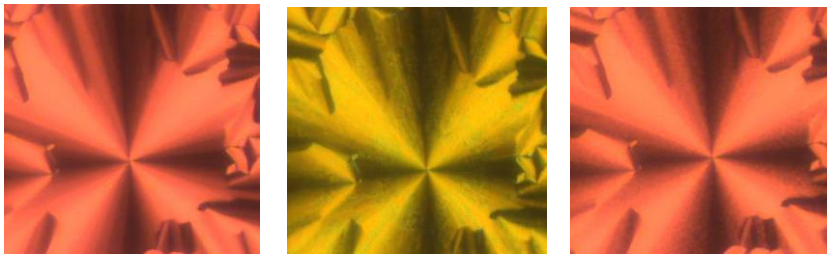
-32 V/µm 0 V/µm +32 V/µm

c) 62 °C (SmC_aP_A+ $Sm(CP)^{hel}$, coexistence))



-32 V/µm 0 V/µm +32 V/µm

d) 45 °C(SmC_aP_A)



-32 V/µm 0 V/µm +32 V/µm

Figure S7. Textures of the distinct mesophases of compound **B10/6** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed under an applied E-field at the indicated voltages (left/right).

3.3 Compound B12/6

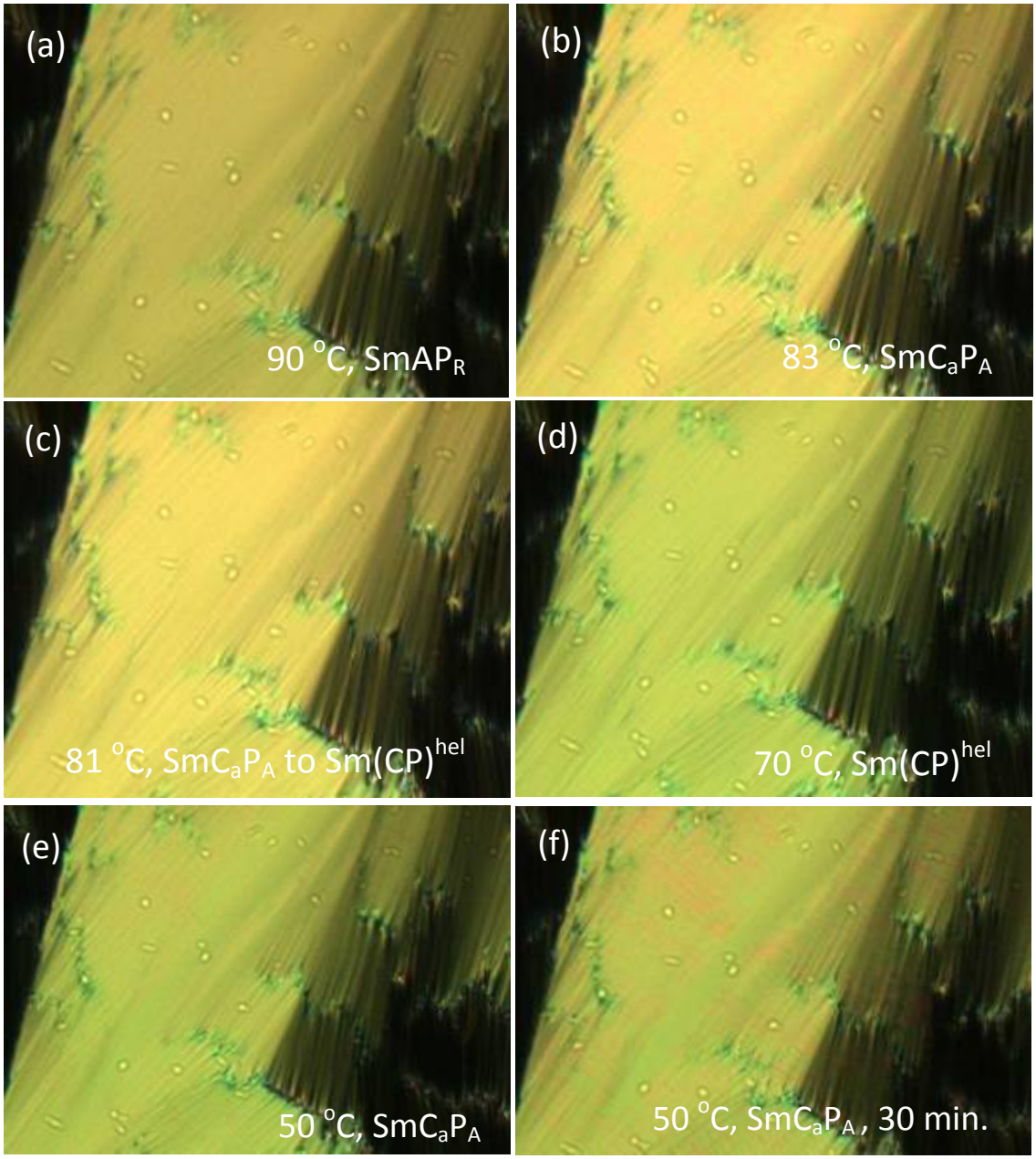


Figure S8. Development of the planar textures of compound **B12/6** with decreasing temperature; note the speckled texture in b), e) and f).

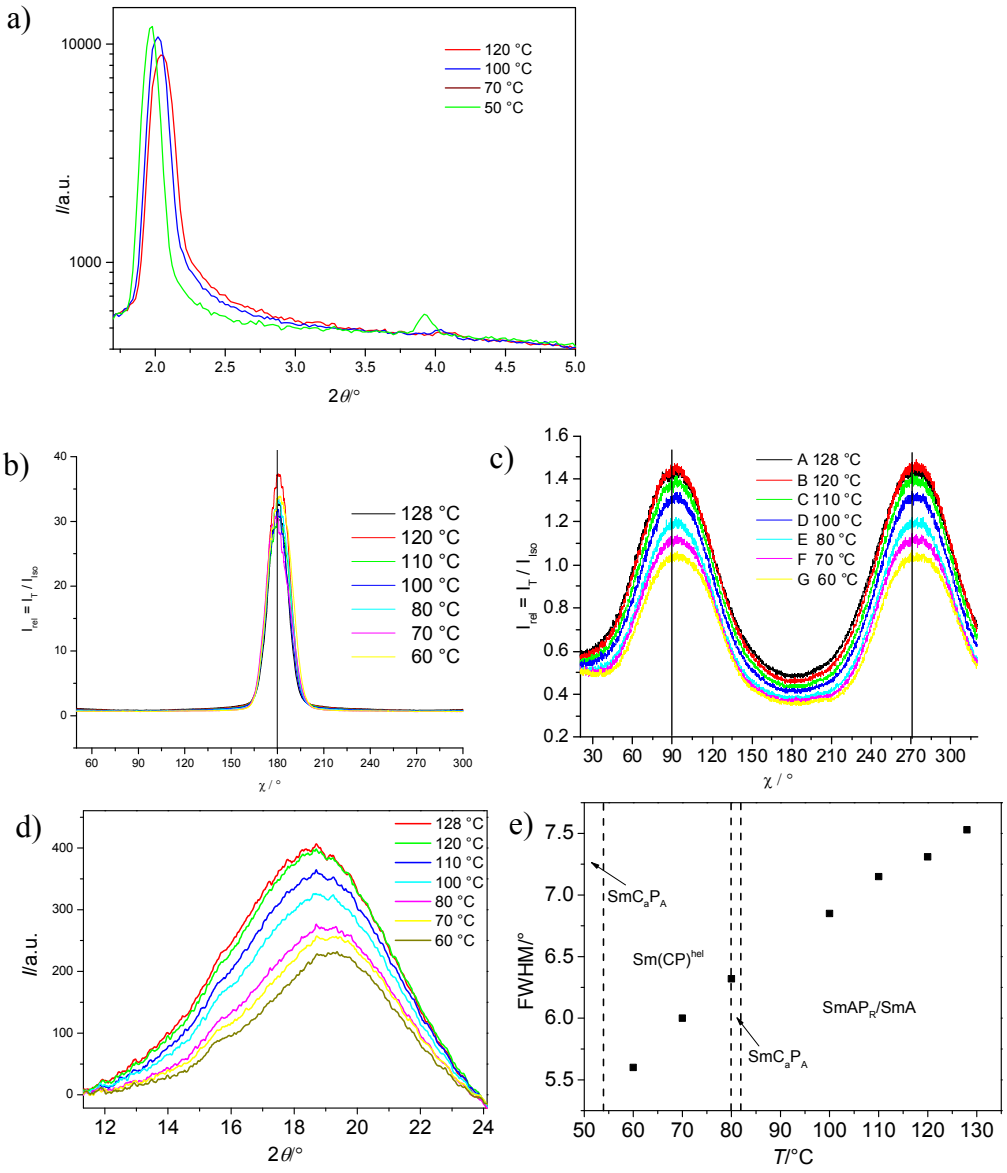


Figure S9. XRD data of compound **B12/6**. a) SAXS pattern; b) intensity distribution of the SAXS along χ (2θ = 1-5°) and c) of the WAXS along χ (2θ = 15-25°); there is no detectable tilt > 5°; d) 2θ scans of the WAXS and e) plot of FWHM of the WAXS depending on the temperature.

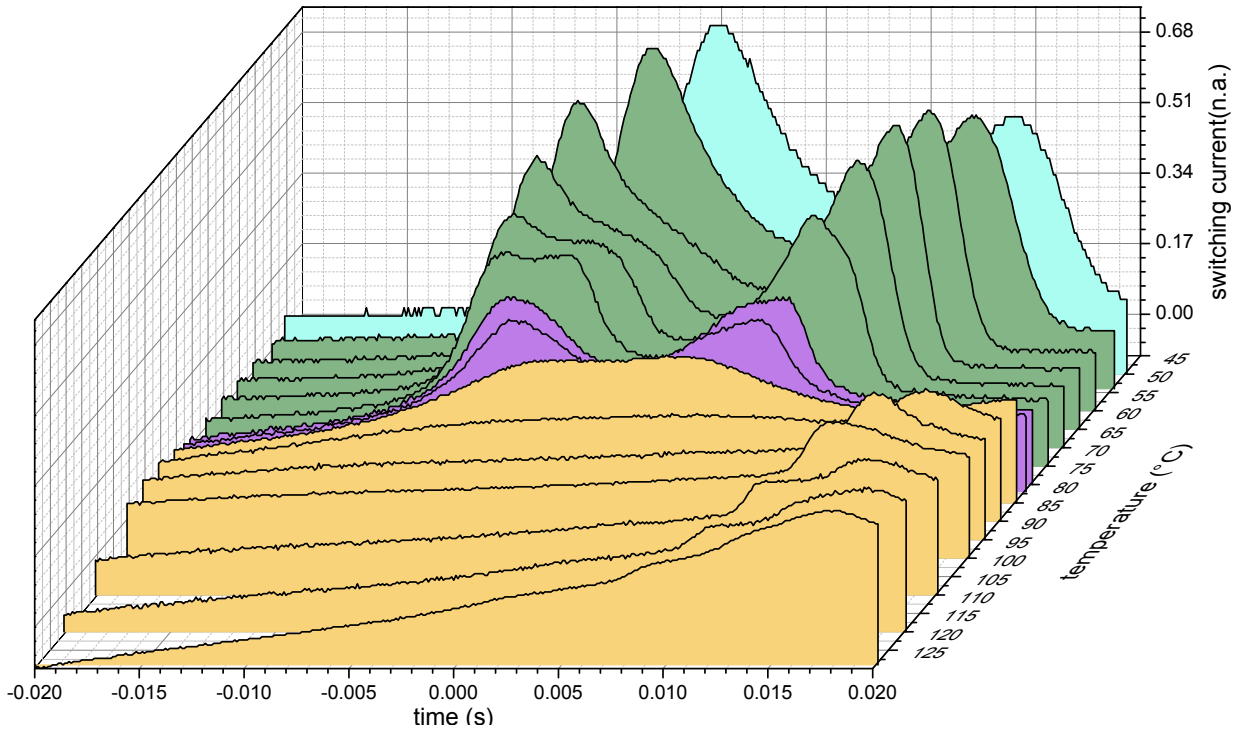


Figure S10. Polarization current response of **B12/6** depending on the temperature as measured in a ITO-coated cell (6 μm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

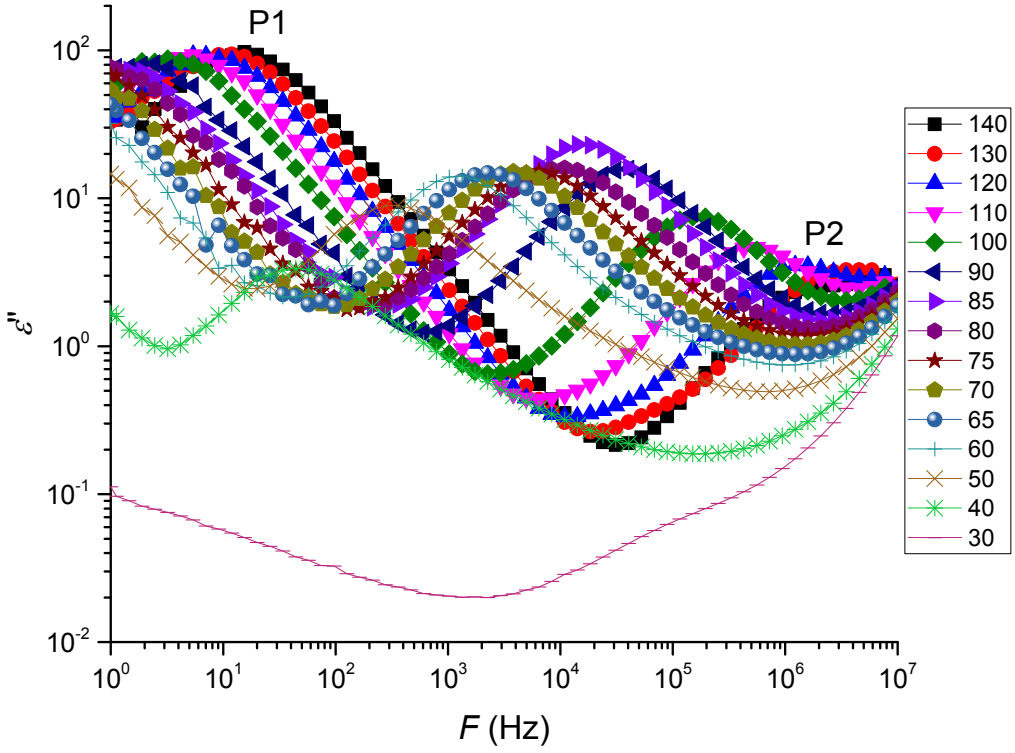


Figure S11. Frequency dependance of the ε″ for selected temperatures as observed in a 10 μm planar cell.

3.4 Compound B14/6

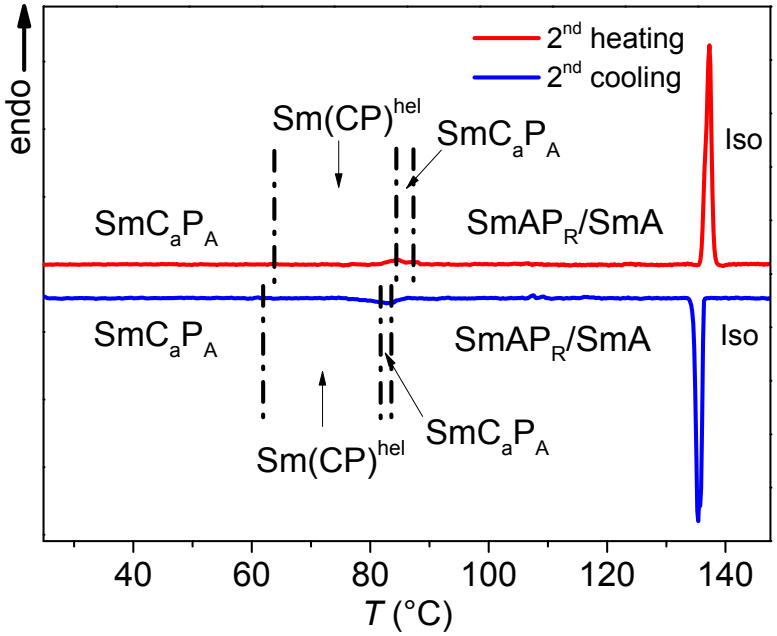


Figure S12. DSC heating and cooling traces of compound **B14/6** recorded at rates of 10 K min^{-1}.

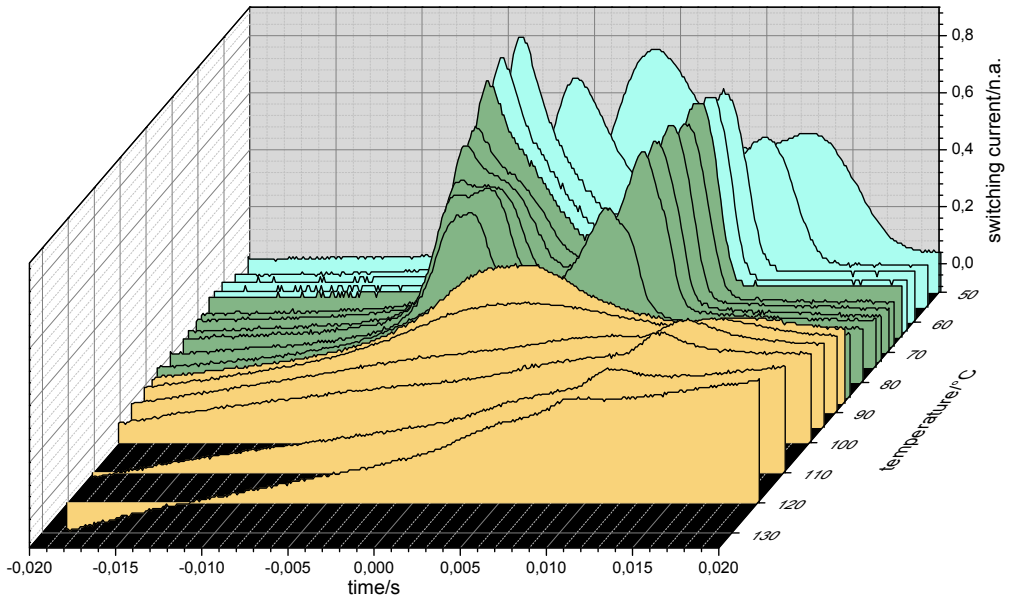


Figure S13. Polarization current response of **B14/6** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.5 Compound B16/6

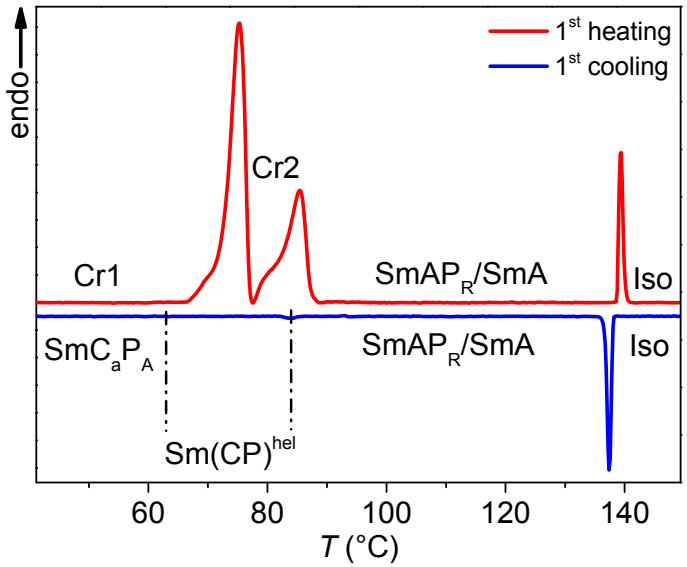


Figure S14. DSC heating and cooling traces of compound **B16/6** recorded at rates of 10 K min^{-1}

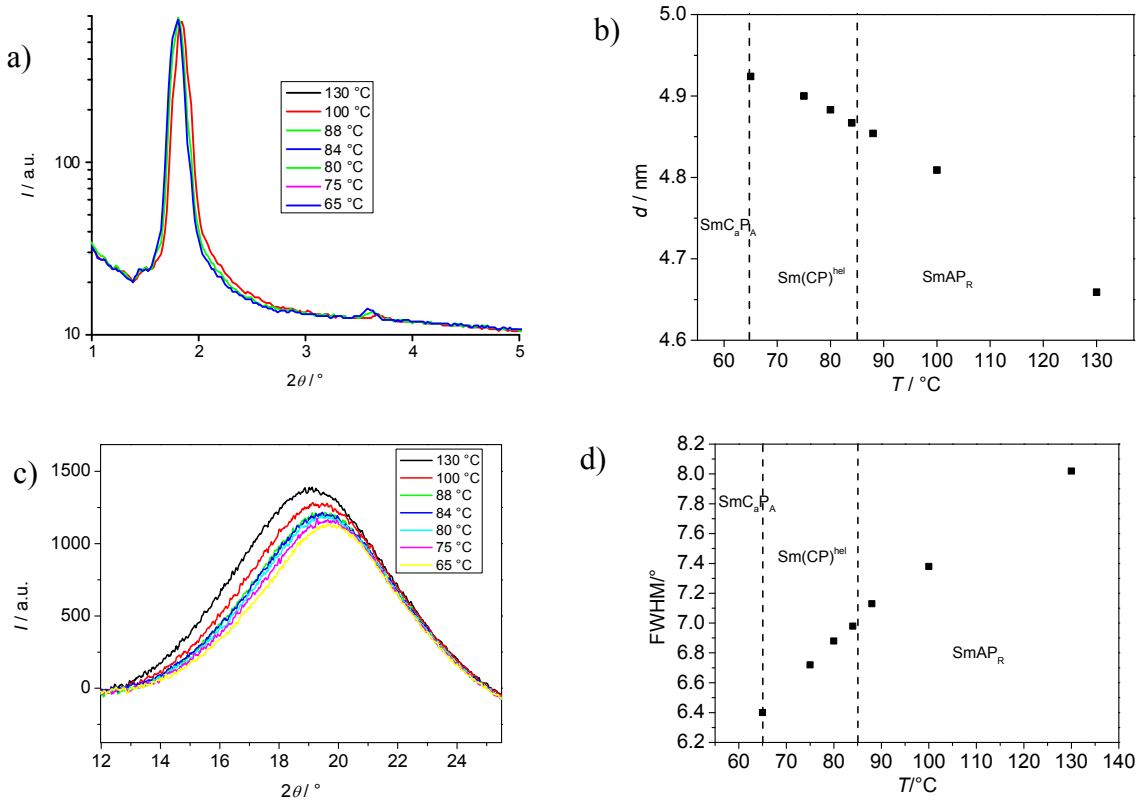


Figure S15. XRD data of compound **B16/6**. a) Plot of the small angle diffraction pattern; b) plot of *d*-values of the layer spacing depending on temperature, c) 2θ distribution and c) FWHM values of the wide angle scattering depending on the temperature.

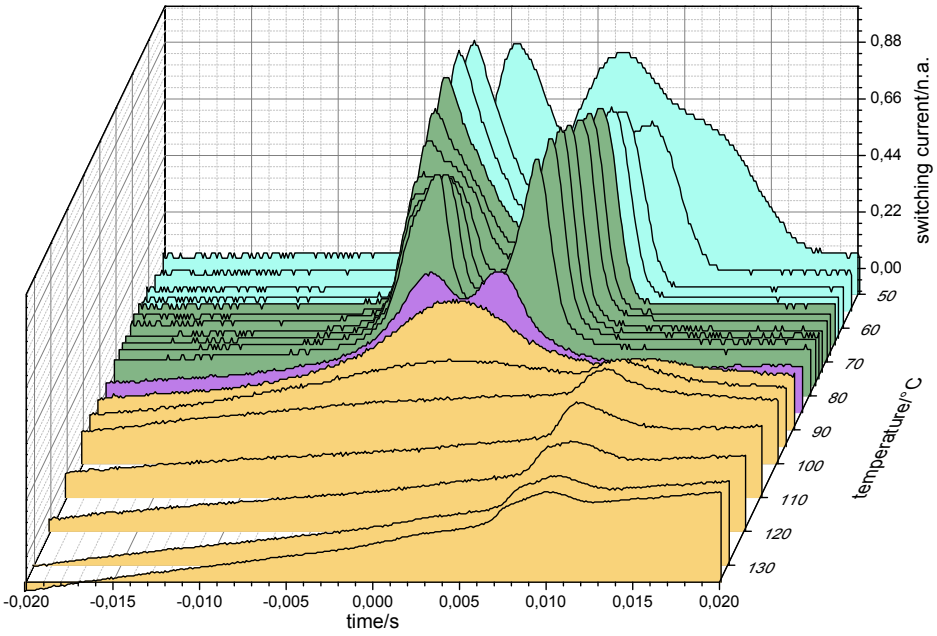


Figure S16. Polarization current response of **B16/6** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.6 Compound B18/6

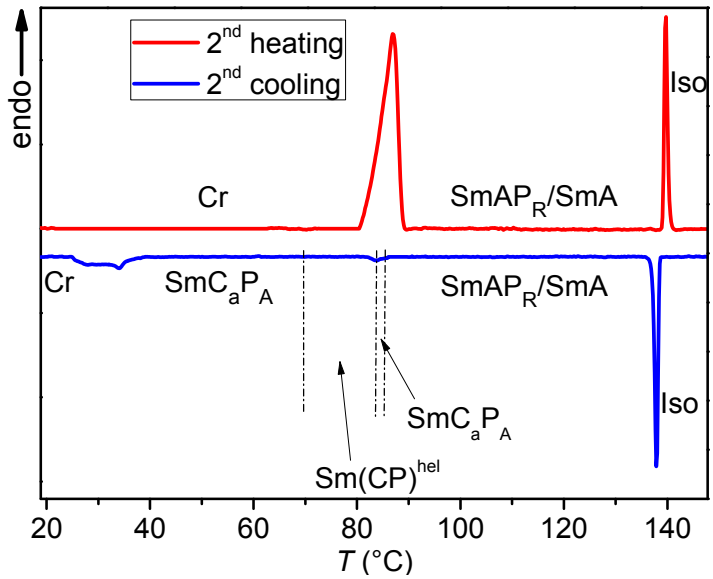


Figure S17. DSC heating and cooling traces of compound **B18/6** recorded at rates of 10 K min^{-1}.

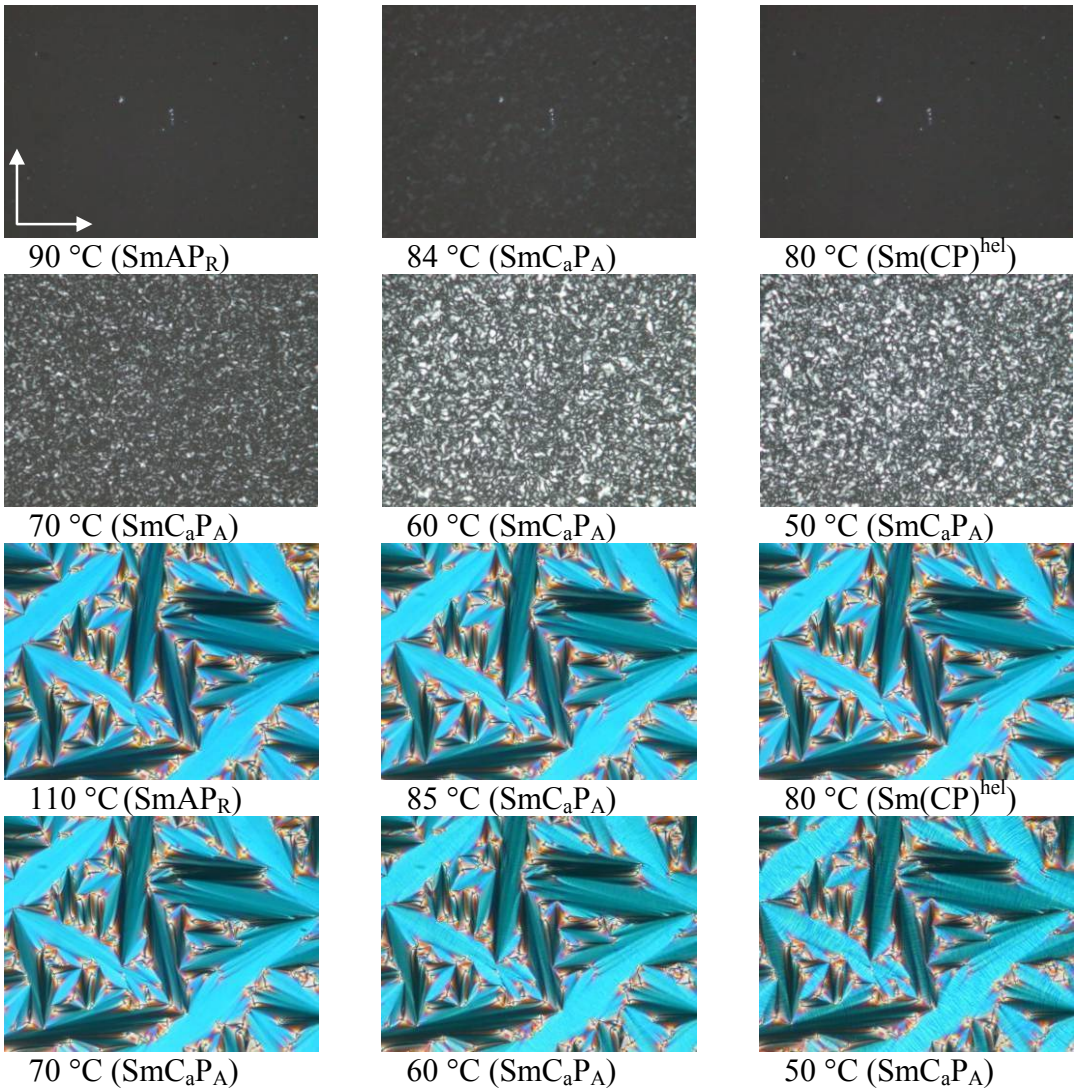


Figure S18. Textures of compound **B18/6** as observed between crossed polarizers depending on temperature; the two top rows show the homeotropic textures and the two bottom rows the planar fan-like textures at the given temperatures in the indicated LC phases;

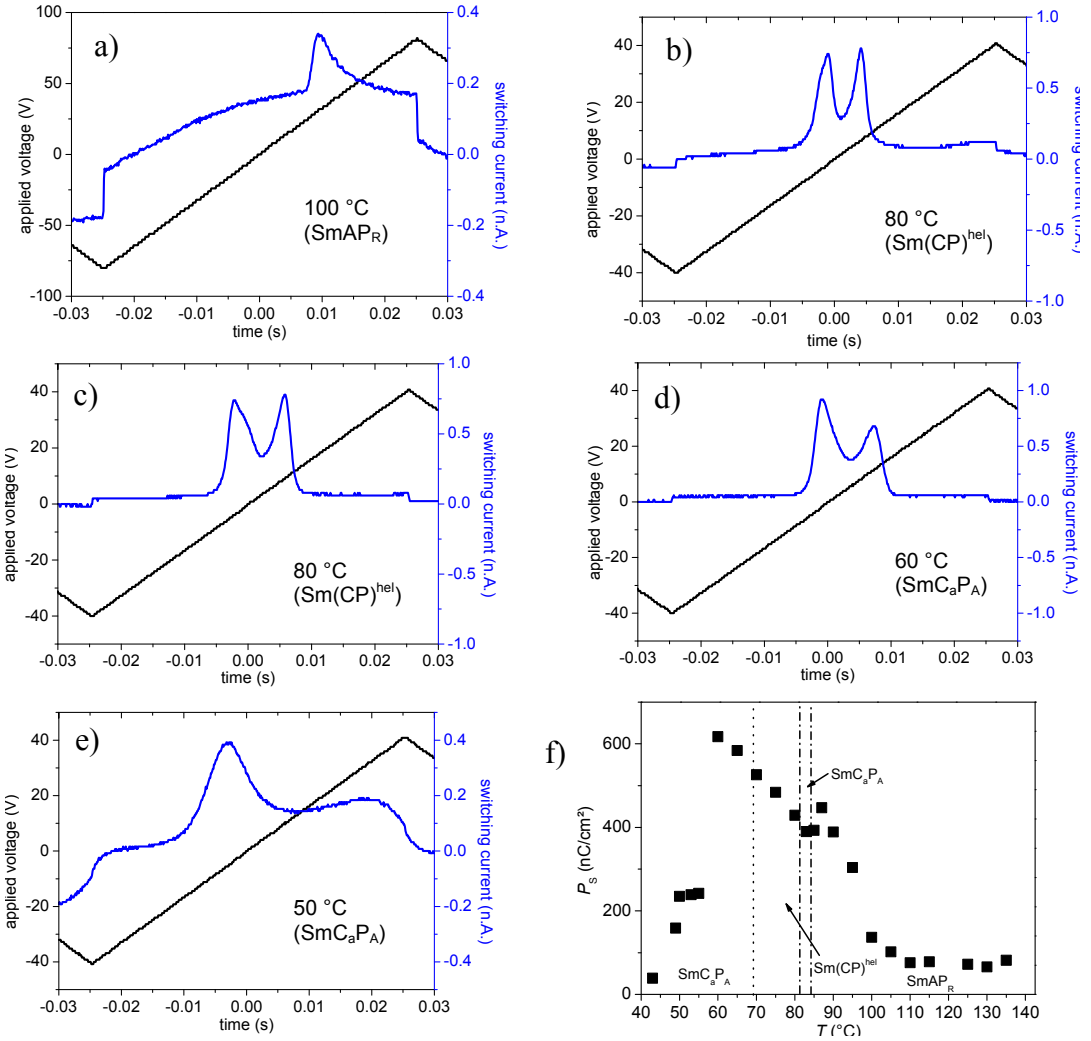
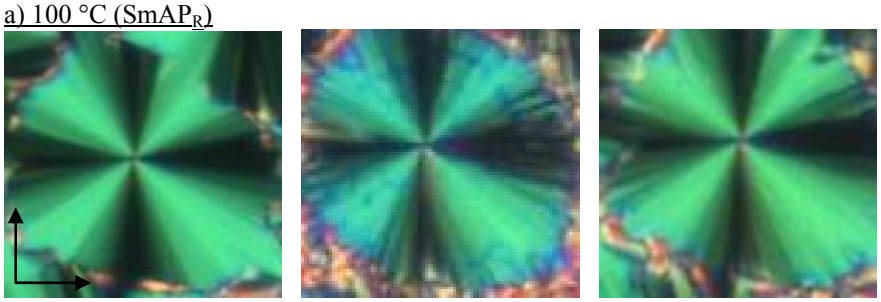


Figure S19. Polarization current response curves of **B18/6** at the indicated temperatures, measured in an ITO-coated cell (6 µm) under a triangular wave voltage and a frequency of 10 Hz at the given temperatures. a) SmAP$_R$-phase (V_{pp} = 160 V) at 100 °C, b-c) Sm(CP)^{hel}-phase (V_{pp} = 80 V), d-e) SmC$_a$P$_A$-phase (V_{pp} = 80 V). The occurrence of only one peak in e) can be explained due to the increased viscosity at low temperatures. f) shows the temperature dependence of the polarization values.

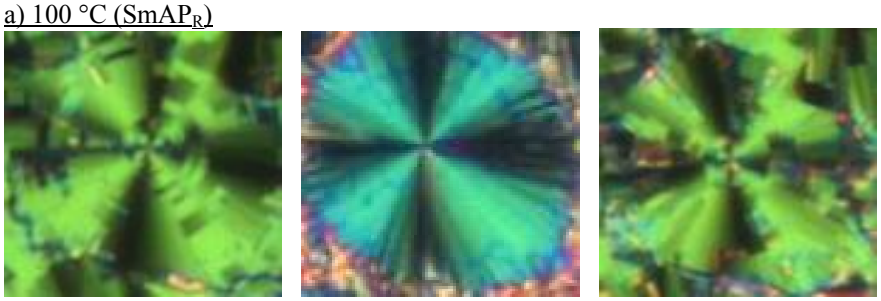
a) 100 °C (SmAP$_R$)



-8 V/µm 0 V/µm +8 V/µm

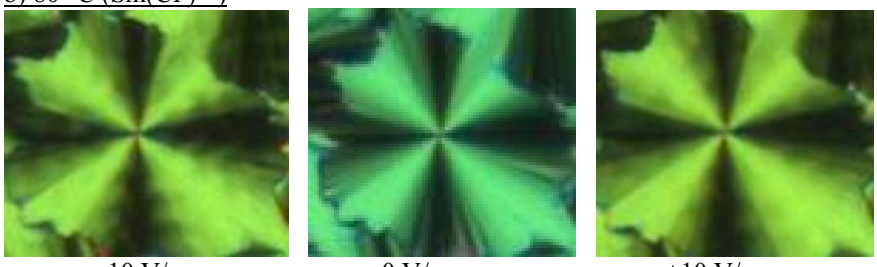
Figure S20. Textures of the SmAP$_R$ of compound **B18/6** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed for under an applied E-field of -/+ 8V/µm (left/right).

a) 100 °C ($SmAP_R$)

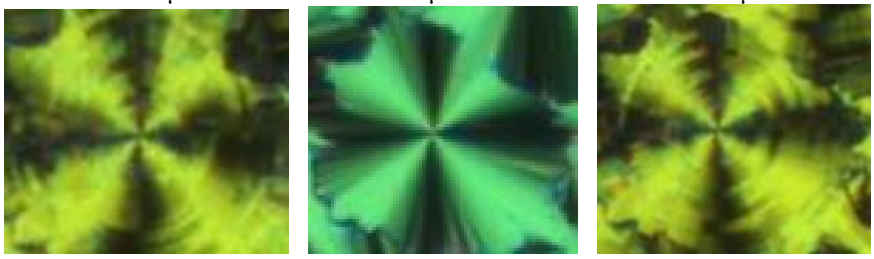


-32 V/µm 0 V/µm +32V/µm

b) 80 °C ($Sm(CP)^{hel}$)

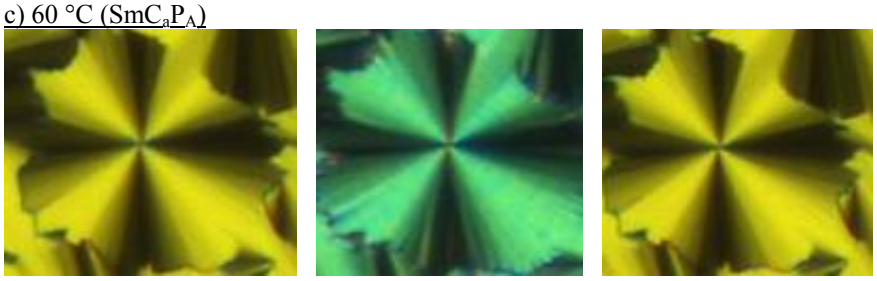


-10 V/µm 0 V/µm +10 V/µm



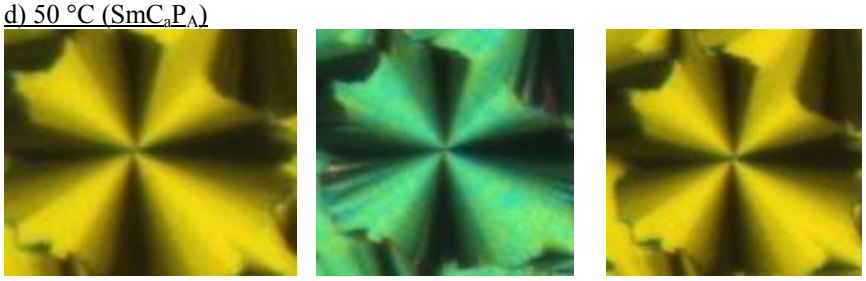
-32 V/µm 0 V/µm +32 V/µm

c) 60 °C (SmC_aP_A)



-32 V/µm 0 V/µm +32 V/µm

d) 50 °C (SmC_aP_A)



-32 V/µm 0 V/µm +32 V/µm

Figure S20 (continued). Textures of the distinct mesophases of compound **B18/6** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed for under an applied E-field at the indicated voltages (left/right).

3.7 Compound B20/6

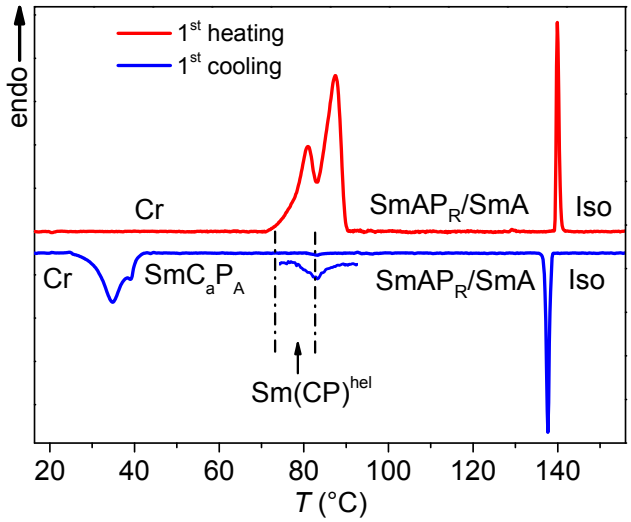


Figure S21. DSC heating and cooling traces of compound **B20/6** recorded at rates of 10 K min^{-1}.

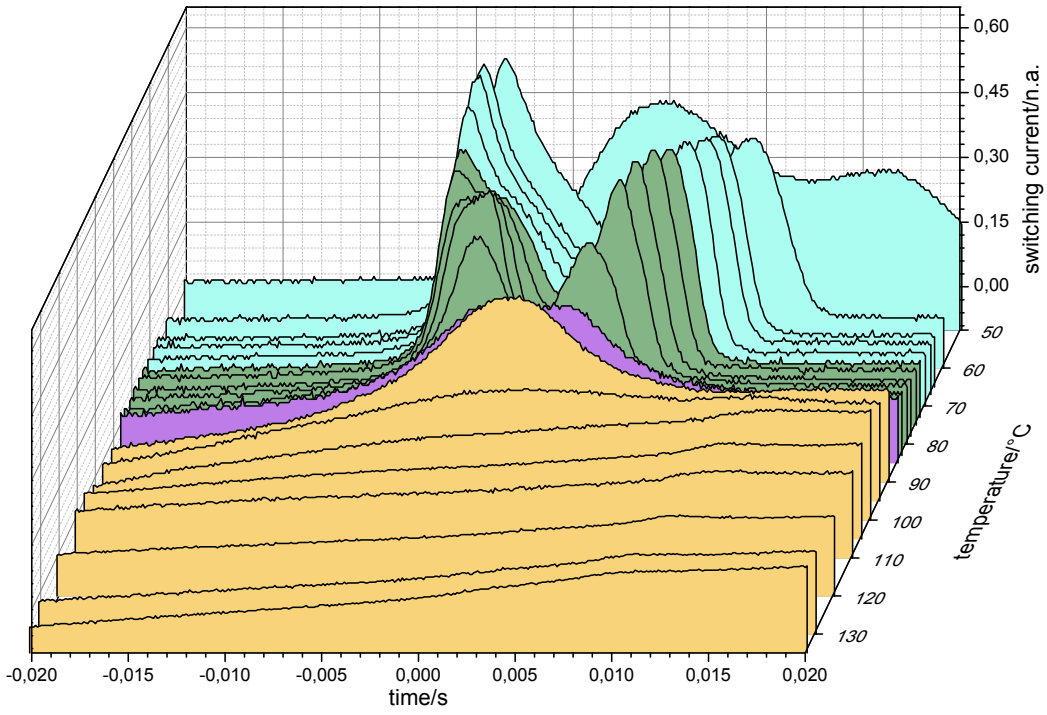


Figure S22. Polarization current response of **B20/6** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.8 Compound B22/6

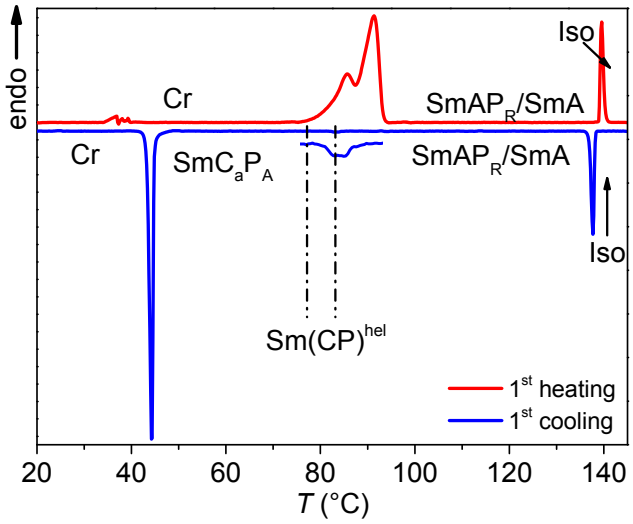


Figure S23. DSC heating and cooling traces of compound **B22/6** recorded at rates of 10 K min^{-1}.

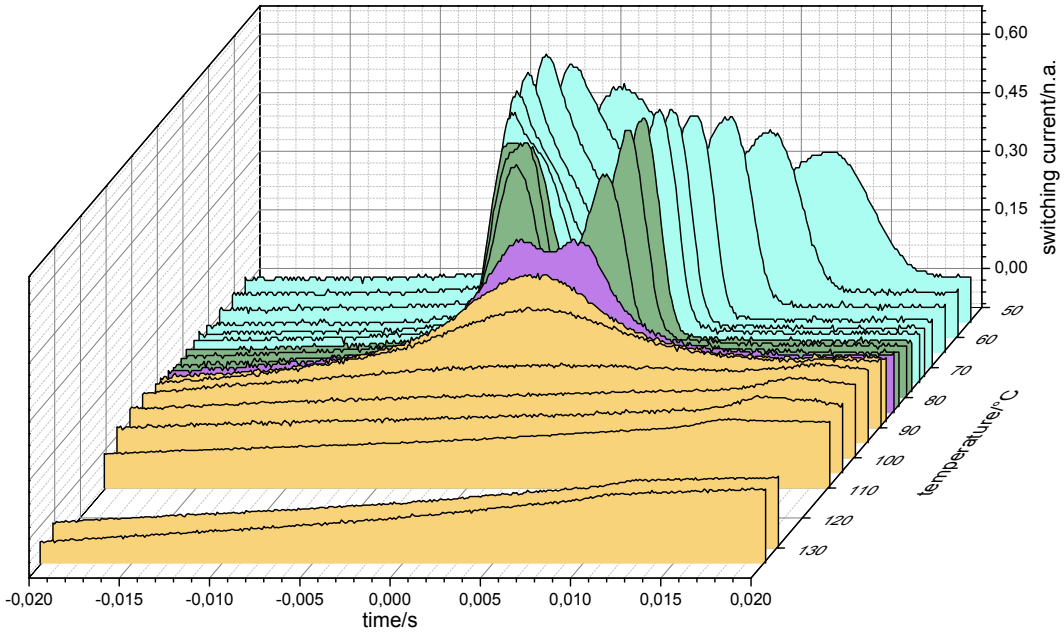


Figure S24. Polarization current response of **B22/6** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

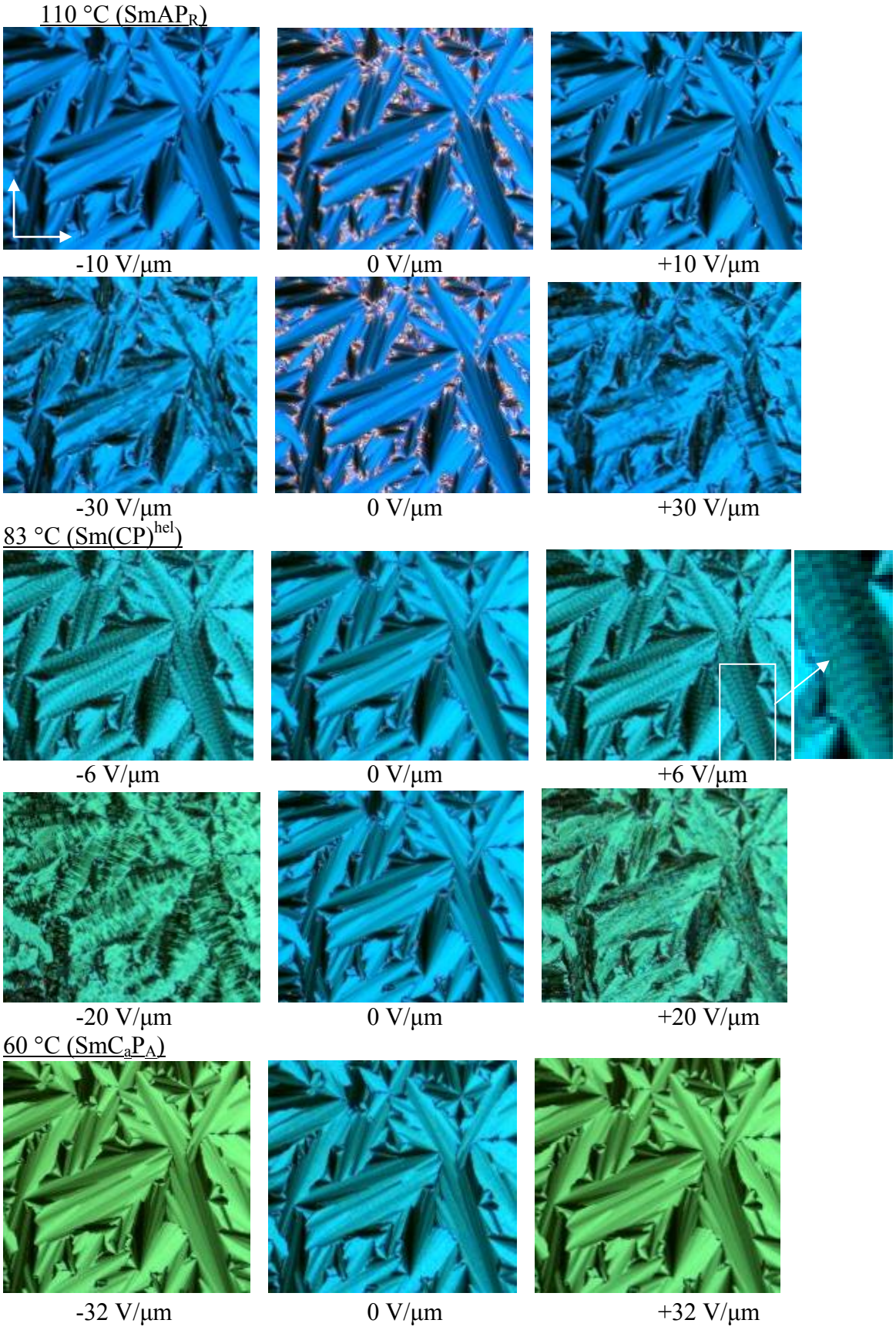


Figure S25. Textures of the distinct mesophases of compound **B22/6** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed for under an applied E-field at the indicated voltages (left/right); the tiger stripe texture can be observed at +/-6V/µm.

3.9 Compound C12/12

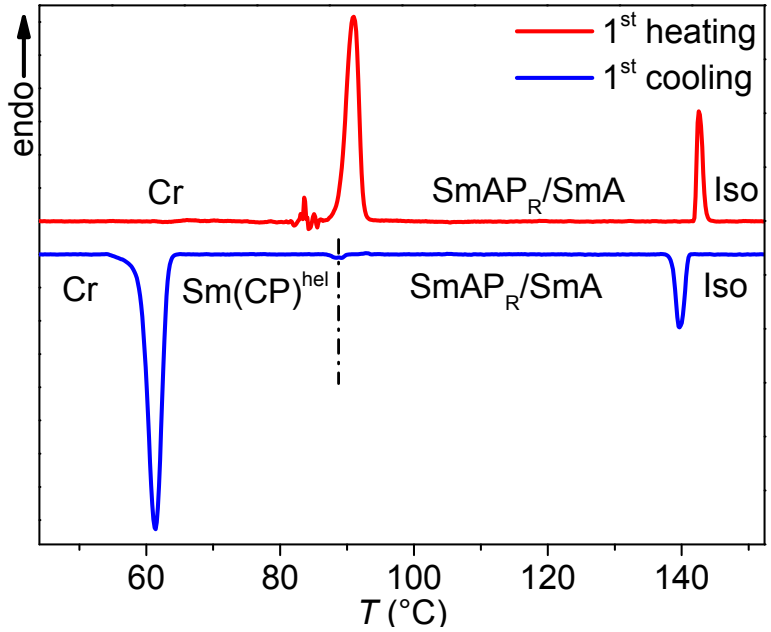


Figure S26. DSC heating and cooling traces of compound **C12/12** recorded at rates of 10 K min^{-1}.

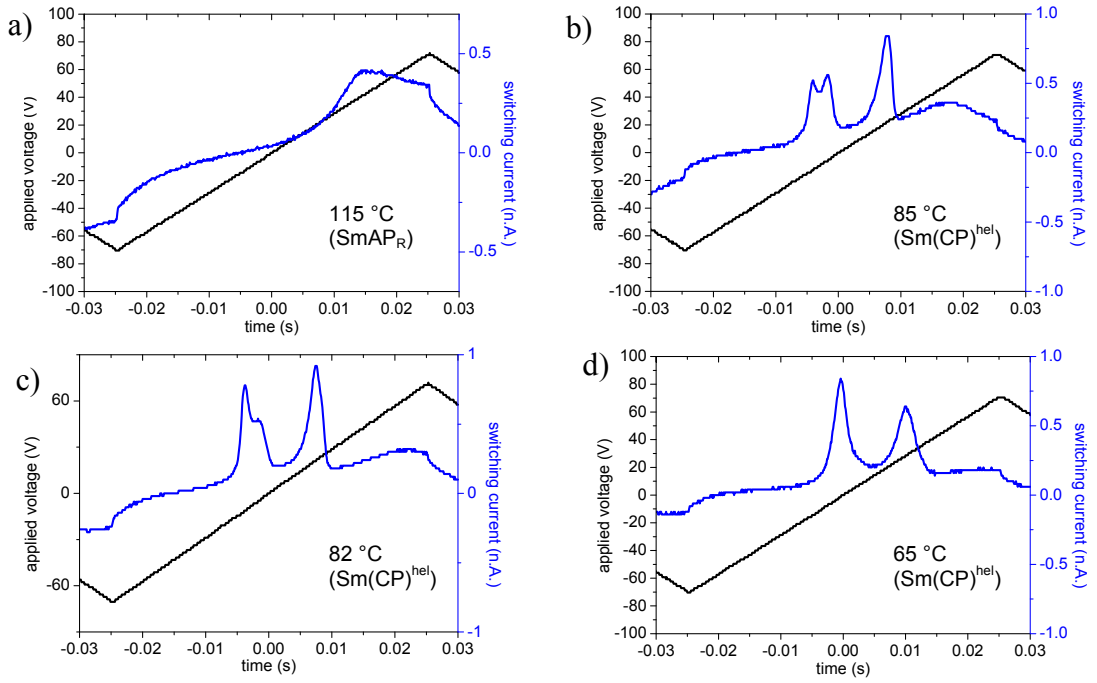


Figure S27. Polarization current response curves of **C12/12** at the indicated temperatures, measured in an ITO-coated cell (6 µm) under a triangular wave voltage of 140 Vpp and a frequency of 10 Hz. a) $SmAP_R$-phase at 115 °C, b-d) $Sm(CP)^{hel}$-phase at b) 85 °C, c) 82 °C and d) 65 °C.

130 °C ($SmAP_R$) 88 °C ($Sm(CP)^{hel}$) 70 °C ($Sm(CP)^{hel}$)

Figure S28. Homeotropic textures under crossed polarizers of compound **C12/12** depending on temperature; the two insets show the planar textures at the indicated temperatures.

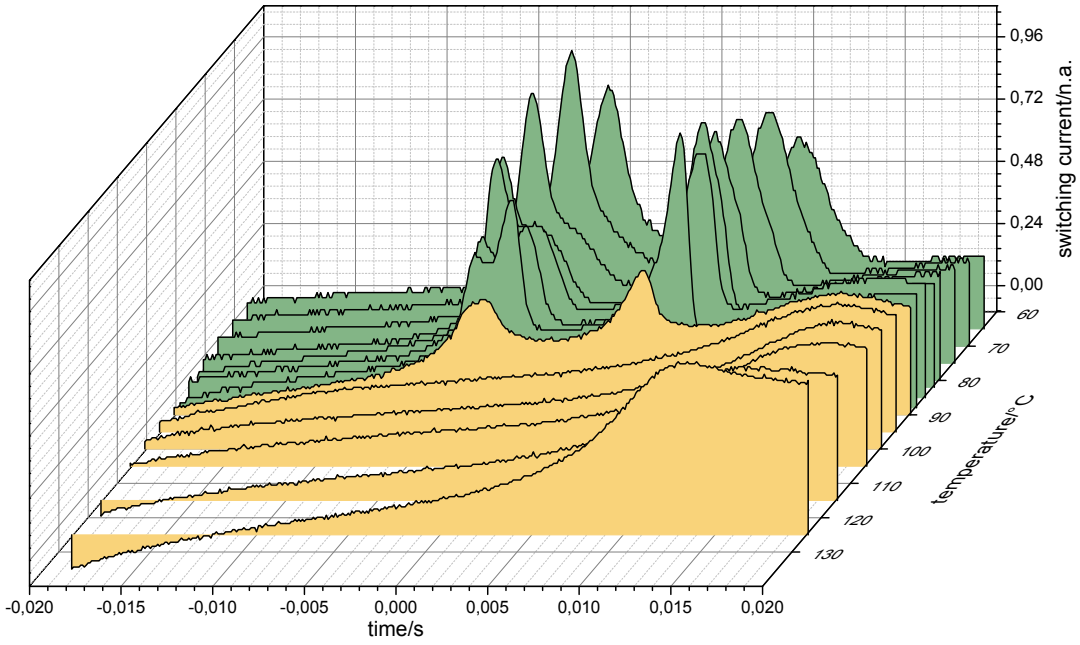


Figure S29. Polarization current response of **C12/12** depending on the temperature as measured in a ITO-coated cell (6 μm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.10 Compound C12/14

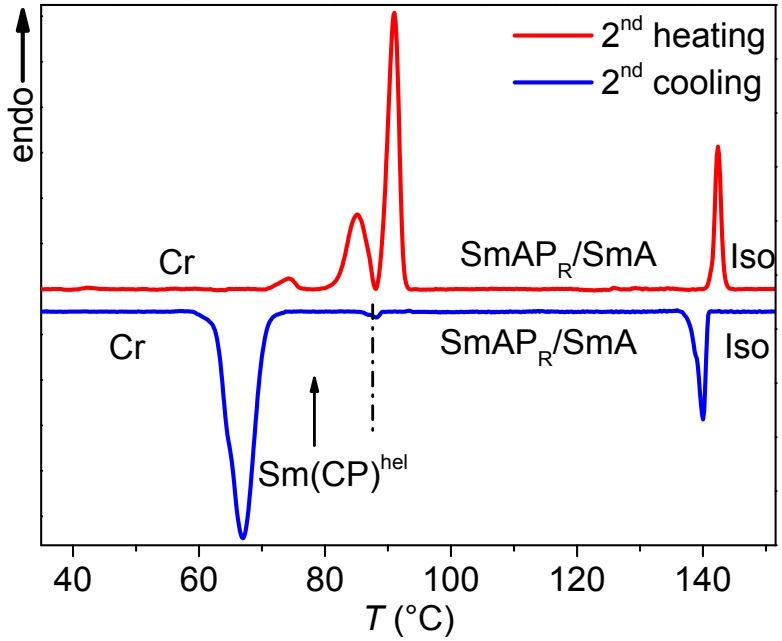


Figure S30. DSC heating and cooling traces of compound **C12/14** recorded at rates of 10 K min^{-1}.

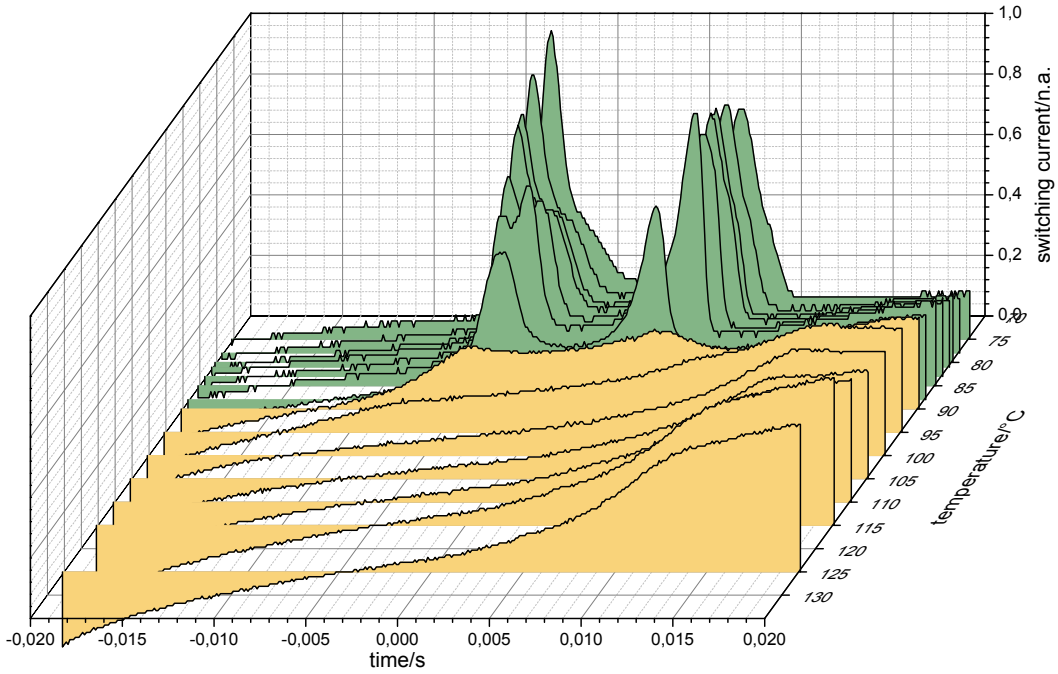


Figure S31. Polarization current response of **C12/14** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.11 Compound C14/14

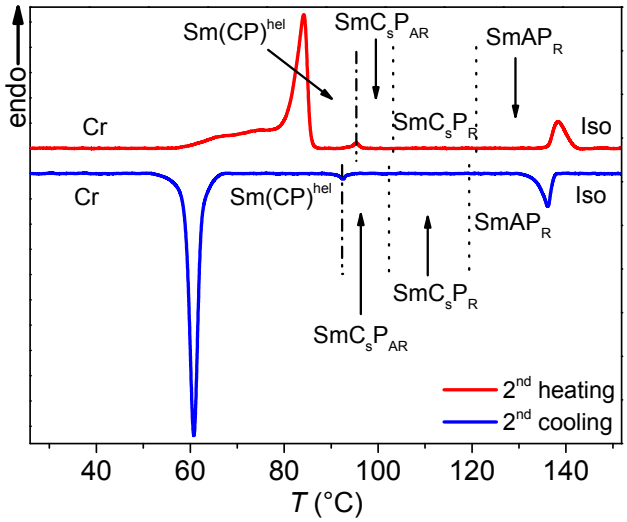


Figure S32. DSC heating and cooling traces of compound **C14/14** recorded at rates of 10 K min^{-1}.

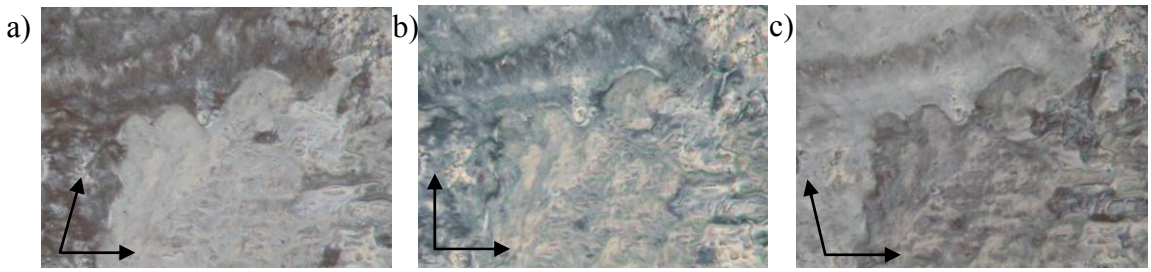


Figure S33. Chiral tilt-domains in the $SmC_sP_R[*]$ phase of **C14/14** at T = 110 °C as observed b) between crossed polarizers and a,c) between slightly uncrossed polarizers with the analyzer twisted by +/- 20 ° out of the perpendicular direction, respectively.

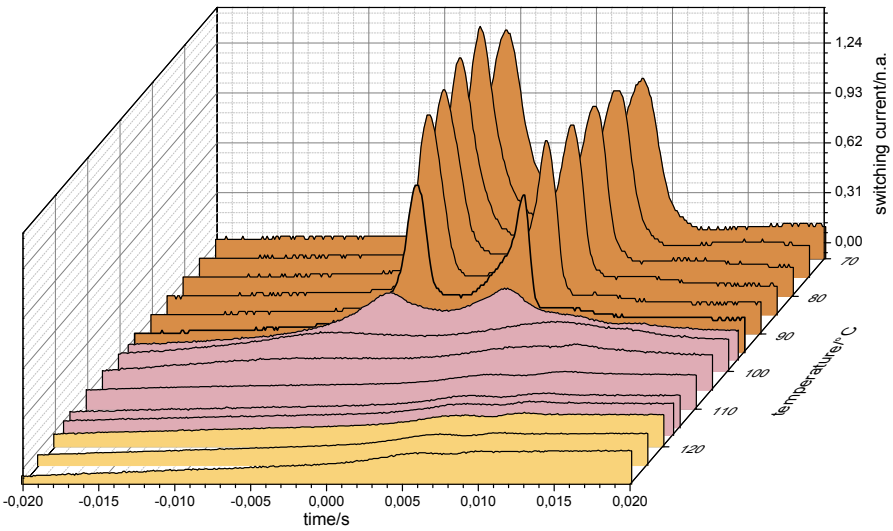


Figure S34. Polarization current response of **B14/14** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.12 Compound C16/14

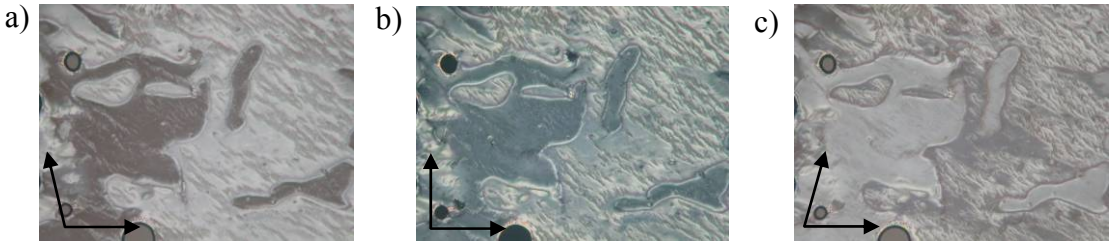


Figure S35. Chiral tilt-domains in the $SmC_sP_R^{[*]}$ phase of **C16/14** at T = 110 °C as observed b) between crossed polarizers and a,c) between slightly uncrossed polarizers with the analyzer twisted by +/- 20 ° out of the perpendicular direction, respectively.

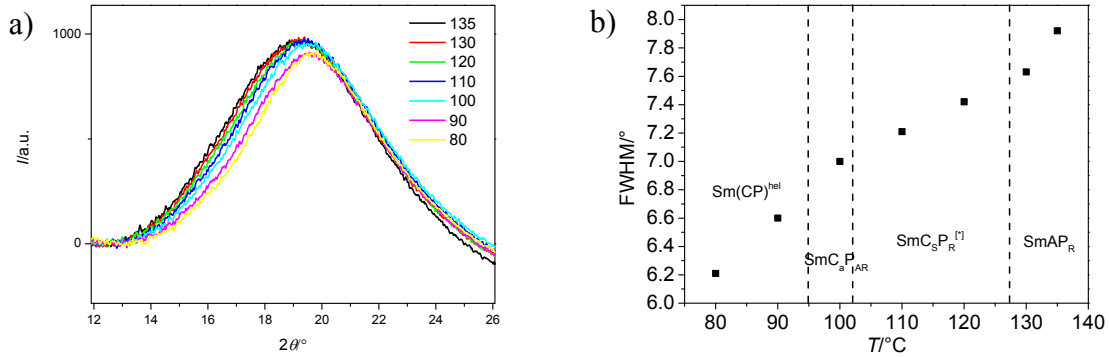


Figure S36. WAXD data of compound **C16/14**. a) 2θ scans and b) plot of FWHM depending on the temperature.

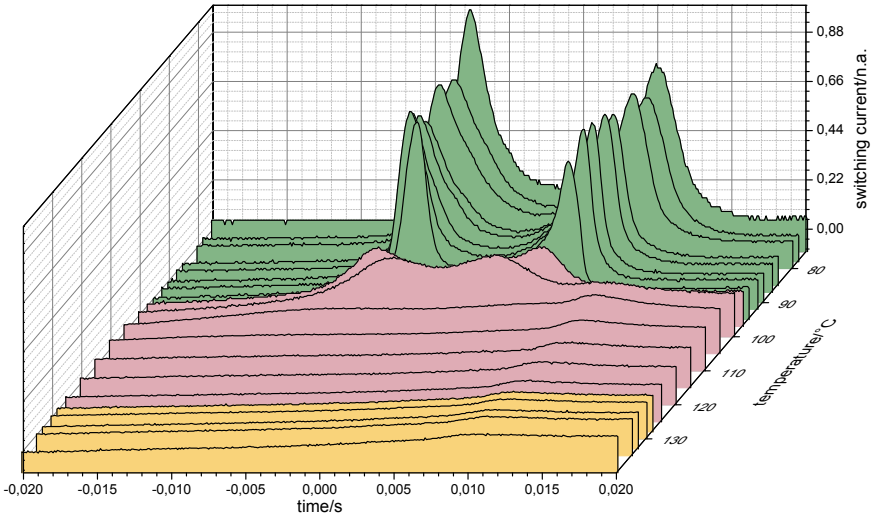


Figure S37. Polarization current response of **C16/14** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

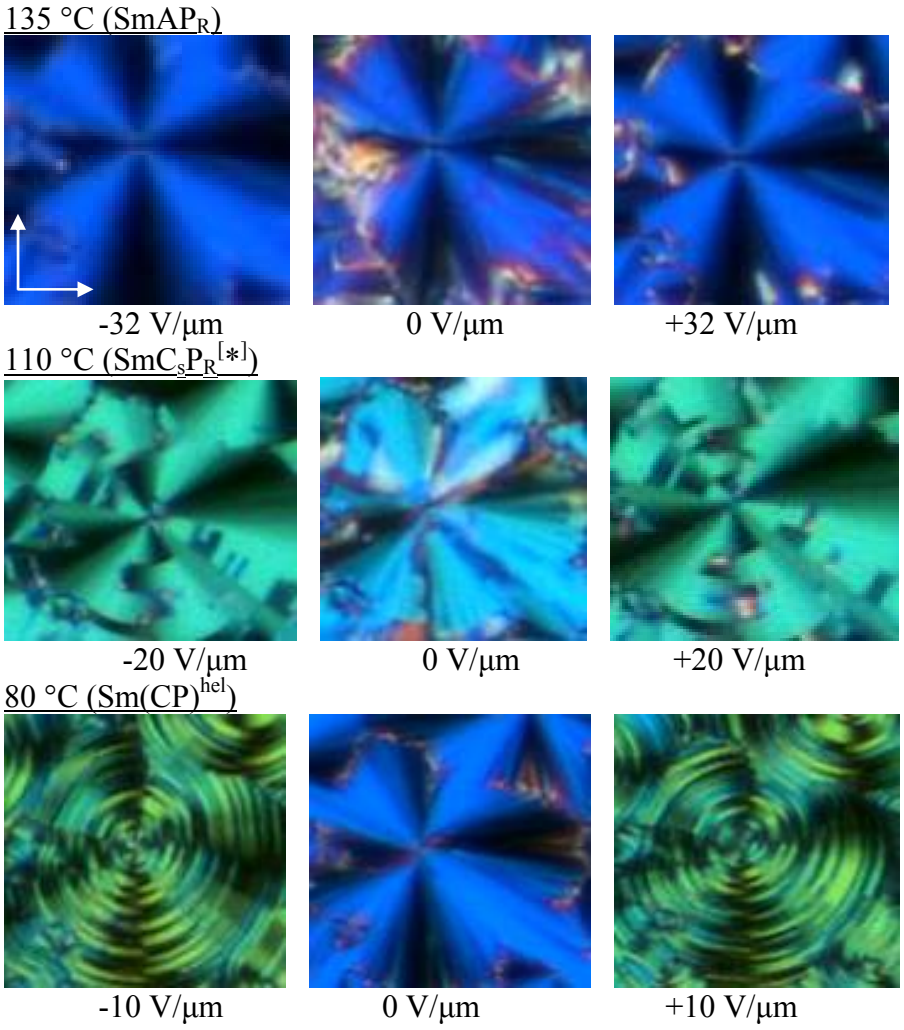
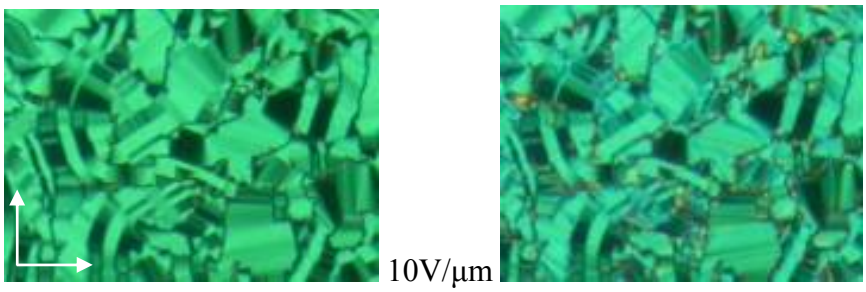


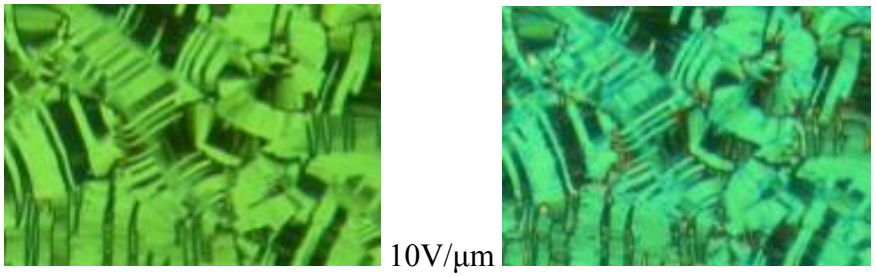
Figure S38. Textures of the distinct mesophases of compound **C16/14** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed for under an applied E-field at the indicated voltages (left/right).

120 °C (SmC$_s$P$_R$[*])



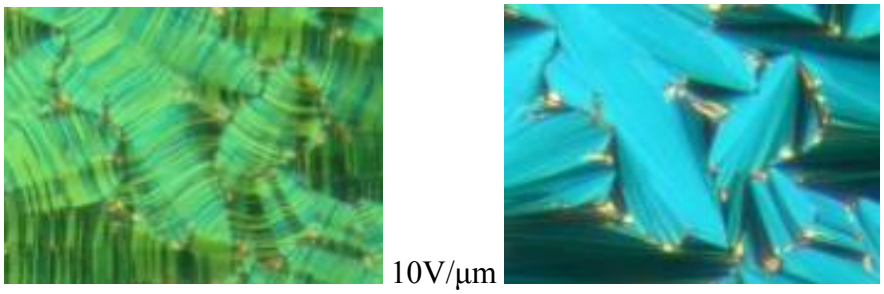
10V/µm 0V/µm

100 °C (SmC$_s$P$_{AR}$)



10V/µm 0V/µm

90 °C (Sm(CP)^{hel})



10V/µm 0V/µm

Figure S39. Change of the textures of compound **C16/14** at the SmC$_s$P$_R$-SmC$_s$P$_{AR}$-Sm(CP)^{hel} transitions in a planar cell as observed between crossed polarizers in the ground state without applied E-field (right) and as observed for under an applied E-field (left); in both non-helical phases the switching does not change the tilt direction as typical for switching around the long axis, whereas in the heliconical phase the reorganization takes place by precision on a cone.

3.13 Compound C18/14

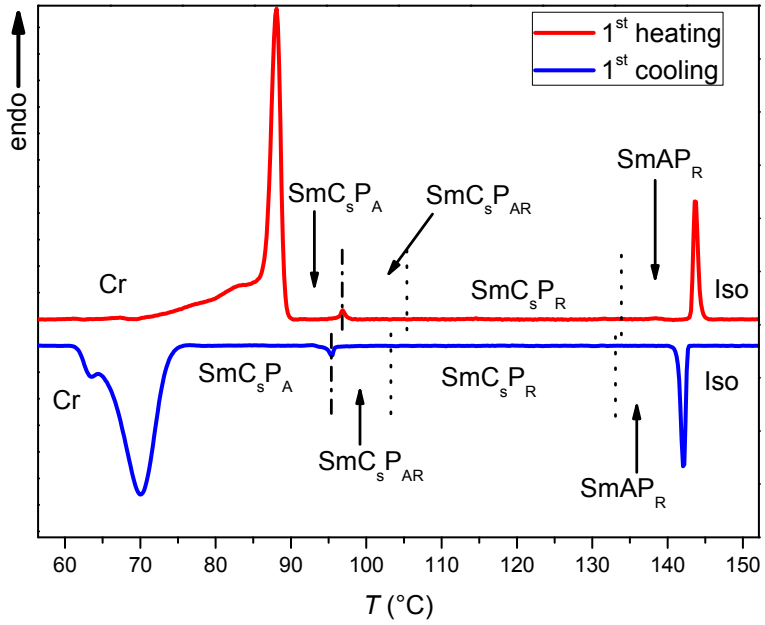


Figure S40. DSC heating and cooling traces of compound **C18/14** recorded at rates of 10 K min^{-1}.

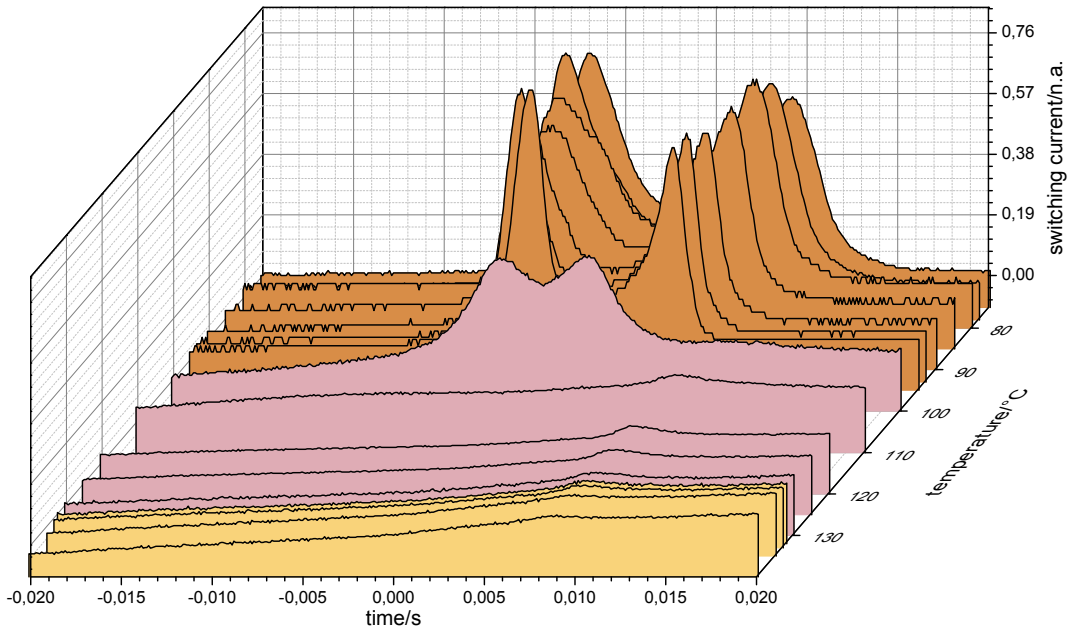
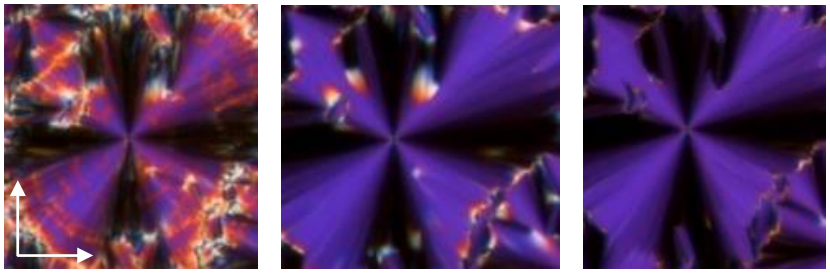


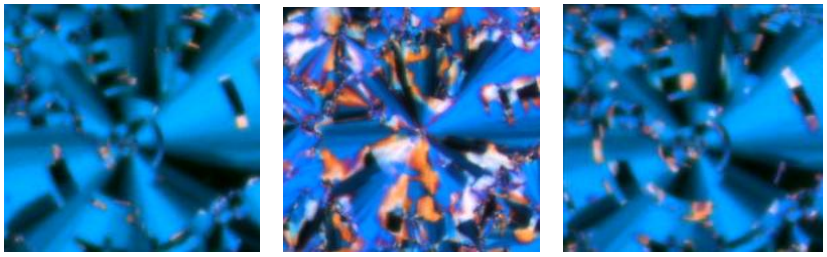
Figure S41. Polarization current response of **C18/14** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

a) 135 °C ($SmAP_R$)

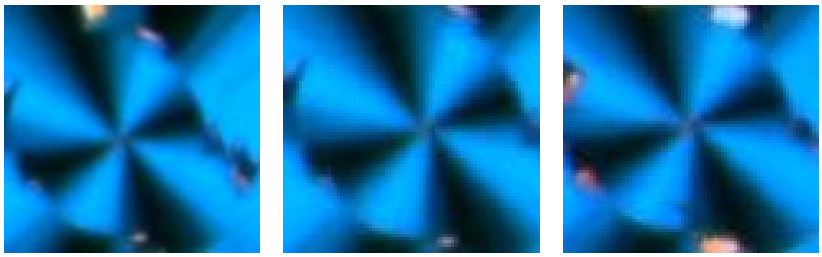


0 V/µm +20 V/µm +32 V/µm

b) 110 °C (SmC_sP_R)



-10 V/µm 0 V/µm +10 V/µm



-10 V/µm 0 V/µm +10 V/µm

Figure S42. Textures of the distinct mesophases of compound **C18/14** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field and as observed under an applied E-field at the indicated voltages; see Fig. 14 for the switching in the SmC_sP_A and field induced $Sm(CP)^{hel}$ phases.

3.14 Compound C22/12

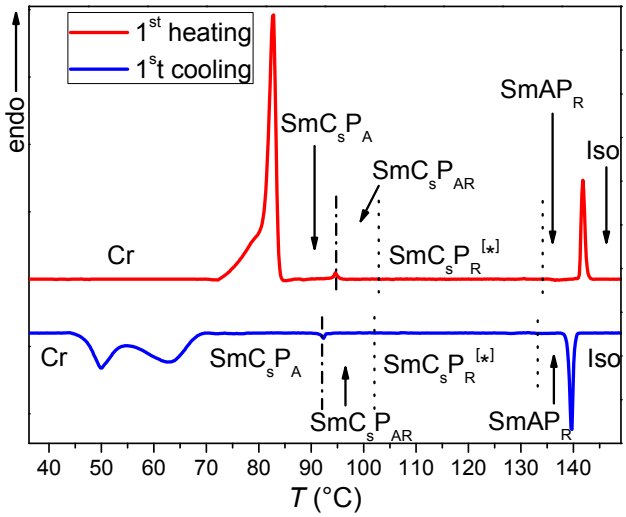


Figure S43. DSC heating and cooling traces of compound **C22/12** recorded at rates of 10 K min^{-1}

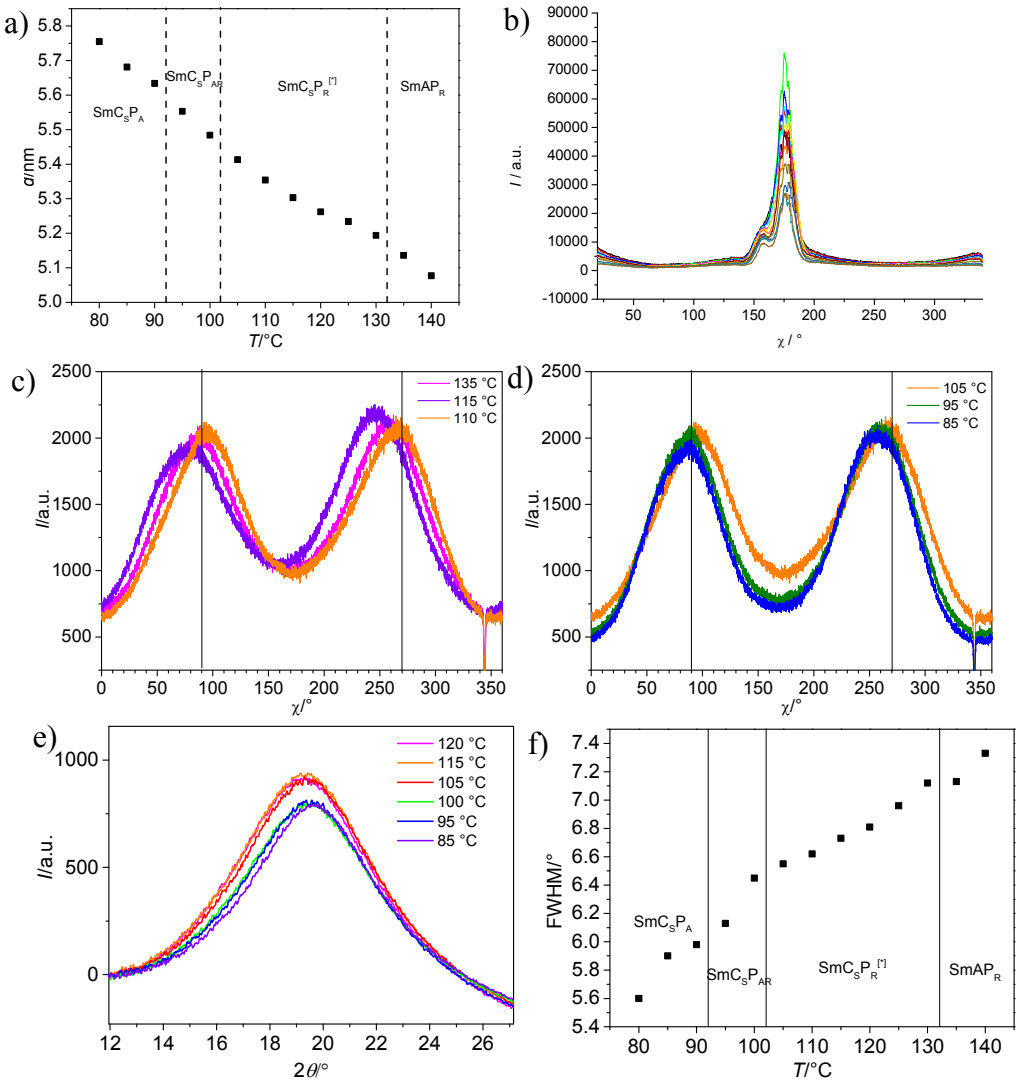


Figure S 44. XRD data of a magnetically aligned sample of compound **C22/12**. a) Plot of *d*-values of the layer spacing depending on temperature, b) intensity distribution of the SAXS (2θ = 1-3°; main maximum at 176°, the small peak is due to misalignment) and c,d) the

WAXS (2θ = 15-25°) depending on the temperature, indicating the presence of tilt; e) 2θ scans of the WAXS and f) FWHM depending on the temperature.

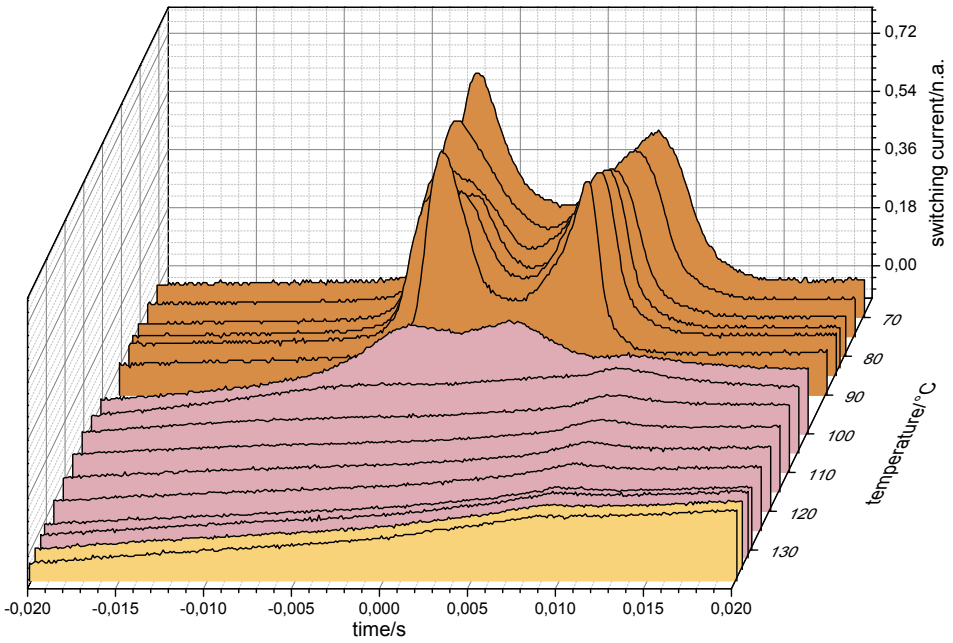
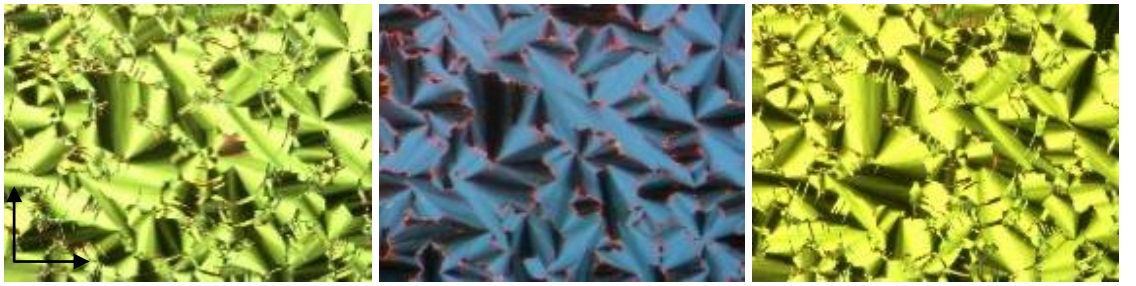
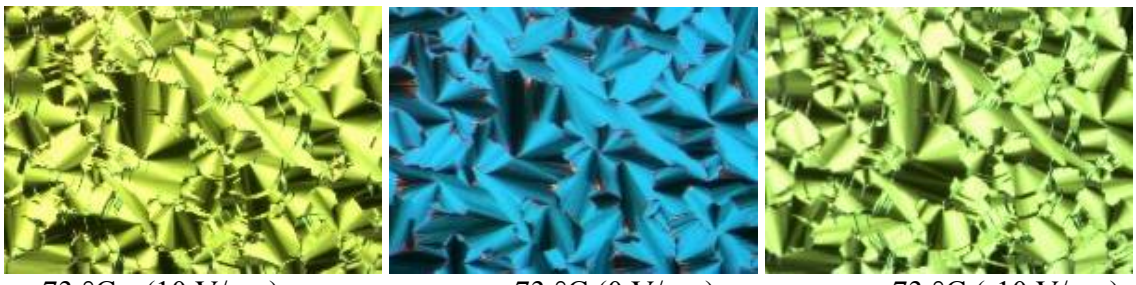


Figure S45. Polarization current response of **C22/12** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.



90 °C (10 V/µm) 90 °C (0 V/µm) 90 °C (-10 V/µm)



73 °C (10 V/µm) 73 °C (0 V/µm) 73 °C (-10 V/µm)

Figure S46. Textures of the field induced $Sm(CP)^{hel}$ phase in the SmC_sP_A range of compound **C22/12** at the given temperatures in a planar cell as observed between crossed polarizers at 0V (middle) and under an applied DC-field at the indicated voltages (left and right). The extinctions parallel to the polarizers at 0V, together with the switching on a cone by rotation of the extinction crosses indicate a field induced $Sm(CP)^{hel}$ phase.

3.15 Compound C18/18

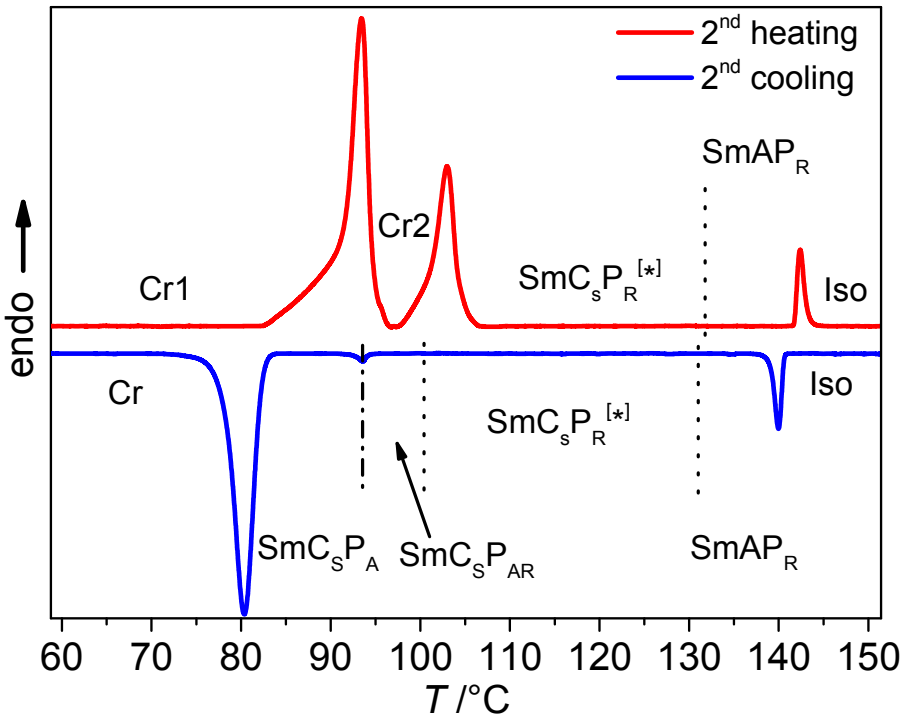


Figure S47. DSC heating and cooling traces of **C18/18** recorded at rates of 10 K min^{-1};

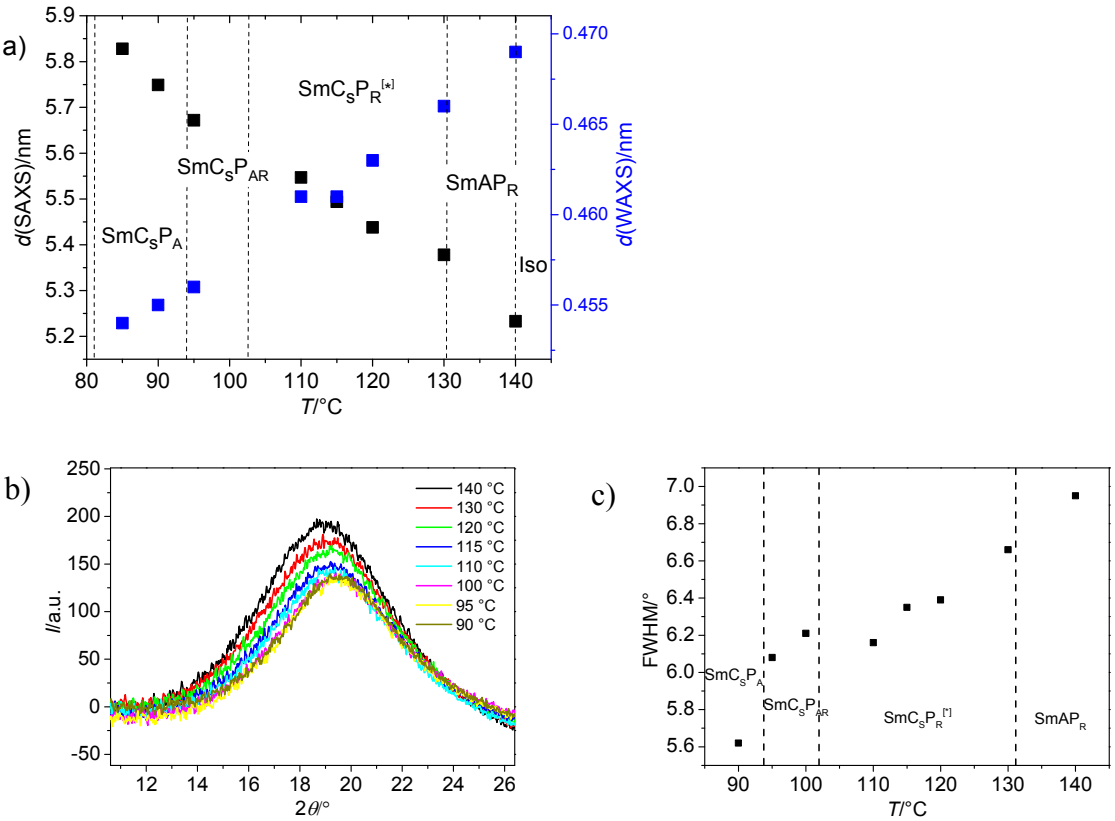


Figure S48. XRD data of compound **C18/18.** a) *d*-values of the layer spacing and of the maxima of the diffuse wide angle scattering in the XRD patterns of depending on temperature; b) 2θ scans of the wide angle scatterings and c) plot of FWHM of the wide angle scatterings depending on the temperature.

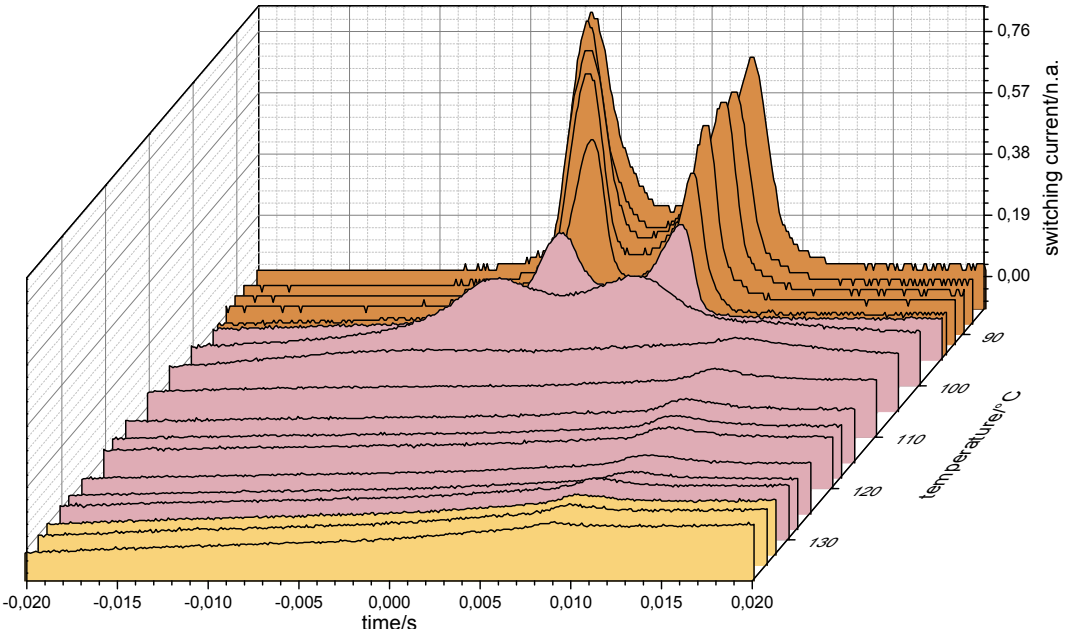


Figure S49. Polarization current response of **B18/18** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

3.16 Compound C22/18

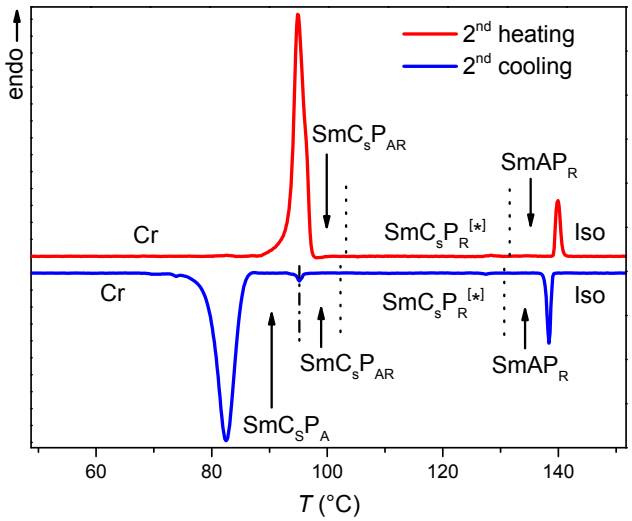


Figure S50. DSC heating and cooling traces of compound **C22/18** recorded at rates of 10 K min^{-1}

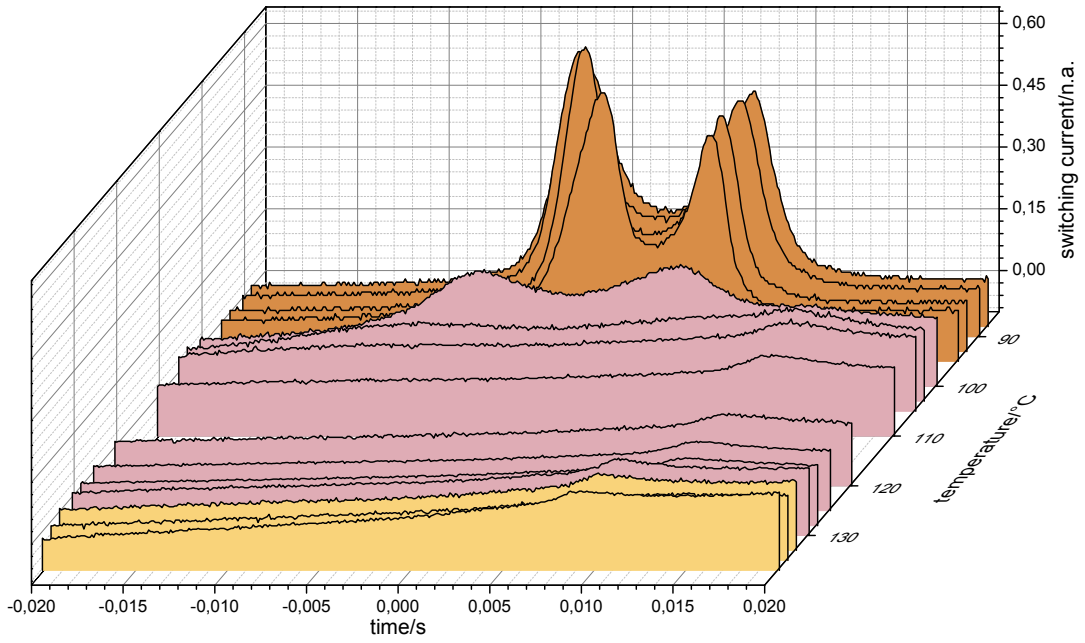


Figure S51. Polarization current response of **B22/18** depending on the temperature as measured in an ITO-coated cell (6 µm) under a triangular wave voltage of 160 V_{pp} and a frequency of 10 Hz.

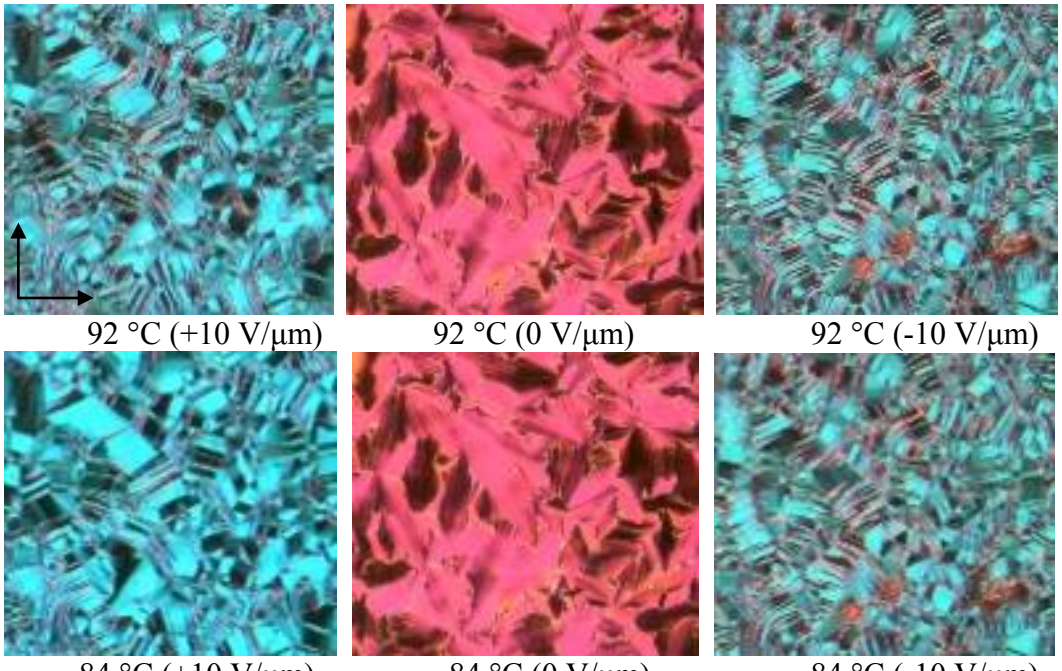


Figure S52. Textures of the field induced $Sm(CP)^{hel}$ phase in the SmC_sP_A range of compound **C22/12** at the given temperatures in a planar cell as observed between crossed polarizers at 0V (middle) and under an applied DC-field at the indicated voltages (left and right). The extinctions parallel to the polarizers at 0V, together with the switching on a cone between opposite tilt domains indicate a field induced $Sm(CP)^{hel}$ phase. This is additionally supported by the tiger-stripe pattern between the tilt domains.

3.17 Compound D18/O6

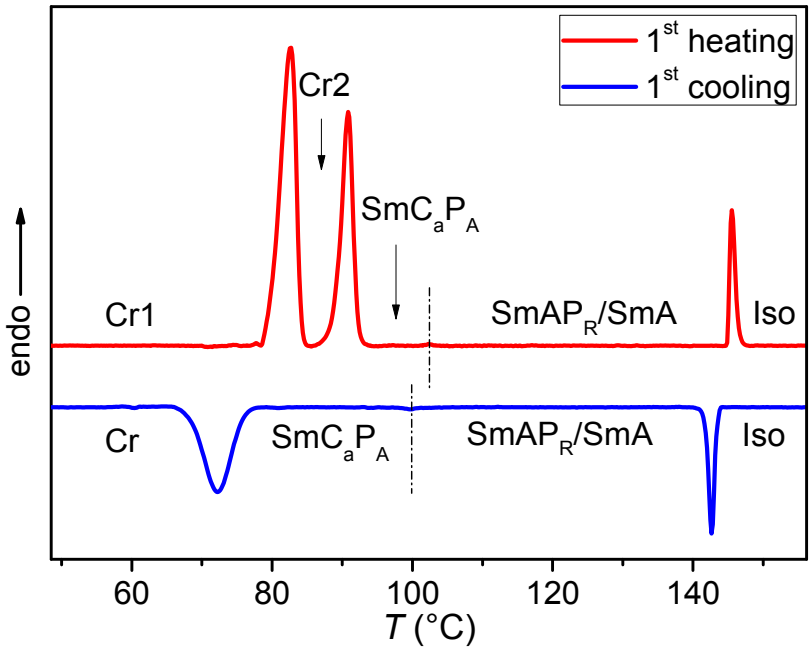


Figure S53. DSC heating and cooling traces of compound **D18/O6** recorded at rates of 10 K min^{-1}.

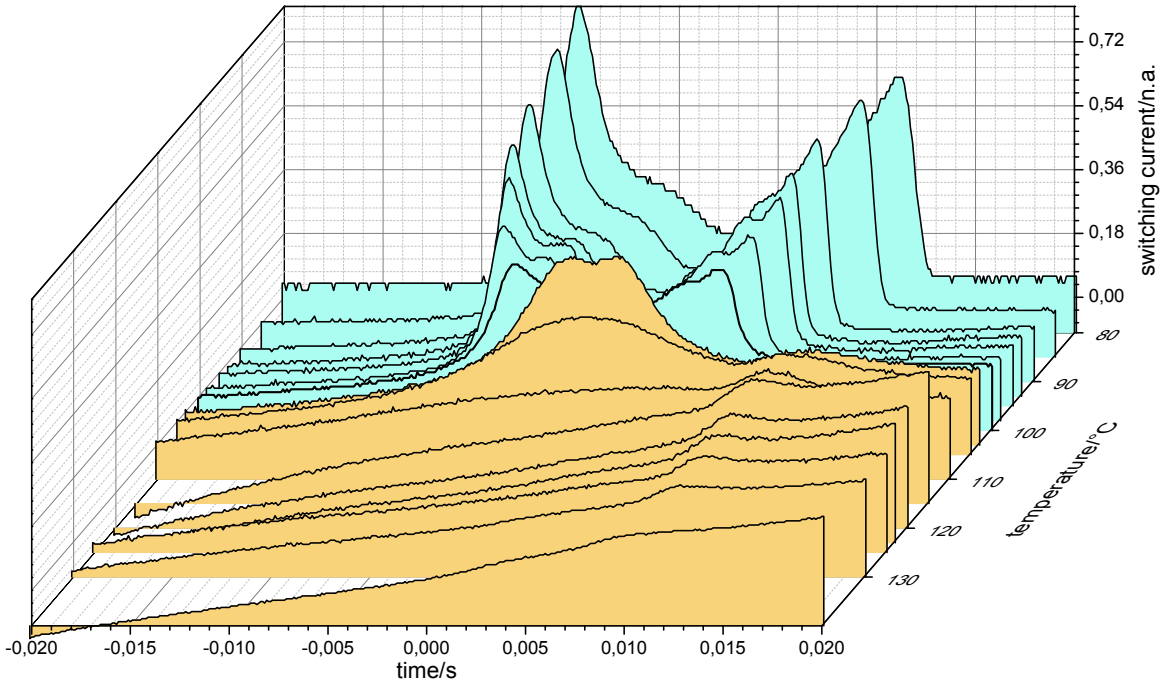


Figure S54. Polarization current response of **D18/O6** depending on the temperature as measured in a ITO-coated cell (6 µm) under a triangular wave voltage of 160 Vpp and a frequency of 10 Hz.

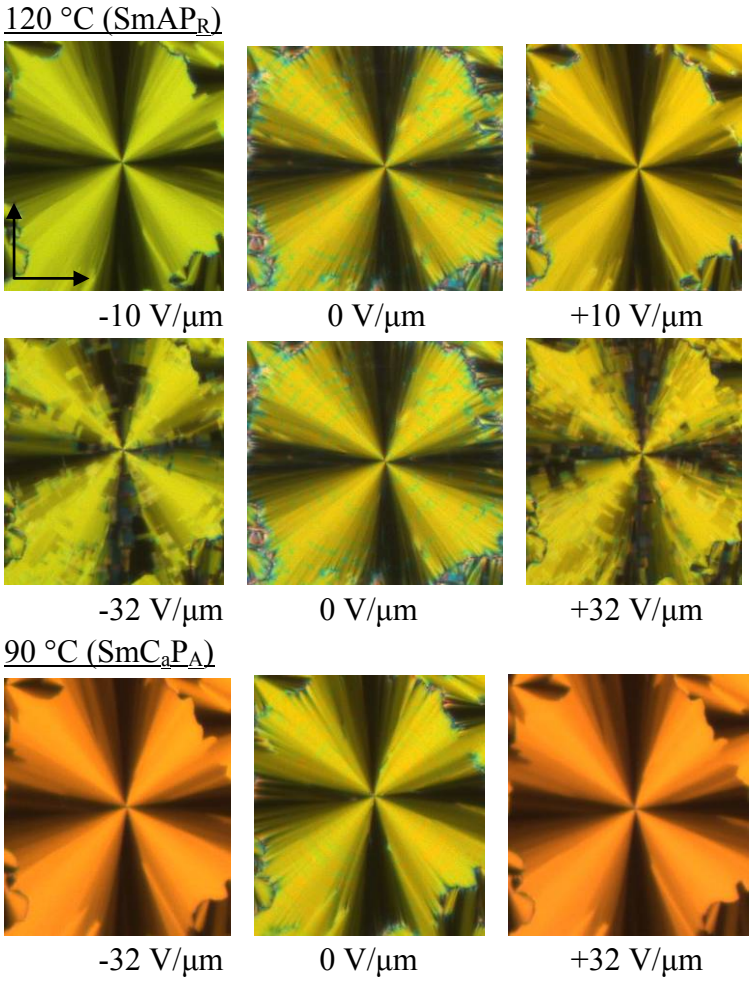


Figure S55. Textures of the distinct mesophases of compound **D18/O6** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed for under an applied E-field at the indicated voltages (left/right).

3.18 Compound DO18/6

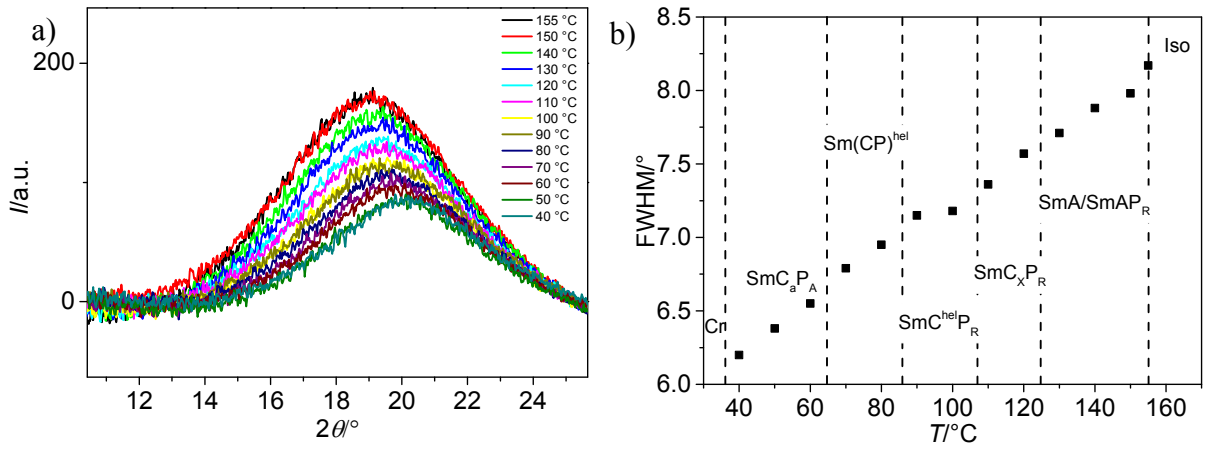


Figure S56. XRD data of compound **DO18/6** a) 2θ scans of the wide angle scatterings, b) plot of FWHM of the WAXS depending on the temperature.

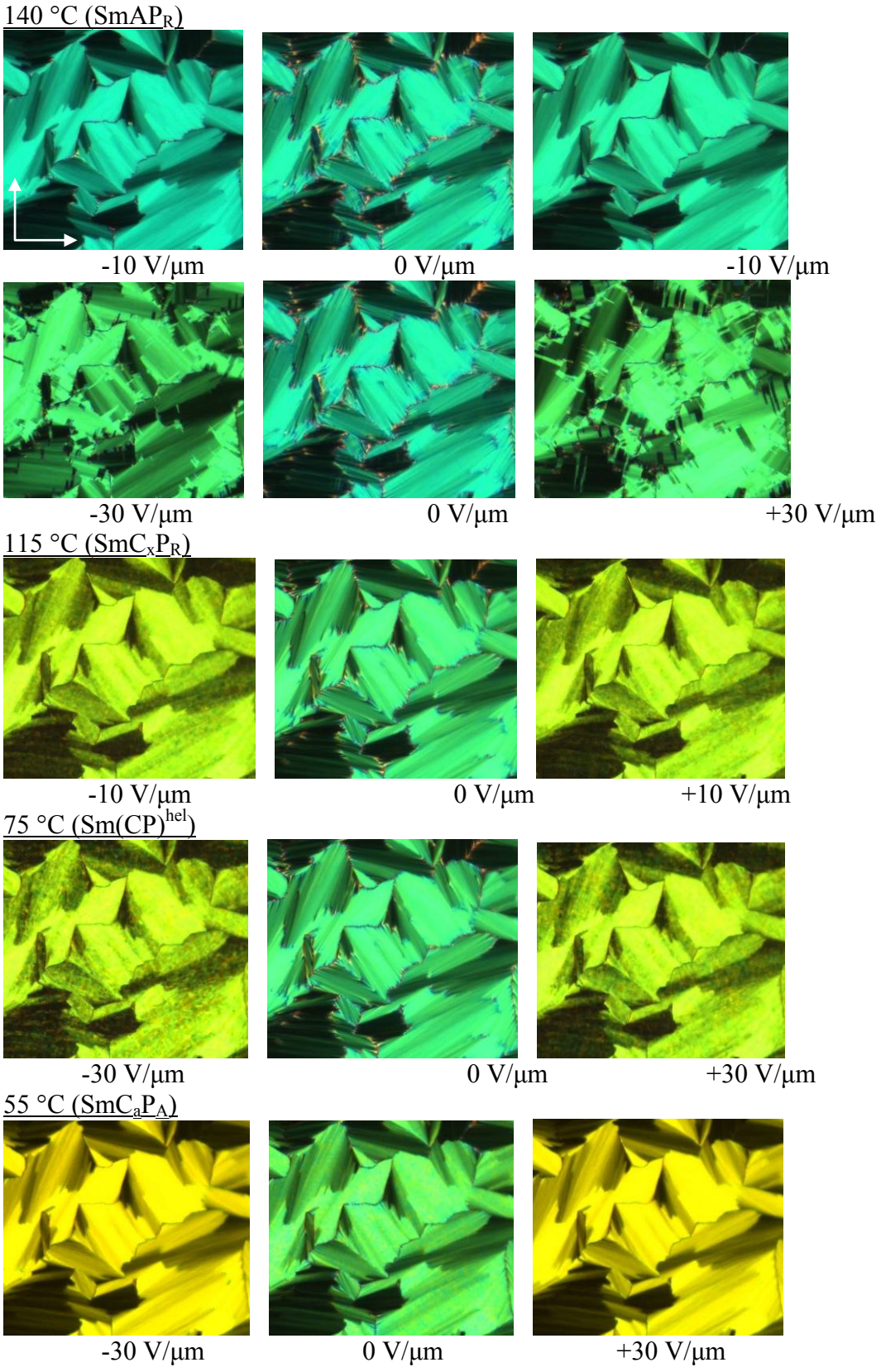


Figure S57. Textures of the distinct mesophases of compound **DO18/6** at the given temperatures in a planar cell as observed between crossed polarizers in the ground state without applied E-field (middle) and as observed for under an applied E-field at the indicated voltages (left/right).

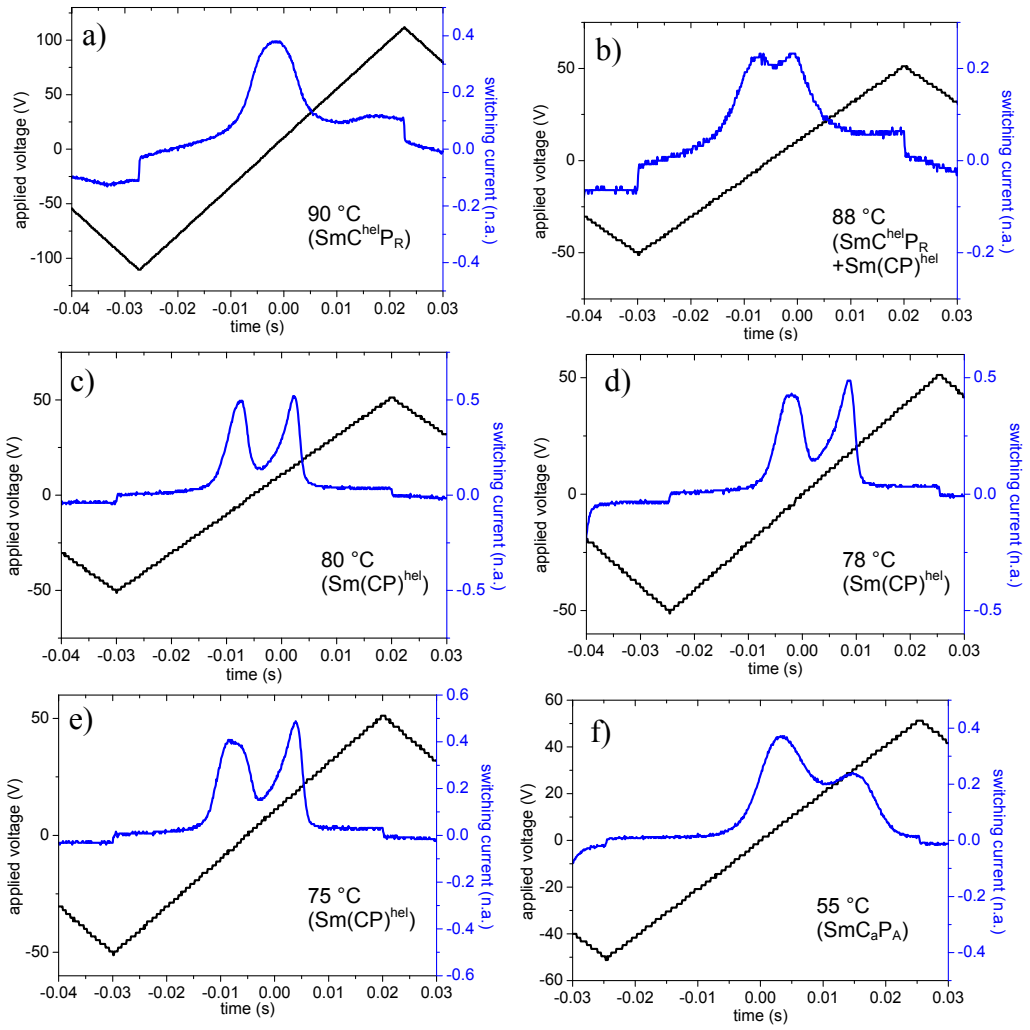


Figure S58. Polarization current response curves of **DO18/6** at the indicated temperatures, measured in a ITO-coated cell (6 µm) under a triangular wave voltage and a frequency of 10 Hz. a) $Sm(CP)^{hel}_{R}$-phase at 90 °C (V_{PP} = 240 V), b) $Sm(CP)^{hel}_{R}$-phase at 88 °C (V_{PP} = 100 V), c) $Sm(CP)^{hel}$-phase at 80 °C (V_{PP} = 100 V), d) $Sm(CP)^{hel}$-phase at 78 °C (V_{PP} = 100 V), e) $Sm(CP)^{hel}$-phase at 75 °C (V_{PP} = 100 V) and f) SmC_aP_A phase at 55 °C (V_{PP} = 100 V).

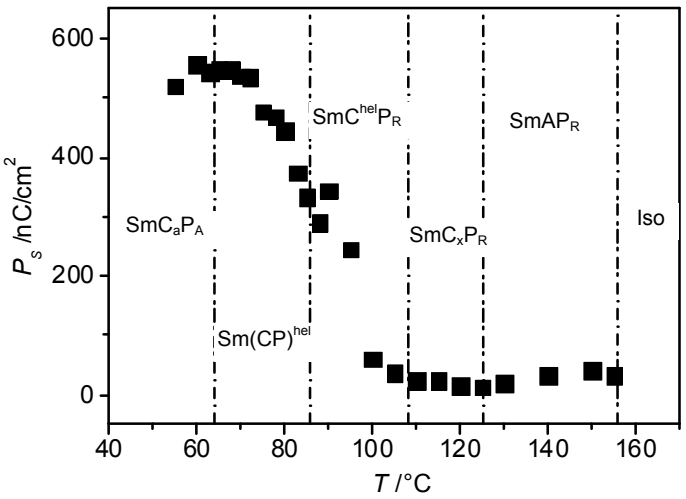


Figure S59. a) Polarization values compound **DO18/6** as measured depending on temperature.

3.19 Compound DO18/O6

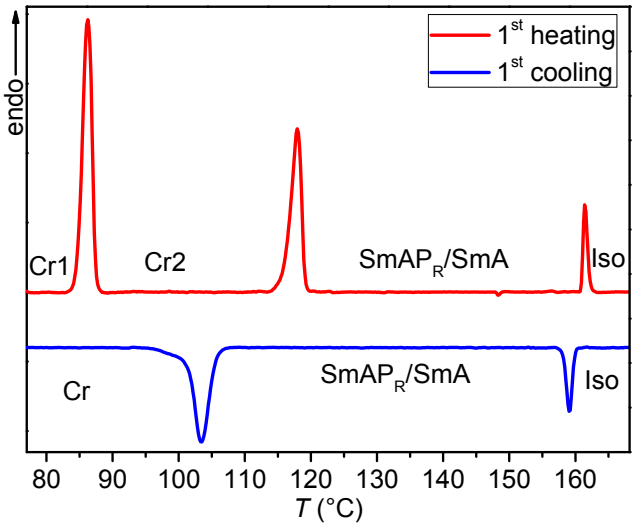
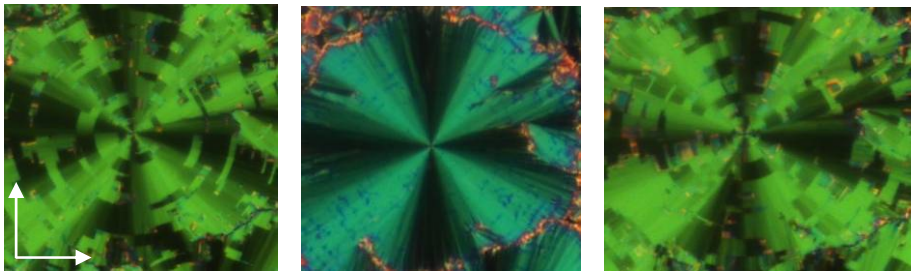


Figure S60. DSC heating and cooling traces of compound **DO18/O6** recorded at rates of 10 K min^{-1}.



-30 V/µm 0 V/µm +30 V/µm

Figure S61. Investigation of the switching in the SmAP$_R$ phase of **DO18/O6** at T = 130°C between crossed polarizers under the indicated conditions; synclinic SmC$_s$P$_F$ states are induced under the applied field (tilt domains,left/right) which relax back at 0V to the de Vries like SmA ground state with randomized polar and tilt directions (middle).

3.20 Compound DO22/O6

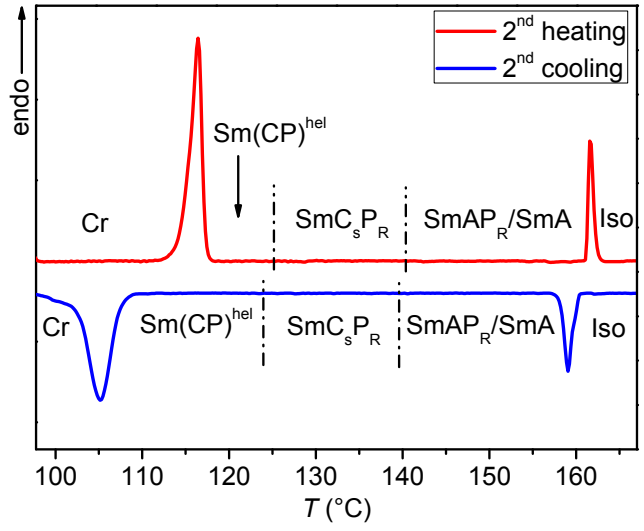


Figure S62: DSC traces of compound **DO22/O6** on heating and cooling at a constant rate of 10 K min^{-1}.

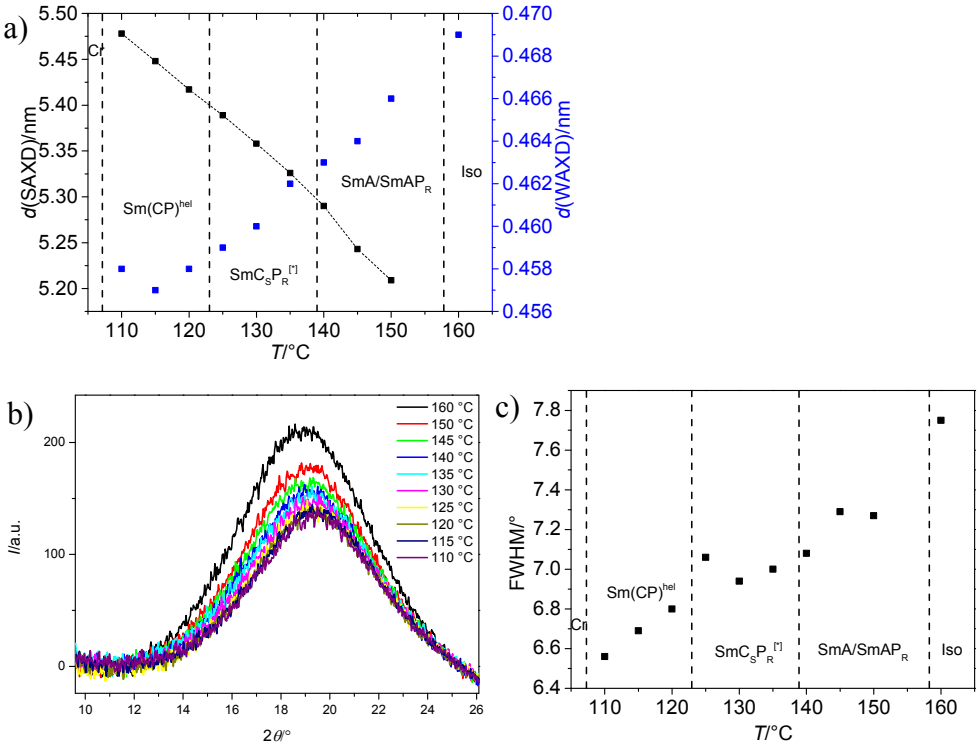


Figure S63. XRD data of compound **DO22/O6** a) plot of *d*-values of layer spacings and maxima of the wide angle scatterings depending on the temperature, b) 2θ scans of the WAXS, d) plot of FWHM depending on the temperature.

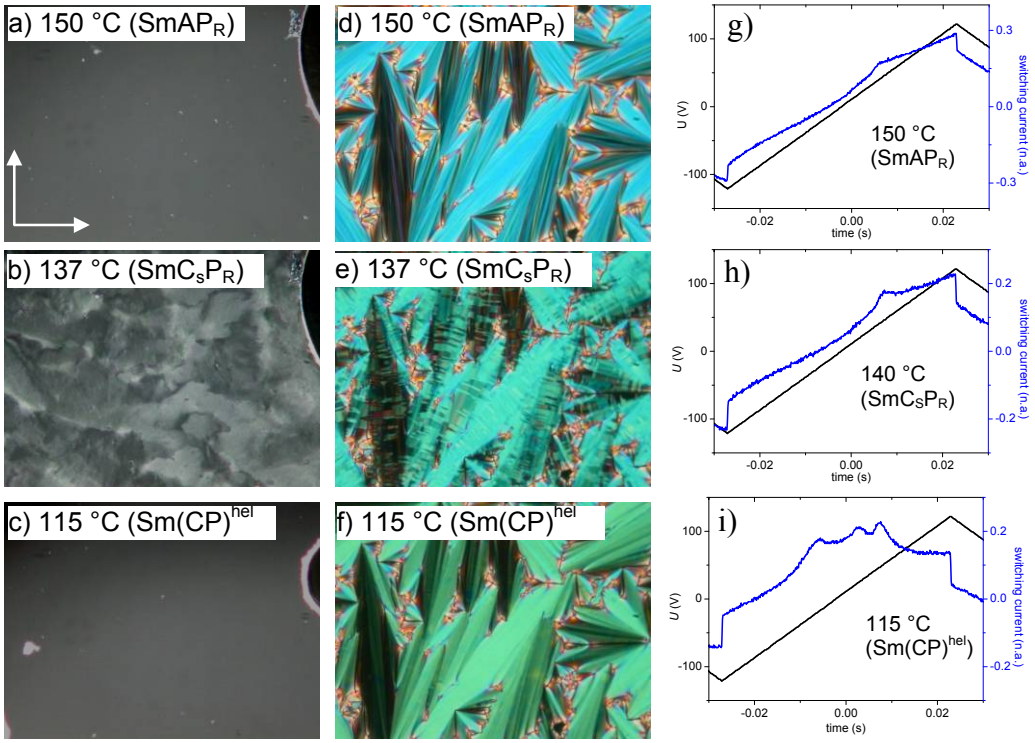


Figure S64. Homeotropic (left, a-c) and planar textures (middle, d-f) as observed between crossed polarizers and corresponding polarization current curves (right, g-i) of compound **DO22/O6** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, non-coated) under a triangular wave voltage and a frequency of 10 Hz. g) $SmAP_R$-phase at 150 °C (V_{PP} = 240 V), h) SmC_sP_R-phase at 140 °C (V_{PP} = 240 V) and i) $Sm(CP)^{hel}$-phase at 115 °C (V_{PP} = 240 V).

3.21 Compound DO12/6

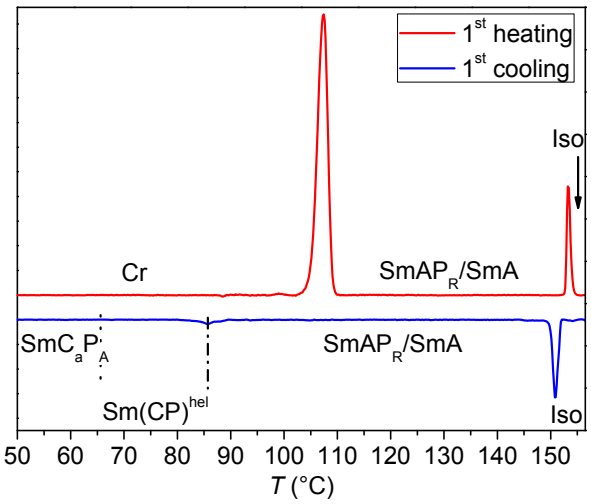


Figure S65. DSC heating and cooling traces of compound **DO12/6** recorded at rates of 10 K min^{-1}.

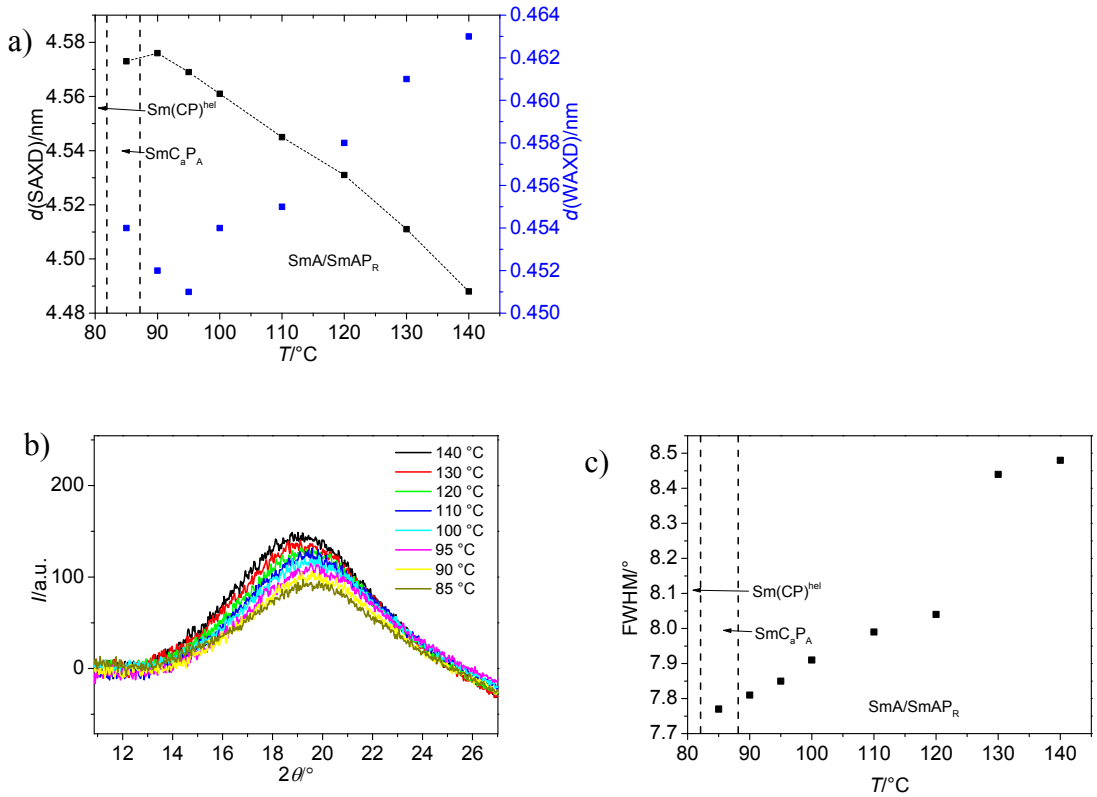


Figure S66. XRD data of compound **DO12/6.** a) plot of *d*-values of layer spacings and maxima of the wide angle scatterings depending on the temperature, b) 2θ scans of the WAXS, d) plot of FWHM depending on the temperature.

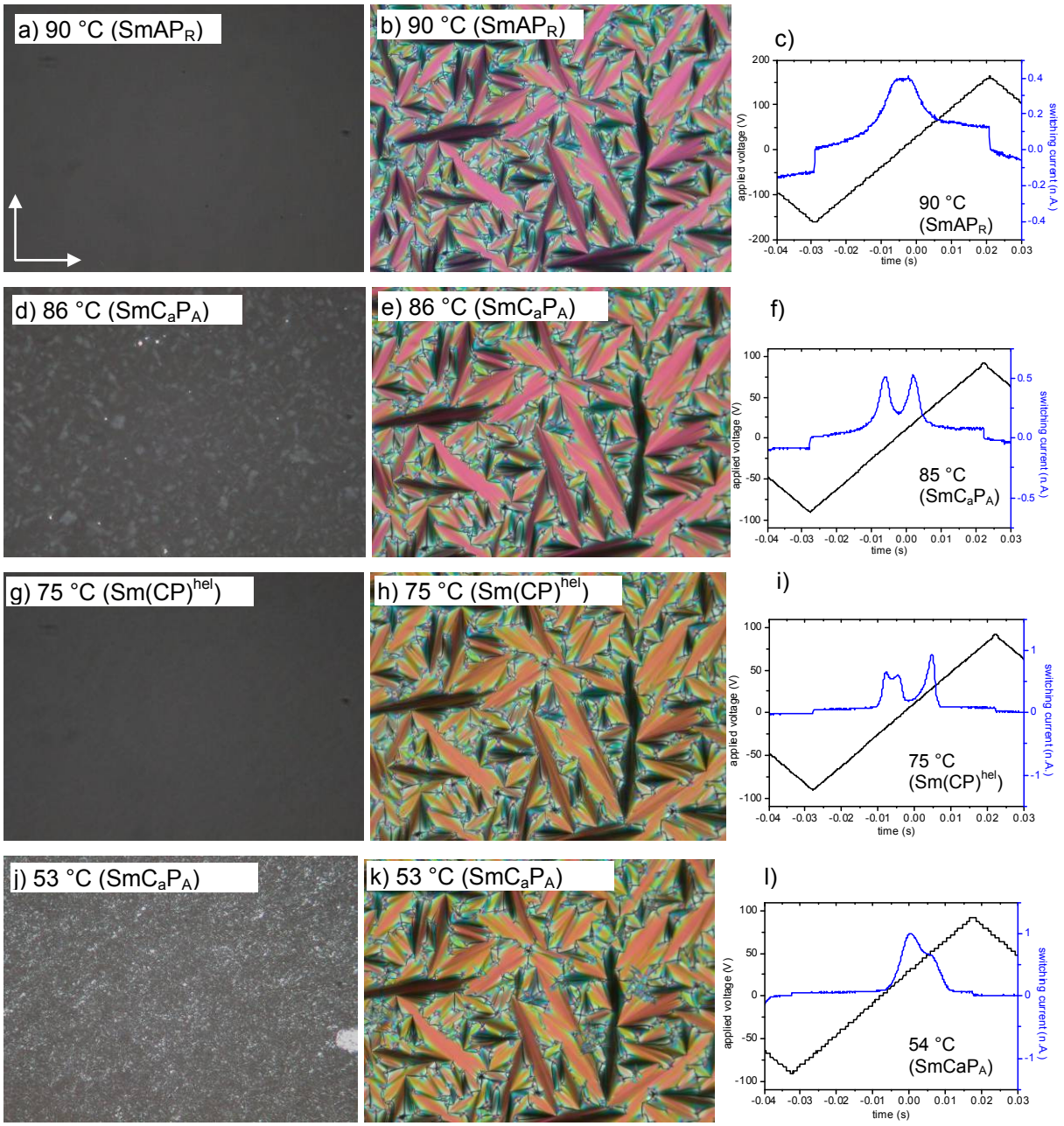


Figure S67. Homeotropic (left) and planar textures (middle) as observed between crossed polarizers and corresponding polarization current curves (right) of compound **DO12/6** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, non-coated) under a triangular wave voltage and a frequency of 10 Hz. c) SmAP$_R$-phase at 90 °C (V_{PP} = 320 V), f) SmC$_a$P$_A$-phase at 85 °C (V_{PP} = 180 V), i) Sm(CP)^{hel}-phase at 75 °C (V_{PP} = 180 V) and l) SmC$_a$P$_A$ at 54 °C (V_{PP} = 180 V).

3.22 Compound DO12/12

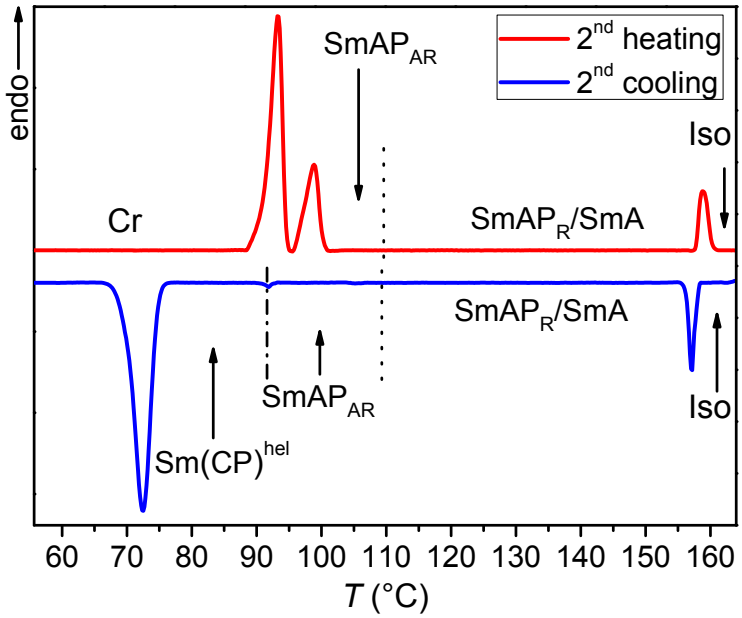


Figure S68. DSC heating and cooling traces of compound **DO12/12** recorded at rates of 10 K min^{-1}.

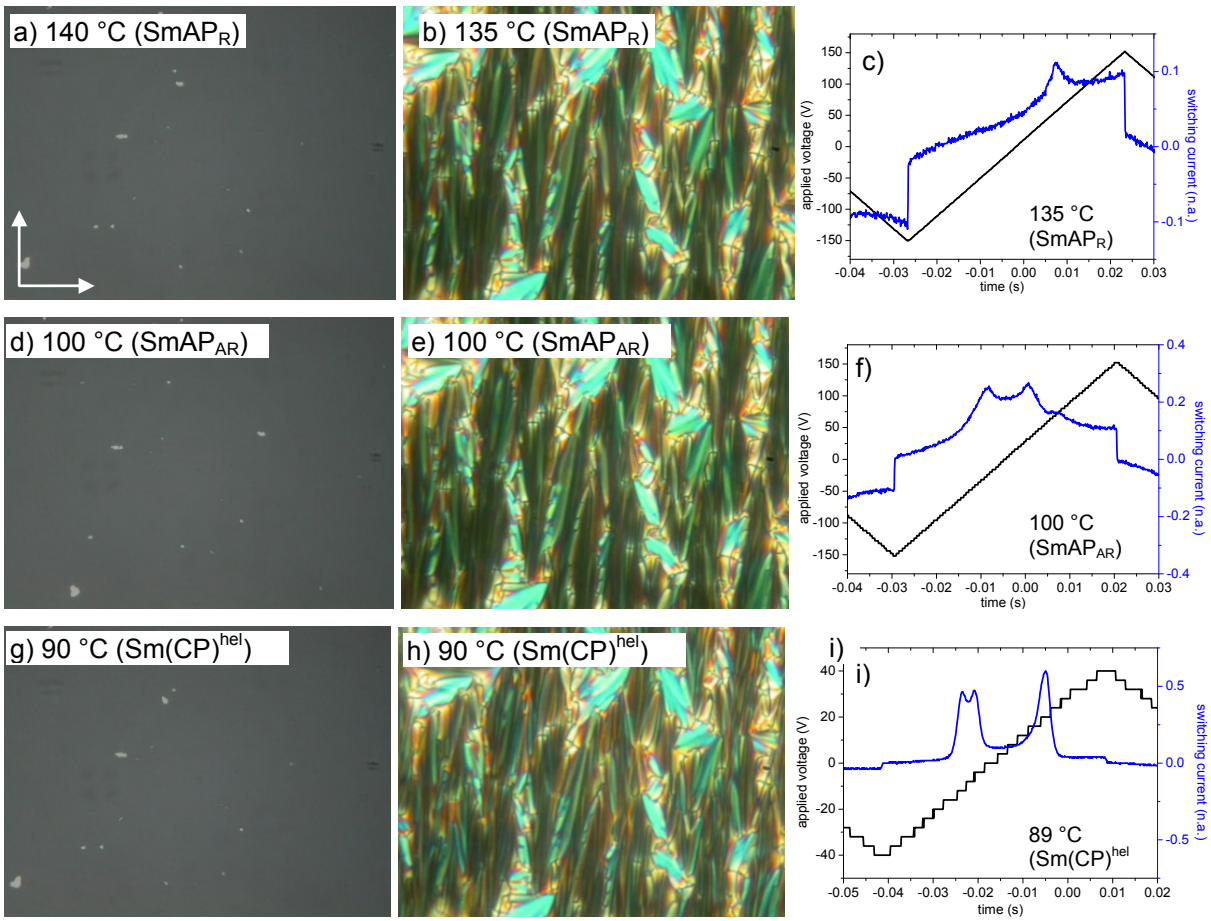


Figure S69. Homeotropic (left) and planar textures (middle) as observed between crossed polarizers and corresponding polarization current curves (right) of compound **DO12/12** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, PI-coated) under a triangular wave voltage and a

frequency of 10 Hz. c) $SmAP_R$-phase at 135 °C (V_{PP} = 300 V), f) $SmAP_{AR}$-phase at 100 °C (V_{PP} = 300 V) and i) $Sm(CP)^{hel}$-phase at 89 °C (V_{PP} = 80 V).

3.23 Compound D12/O12

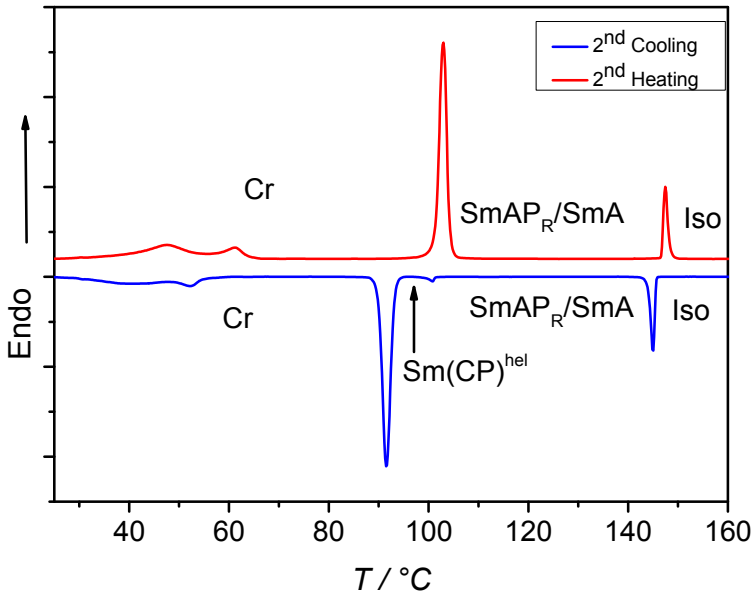


Figure S70. DSC heating and cooling traces of compound **D12/O12** recorded at rates of 10 K min^{-1}.

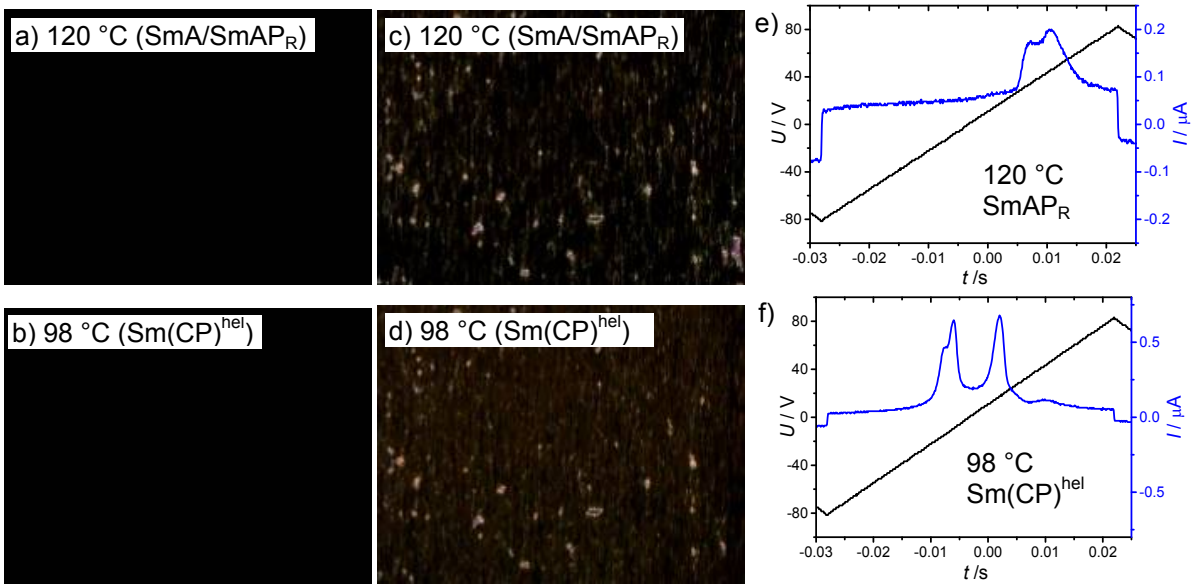


Figure S71. Homeotropic (left, a-b) and planar textures (middle, c-d) as observed between crossed polarizers and corresponding polarization current curves (right, e-f) of compound **D12/O12** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, PI-coated) under a triangular wave voltage and a frequency of 10 Hz; the double peak + single peak confirm the ferroelectric switching as ypical for the $Sm(CP)^{hel}$ phase.

3.24 Compound DO12/O12

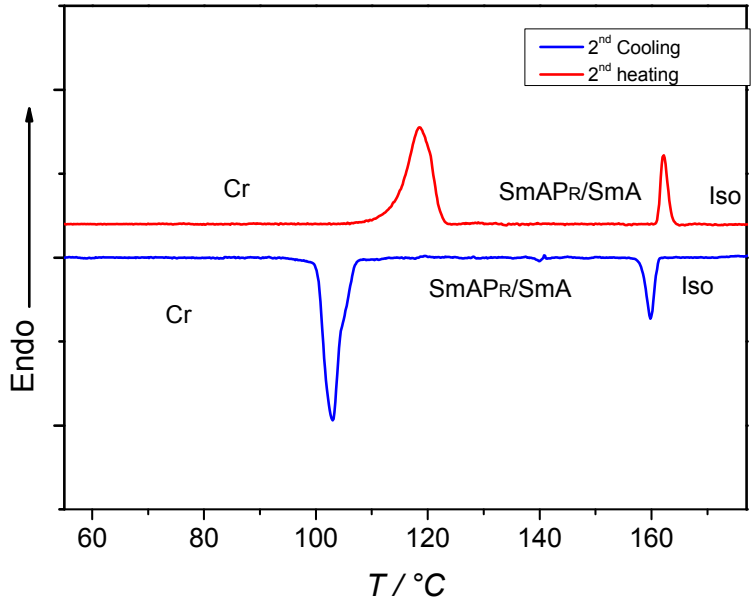
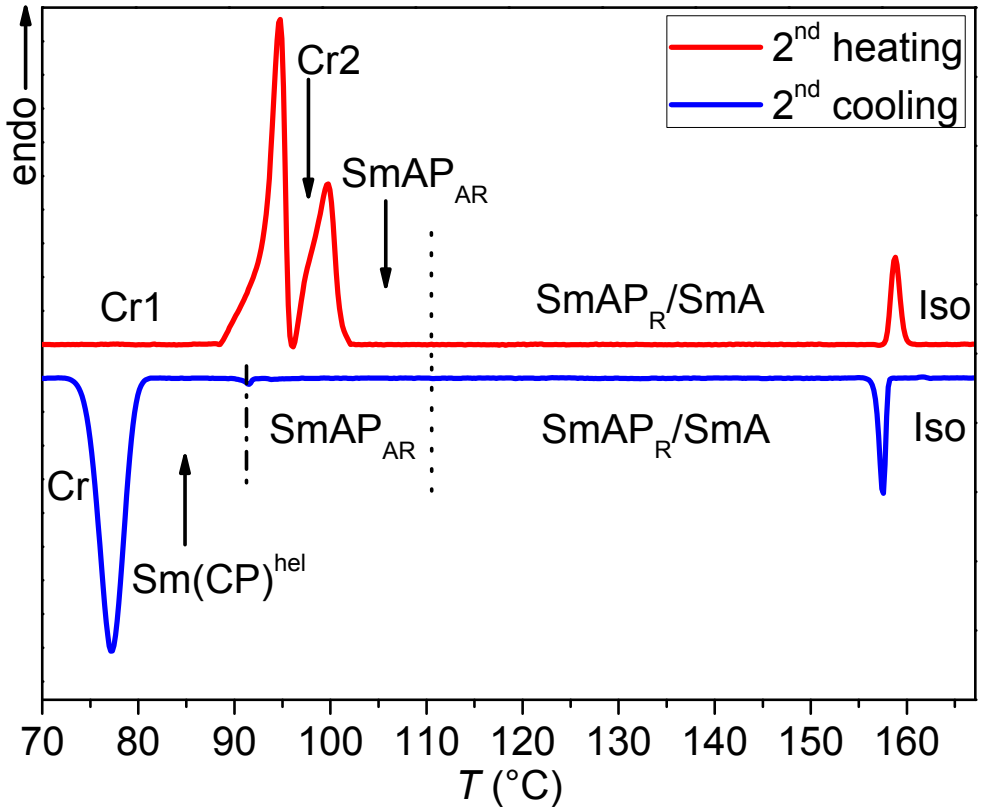


Figure S72. DSC heating and cooling traces of compound **DO12/O12** recorded at rates of 10 K min^{-1}.

3.25 Compound DO12/14



Fiure S73. DSC heating and cooling traces of compound **DO12/14** recorded at rates of 10 K min^{-1}.

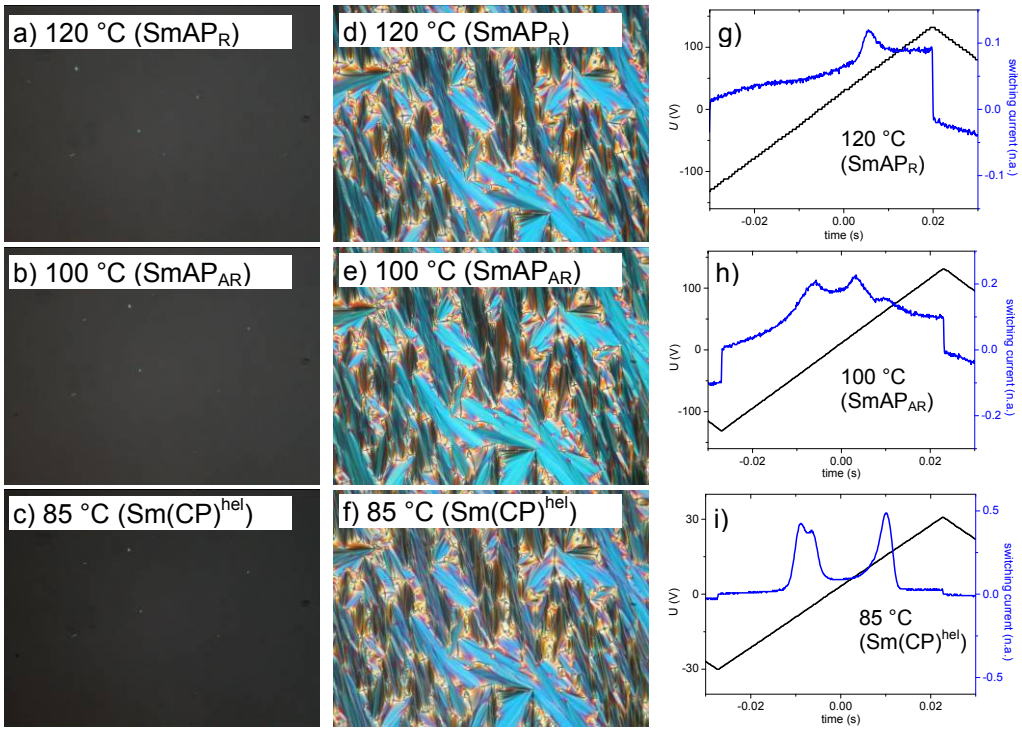


Figure S74. Homeotropic (left, a-c) and planar textures (middle, d-f) as observed between crossed polarizers and corresponding polarization current curves (right, g-i) of compound **DO12/14** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, PI-coated) under a triangular wave voltage and a frequency of 10 Hz. g) SmAP$_R$-phase at 120 °C (V_{PP} = 260 V), h) SmAP$_{AR}$-phase at 100 °C (V_{PP} = 260 V) and i) Sm(CP)^{hel}-phase at 85 °C (V_{PP} = 60 V).

3.26 Compound DO14/O14

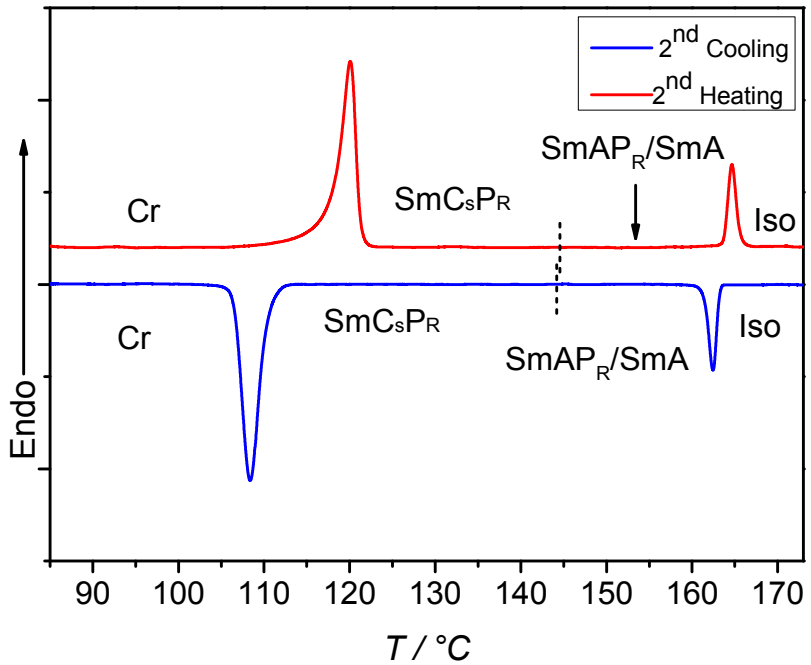


Figure S75. DSC heating and cooling traces of compound **DO14/O14** recorded at rates of 10 K min^{-1}.

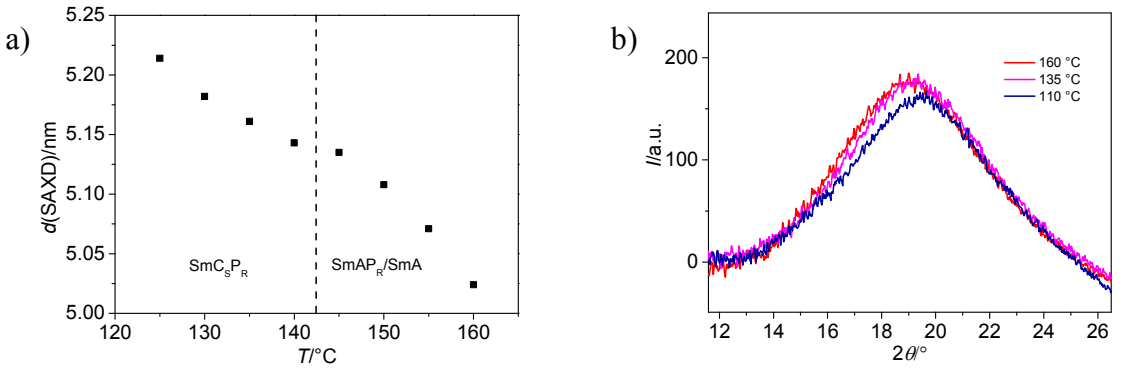


Figure S76. XRD data of compound **DO14/O14.** a) Plot of layer spacings depending on the temperature, measured on heating, b) 2θ scans of the wide angle scattering.

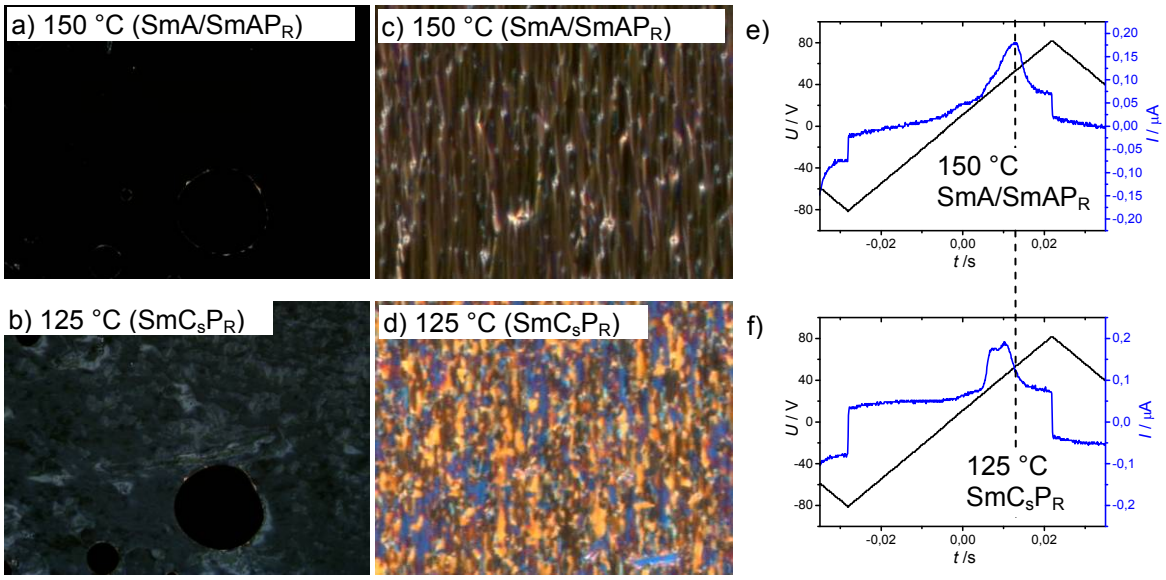


Figure S77. Homeotropic (left, a-b) and planar textures (middle, c-d) as observed between crossed polarizers and corresponding polarization current curves (right, e-f) of compound **DO14/O14** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, PI-coated) under a triangular wave voltage and a frequency of 10 Hz.

3.27 Compound E12/12

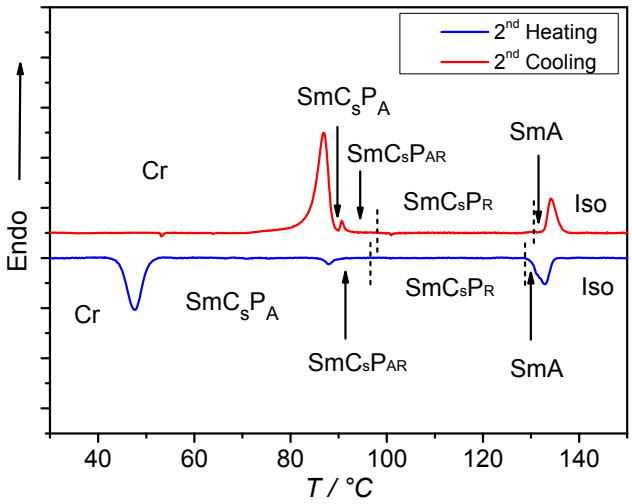


Figure S78. DSC heating and cooling traces of compound **F12/12** recorded at rates of 10 K min^{-1}.

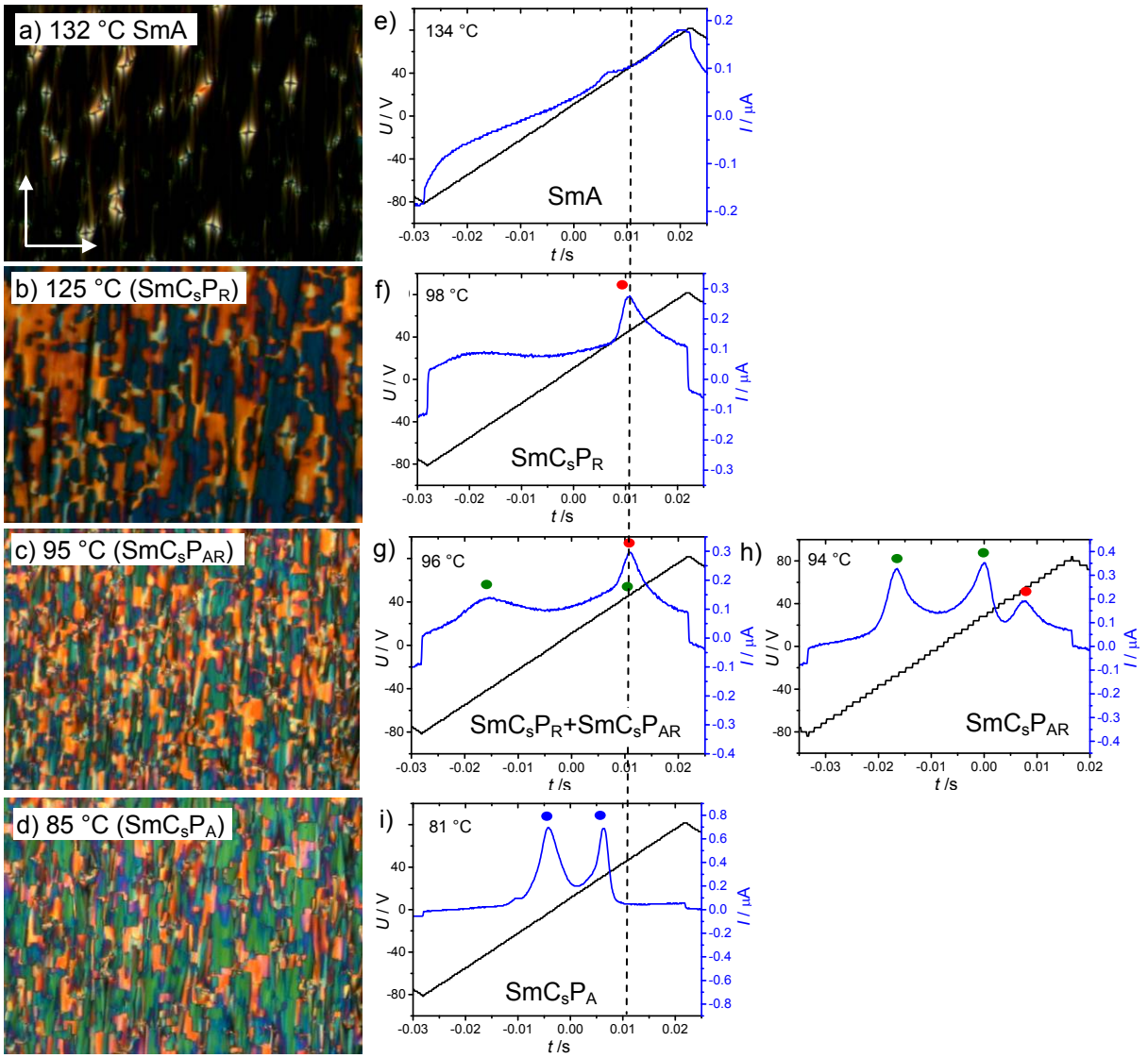
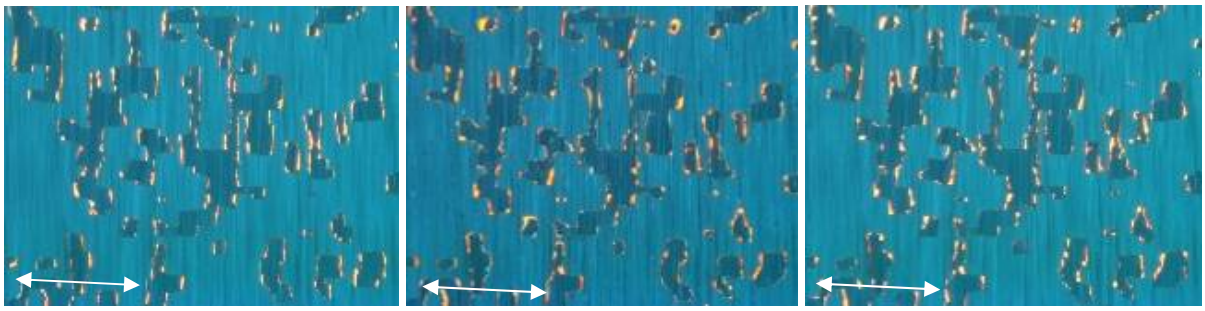


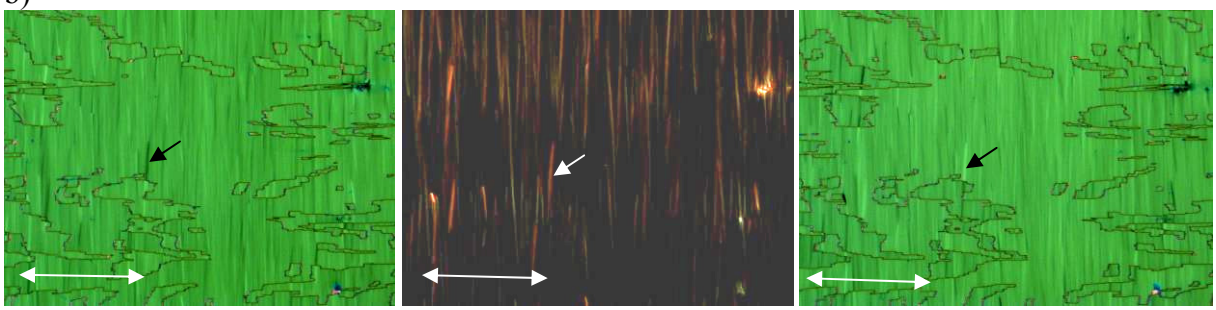
Figure S79. a-d) Planar textures as observed between crossed polarizers and e-i) polarization current curves of compound **E12/12** at the given temperatures in the indicated LC phases. The polarization current response was measured in an ITO-coated cell (6 µm, PI-coated) under a triangular wave voltage and a frequency of 10 Hz; red dots single peak of the SmC_sP_R range, green switching in the SmC_sP_{AR} range and blue antiferroelectric switching in SmC_sP_A.

a)



SmC_sP_F: 125 °C (10 V/µm) SmC_sP_R: 125 °C (0 V/µm) SmC_sP_F:125 °C (-10 V/µm)

b)



SmC_sP_F: 70 °C (10 V/µm) $Sm(CP)^{hel}$: 70 °C (0 V/µm) SmC_sP_F: 70 °C (-10 V/µm)

Figure S80. Switching of compound **E12/12** in a planar cell as observed between crossed polarizers at the indicated field strengths in the distinct phases and field induced states: a) Tilt domain textures of the SmC_sP_R phase at 125 °C showing a reorganization around the long axis. Though the birefringence slightly increases in the switched states there is no change of the position of the tilt domains showing the reorganization around the long axis. b) SmC_sP_A phase at 70 °C as observed under an applied E-field at the indicated voltages; after switching off the applied field the director becomes aligned parallel to the analyzer direction and the planar texture becomes dark due to the field induced $Sm(CP)^{hel}$ structure.

3.28 Compound EO12/12

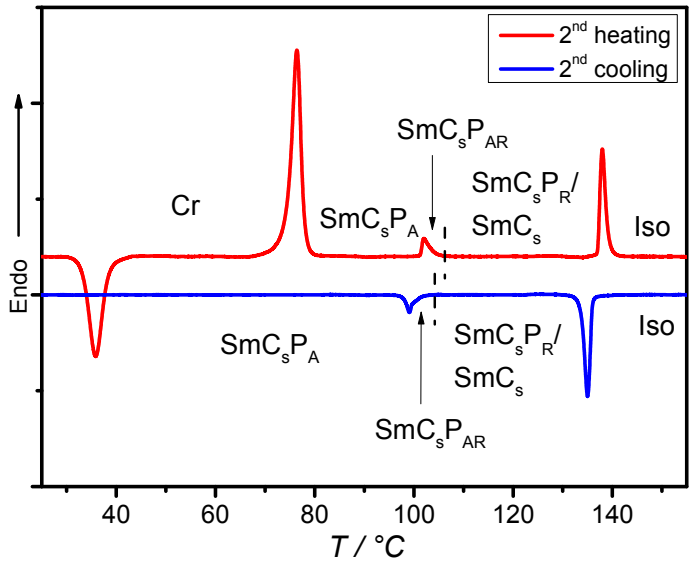


Figure S81. DSC heating and cooling traces of compound **EO12/12** recorded at rates of 10 K min^{-1}.

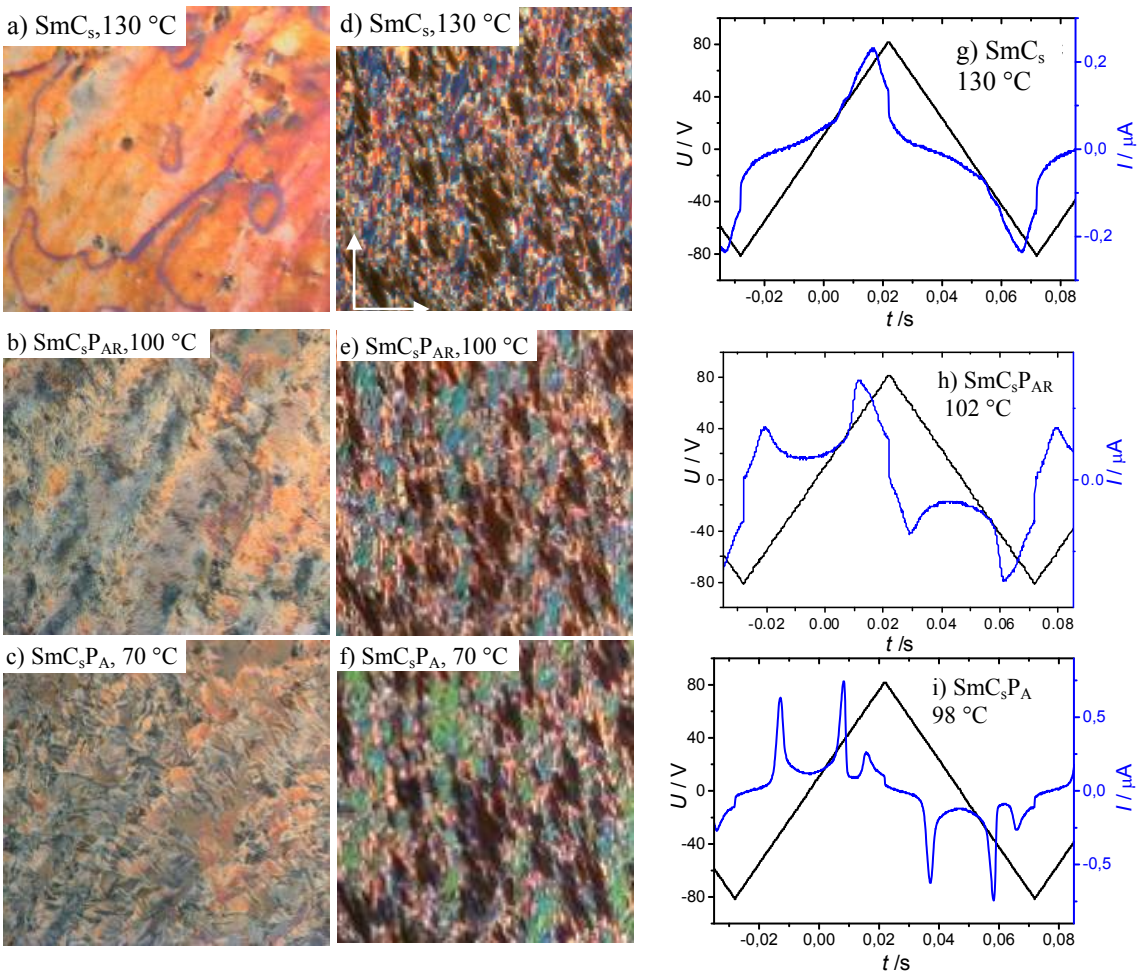


Figure S82. Homeotropic (left) and planar textures (middle) as observed between crossed polarizers and corresponding polarization current curves (right) of compound **EO12/12** at the given temperatures in the indicated LC phases; 160 Vpp, in a 6 µm PI-coated ITO cell.

90 °C (10 V/µm) 90 °C (0 V/µm) 90 °C (-10 V/µm)

Figure S83. Textures of the SmC_sP_A phase of compound **EO12/12** in a planar cell as observed between crossed polarizers at the indicated field strengths. Though the birefringence increases in the switched states there is no change of the position of the extinctions showing the $SmC_sP_A \leftrightarrow SmC_sP_F$ switching by rotation around the long axis.

3.29 Compound EO12/O12

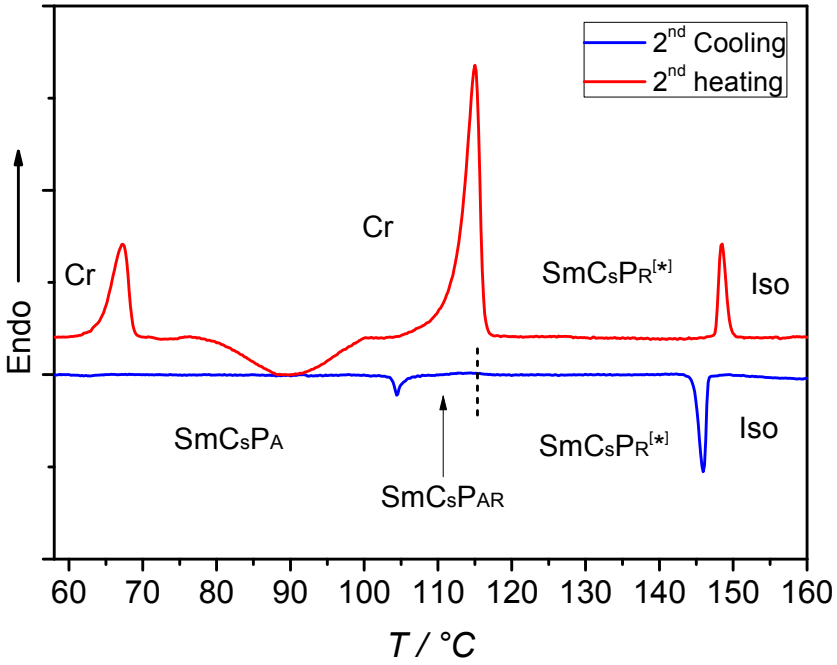


Figure S84. DSC heating and cooling traces of compound **EO12/O12** recorded at rates of 10 K min^{-1}.

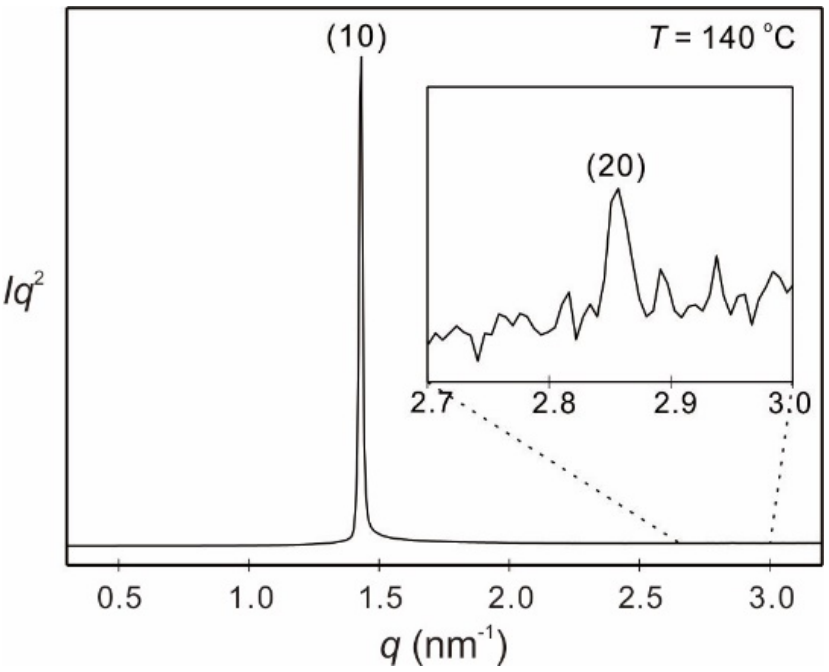
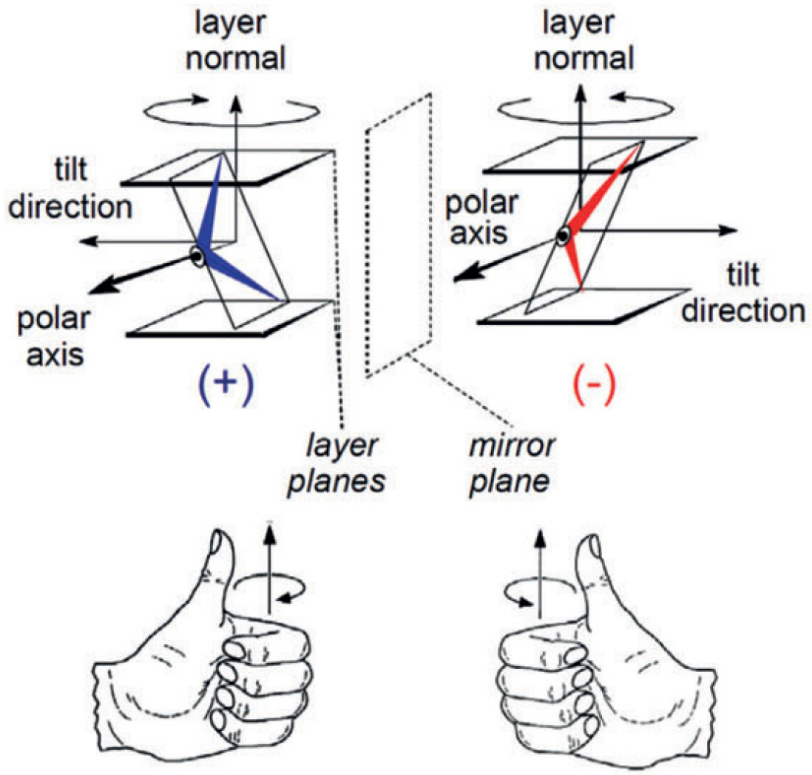


Figure S85. SAXS pattern of **EO12/O12** at 140 °C showing the weak (20) layer reflection and indicating the absence of a 2d-lattice (investigated with synchrotron source).

4. Additional illustrations



Scheme S3. Layer chirality and the structures of the polar SmC phases of bent-core mesogens. The orthogonal combination of tilt and polar order leads to reduced C_{2v} symmetry and superstructural chirality of the layers (adapted from ref.[S14]); blue/red color indicates the chirality sense; reproduced from Ref. S14 with permission from The Royal Society of Chemistry

5. References

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