Supporting Information

Cluster phases of 4-cyanoresorcinol derived hockey-stick liquid crystals

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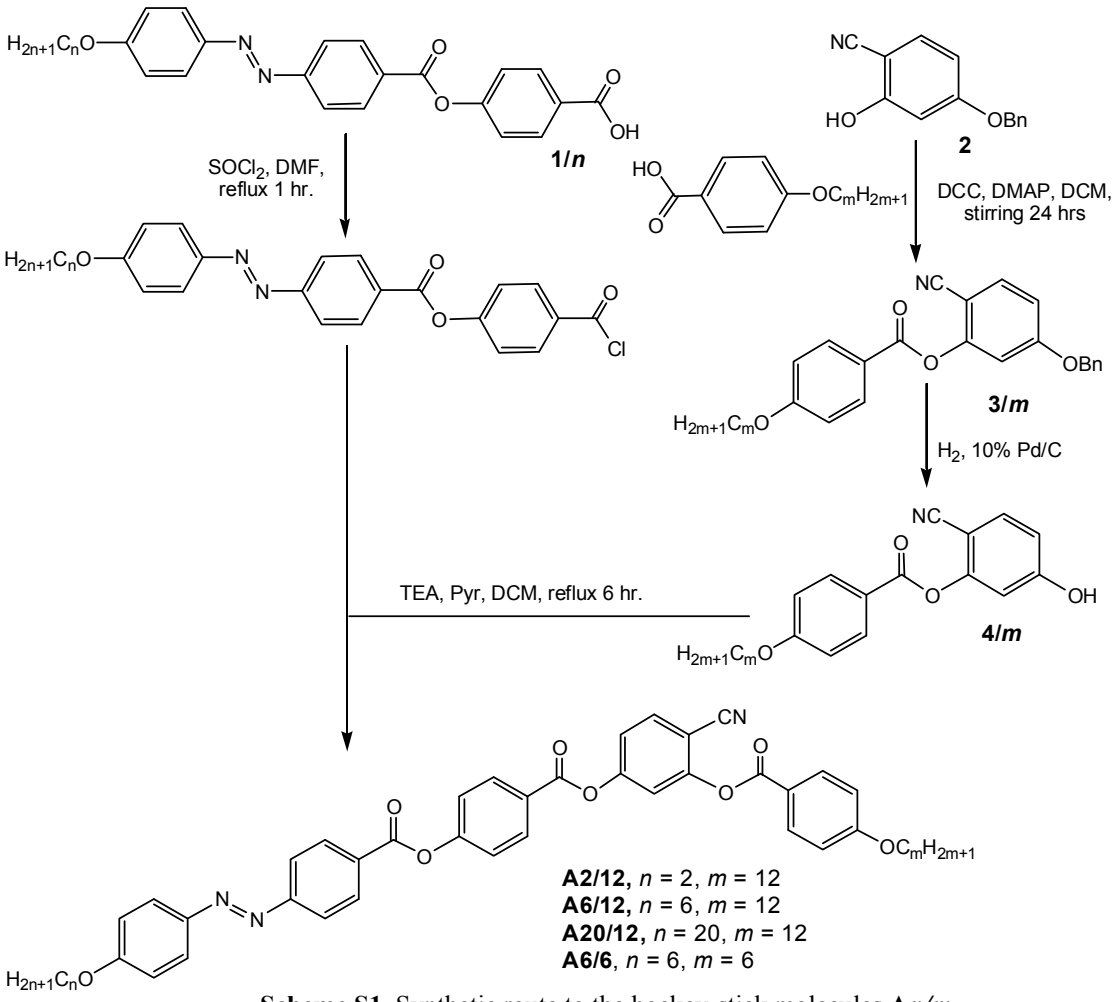
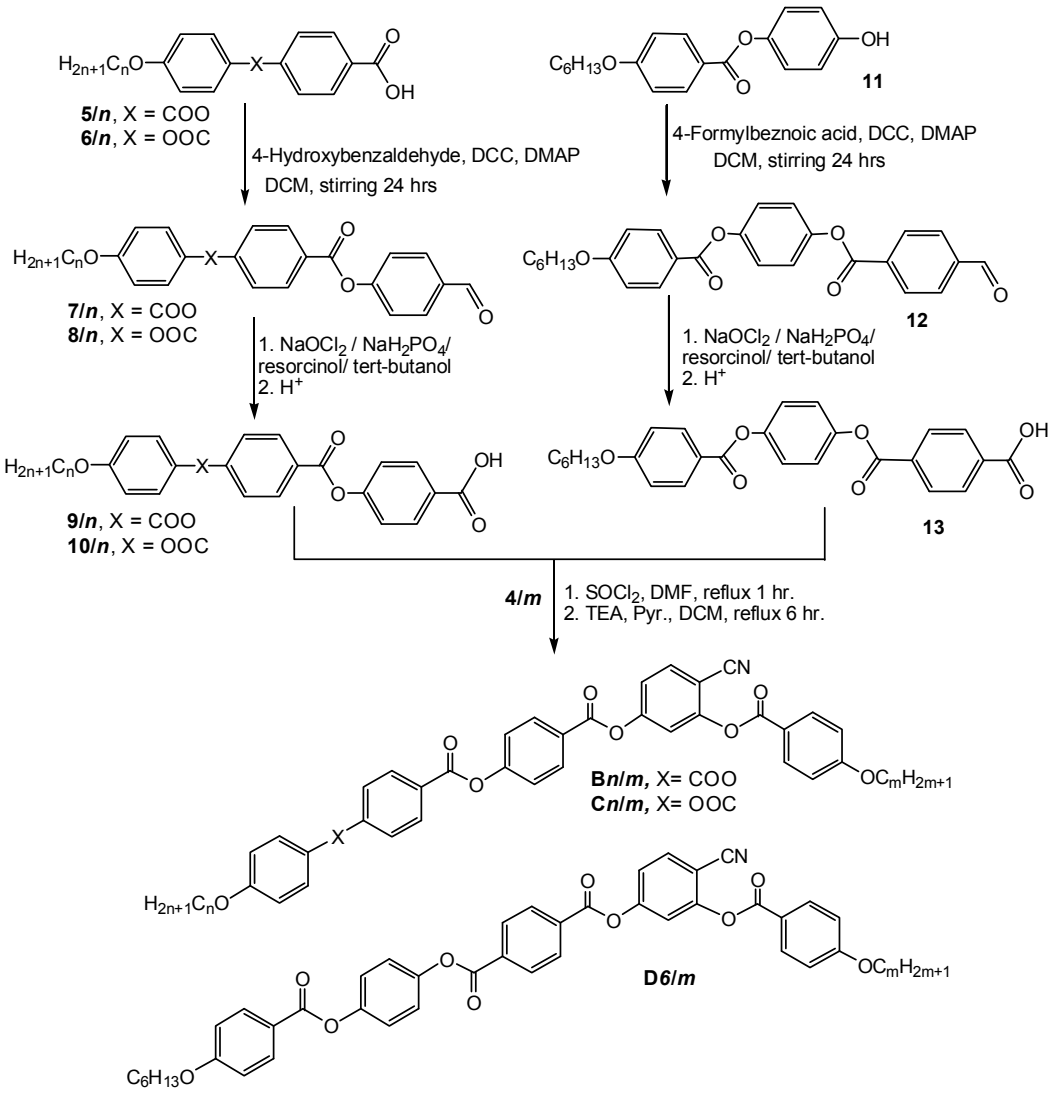
Contents

1. Synthesis and analytical data

The azobenzene containing derived benzoic acids are synthesized according to the methods described before.[S1] The synthesis of the other intermediates as well as of the final molecules is shown in Schemes S1- S4. **Note** that the numbering of the intermediate compounds used here is different from that used in Scheme 2 of the main text.



Scheme S1. Synthetic route to the hockey-stick molecules **A*n/m***.



Scheme S2. Synthetic route to the hockey-stick molecules **B*n/m*-D*n/m***.

1.1. 5-Benzyloxyphenyl-2-cyano-4'-alkoxybenzoates 3/*m*

As shown in Scheme S1 4-benzyloxy-2-hydroxybenzonitrile **2**[S2] was esterified with 4-alkoxybenzoic acids using DCC and a catalytic amount of DMAP in dichloromethane (DCM) as a solvent and stirring for 24 hours. The crude white powder obtained after removing the solvent was purified by column chromatography using DCM as eluent followed by recrystallization from ethanol. The analytical data for 5-benzyloxyphenyl-2-cyano-4'-dodecyloxybenzoate (**3**/***12***) as an example are as following:

Colourless crystals, yield 74.2 %, m.p. 68 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 8.5 Hz, 2H, Ar-H), 7.61 (d, J = 8.7 Hz, 1H, Ar-H), 7.46 – 7.33 (m, 5H, Ar-H), 7.12 (d, J = 2.4 Hz, 1H, Ar-H), 6.99 (d, J = 8.5 Hz, 2H, Ar-H), 6.93 (dd, J = 8.7, 2.4 Hz, 1H, Ar-H), 5.13 (s, 2H, Ph-$\underline{CH_2}$), 4.06 (t, J = 6.6 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.88 – 1.76 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.57 – 1.21 (m, 18H, CH_2), 0.90 (t, J = 6.9 Hz, 3H, CH_3).

1.2. 2-Cyano-5-hydroxyphenyl-4'-alkoxybenzoates 4/*m*

A suspension of compound **3**/***m*** (3.48 mmol) and Pd/C (10% Pd, 0.3 g) in 80 mL THF was flushed with hydrogen. The mixture was stirred at 45 °C at normal pressure for 24 hours, followed by filtration off the catalyst and evaporation of the solvent. The crude product was

purified by flash chromatography (silica gel, $CHCl_3$/PE 8:2) to give **4/*m*** as white powders. As an example the analytical data for 2-cyano-5-hydroxyphenyl-4'-dodecyloxybenzoate are as following:

White powder, yield 91 %, m.p. 87 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.7 Hz, 2H, Ar-H), 7.57 (d, J = 6.6 Hz, 1H, Ar-H), 7.02 – 6.96 (m, 3H, Ar-H), 6.79 (dd, J = 8.6, 2.4 Hz, 1H, Ar-H), 6.19 (s, 1H, Ar-OH), 4.06 (t, J = 6.6 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.88 – 1.76 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.53 – 1.21 (m, 18H, CH_2), 0.90 (t, J = 7.0 Hz, 3H, CH_3).

1.3. Substituted benzoic acids **9/*n*, 10/*n* and 13** *without azo units*

The acids **9/*n*, 10/*n*** and **13** were synthesized as shown in Scheme 2. For example the acids with n = 6 i.e. **9/6**, **10/6** and **13** were prepared by first synthesizing their corresponding aldehydes by esterification of 4-(4'-n-hexyloxybenzoyloxy)benzoic acid (**5/6**)[S2] or 4-(4'-hexyloxyphenoxycarbonyl)benzoic acid (**6/6**)[S3] or 4-(4'-n-hexyloxybenzoyloxy)phenol (**11**)[S4] with 4-hydroxybenzaldehyde or 4-formylbenzoic acid using DCC and a catalytic amount of DMAP. The obtained aldehydes were then oxidized to their corresponding acids using the same method described for the acids **1/*n***.[S1a] All aldehydes were purified with cloumn chromotography using dichloromethane followed by recrystallization from ethanol, while no purification was needed for any of the obtained acids and they were used for the next steps without further purifications. The analytical data obtained for the aldehydes **7/6**, **8/6** and **12** as well as for the acids **9/*6*, 10/*6*** and **13** are given below:

7/6: Colourless crystals, yield 65.6%, phase behaviour: Cr 108 °C SmC 116 °C N 145 °C isotropic. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H, Ar-CHO), 8.28 (d, J = 5.8 Hz, 2H, Ar-H), 8.15 (d, J = 8.8 Hz, 2H, Ar-H), 7.99 (d, J = 8.6 Hz, 2H, Ar-H), 7.46 – 7.36 (m, 4H, Ar-H), 6.99 (d, J = 8.9 Hz, 2H, Ar-H), 4.06 (t, J = 6.5 Hz, 4H, Ar-O$\underline{CH_2}CH_2$), 1.88 – 1.76 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.57 – 1.31 (m, 6H, CH_2), 0.92 (t, J = 7.1 Hz, 3H, CH_3).

8/6: Colourless crystals, yield 59.9%, phase behaviour: Cr 172 °C N 217 °C isotropic. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 10.06 (s, 1H, Ar-CHO), 8.45 – 8.25 (m, 4H, Ar-H), 8.02 (d, J = 8.8, 2H, Ar-H), 7.47 (d, J = 8.9, 2H, Ar-H), 7.16 (d, J = 8.7, 2H, Ar-H), 6.96 (d, J = 8.8, 2H, Ar-H), 3.99 (t, J = 6.6 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.95 – 1.71 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.65 – 1.17 (m, 6H, CH_2), 0.93 (t, J = 9.6, 3H, CH_3).

12: Colourless crystals, yield 51.65%, phase behaviour: Cr 132 °C N 136 °C isotropic. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.15 (s, 1H, Ar-CHO), 8.37 (d, J = 14.5, 2H, Ar-H), 8.15 (d, J = 14.5, 2H, Ar-H), 8.04 (d, J = 8.5, 2H, Ar-H), 7.29 (s, 4H, Ar-H), 6.98 (d, J = 8.5, 2H, Ar-H), 4.05 (t, J = 6.7, 2H, Ar-O$\underline{CH_2}CH_2$), 1.88 – 1.75 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.57 – 1.30 (m, 6H, CH_2), 0.92 (t, J = 7.2, 3H, CH_3).

9/*6*: Colorless powder, yield 97%, ^{1}H-NMR (400 MHz, DMSO-d_6): δ 13.04 (s, 1H, Ar-COOH), 8.23 (d, J = 8.7 Hz, 2H, Ar-H), 8.12 – 7.99 (m, 4H, Ar-H), 7.52 (d, J = 8.7 Hz, 2H, Ar-H), 7.44 (d, J = 8.6 Hz, 2H, Ar-H), 7.11 (d, J = 5.9 Hz, 2H, Ar-H), 4.09 (t, J = 6.5 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.80 – 1.67 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.49 – 1.24 (m, 6H, CH_2), 0.87 (t, J = 7.0 Hz, 3H, CH_3).

10/*6*: Colorless powder, yield 96.8%, ^{1}H-NMR (500 MHz, DMSO-d_6): δ 12.90 (s, 1H, Ar-COOH), 8.39 – 8.25 (m, 4H, Ar-H), 8.05 (d, J = 8.7 Hz, 2H, Ar-H), 7.47 (d, J = 8.7 Hz, 2H, Ar-H), 7.21 (d, J = 9.0 Hz, 2H, Ar-H), 6.98 (d, J = 9.1 Hz, 2H, Ar-H), 3.96 (t, J = 6.5 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.81 – 1.61 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.50 – 1.18 (m, 6H, , CH_2), 0.87 (t, J = 7.0 Hz, 3H, CH_3).

13: Colorless powder, yield 97.4%, ^{1}H-NMR (400 MHz, DMSO-d_6): δ 12.00 (s, 1H, Ar-COOH), 8.23 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.12 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.06 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.43 – 7.29 (m, 4H, Ar-H), 7.09 (d, *J* = 7.8 Hz, 2H, Ar-H), 4.07 (t, *J* = 6.5 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.78 – 1.66 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.46 – 1.23 (m, 6H, CH_2), 0.86 (t, *J* = 7.1 Hz, 3H, CH_3).

1.4. Hockey-stick molecules A*n/m*-D*n/m*

General procedure: 1.0 mmol of the corresponding acid **1**/***n***, **9**/***n***, **10**/***n*** or **13** was heated under reflux with thionyl chloride (3 mL) and a catalytic amount of *N,N*-dimethylformamide (DMF) for one hour. The excess of thionyl chloride was removed by distillation under reduced pressure. The obtained acid chloride was then dissolved in dry dichloromethane (DCM, 20 mL) followed by addition of **4**/***m*** (1.0 mmol) previously dissolved in DCM, triethylamine (TEA, 1.2 mmol) and a catalytic amount of pyridine (pyr.) and the reaction mixture was then refluxed for 6 hours under argon atmosphere. The reaction progress was checked with TLC and at the end of the reaction the solution was cooled to room temperature, washed with 10% HCl (2 × 50 mL) and three times with cold water followed by extraction with dichloromethane (3 × 50 mL) and finally dried over anhydrous sodium sulphate. The crude residue was chromatographed on silica gel using DCM followed by recrystallization from chloroform/ethanol mixture. The analytical data obtained for the synthesized new materials are as follows:

A2/12: Orange crystals, yield 64.5%, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.37 (d, *J* = 6.6 Hz, 2H, Ar-H), 8.30 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.21 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.04 – 7.96 (m, 4H, Ar-H), 7.80 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.46 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.32 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.07 – 6.98 (m, 4H, Ar-H), 4.17 (q, *J* = 7.0 Hz, 2H, Ar-O$\underline{CH_2}CH_3$), 4.07 (t, *J* = 6.6 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.88 – 1.79 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.58 – 1.22 (m, 21H, CH_2 and CH_3), 0.90 (t, *J* = 6.9 Hz, 3H, CH_3). Elemental Analysis: Calc. for **$C_{48}H_{49}N_3O_8$** C, 72.43; H, 6.21; N, 5.28. Found C, 72.36; H, 6.15; N, 5.30 %.

A6/12: Orange crystals, yield 64.8%, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.31 (d, *J* = 7.8 Hz, 2H, Ar-H), 8.21 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.04 – 7.93 (m, 4H, Ar-H), 7.80 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.46 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.32 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.08 – 6.95 (m, 4H, Ar-H), 4.12 – 4.02 (m, 4H, Ar-O$\underline{CH_2}CH_2$), 1.90 – 1.77 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.59 – 1.20 (m, 24H, CH_2), 0.98 – 0.85 (m, *J* = 20.9, 7.0 Hz, 6H, CH_3). Elemental Analysis: Calc. for **$C_{52}H_{57}N_3O_8$** C, 73.30; H, 6.74; N, 4.93. Found C, 73.30; H, 6.63; N, 4.88 %.

A20/12: Orange crystals, yield 66.4%, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.36 (d, *J* = 10.0 Hz, 2H, Ar-H), 8.30 (d, *J* = 8.8 Hz, 2H, Ar-H), 8.21 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.04 – 7.96 (m, 4H, Ar-H), 7.80 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.46 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.32 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.08 – 6.96 (m, 4H, Ar-H), 4.12 – 4.00 (m, 4H, Ar-O$\underline{CH_2}CH_2$), 1.90 – 1.78 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.60 – 1.19 (m, 52H, CH_2), 0.95 – 0.83 (m, 6H, CH_3). Elemental Analysis: Calc. for **$C_{66}H_{85}N_3O_8$** C, 75.61; H, 8.17; N, 4.01. Found C, 75.50; H, 8.14; N, 4.37 %.

A6/6: Orange crystals, yield 65.0%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 6.7 Hz, 2H, Ar-H), 8.29 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.19 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.02 – 7.93 (m, 4H, Ar-H), 7.78 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.54 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.44 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.06 – 6.96 (m, 4H, Ar-H), 4.10 – 4.01 (m,

4H, Ar-O$\underline{CH_2}CH_2$), 1.89 – 1.77 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.57 – 1.30 (m, 14H, CH_2), 0.98 – 0.86 (m, 6H, CH_3). Elemental Analysis: Calc. for **$C_{46}H_{45}N_3O_8$** C, 71.95; H, 5.91; N, 5.47. Found C, 71.89; H, 5.82; N, 5.47 %.

B6/6: Colorless crystals, yield 62.3%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.32 – 8.25 (m, 4H, Ar-H), 8.22 – 8.13 (m, 4H, Ar-H), 7.78 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.53 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.45 – 7.37 (m, 4H, Ar-H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.02 – 6.96 (m, 4H, Ar-H), 4.10 – 4.01 (m, *J* = 6.6, 1.1 Hz, 4H, Ar-O$\underline{CH_2}CH_2$), 1.88 – 1.78 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.56 – 1.30 (m, 12H, CH_2), 0.96 – 0.88 (m, 6H, CH_3). Elemental Analysis: Calc. for **$C_{47}H_{45}NO_{10}$** C, 72.02; H, 5.79; N, 1.79. Found C, 72.00; H, 5.75; N, 1.70 %.

B6/12: Colorless crystals, yield 63.0%, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.33 – 8.26 (m, 4H, Ar-H), 8.23 – 8.15 (m, 4H, Ar-H), 7.79 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.55 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.46 – 7.39 (m, 4H, Ar-H), 7.31 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 7.03 – 6.98 (m, 4H, Ar-H), 4.10 – 4.04 (m, 4H, Ar-O$\underline{CH_2}CH_2$), 1.89 – 1.80 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.57 – 1.22 (m, 36H, CH_2), 0.98 – 0.86 (m, 6H, CH_3). Elemental Analysis: Calc. for **$C_{53}H_{57}NO_{10}$** C, 73.34; H, 6.62; N, 1.61. Found C, 73.25; H, 6.55; N, 1.52 %.

C6/6: Colorless crystals, yield 62.5%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40 – 8.26 (m, 6H), 8.24 – 8.14 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.19 – 7.11 (m, 2H), 7.05 – 6.91 (m, 4H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.90 – 1.73 (m, 4H), 1.59 – 1.29 (m, 12H), 1.00 – 0.85 (m, *J* = 10.7, 3.5 Hz, 6H). Elemental Analysis: Calc. for **$C_{47}H_{45}NO_{10}$** C, 72.02; H, 5.79; N, 1.79. Found C, 71.97; H, 5.74; N, 1.73 %.

C6/12: Colorless crystals, yield 62.8%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40 – 8.25 (m, 6H), 8.24 – 8.12 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 4.8 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.05 – 6.89 (m, 4H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.72 (m, 4H), 1.60 – 1.15 (m, 24H), 1.00 – 0.80 (m, 6H). CH_2), 0.98 – 0.86 (m, 6H, CH_3). Elemental Analysis: Calc. for **$C_{53}H_{57}NO_{10}$** C, 73.34; H, 6.62; N, 1.61. Found C, 73.27; H, 6.60; N, 1.55 %.

C12/6: Colorless crystals, yield 63.1%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40 – 8.25 (m, 6H), 8.24 – 8.16 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.04 – 6.90 (m, 4H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.70 (m, 4H), 1.60 – 1.18 (m, 24H), 0.99 – 0.81 (m, 6H). Elemental Analysis: Calc. for **$C_{53}H_{57}NO_{10}$** C, 73.34; H, 6.62; N, 1.61. Found C, 73.29; H, 6.58; N, 1.56 %.

C12/12: Colorless crystals, yield 63.3%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40 – 8.25 (m, 6H), 8.23 – 8.14 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.30 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.19 – 7.10 (m, 2H), 7.04 – 6.90 (m, 4H), 4.06 (t, *J* = 6.6 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.88 – 1.72 (m, 4H), 1.60 – 1.16 (m, 36H), 0.88 (q, *J* = 6.2 Hz, 6H). Elemental Analysis: 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, 1.46 %.

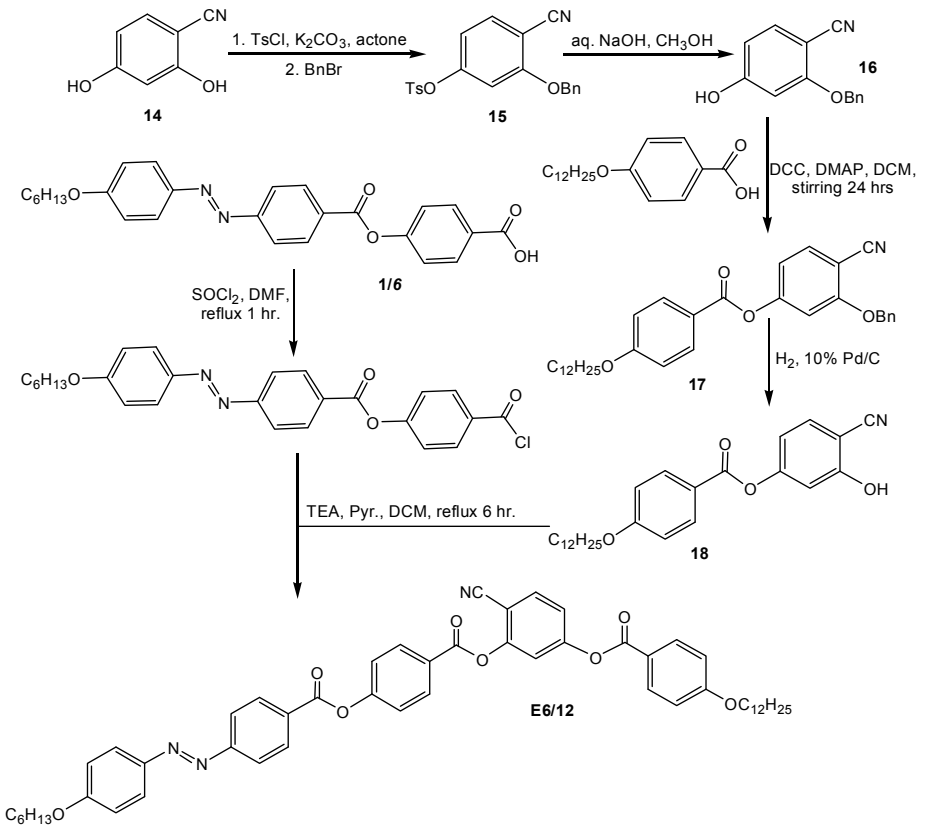
D6/6: Colorless crystals, yield 61.5%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 – 8.28 (m, 4H, Ar-H), 8.22 – 8.12 (m, 4H, Ar-H), 7.80 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.57 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.35 – 7.28 (m, 5H, Ar-H), 7.04 – 6.94 (m, 4H, Ar-H), 4.09 – 4.01 (m, 4H, Ar-O$\underline{CH_2}CH_2$), 1.90 – 1.75 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.56 – 1.30 (m, 12H, CH_2), 0.98 – 0.86 (m,

6H, CH_3). Elemental Analysis: Calc. for **$C_{47}H_{45}NO_{10}$** C, 72.02; H, 5.79; N, 1.79. Found C, 71.97; H, 5.73; N, 1.78 %.

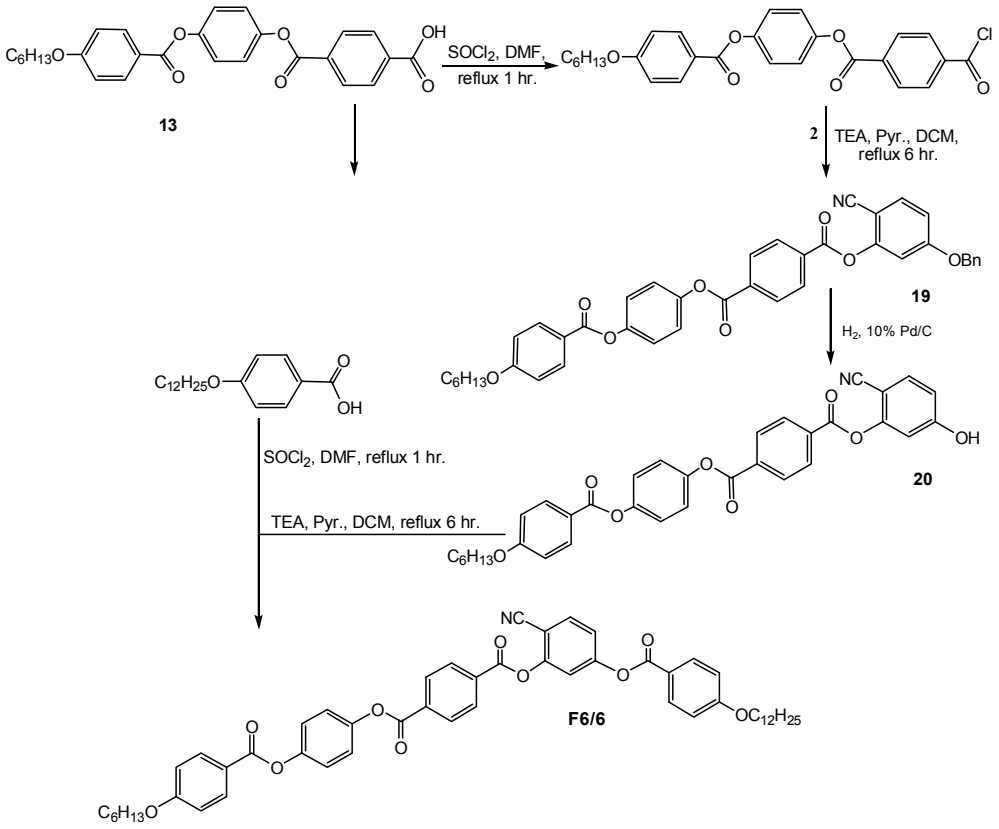
D6/12: Colorless crystals, yield 64.1%, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.40 – 8.31 (m, 4H, Ar-H), 8.23 – 8.13 (m, 4H, Ar-H), 7.81 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.59 (d, *J* = 2.2 Hz, 1H, Ar-H), 7.36 – 7.29 (m, 5H, Ar-H), 7.04 – 6.96 (m, 4H, Ar-H), 4.10 – 4.03 (m, 4H, Ar-O$\underline{CH_2}CH_2$), 1.89 – 1.78 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.58 – 1.21 (m, 24H, CH_2), 0.98 – 0.80 (m, 6H, CH_3). Elemental Analysis: Calc. for **$C_{53}H_{57}NO_{10}$** C, 73.34; H, 6.62; N, 1.61. Found C, 73.30; H, 6.55; N, 1.58 %.

1.5. Hockey-stick molecules with inverted direction of the cyano group (E6/12 and F6/6)

The synthesis of the related hockey-stick materials **E6/12** and **F6/6** with inverted direction of the cyano group is shown in Schemes S3 and S4, using the same procedure described for the hockey-stick molecules **A*n/m*-D*n/m***. The synthesis details as well as the analytical data for the intermediates and for **E6/12** and **F6/6** compounds are given below.



Scheme S3. Synthetic route to the hockey-stick molecule **E6/12**.



Scheme S24. Synthetic route to the hockey-stick molecule **F6/6**.

1.5.1. 2-Benzyloxy-4-(p-toluenesulfonyloxy)benzonitrile (15)

As shown in Scheme S3, 4-cyanoresorcinol **14**[S2] (3.58 g, 26.5 mmol), p-toluenesulfonylchloride (5.57 g, 29.2 mmol) and K_2CO_3 (10.99 g, 79.5 mmol) were mixed in acetone (250 mL) and refluxed for 18 hours under argon atmosphere. To the reaction mixture was added benzylbromide (6.3 mL, 53.0 mmol), and then refluxed for another 18 hours. The reaction solution was filtered and concentrated under reduced pressure. Then water was added, and the organic layer was extracted with ethyl acetate three times, washed with water and brine, and then dried over Na_2SO_4. The solvent was concentrated under reduced pressure and purified by silica-gel chromatography (hexane/ethyl acetate = 10/1) to give a colourless oil. Yield 93 %, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.3 Hz, 2H, Ar-H), 7.48 (d, J = 8.5 Hz, 1H, Ar-H), 7.45 – 7.29 (m, 7H, Ar-H), 6.83 (d, J = 2.1 Hz, 1H, Ar-H), 6.58 (dd, J = 8.5, 2.1 Hz, 1H, Ar-H), 5.13 (s, 2H, Ph-CH_2), 2.48 (s, 3H, CH_3).

1.5.2. 2-Benzyloxy-4-hydroxybenzonitrile (16)

To a solution of 2-benzyloxy-4-(p-toluenesulfonyloxy)benzonitrile **15** (3.50 g, 9.2 mmol) in methanol (230 mL) was added 2N NaOH (48 mL) at room temperature under argon atmosphere. The reaction solution was stirred for 20 hours, and then concentrated under reduced pressure then 2N HCl solution was added till pH ≈ 1. The organic layer was extracted with CH_2Cl_2, washed with water and brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure to give pure white solid. Yield 98.3%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.27 (m, 6H, Ar-H), 6.87 (s, 1H, Ar-OH), 6.55 – 6.41 (m, 2H, Ar-H), 5.12 (s, 2H, $PhCH_2$).

1.5.3. 3-Benzyloxyphenyl-4-cyano-4'-dodecyloxybenzoate (17)

Prepared using the method described for **3/*m*** starting from 2-benzyloxy-4-hydroxybenzonitrile (**16**). Colourless crystals, yield 90.58%, m.p. 90 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.12 (d, 2H, *J* = 8.9 Hz, Ar-H), 7.64 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.51 – 7.32 (m, 5H, Ar-H), 7.02 – 6.95 (m, 3H, Ar-H), 6.92 (dd, *J* = 8.4, 1.9 Hz, 1H, Ar-H), 5.22 (s, 2H, $PhCH_2$), 4.06 (t, *J* = 6.6 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.89 – 1.77 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.58 – 1.21 (m, 18H, CH_2), 0.90 (t, *J* = 6.9 Hz, 3H, CH_3).

1.5.4. 4-Cyano-3-hydroxyphenyl-4'-dodecyloxybenzoate (18)

Prepared using the method described for **4/*m***. White powder, yield 97.4%, m.p. 94 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.55 (d, 1H, Ar-H), 6.96 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.92 – 6.84 (m, 2H, Ar-H), 6.60 (s, 1H, Ar-OH), 4.04 (t, 2H, Ar-O$\underline{CH_2}CH_2$), 1.87 – 1.76 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.54 – 1.19 (m, 18H, CH_2), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3).

1.5.5. 5-Benzyloxyphenyl-2-cyano-4'-[4-(4-hexyloxybenzoyl)phenoxycarbonyl]benzoate (19)

Prepared using the esterification method described for the synthesis of compounds **A*n*/*m***. Colourless crystals, yield 41.3%, phase behaviour: Cr 148 °C N 191 °C isotropic. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.43 – 8.34 (m, 4H, Ar-H), 8.20 – 8.12 (m, 2H, Ar-H), 7.66 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.47 – 7.36 (m, 5H, Ar-H), 7.36 – 7.28 (m, 4H, Ar-H), 7.14 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.03 – 6.95 (m, 3H, Ar-H), 5.16 (s, 2H, $PhCH_2$), 4.07 (t, *J* = 6.6 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.90 – 1.77 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.60 – 1.31 (m, 6H, CH_2), 0.99 – 0.87 (t, *J* = 5.5 Hz, 3H, CH_3).

1.5.6. 2-Cyano-5-hydroxyphenyl -4'-[4-(4-hexyloxybenzoyl)phenoxycarbonyl]benzoate 20

Prepared using the deprotection method described for the synthesis of compound **4/*m***. Colourless crystals, yield 32.7%, phase behaviour: Cr 169 °C N 313 °C isotropic. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.41 – 8.27 (m, 4H, Ar-H), 8.14 (d, *J* = 6.8 Hz, 2H, Ar-H), 8.05 (s, 1H, Ar-H), 7.56 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.35 – 7.23 (m, 4H, Ar-H), 6.99 (d, 7.1 Hz, 2H, Ar-H), 6.82 (dd, *J* = 8.6, 2.3 Hz, 1H, Ar-H), 5.44 (s, 1H, OH, Ar-OH), 4.05 (t, *J* = 6.4 Hz, 2H, Ar-O$\underline{CH_2}CH_2$), 1.89 – 1.76 (m, 2H, Ar-OCH$_2\underline{CH_2}$), 1.59 – 1.29 (m, 6H, CH_2), 0.98 – 0.88 (t, *J* = 6.3 Hz, 3H, CH_3).

1.5.7. Compounds E6/12 and F6/6

E6/12.- Orange crystals, yield 67.7%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.39 – 8.31 (m, 4H, Ar-H), 8.13 (d, *J* = 9.2, 2H, Ar-H), 8.03 – 7.94 (m, 4H, Ar-H), 7.78 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.52 (d, *J* = 1.9 Hz, 1H, Ar-H), 7.46 (d, *J* = 8.2, 2H, Ar-H), 7.31 (dd, *J* = 8.6, 2.2 Hz, 1H, Ar-H), 7.06 – 6.95 (m, 4H, Ar-H), 4.11 – 3.98 (m, 4H, Ar-O$\underline{CH_2}CH_2$), 1.90 – 1.76 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.57 – 1.21 (m, 24H, CH_2), 0.99 – 0.84 (m, 6H, CH_3). Elemental Analysis: Calc. for $\mathbf{C_{52}H_{57}N_3O_8}$ C, 73.30; H, 6.74; N, 4.93. Found C, 73.26; H, 6.65; N, 4.90 %.

F6/6.- White powder, yield 65.2%, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.44 – 8.31 (m, 4H, Ar-H), 8.19 – 8.08 (m, 4H, Ar-H), 7.80 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.54 (d, *J* = 2.2 Hz,

1H, Ar-H), 7.37 – 7.27 (m, 5H, Ar-H), 7.03 – 6.94 (m, 4H, Ar-H), 4.06 (t, J = 6.6 Hz, 4H, Ar-O$\underline{CH_2}CH_2$), 1.90 – 1.76 (m, 4H, Ar-OCH$_2\underline{CH_2}$), 1.59 – 1.29 (m, 12H, CH_2), 1.00 – 0.84 (m, J = 5.9 Hz, 6H, CH_3). Elemental Analysis: Calc. for **$C_{53}H_{57}NO_{10}$** C, 73.34; H, 6.62; N, 1.61. Found C, 73.31; H, 6.60; N, 1.59 %.

1.6. NMR spectra of the HSLCs

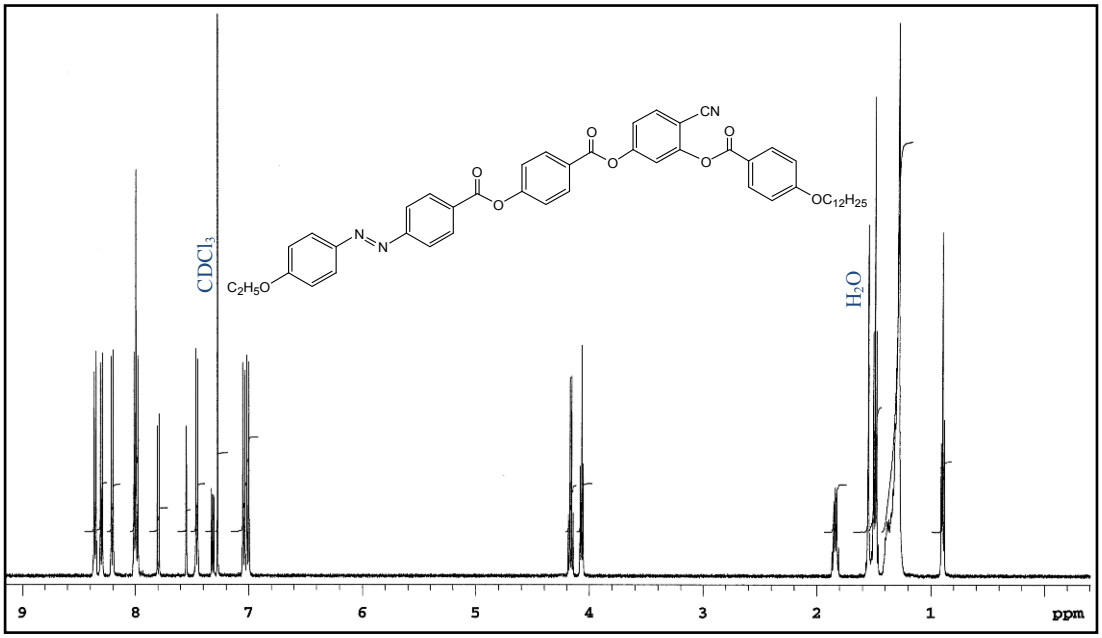


Figure S1. ^{1}H-NMR Spectrum of **A2/12** in $CDCl_3$.

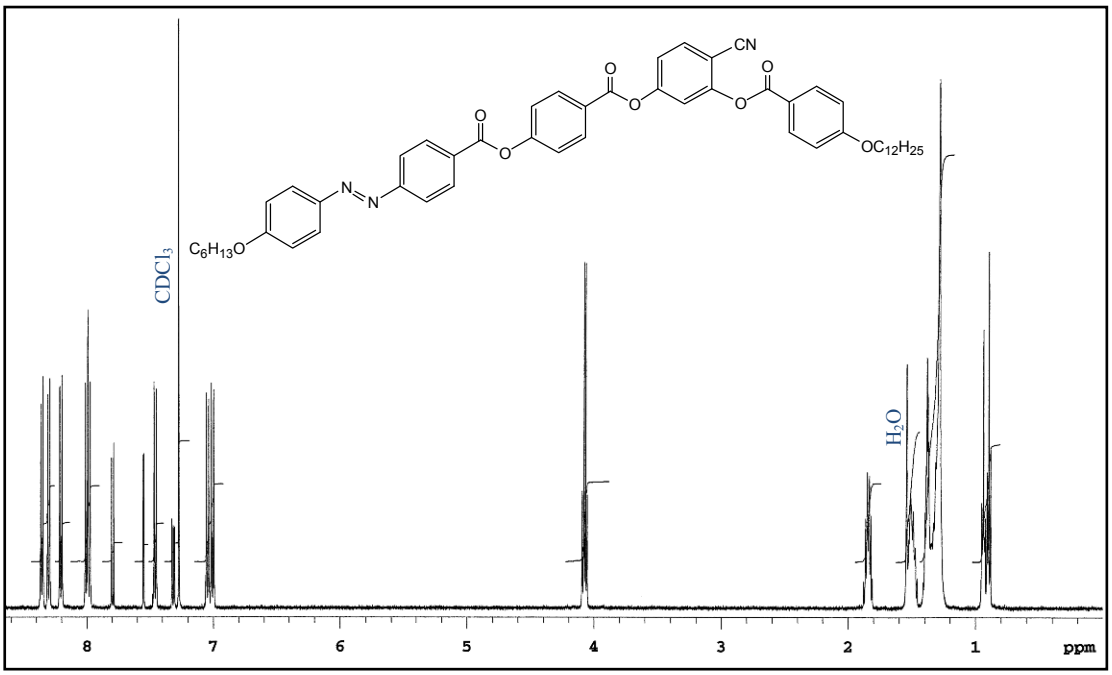


Figure S2. ^{1}H-NMR Spectrum of **A6/12** in $CDCl_3$.

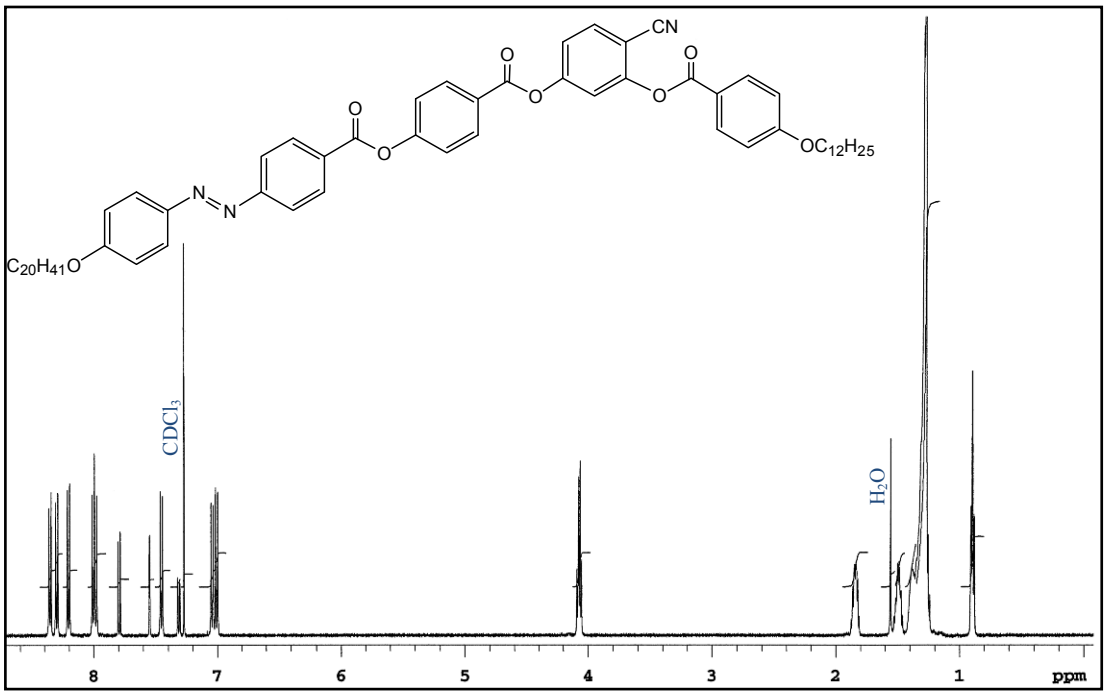


Figure S3. ^{1}H-NMR Spectrum of **A20/12** in $CDCl_3$.

Figure S4. ^{1}H-NMR Spectrum of **A6/6** in $CDCl_3$.

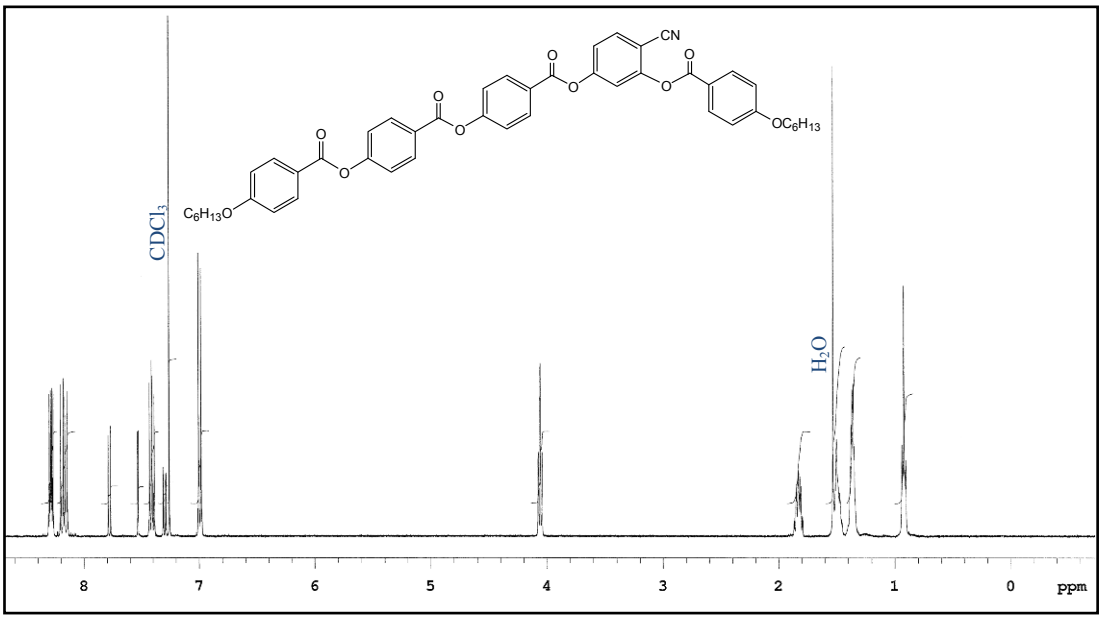


Figure S5. ^{1}H-NMR Spectrum of **B6/6** in $CDCl_3$.

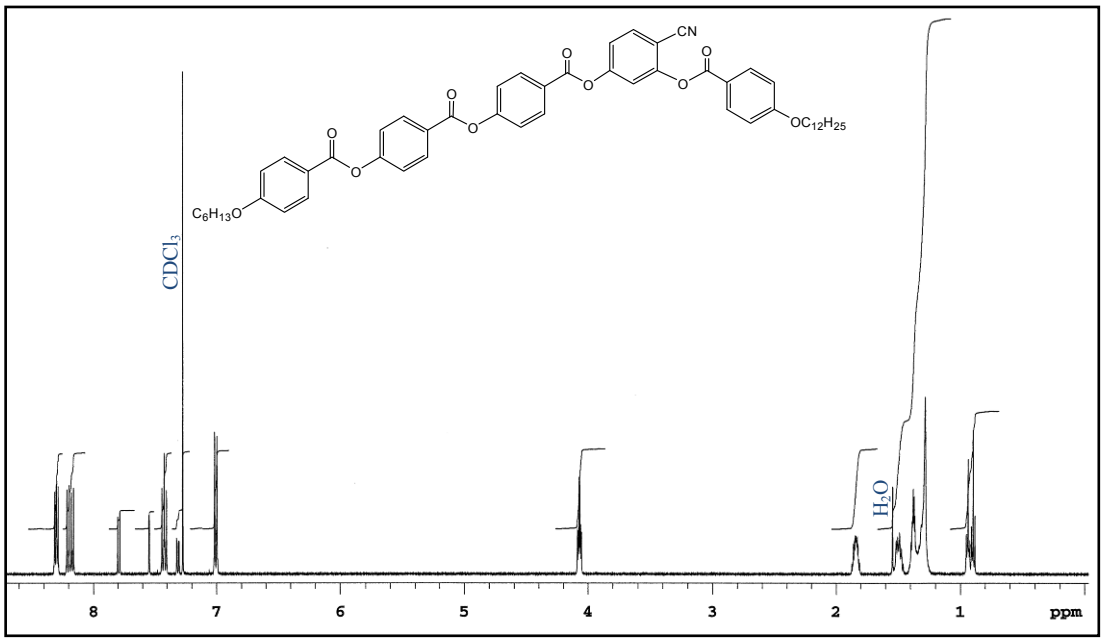


Figure S6. ^{1}H-NMR Spectrum of **B6/12** in $CDCl_3$.

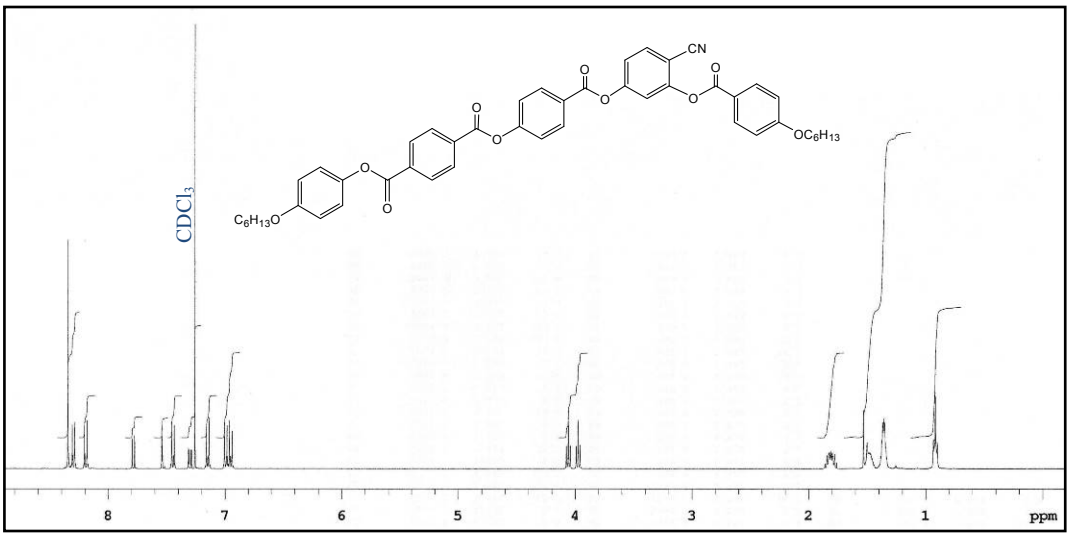


Figure S7. ^{1}H-NMR Spectrum of **C6/6** in $CDCl_3$.

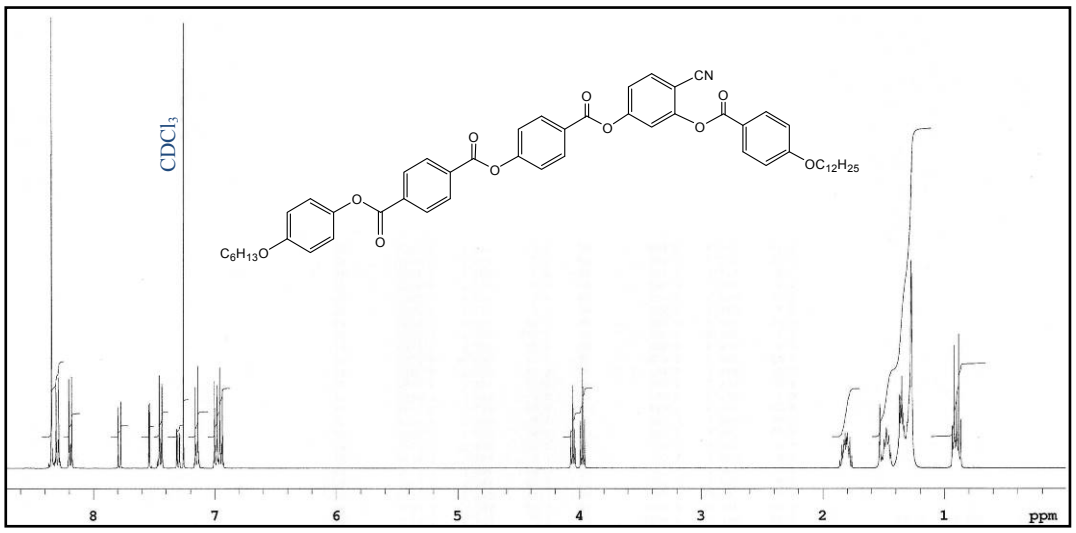


Figure S8. ^{1}H-NMR Spectrum of **C6/12** in $CDCl_3$.

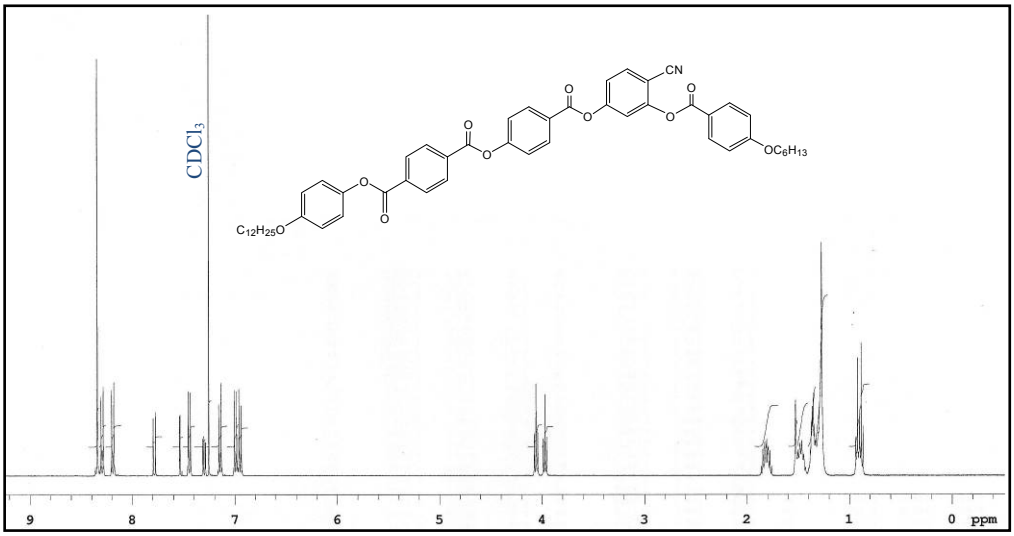


Figure S9. ^{1}H-NMR Spectrum of **C12/6** in $CDCl_3$.

Figure S10. ^{1}H-NMR Spectrum of **C12/12** in $CDCl_3$.

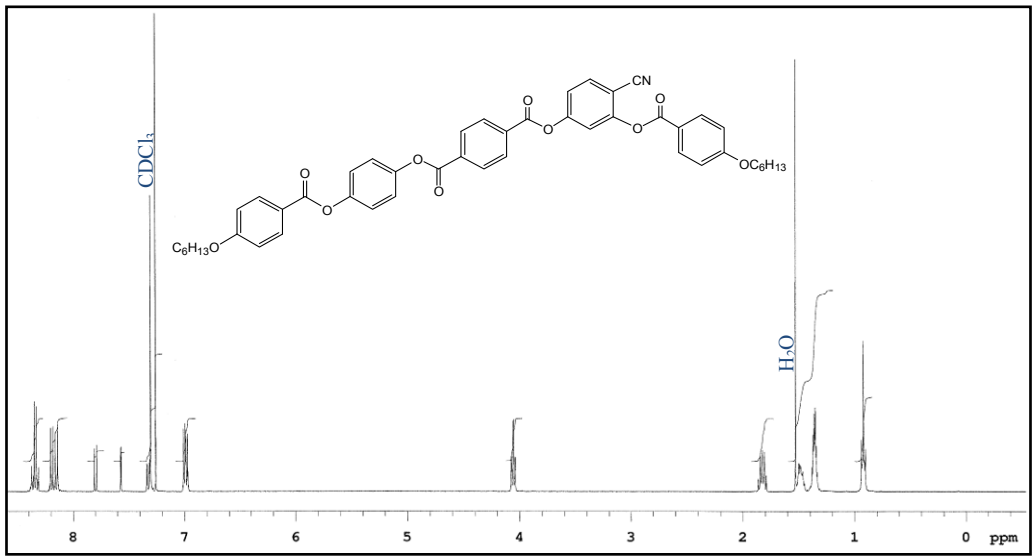


Figure S11. ^{1}H-NMR Spectrum of **D6/6** in $CDCl_3$.

Figure S12. ^{1}H-NMR Spectrum of **D6/12** in $CDCl_3$.

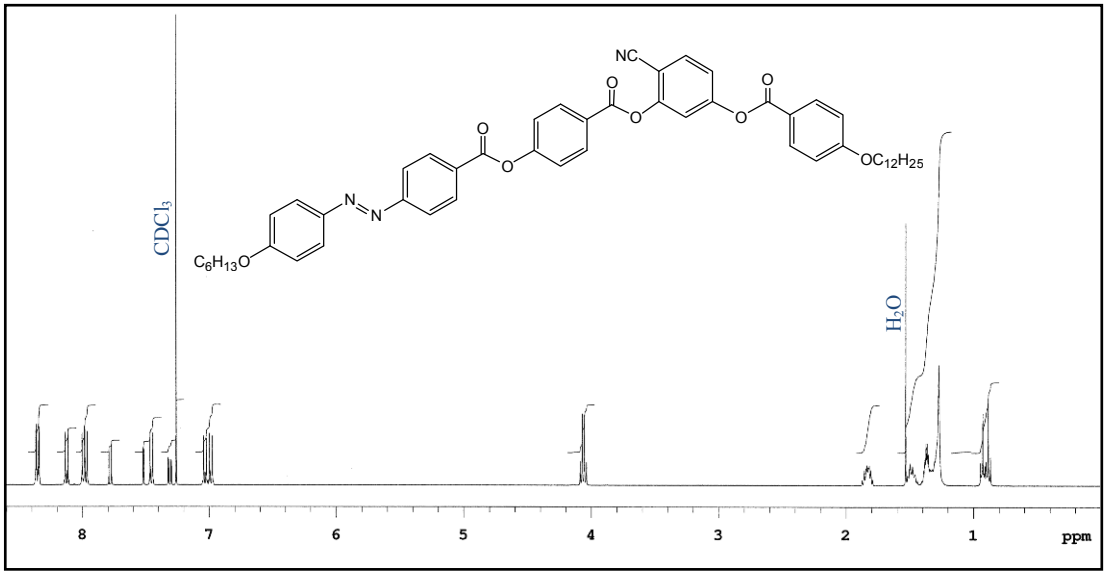


Figure S13. ^{1}H-NMR Spectrum of **E6/12** in $CDCl_3$.

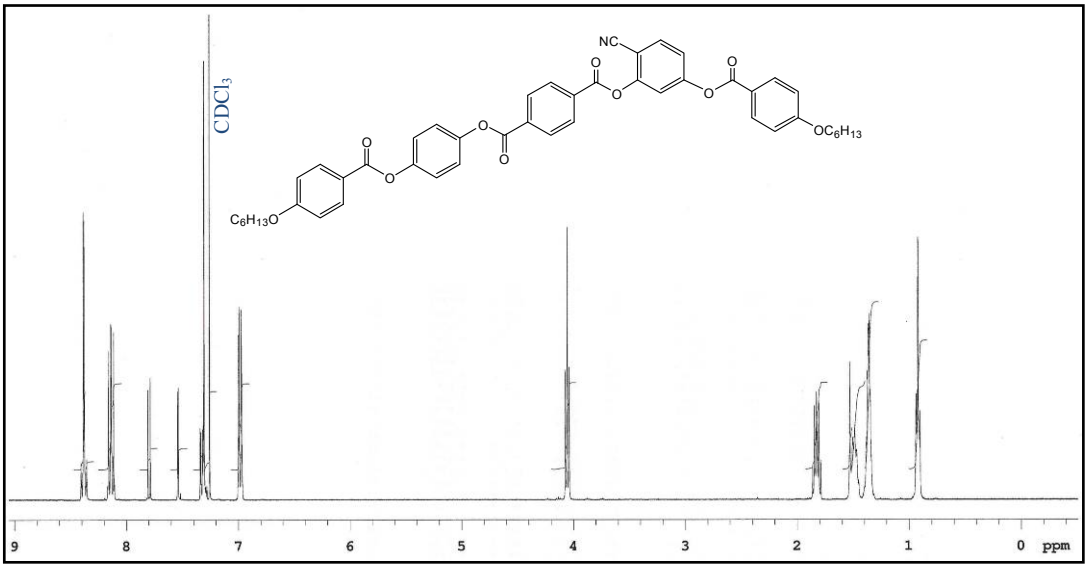


Figure S14. ^{1}H-NMR Spectrum of **F6/6** in $CDCl_3$.

2. Additional data

2.1 Textures and DSC data

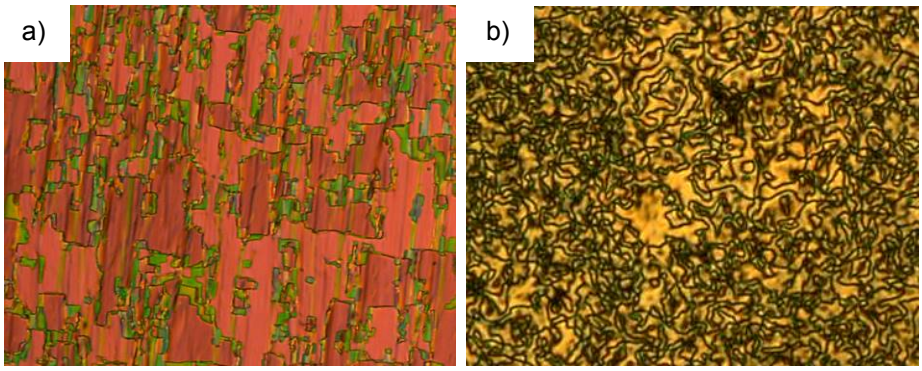


Figure S15. Optical micrographs observed for the SmC_s phase at T = 150 ºC of compound **A20/12**: a) in a planar cell (6 μm PI coated ITO cell) and b) in a homeotropic cell (between ordinary non-treated microscopy slides).

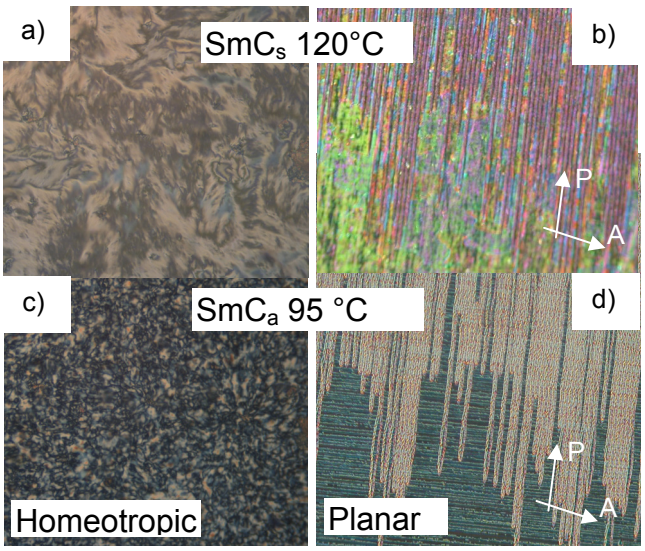


Figure S16. Textures of **D6/6** as observed in the SmC_s and SmC_a phase, a,c) homeotropic alignment between ordinary microscopy glass slides and b,d) planar alignment in PI coated 6 μm ITO cells.

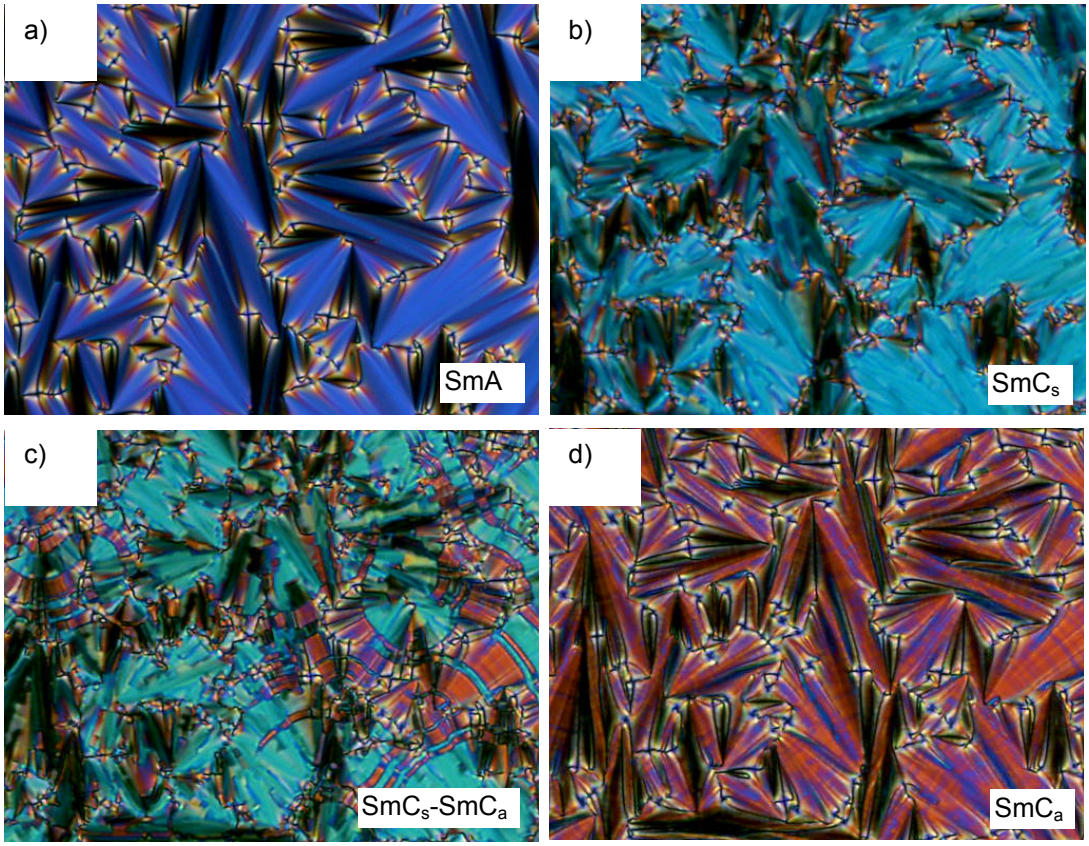


Figure S17. Optical micrographs observed in a planar cell (6 μm PI coated ITO cell) for compound **D6/12** in: a) the SmA phase at 205 °C; b) the SmC_s phase at 155 °C; c) at the SmC_s - SmC_a phase transition at 65 °C (anchoring transition) and d) the SmC_a phase at 55 °C.

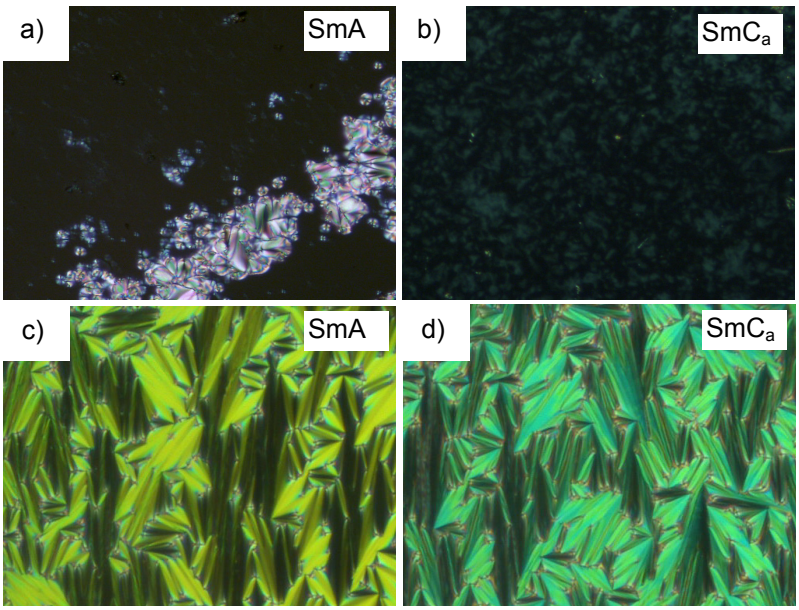


Figure S18. Optical micrographs of the SmA-SmC_a transition of compound **B6/6**. a,b) as observed in a homeotropic cell and c,d) in a planar cell (6 μm PI coated ITO cell): a) SmA phase at 170 °C; b) the SmC_a phase at 130 °C; c) SmA phase at 170 °C; b) the SmC_a phase at 130 °C.

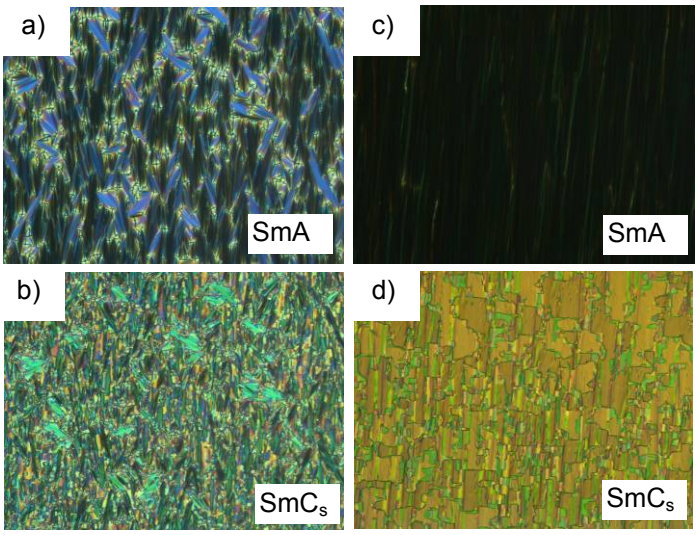


Figure S19. Textures as observed in the LC phases of a,b) compound **C12/12** in a 6μm PI-coated cell after an application of a DC field (E = +10 Vμm^{-1}) a) in the SmA phase at T = 190 °C and b) in the SmC_S phase at T = 160 °C and c,d) compound **A20/12** c) in the SmA phase at T = 187 °C and d) in the SmC_S phase at T = 170 °C.

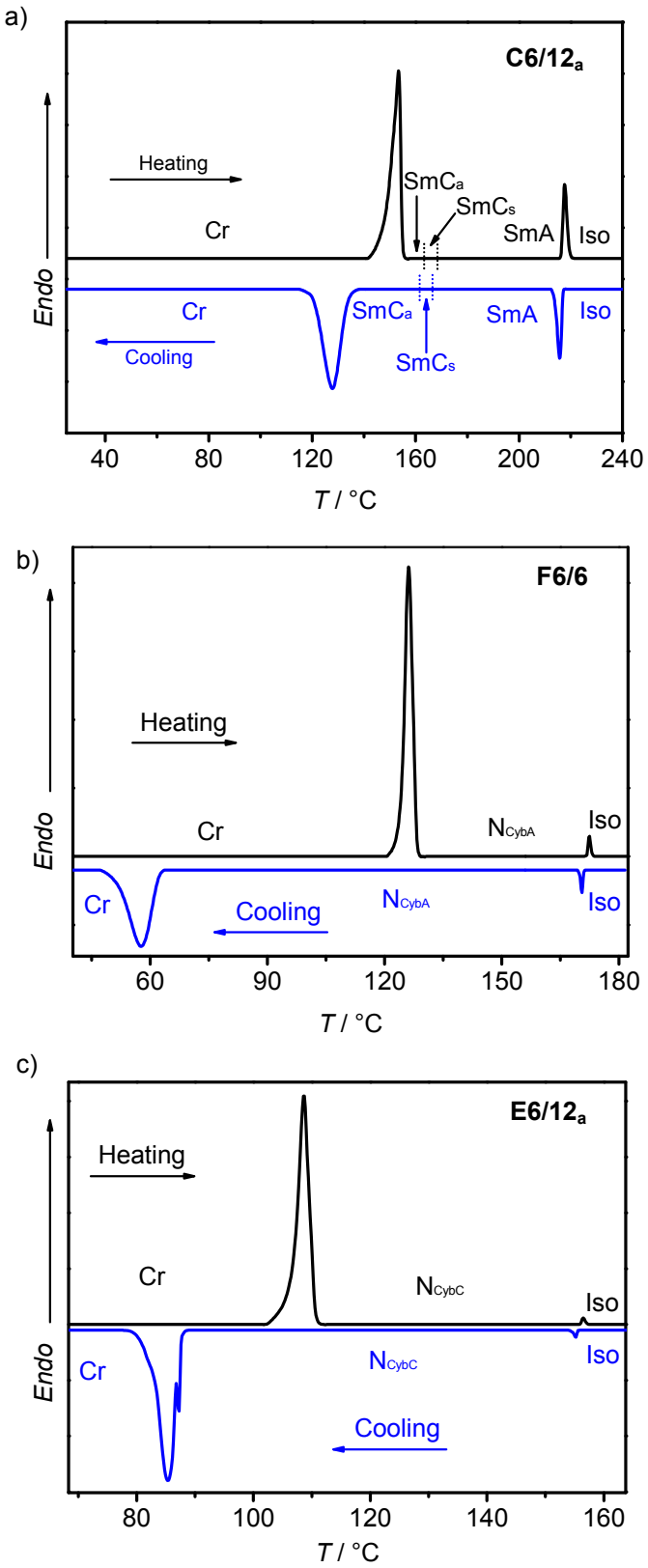


Figure S20. Representative DSC traces: a) **C6/12; b) F6/6** and **c) E6/12.**

2.2 XRD Data

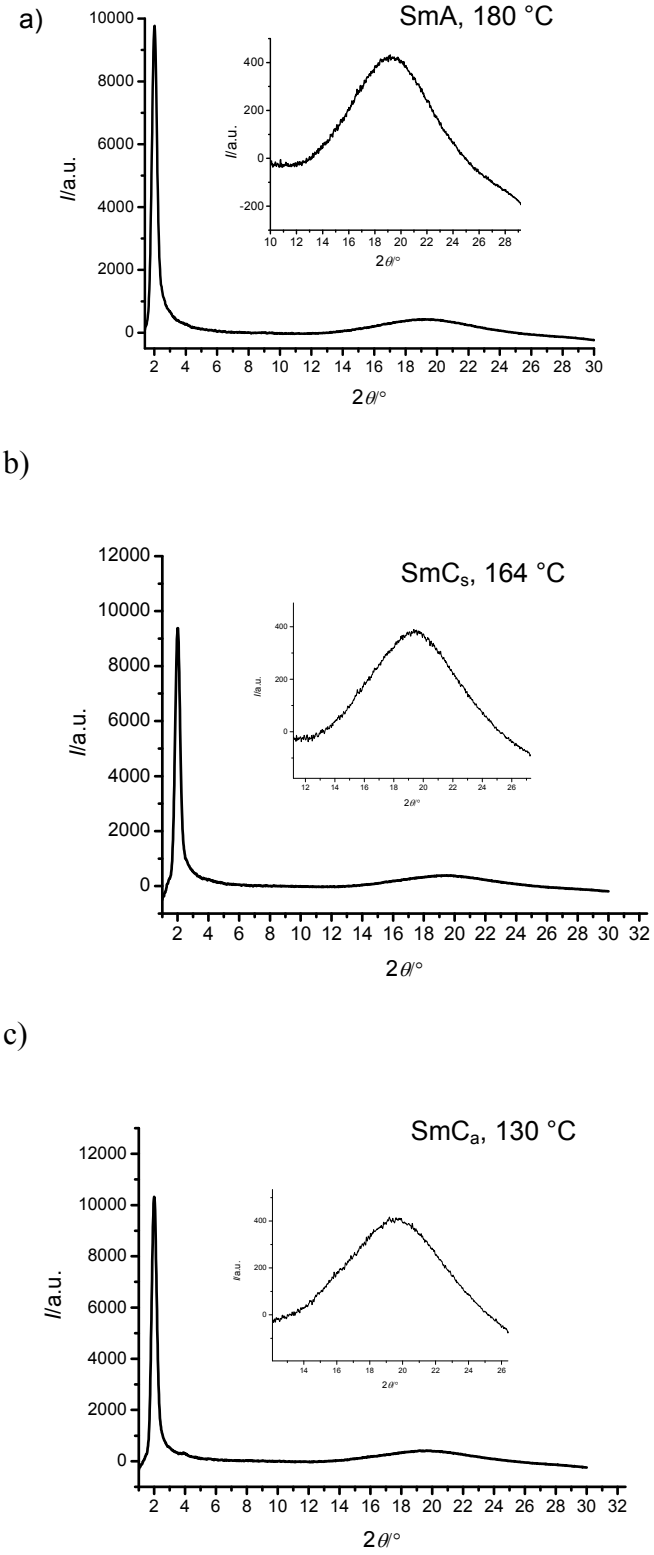


Figure S21. XRD patterns of **A6/6** in the distinct LC phases: a) SmA phase at T = 180 °C; b) SmC_s phase at T = 164 °C and c) SmC_a phase at T = 130 °C.

Table S1. XRD data of the investigated compounds.

Comp.	*T*/°C	2*θ*/°	*θ*/°	hk	*d*-value/nm	phase	*d*/nm
A6/6	180	2,003 19,190	1,002 9,595	10 diff	4,411 0,462	SmA	4.41
	164	1,980 19.311	0,990 9.655	10 diff	4,461 0.460	SmC_s	4.46
	130	1.980 3.964 19.516	0.990 1.982 9.758	10 20 diff	4.462 2.229 0.455	SmC_a	4.46
D6/6	180	2.105 19.152	1.052 9.576	10 diff	4.198 0.463	SmA	4.20
	130	2.232 4.444 19.528	1.116 2.222 9.764	10 20 diff	3.958 1.988 0.455	SmC_s	3.96
	90	2.281 4.523 19.899	1.141 2.262 9.950	10 20 diff	3.873 1.954 0.446	SmC_a	3.87
E6/12	140	2.424 19.217	1.212 9.608	10 diff	3.645 0.462	N_{CybC}	3.65
F6/6	150	2.690 4.420 19.300	1.345 2.210 9.650	10 20 diff	3.284 1.999 0.460	N_{CybC}	3.28

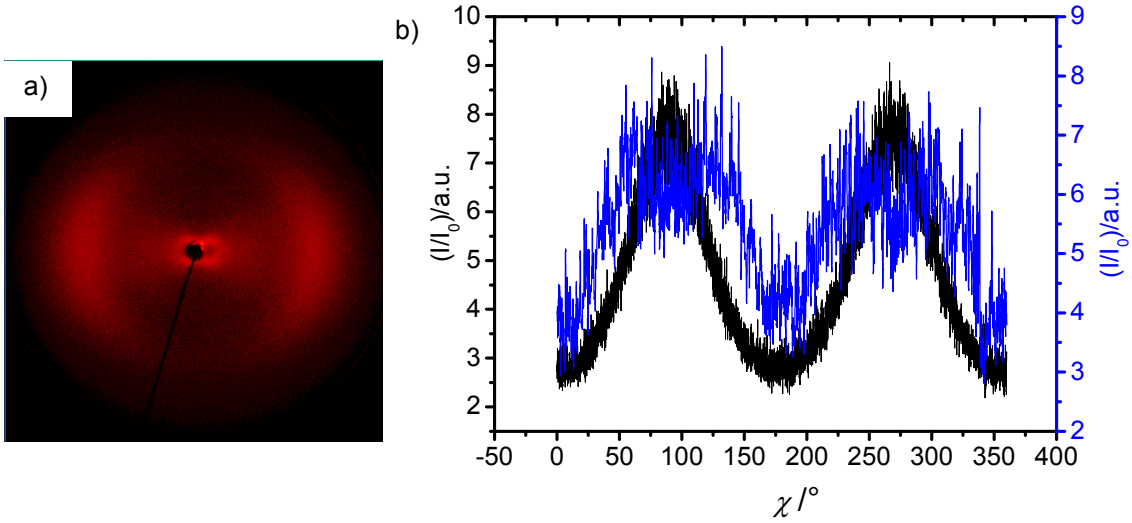


Figure S22. XRD investigations of the nematic phase of compound **E6/12**: a) diffraction pattern at 95 °C; b) intensity distribution of the diffuse scatterings along χ, black curve wide angle scattering (15-25° 2θ) and blue curve small angle scattering (2-5° 2θ).

2.3 Electrooptical investigations

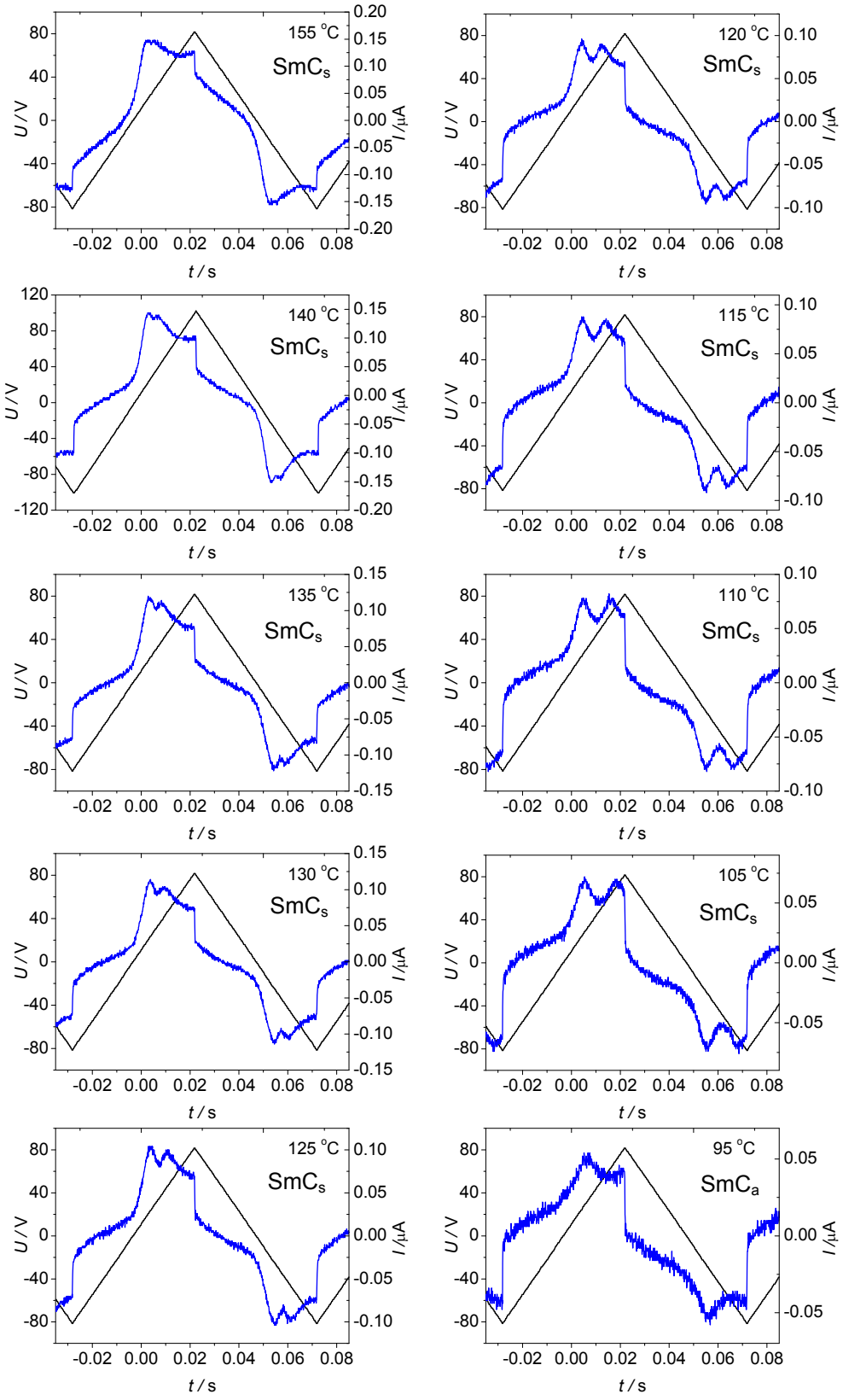


Figure S23. Polarization current curves of compound **D6/6** in as observed in the temperature range between 155 and 95 °C on cooling.

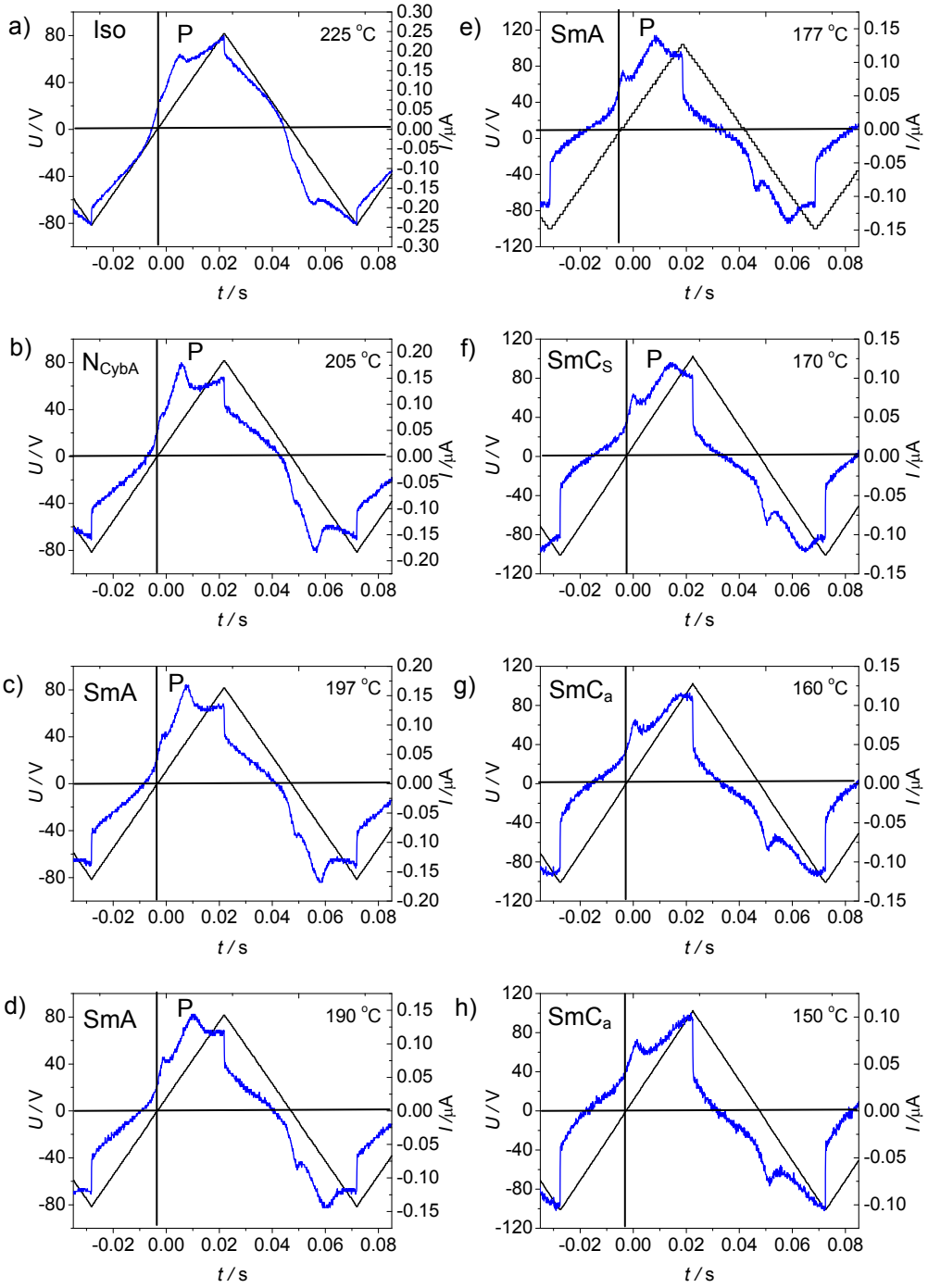


Figure S24. Polarization current curves of compound **A6/6** in as observed in the temperature range between 225 and 150 °C.

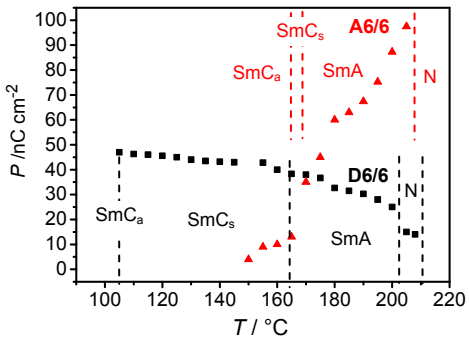


Figure 25. Development of the area under the current peaks (assuming a polarization, but also involving a contribution of ionic conductivity which is not separated) of compounds **A6/6** and **D6/6**.

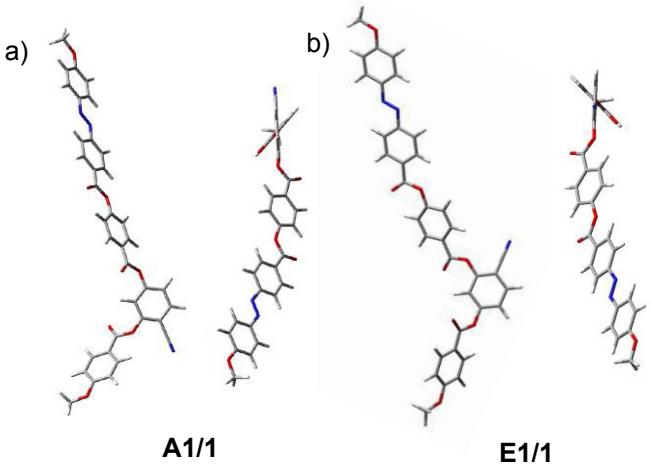


Figure 26: Local minima of the chiral conformation of the energy minimized molecular conformers at the B3LYP/LANL2DZ level of theory of the model compounds a) **A1/1** and b) **E1/1** as observed under two distinct perspectives. Left, perpendicular to the plane of the resorcinol core indicating changes of the bending angle and right, along the shorter wing and parallel to the plane of the resorcinol core, indicating the twist between the planes.

2.4. Photoisomerization studies

The photosensitivity of the prepared azobenzene containing HSLCs was confirmed by measuring UV-vis absorption spectroscopy of compound **E6/12** as a representative example. As shown in Fig. S25 the UV-vis spectra of **E6/12** dissolved in chloroform solution was measured at three different states: a) freshly prepared, b) after exposure to 365 nm light for one hour and finally c) after storing the sample in dark overnight. In the first spectrum a maximum absorption at 367 nm is observed as a result of the π-π^* transition of the chromophore in the molecule confirming the presence of the trans isomer, while in the second spectrum the absorption at 367 nm almost disappears and another absorption band at 465 nm starts to develop as a result of *trans-cis* photoisomerization. The formed less stable cis-isomer relaxes back to the more stable trans- isomer after storing the solution in dark overnight, where very similar spectrum to that observed for the freshly prepared solution is obtained. These observations are very similar to that reported for the other azobenzene-based hockey-stick molecules[S1,S5] and azobenzene-containing BCLCs derived from 4-cyanoresorcinol.[S6]

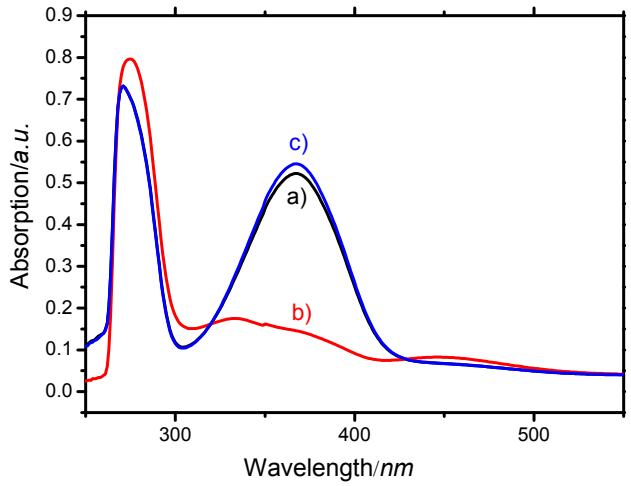


Figure S27. UV-vis spectra (absorbance vs. wavelength) of **E6/12** dissolved in chloroform (0.02 mM solution) at 25 ºC. a) Freshly prepared sample, *trans*-isomer before irradiation, black line; b) *cis*-isomer as obtained after one hour irradiation with light of 365 nm wavelength, red line; c) trans-isomer after keeping the sample in dark overnight, blue line.

3. References

S1 a) M. Alaasar, S. Poppe, C. Tschierske, *Liq. Cryst.*, 2017, 44, 729; b) M. Alaasar, M. Prehm, M. Brautzsch and C. Tschierske. *J. Mater. Chem. C,* **2014**, *2*, 5487.

S2 C. Keith, A. Lehmann, U. Baumeister, M. Prehm and C. Tschierske, *Soft Matter*, **2010**, *6*, 1704.

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