

## Supplemental material

### Competing Synclinic and Anticlinic Interactions in Smectic Phases of Bent-Core Mesogens

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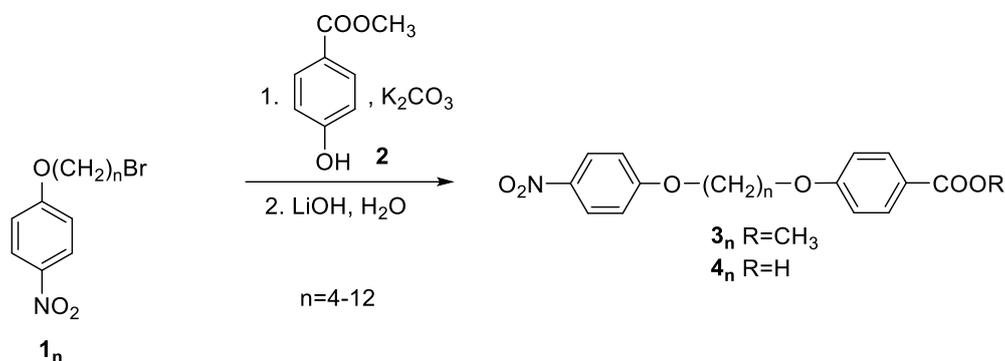
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## 1. Synthesis

### 1.1. Synthesis of the lengthening arms

Syntheses of the acids **4<sub>n</sub>** were achieved by series of transformations shown in Scheme S1.



Scheme S1. Synthesis scheme of the lengthening arms **3** and **4**.

#### Methyl 4-[5-(4-nitrophenyloxy)pentyl]oxy]benzoate (**3<sub>5</sub>**)

A mixture of bromide **1<sub>5</sub>** (1.70 g; 5.9 mmol), methyl 4-hydroxybenzoate (**2**) (1.52 g; 10 mmol), anhydrous potassium carbonate (1.80 g; 13 mmol), sodium iodide (150 mg) and dry *N,N*-dimethylformamide (25 ml) was heated under stirring at 90°C for 6 h. After cooling to room temperature, the solvent was evaporated at reduced pressure. The residue was extracted with hot chloroform (3 × 50 ml), the combined solution was washed subsequently with water (20 ml), brine (30 ml), and dried with anhydrous magnesium sulphate. The solvent was removed and the product was purified by column chromatography (toluene/*tert*-butyl methyl ether 100/3) and crystallisation from ethyl acetate to yield 1.83 g (86%) of **3<sub>5</sub>**, m.p. 122-123.5°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.70 (m, 2 H, CH<sub>2</sub>), 1.89 (m, 2 H, CH<sub>2</sub>), 1.91 (m, 2 H, CH<sub>2</sub>), 3.88 (s, 3 H, OCH<sub>3</sub>), 4.05 (t, 2 H, *J*=6.4, OCH<sub>2</sub>), 4.08 (t, 2 H, *J*=6.2), 6.90 (d, 2 H, *J*=8.8), 6.93 (d, 2 H, *J*=8.8), 7.97 (d, 2 H, *J*=8.8), 8.19 (d, 2 H, *J*=8.8). Elemental analysis: for C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub> (359.38): calculated/found: C 63.50/63.39, H 5.89/5.83, N 3.90/3.81%.

In the same way, other homologues **3<sub>n</sub>** have been prepared.

**3<sub>4</sub>**: Yield 85%, m.p. 137-137.5°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 2.03 (m, 4 H, (CH<sub>2</sub>)<sub>2</sub>), 3.88 (s, 3 H, OCH<sub>3</sub>), 4.11 (m, 4 H, 2 × OCH<sub>2</sub>), 6.89 (d, 2 H, *J*=8.8), 6.93 (d, 2 H, *J*=9.3), 7.98 (d, 2 H, *J*=8.8), 8.19 (d, 2 H, *J*=9.3). Elemental analysis: for C<sub>18</sub>H<sub>19</sub>NO<sub>6</sub> (345.36): calculated/found: C 62.60/62.55, H 5.55/5.39, N 4.06/3.94%.

**3<sub>6</sub>**: Yield 75%, m.p. 153.5-154°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.58 (m, 4 H, (CH<sub>2</sub>)<sub>2</sub>), 1.86 (m, 4 H, 2 × CH<sub>2</sub>), 3.88 (s, 3 H, OCH<sub>3</sub>), 4.05 (t, 2 H, *J*=6.4, OCH<sub>2</sub>), 4.08 (t, 2 H, *J*=6.2), 6.89 (d, 2 H, *J*=8.8), 6.93 (d, 2 H, *J*=9.3), 7.98 (d, 2 H, *J*=8.8), 8.19 (d, 2 H, *J*=9.3). Elemental analysis: for C<sub>20</sub>H<sub>23</sub>NO<sub>6</sub> (373.41): calculated/found: C 64.33/64.30, H 6.21/6.08, N 3.75/3.67%.

**3<sub>7</sub>**: Yield 82%, m.p. 110-111°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.53 (m, 6 H, (CH<sub>2</sub>)<sub>3</sub>), 1.85 (m, 4 H, 2 × CH<sub>2</sub>), 3.88 (s, 3 H, CH<sub>3</sub>), 4.03 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.06 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 6.89 (d, 2 H, *J*=8.9), 6.93 (d, 2 H, *J*=9.2), 7.97 (d, 2 H, *J*=8.9), 8.19 (d, 2 H, *J*=9.3). Elemental analysis: for C<sub>21</sub>H<sub>25</sub>NO<sub>6</sub> (387.43): calculated/found: C 65.10/64.96, H 6.50/6.46, N 3.62/3.50%.

**3<sub>8</sub>**: Yield 90%, m.p. 137-138°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.38-1.53 (m, 8 H, (CH<sub>2</sub>)<sub>4</sub>), 1.81 (m, 4 H, 2 × CH<sub>2</sub>), 3.88 (s, 3 H, CH<sub>3</sub>), 4.01 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.04 (t, 2 H, *J*=7.0, OCH<sub>2</sub>),

6.89 (d, 2 H,  $J=9.3$ ), 6.93 (d, 2 H,  $J=9.3$ ), 7.97 (d, 2 H,  $J=8.8$ ), 8.19 (d, 2 H,  $J=9.3$ ). Elemental analysis: for  $C_{22}H_{27}NO_6$  (401.46): calculated/found: C 65.82/65.66, H 6.78/6.59, N 3.49/3.36%.

**39:** Yield 90%, m.p. 121-122°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 1.37 (m, 6 H, 3  $\times$   $CH_2$ ), 1.47 (m, 4 H, 2  $\times$   $CH_2$ ), 1.81 (m, 4 H, 2  $\times$   $CH_2$ ), 3.88 (s, 3 H,  $CH_3$ ), 4.00 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 4.02 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 6.89 (d, 2 H,  $J=8.8$ ), 6.93 (d, 2 H,  $J=9.3$ ), 7.95 (d, 2 H,  $J=8.8$ ), 8.19 (d, 2 H,  $J=9.3$ ). Elemental analysis: for  $C_{23}H_{29}NO_6$  (415.49): calculated/found: C 66.49/66.40, H 7.04/6.89, N 3.37/3.19%.

**310:** Yield 81%, m.p. 121.5-123.5°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 1.34 (m, 8 H, 4  $\times$   $CH_2$ ), 1.47 (m, 4 H, 2  $\times$   $CH_2$ ), 1.80 (m, 4 H, 2  $\times$   $CH_2$ ), 3.88 (s, 3 H,  $CH_3$ ), 4.00 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 4.04 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 6.89 (d, 2 H,  $J=8.8$ ), 6.93 (d, 2 H,  $J=9.3$ ), 7.97 (d, 2 H,  $J=9.3$ ), 8.19 (d, 2 H,  $J=9.3$ ). Elemental analysis: for  $C_{24}H_{31}NO_6$  (429.52): calculated/found: C 67.11/67.00, H 7.27/7.29, N 3.26/3.14%.

**311:** Yield 79%, m.p. 127.5-128.5°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 1.37 (m, 8 H, 5  $\times$   $CH_2$ ), 1.47 (m, 4 H, 2  $\times$   $CH_2$ ), 1.81 (m, 4 H, 2  $\times$   $CH_2$ ), 3.88 (s, 3 H,  $CH_3$ ), 4.00 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 4.02 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 6.89 (d, 2 H,  $J=8.8$ ), 6.93 (d, 2 H,  $J=9.3$ ), 7.95 (d, 2 H,  $J=8.8$ ), 8.19 (d, 2 H,  $J=9.3$ ). Elemental analysis: for  $C_{25}H_{33}NO_6$  (443.54): calculated/found: C 67.70/67.56, H 7.50/7.37, N 3.16/3.03%.

**312:** Yield 64%, m.p. 114-115°C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 1.34 (m, 12 H, 6  $\times$   $CH_2$ ), 1.47 (m, 4 H, 2  $\times$   $CH_2$ ), 1.80 (m, 4 H, 2  $\times$   $CH_2$ ), 3.88 (s, 3 H,  $CH_3$ ), 4.00 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 4.04 (t, 2 H,  $J=7.0$ ,  $OCH_2$ ), 6.89 (d, 2 H,  $J=8.8$ ), 6.93 (d, 2 H,  $J=9.3$ ), 7.97 (d, 2 H,  $J=9.3$ ), 8.19 (d, 2 H,  $J=9.3$ ). Elemental analysis: for  $C_{26}H_{35}NO_6$  (457.57): calculated/found: C 68.25/68.09, H 7.71/7.59, N 3.06/3.00%.

#### 4-[5-(4-Nitrophenyloxy)pentyl]oxy]benzoic acid (**45**)

A mixture of ester **35** (1.80 g; 5.01 mmol), lithium hydroxide (1.20 g; 50 mmol), THF (120 ml) and water (30 mmol) was stirred and heated to boiling for 24 h. While hot, the mixture was acidified with 7% aq. hydrochloric acid (35 ml) and stirred for 5 min. After cooling, the layers were separated, the aqueous layer was extracted with chloroform (3  $\times$  120 ml). The combined solution was washed with brine (100 ml) and dried with anhydrous magnesium sulphate. The solvent was removed, and the residue was crystallised from 2-methoxyethanol, the deposited crystals were filtered and washed with a small amount of the solvent. After drying under reduced pressure, 1.59 g (92%) of acid **45** was obtained, m.p. 196-197°C.  $^1H$  NMR (300 MHz,  $DMSO-d_6$ ): 1.55 (m, 2 H,  $CH_2$ ), 1.78 (m, 4 H,  $(CH_2)_2$ ), 4.04 (t, 2 H,  $J=6.4$ ,  $OCH_2$ ), 4.10 (t, 2 H,  $J=6.4$ ,  $OCH_2$ ), 6.98 (d, 2 H,  $J=8.8$ ), 7.13 (d, 2 H,  $J=8.8$ ), 7.85 (d, 2 H,  $J=8.8$ ), 8.18 (d, 2 H,  $J=8.8$ ), 12.55 (bs, 1 H, OH). Elemental analysis: for  $C_{18}H_{19}NO_6$  (345.36): calculated/found: C 62.60/62.40, H 5.55/5.59, N 4.06/3.99%.

In this way, the other acid **4n** were obtained.

**44:** Yield 86%, m.p. 253°C (2-methoxyethanol).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ ): 1.89 (m, 4 H,  $(CH_2)_2$ ), 4.10 (t, 2 H,  $OCH_2$ ), 4.18 (t, 2 H,  $OCH_2$ ), 6.99 (d, 2 H,  $J=8.8$ ), 7.14 (d, 2 H,  $J=8.8$ ), 7.86 (d, 2 H,  $J=8.8$ ), 8.18 (d, 2 H,  $J=8.8$ ), 12.57 (bs, 1 H, OH). Elemental analysis: for  $C_{17}H_{17}NO_6$  (331.33): calculated/found: C 61.63/61.49, H 5.17/5.26, N 4.23/4.19%.

**46:** Yield 95%, m.p. 179-192°C (2-methoxyethanol).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ ): 1.46 (m, 4 H,  $(CH_2)_2$ ), 1.74 (m, 4 H,  $(CH_2)_2$ ), 4.01 (t, 2 H,  $J=6.4$ ,  $OCH_2$ ), 4.10 (t, 2 H,  $J=6.4$ ,  $OCH_2$ ), 6.97 (d, 2 H,  $J=8.8$ ), 7.11 (d, 2 H,  $J=8.8$ ), 7.81 (d, 2 H,  $J=8.8$ ), 8.17 (d, 2 H,  $J=8.8$ ), 12.55 (bs, 1 H, OH). Elemental analysis: for  $C_{19}H_{21}NO_6$  (356.38): calculated/found: C 63.50/63.39, H 5.89/5.67, N 3.90/3.80%.

**47:** Yield 92%, m.p. 159-160°C (ethanol). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.43 (m, 6 H, (CH<sub>2</sub>)<sub>3</sub>), 1.74 (m, 4 H, (CH<sub>2</sub>)<sub>2</sub>), 4.00 (t, 2 H, *J*=6.4, OCH<sub>2</sub>), 4.09 (t, 2 H, *J*=6.4, OCH<sub>2</sub>), 6.96 (d, 2 H, *J*=8.8), 7.10 (d, 2 H, *J*=8.8), 7.82 (d, 2 H, *J*=8.8), 8.16 (d, 2 H, *J*=8.8), 12.55 (bs, 1 H, OH). Elemental analysis: for C<sub>20</sub>H<sub>23</sub>NO<sub>6</sub> (373.41): calculated/found: C 64.33/64.21, H 6.21/6.19, N 3.75/3.58%.

**48:** Yield 95%, m.p. 179-181°C (ethanol). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.29 (m, 4 H, 2 × CH<sub>2</sub>), 1.39 (m, 4 H, 2 × CH<sub>2</sub>), 1.70 (m, 4 H, 2 × CH<sub>2</sub>), 4.00 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.09 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 6.96 (d, 2 H, *J*=8.8), 7.06 (d, 2 H, *J*=9.3), 7.85 (d, 2 H, *J*=9.2), 8.17 (d, 2 H, *J*=8.8), 12.55 (bs, 1 H, OH). Elemental analysis: for C<sub>21</sub>H<sub>25</sub>NO<sub>6</sub> (387.44): calculated/found: C 65.10/64.94, H 6.50/6.48, N 3.62/3.42%.

**49:** Yield 92%, Cr 145 N 153 Iso (ethanol). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.28 (m, 6 H, 3 × CH<sub>2</sub>), 1.38 (m, 4 H, 2 × CH<sub>2</sub>), 1.69 (m, 4 H, 2 × CH<sub>2</sub>), 4.00 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.08 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 6.96 (d, 2 H, *J*=8.8), 7.05 (d, 2 H, *J*=9.3), 7.84 (d, 2 H, *J*=9.2), 8.16 (d, 2 H, *J*=8.8), 12.55 (bs, 1 H, OH). Elemental analysis: for C<sub>22</sub>H<sub>27</sub>NO<sub>6</sub> (401.46): calculated/found: C 65.82/65.66, H 6.78/6.68, N 3.49/3.33%.

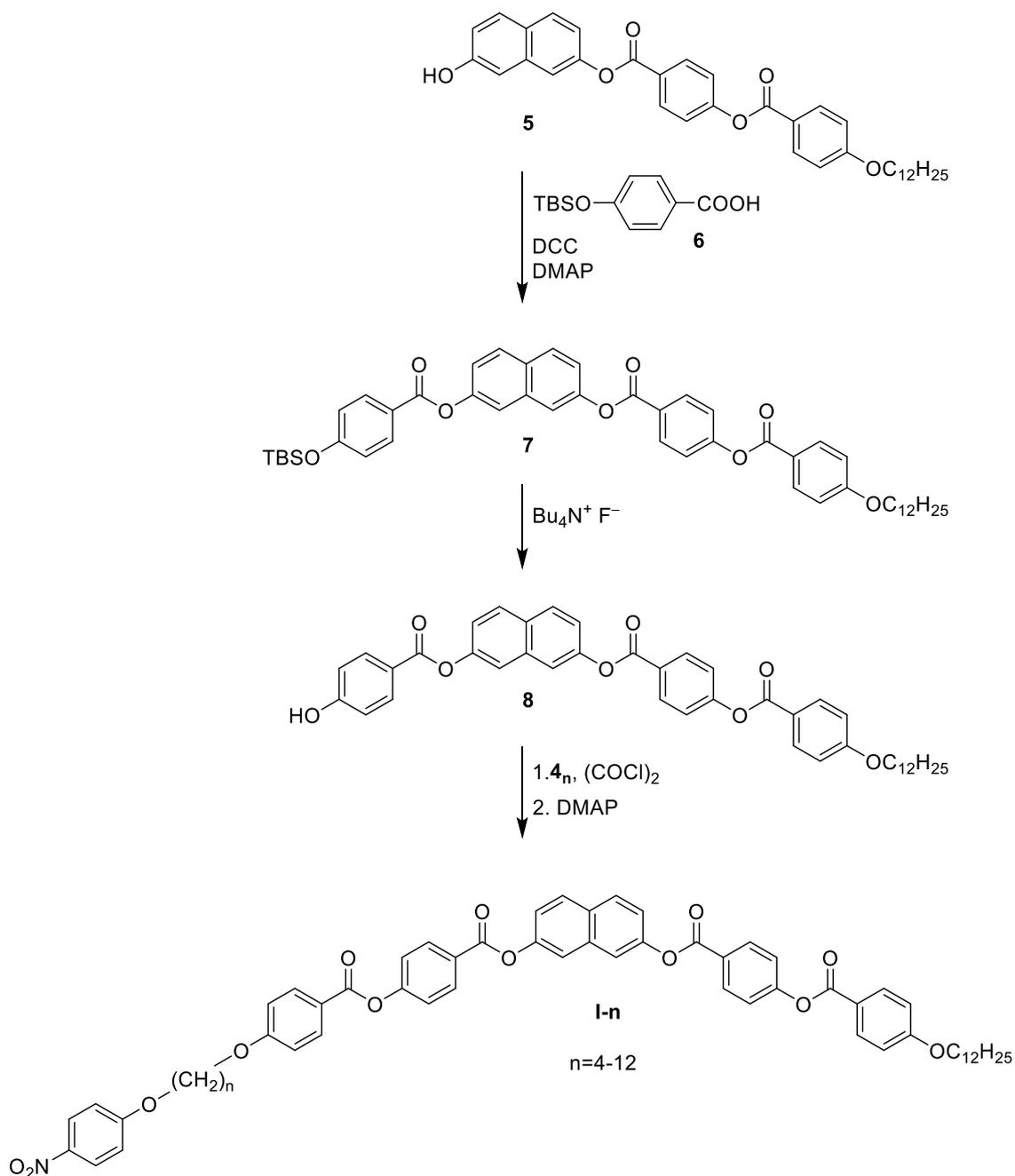
**410:** Yield 90%, Cr 158 N 163 Iso (ethanol). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.27 (m, 8 H, 4 × CH<sub>2</sub>), 1.37 (m, 4 H, 2 × CH<sub>2</sub>), 1.69 (m, 4 H, 2 × CH<sub>2</sub>), 4.00 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.08 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 6.96 (d, 2 H, *J*=8.8), 7.05 (d, 2 H, *J*=9.3), 7.84 (d, 2 H, *J*=9.2), 8.16 (d, 2 H, *J*=8.8), 12.55 (bs, 1 H, OH). Elemental analysis: for C<sub>23</sub>H<sub>29</sub>NO<sub>6</sub> (415.49): calculated/found: C 66.49/66.40, H 7.04/6.81, N 3.37/3.26%.

**411:** Yield 81%, m.p. 253°C (ethanol). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.26 (m, 10 H, 5 × CH<sub>2</sub>), 1.37 (m, 4 H, 2 × CH<sub>2</sub>), 1.69 (m, 4 H, 2 × CH<sub>2</sub>), 3.99 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.08 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 6.97 (d, 2 H, *J*=9.3), 7.08 (d, 2 H, *J*=9.3), 7.84 (d, 2 H, *J*=8.8), 8.17 (d, 2 H, *J*=8.8), 12.55 (bs, 1 H, OH). Elemental analysis: for C<sub>24</sub>H<sub>31</sub>NO<sub>6</sub> (429.52): calculated/found: C 67.11/66.99, H 7.27/7.16, N 3.26/3.17%.

**412:** Yield 92%, m.p. 139-153°C (ethanol). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): 1.25 (m, 12 H, 6 × CH<sub>2</sub>), 1.38 (m, 4 H, 2 × CH<sub>2</sub>), 1.70 (m, 4 H, 2 × CH<sub>2</sub>), 4.00 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 4.09 (t, 2 H, *J*=7.0, OCH<sub>2</sub>), 6.97 (d, 2 H, *J*=8.8), 7.11 (d, 2 H, *J*=9.3), 7.85 (d, 2 H, *J*=9.2), 8.17 (d, 2 H, *J*=8.8), 12.55 (bs, 1 H, OH). Elemental analysis: for C<sub>25</sub>H<sub>33</sub>NO<sub>6</sub> (443.54): calculated/found: C 67.70/67.56, H 7.50/7.41, N 3.16/3.03%.

## 1.2. Synthesis of target materials

Scheme S2 summarizes the synthetic transformations leading to the final compounds **I-n**.



Scheme S2. Scheme of the synthetic route leading to the final products.

**{7-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-yl} 4-(*tert*-butyldimethylsilyloxy)benzoate (7)**

A mixture of naphthol **5** (0.78 g; 1.37 mmol), acid **6** (0.45 g; 1.78 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.51 g; 2.43 mmol) and 4-dimethylaminopyridine (DMAP) (50 mg; 0.41 mmol) in dry dichloromethane (70 ml) was stirred at room temperature in the inert argon atmosphere for 3 h. The deposited dicyclohexylurea was filtered and washed with dichloromethane (3 × 15 ml). The filtrate was evaporated and the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, gradient elution 100/2 to 100/8). Yield 700 mg (73%) of **7**, m.p. 136-140 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.28 (s, 6 H, 2 × CH<sub>3</sub>), 0.89 (t, 3 H, *J*=7.0, CH<sub>3</sub>), 1.01 (s, 9 H, (CH<sub>3</sub>)<sub>3</sub>C), 1.28 (m, 16 H, (CH<sub>2</sub>)<sub>8</sub>), 1.44 (m, 2 H,

CH<sub>2</sub>), 1.83 (m, 2 H, CH<sub>2</sub>), 4.06 (t, 2 H, *J*=6.4, OCH<sub>2</sub>), 6.89 (d, 2 H, *J*=8.8), 6.99 (d, 2 H, *J*=9.3), 7.36 (dt, 2 H, *J*=8.8, *J*=2.1), 7.39 (d, 2 H, *J*=8.8), 7.68 (t, 2 H, *J*=2.3), 7.92 (dd, 2 H, *J*=8.8), 8.13 (d, 2 H, *J*=9.3), 8.16 (d, 2 H, *J*=8.8), 8.33 (d, 2 H, *J*=8.8).

### **{7-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-yl} 4-hydroxybenzoate (8)**

To a solution of ester **7** (600 mg; 0.75 mmol) in a mixture of THF (50 ml) and water (10 ml), a 1M solution of tetrabutylammonium fluoride in tetrahydrofuran (0.25 ml) was added and the mixture was stirred at room temperature for 1 h. The solution was diluted with water and extracted with ethyl acetate (4 × 30 ml). The combined organic solution was washed with brine (50 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the product was purified by column chromatography (chloroform/acetone 100/3) to yield 490 mg (95%) of **8**, m.p. 209-210°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.90 (t, 3 H, *J*=7.0, CH<sub>3</sub>), 1.28 (m, 16 H, (CH<sub>2</sub>)<sub>8</sub>), 1.44 (m, 2 H, CH<sub>2</sub>), 1.83 (m, 2 H, CH<sub>2</sub>), 4.06 (t, 2 H, *J*=6.4, OCH<sub>2</sub>), 6.95 (d, 2 H, *J*=8.8), 6.99 (d, 2 H, *J*=8.8), 7.38 (dt, 2 H, *J*=8.8, *J*=2.1), 7.39 (d, 2 H, *J*=8.8), 7.68 (t, 2 H, *J*=2.3), 7.92 (dd, 2 H, *J*=8.8), 8.13 (d, 2 H, *J*=9.3), 8.16 (d, 2 H, *J*=8.8), 8.33 (d, 2 H, *J*=8.8).

### **1.3. Target compounds I-n**

To a mixture of acid **4<sub>n</sub>**, DMAP (10 mg) in dry dichloromethane (15 ml), oxalyl chloride (0.5 ml; 5.8 mmol) was added and the mixture was stirred at room temperature in an argon atmosphere for 6 h. The mixture was evaporated, toluene (5 ml) was added and evaporated. The crude acid chloride was dissolved in dry dichloromethane (5 ml) and added to a solution of naphthol **8** (0.7 mmol) and DMAP (150 mmol; 1.23 mmol) in dry dichloromethane (20 ml). The mixture was stirred at 40 °C for 2 h in the inert argon atmosphere, cooled to room temperature and washed aq. saturated solution of sodium hydrogen carbonate (20 ml). The aqueous layer was washed with dichloromethane (3 × 20 ml) and the combined organic solution was washed with saturated aq. solution of sodium chloride and dried with anhydrous magnesium sulphate. After removing the solvent, the crude product was purified by column chromatography (elution with a toluene/dichloromethane/*tert*-butyl methyl ether 50/50/1 mixture) and final multiple crystallisations from an ethanol/acetone/toluene mixture.

**7-(4-{4-[7-(4-Nitrophenyloxy)butyloxy]}benzoyloxy)benzoyloxynaphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-4)**. Yield 75%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H, *J*=6.7, CH<sub>3</sub>), 1.29-1.42 (m, 16 H, 8 × CH<sub>2</sub>), 1.46 (m, 2 H, CH<sub>2</sub>), 1.83 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 2.06 (m, 4 H, 2 × OCH<sub>2</sub>CH<sub>2</sub>), 4.06 (t, 2 H, *J*=6.5, OCH<sub>2</sub>), 4.16 (m, 4 H, 2 × OCH<sub>2</sub>), 6.98 (m, 6 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.18 (m, 6 H, H-Ar), 8.34 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.54 (C<sub>q</sub>), 164.52 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.24 (C<sub>q</sub>), 163.92 (C<sub>q</sub>), 163.82 (C<sub>q</sub>), 163.45 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.38 (C<sub>q</sub>), 149.26 (C<sub>q</sub>), 149.24 (C<sub>q</sub>), 141.48 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.48 (2 × CH<sub>benz</sub>), 132.42 (2 × CH<sub>benz</sub>), 131.89 (2 × CH<sub>benz</sub>), 131.88 (2 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.84 (C<sub>q</sub>), 126.76 (C<sub>q</sub>), 125.95 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.12 (2 × CH<sub>benz</sub>), 121.29 (C<sub>q</sub>), 121.23 (2 × CH<sub>naph</sub>), 120.89 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.37 (2 × CH<sub>benz</sub>), 114.35 (2 × CH<sub>benz</sub>), 68.38 (OCH<sub>2</sub>), 68.24 (OCH<sub>2</sub>), 67.63 (OCH<sub>2</sub>), 31.91 (CH<sub>2</sub>), 29.65-29.35 (6 × CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 25.78 (CH<sub>2</sub>), 25.76 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>60</sub>H<sub>59</sub>NO<sub>13</sub> (1002.14): calculated/found: C 71.91/71.86, H 5.93/5.76, N 1.40/1.31%.

**7-(4-{4-[7-(4-Nitrophenyloxy)pentylloxy]}benzoyloxy)benzoyloxynaphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-5)**. Yield 70%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>):

0.88 (t, 3 H,  $J=6.8$ , CH<sub>3</sub>), 1.42-1.18 (m, 16 H, 8 × CH<sub>2</sub>), 1.47 (m, 2 H, CH<sub>2</sub>), 1.71 (m, 2 H, CH<sub>2</sub>), 1.83 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.94 (m, 4 H, 2 × OCH<sub>2</sub>CH<sub>2</sub>), 4.06 (t, 2 H,  $J=6.6$ , OCH<sub>2</sub>), 4.12 (m, 4 H, 2 × OCH<sub>2</sub>), 6.97 (m, 6 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.19 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.53 (C<sub>q</sub>), 164.52 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.26 (C<sub>q</sub>), 164.03 (C<sub>q</sub>), 163.82 (C<sub>q</sub>), 163.58 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.39 (C<sub>q</sub>), 149.26 (C<sub>q</sub>), 149.24 (C<sub>q</sub>), 141.40 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.45 (2 × CH<sub>benz</sub>), 132.42 (2 × CH<sub>benz</sub>), 131.89 (2 × CH<sub>benz</sub>), 131.88 (2 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.82 (C<sub>q</sub>), 126.76 (C<sub>q</sub>), 125.93 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.13 (2 × CH<sub>benz</sub>), 121.20 (2 × CH<sub>naph</sub>), 121.15 (C<sub>q</sub>), 120.89 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.41 (2 × CH<sub>benz</sub>), 114.36 (4 × CH<sub>benz</sub>), 68.54 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 67.96 (OCH<sub>2</sub>), 31.91 (CH<sub>2</sub>), 29.66-29.35 (6 × CH<sub>2</sub>), 29.08 (CH<sub>2</sub>), 28.80 (CH<sub>2</sub>), 28.74 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 22.66 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>61</sub>H<sub>61</sub>NO<sub>13</sub> (1016.17): calculated/found: C 72.10/71.97, H 6.05/6.07, N 1.38/1.30%.

**7-(4-{4-[7-(4-Nitrophenyloxy)hexyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-6).** Yield 77%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H,  $J=6.8$ , CH<sub>3</sub>), 1.19-1.42 (m, 16 H, 8 × CH<sub>2</sub>), 1.48 (m, 2 H, CH<sub>2</sub>), 1.59 (m, 4 H, CH<sub>2</sub>), 1.85 (m, 6 H, 3 × OCH<sub>2</sub>CH<sub>2</sub>), 4.07 (m, 6 H, 3 × OCH<sub>2</sub>), 6.99 (m, 6 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.19 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.54 (C<sub>q</sub>), 164.52 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.28 (C<sub>q</sub>), 164.10 (C<sub>q</sub>), 163.81 (C<sub>q</sub>), 163.66 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.40 (C<sub>q</sub>), 149.24 (C<sub>q</sub>), 149.26 (C<sub>q</sub>), 141.36 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.44 (2 × CH<sub>benz</sub>), 132.42 (2 × CH<sub>benz</sub>), 131.89 (2 × CH<sub>benz</sub>), 131.88 (2 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.82 (C<sub>q</sub>), 126.77 (C<sub>q</sub>), 125.92 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.13 (2 × CH<sub>benz</sub>), 121.22 (2 × CH<sub>naph</sub>), 121.08 (C<sub>q</sub>), 120.90 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.36 (4 × CH<sub>benz</sub>), 68.63 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 68.08 (OCH<sub>2</sub>), 31.91 (CH<sub>2</sub>), 29.65-29.35 (6 × CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 29.01 (CH<sub>2</sub>), 28.92 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 25.78 (CH<sub>2</sub>), 25.74 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>62</sub>H<sub>63</sub>NO<sub>13</sub> (1030.19): calculated/found: C 72.29/72.17, H 6.16/6.602, N 1.36/1.26%.

**7-(4-{4-[7-(4-Nitrophenyloxy)heptyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-7).** Yield 60%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.89 (t, 3 H,  $J=7.0$ , CH<sub>3</sub>), 1.28 (m, 18 H, 9 × CH<sub>2</sub>), 1.46 (m, 6 H, 3 × CH<sub>2</sub>), 1.83 (m, 6 H, 3 × CH<sub>2</sub>), 4.06 (m, 6 H, 3 × OCH<sub>2</sub>), 6.94 (d, 2 H,  $J=9.4$ ), 6.99 (d, 4 H,  $J=9.0$ ), 7.38 (dd, 2 H,  $J=8.8$ ,  $J=2.2$ ), 7.40 (d, 4 H,  $J=8.6$ ), 7.70 (d, 2 H,  $J=2.0$ ), 7.95 (d, 2 H,  $J=8.6$ ), 8.16 (d, 2 H,  $J=8.8$ ), 8.17 (d, 2 H,  $J=8.8$ ), 8.20 (d, 2 H,  $J=9.4$ ), 8.33 (d, 4 H,  $J=8.6$ ). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): 164.5 (2 × C), 164.3 (2 × C), 164.1 (C), 163.8 (C), 163.7 (C), 155.5 (C), 155.4 (C), 149.3 (3 × C), 144.4 (6 × CH), 134.4 (C), 132.4 (4 × CH), 131.9 (4 × CH), 129.6 (C), 129.4 (2 × CH), 126.8 (2 × C), 125.8 (2 × CH), 122.1 (4 × CH), 121.2 (2 × CH), 121.1 (C), 120.9 (C), 118.6 (2 × CH), 68.7 (CH<sub>2</sub>), 68.4 (CH<sub>2</sub>), 68.2 (CH<sub>2</sub>), 31.9 (CH<sub>2</sub>), 29.7-28.9 (10 × CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 25.9 (2 × CH<sub>2</sub>), 22.7 (CH<sub>2</sub>), 14.1 (CH<sub>3</sub>). Elemental analysis: for C<sub>63</sub>H<sub>65</sub>NO<sub>13</sub> (1044.22): calculated/found: C 72.47/72.33, H 6.27/6.11, N 1.34/1.27%.

**7-(4-{4-[7-(4-Nitrophenyloxy)octyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-8).** Yield 66%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H,  $J=6.8$ , CH<sub>3</sub>), 1.22-1.55 (m, 26 H, 13 × CH<sub>2</sub>), 1.86 (m, 6 H, 3 × OCH<sub>2</sub>CH<sub>2</sub>), 4.06 (m, 6 H, 3 × OCH<sub>2</sub>), 6.94 (d, 2 H,  $J=9.3$ , H-Ar), 6.99 (m, 4 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.19 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.54 (C<sub>q</sub>), 164.52 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.30 (C<sub>q</sub>), 164.17 (C<sub>q</sub>), 163.81 (C<sub>q</sub>), 163.74 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.42 (C<sub>q</sub>), 149.26 (C<sub>q</sub>), 149.25 (C<sub>q</sub>), 141.31 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.43 (2 × CH<sub>benz</sub>), 132.42 (2 × CH<sub>benz</sub>), 131.88 (4 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44

(2 × CH<sub>naph</sub>), 126.80 (C<sub>q</sub>), 126.77 (C<sub>q</sub>), 125.91 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.14 (2 × CH<sub>benz</sub>), 121.21 (2 × CH<sub>naph</sub>), 120.99, 120.90, 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.38 (2 × CH<sub>benz</sub>), 114.36 (2 × CH<sub>benz</sub>), 68.79 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 68.26 (OCH<sub>2</sub>), 31.91 (CH<sub>2</sub>), 29.65-29.35 (6 × CH<sub>2</sub>), 29.25 (CH<sub>2</sub>), 29.23 (CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 29.06 (CH<sub>2</sub>), 28.95 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 25.93 (CH<sub>2</sub>), 25.87 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>64</sub>H<sub>67</sub>NO<sub>13</sub> (1058.25): calculated/found: C 72.64/72.50, H 6.38/6.30, N 1.32/1.24%.

**7-(4-{4-[7-(4-Nitrophenyloxy)nonyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-9).** Yield 78%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H, *J*=6.8, CH<sub>3</sub>), 1.22-1.43 (m, 22 H, 11 × CH<sub>2</sub>), 1.46 (m, 6 H, CH<sub>2</sub>), 1.83 (m, 6 H, 3 × OCH<sub>2</sub>CH<sub>2</sub>), 4.05 (m, 6 H, 3 × OCH<sub>2</sub>), 6.94 (d, 2 H, *J*=9.3, H-Ar), 6.99 (m, 4 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.19 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.54 (C<sub>q</sub>), 164.53 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.31 (C<sub>q</sub>), 164.19 (C<sub>q</sub>), 163.81 (C<sub>q</sub>), 163.76 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.42 (C<sub>q</sub>), 149.25 (2 × C<sub>q</sub>), 141.29 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.42 (4 × CH<sub>benz</sub>), 131.88 (4 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.80 (C<sub>q</sub>), 126.77 (C<sub>q</sub>), 125.91 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.14 (2 × CH<sub>benz</sub>), 121.21 (2 × CH<sub>naph</sub>), 120.97 (C<sub>q</sub>), 120.90 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.38 (2 × CH<sub>benz</sub>), 114.36 (2 × CH<sub>benz</sub>), 68.82 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 68.30 (OCH<sub>2</sub>), 31.91 (CH<sub>2</sub>), 29.66-29.24 (11 × CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 28.96 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 25.91 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>65</sub>H<sub>69</sub>NO<sub>13</sub> (1072.27): calculated/found: C 72.81/72.72, H 6.49/6.44, N 1.31/1.21%.

**7-(4-{4-[7-(4-Nitrophenyloxy)decyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-10).** Yield 66%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H, *J*=6.8, CH<sub>3</sub>), 1.21-1.43 (m, 24 H, 12 × CH<sub>2</sub>), 1.47 (m, 6 H, CH<sub>2</sub>), 1.82 (m, 6 H, 3 × OCH<sub>2</sub>CH<sub>2</sub>), 4.05 (m, 6 H, 3 × OCH<sub>2</sub>), 6.94 (d, 2 H, *J*=9.3, H-Ar), 6.99 (m, 4 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.19 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.54 (C<sub>q</sub>), 164.53 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.31 (C<sub>q</sub>), 164.20 (C<sub>q</sub>), 163.81 (C<sub>q</sub>), 163.77 (C<sub>q</sub>), 155.44 (C<sub>q</sub>), 155.42 (C<sub>q</sub>), 149.25 (2 × C<sub>q</sub>), 141.29 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.42 (4 × CH<sub>benz</sub>), 131.88 (4 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.80 (C<sub>q</sub>), 126.77 (C<sub>q</sub>), 125.91 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.14 (2 × CH<sub>benz</sub>), 121.21 (2 × CH<sub>naph</sub>), 120.96 (C<sub>q</sub>), 120.90 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.39 (2 × CH<sub>benz</sub>), 114.36 (2 × CH<sub>benz</sub>), 68.84 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 68.33 (OCH<sub>2</sub>), 31.91 (CH<sub>2</sub>), 29.65-29.29 (12 × CH<sub>2</sub>), 29.07 (CH<sub>2</sub>), 28.96 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 25.91 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>66</sub>H<sub>71</sub>NO<sub>13</sub> (1086.30): calculated/found: C 72.98/72.90, H 6.59/6.49, N 1.29/1.23%.

**7-(4-{4-[7-(4-Nitrophenyloxy)undecyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-11).** Yield 78%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H, *J*=6.8 Hz, CH<sub>3</sub>), 1.23-1.42 (m, 26 H, 13 × CH<sub>2</sub>), 1.46 (m, 6 H, CH<sub>2</sub>), 1.82 (m, 6 H, 3 × OCH<sub>2</sub>CH<sub>2</sub>), 4.05 (m, 6 H, 3 × OCH<sub>2</sub>), 6.94 (d, 2 H, *J*=9.3, H-Ar), 6.99 (m, 4 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.19 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.54 (C<sub>q</sub>), 164.53 (C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.31 (C<sub>q</sub>), 164.20 (C<sub>q</sub>), 163.81 (C<sub>q</sub>), 163.78 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.42 (C<sub>q</sub>), 149.25 (2 × C<sub>q</sub>), 141.28 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.42 (4 × CH<sub>benz</sub>), 131.88 (4 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.79 (C<sub>q</sub>), 126.77 (C<sub>q</sub>), 125.90 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.14 (2 × CH<sub>benz</sub>), 121.21 (2 × CH<sub>naph</sub>), 120.95 (C<sub>q</sub>), 120.90 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.39 (2 × CH<sub>benz</sub>), 114.36 (2 × CH<sub>benz</sub>), 68.86 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 68.35 (OCH<sub>2</sub>), 31.92 (CH<sub>2</sub>), 29.66-29.30 (13 × CH<sub>2</sub>), 29.08 (CH<sub>2</sub>), 28.96 (CH<sub>2</sub>), 25.97 (CH<sub>2</sub>), 25.91 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13

(CH<sub>3</sub>). Elemental analysis: for C<sub>67</sub>H<sub>73</sub>NO<sub>13</sub> (1100.33): calculated/found: C 73.14/73.03, H 6.69/6.58, N 1.27/1.18%.

**7-(4-{4-[7-(4-Nitrophenyloxy)dodecyloxy]}benzoyloxy)benzoyloxynaphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (I-12).** Yield 65%. <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>): 0.88 (t, 3 H, *J*=6.8 Hz, CH<sub>3</sub>), 1.22-1.42 (m, 28 H, 14 × CH<sub>2</sub>), 1.47 (m, 6 H, CH<sub>2</sub>), 1.82 (m, 6 H, 3 × OCH<sub>2</sub>CH<sub>2</sub>), 4.05 (m, 6 H, 3 × OCH<sub>2</sub>), 6.94 (d, 2 H, *J*=9.3, H-Ar), 6.99 (m, 4 H, H-Ar), 7.39 (m, 6 H, H-Ar), 7.70 (m, 2 H, H-Ar), 7.95 (m, 2 H, H-Ar), 8.18 (m, 6 H, H-Ar), 8.33 (m, 4 H, H-Ar). <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>): 164.53 (2 × C<sub>q</sub>), 164.33 (C<sub>q</sub>), 164.31 (C<sub>q</sub>), 164.21 (C<sub>q</sub>), 163.81 (C<sub>q</sub>), 163.78 (C<sub>q</sub>), 155.45 (C<sub>q</sub>), 155.43 (C<sub>q</sub>), 149.25 (2 × C<sub>q</sub>), 141.27 (C<sub>q</sub>), 134.39 (C<sub>q</sub>), 132.42 (4 × CH<sub>benz</sub>), 131.88 (4 × CH<sub>benz</sub>), 129.61 (C<sub>q</sub>), 129.44 (2 × CH<sub>naph</sub>), 126.79 (C<sub>q</sub>), 126.77 (C<sub>q</sub>), 125.90 (2 × CH<sub>benz</sub>), 122.15 (2 × CH<sub>benz</sub>), 122.14 (2 × CH<sub>benz</sub>), 121.21 (2 × CH<sub>naph</sub>), 120.94 (C<sub>q</sub>), 120.90 (C<sub>q</sub>), 118.60 (2 × CH<sub>naph</sub>), 114.40 (2 × CH<sub>benz</sub>), 114.39 (2 × CH<sub>benz</sub>), 114.36 (2 × CH<sub>benz</sub>), 68.86 (OCH<sub>2</sub>), 68.38 (OCH<sub>2</sub>), 68.36 (OCH<sub>2</sub>), 31.92 (CH<sub>2</sub>), 29.66-29.31 (14 × CH<sub>2</sub>), 29.08 (CH<sub>2</sub>), 28.96 (CH<sub>2</sub>), 25.98 (CH<sub>2</sub>), 25.91 (CH<sub>2</sub>), 22.69 (CH<sub>2</sub>), 14.13 (CH<sub>3</sub>). Elemental analysis: for C<sub>68</sub>H<sub>75</sub>NO<sub>13</sub> (1114.35): calculated/found: C 73.29/73.17, H 6.78/6.72, N 1.26/1.19%.

The chiral dopant is purchased from Dachen with a label S5011. The concentration of chiral dopant was less than 1 %, which did not modify the phase transition temperatures and mesophases ranges.

## 2. Experimental methods and equipment

### 2.1. Differential scanning calorimetry (DSC)

For all synthesised compounds we performed differential scanning calorimetry (DSC), for which Perkin-Elmer calorimeter was used. Samples of 2-5 mg were hermetically sealed in aluminium pans, put into the calorimeter chamber, and subjected to the nitrogen atmosphere. Temperature and enthalpy changes were calibrated to the extrapolated onsets for water, indium, and zinc. We performed two heating-cooling runs at a rate of 5 K/min. The phases were identified from the textures observed under a polarizing optical microscope Nikon Eclipse. The glass cells were prepared from the glasses with ITO transparent electrodes and were filled with studied compounds in the isotropic (Iso) phase by capillary action. The Linkam heating/cooling stages with temperature stabilization ±0.1 K were utilized.

### 2.2. Polarized light microscopy and birefringence measurement

Optical textures were observed using a polarized-light microscope, Zeiss AxioImager A2m, equipped with a Linkam heating stage. Commercially available cells (provided by Warsaw Military University of Technology, WAT), with 1.5 – 10 μm thickness, and polymer aligning layers for planar (HG cells) or homeotropic anchoring (HT cells) were used. The temperature dependence of optical birefringence was measured for planarly aligned cells, using a photoelastic modulator (PEM-90, Hinds) based setup; a halogen lamp (Hamamatsu LC8) equipped with a narrow bandpass filter (633 nm) was used as a light source. Intensity of the transmitted light was registered with a photodiode (FLC Electronics PIN-20) and deconvoluted

with a lock-in amplifier (EG&G 7265) into 1f and 2f components (where  $f=50\text{kHz}$  is a working frequency of the photoelastic modulator), which allowed us to determine a retardation induced by the sample. Knowing the sample thickness, the retardation was recalculated into the optical birefringence. Additionally, optical birefringence and the orientation of the optical axis was also determined in microdomains (of order of few microns) using CRI Abrio system utilizing LC compensator, attached to the microscope.

### 2.3. X-ray diffraction

The temperature dependence of the smectic layer thickness was determined from small angle X-ray diffraction (SAXRD) experiments, performed with a Bruker D8 Discover system (CuK $\alpha$  radiation, Goebel mirror monochromator, scintillation counter) working in the reflection mode. Samples were prepared in a form of thin film on silicon waver, their temperature was controlled using Anton Paar DCS350 heating stage, with precision of  $\pm 0.1$  K. Wide angle diffractograms (WAXRD) were collected with a Bruker D8 GADDS system (CuK $\alpha$  radiation, Goebel mirror monochromator, point beam collimator, VANTEC2000 area detector). Samples were prepared as droplets on a heated surface and their temperature was stabilized with modified Linkam heating stage during the measurements.

High-resolution small angle XRD patterns were also recorded for the selected homologue using synchrotron radiation source at Advanced Light Source, LBNL, USA. Experiments were carried out on the SAXS beamline (7.3.3) at the energy of the incident beam 10 keV, the XRD patterns were collected using the Pilatus 2M detector, placed at the distance 2575 mm from the sample. The resonant soft x-ray scattering (RSOXS) experiments were also carried out at ALS facilities, on the beamline 11.0.1.2. The energy of the incident beam was tuned to the K-edge absorption band of carbon (283 eV). Samples with the thickness lower than 1  $\mu\text{m}$  were prepared on SiN membranes. The scattered intensity was recorded using the Princeton PI-MTE CCD detector.

### 2.4. Dielectric spectroscopy

An impedance analyser Schlumberger 1260 was utilized to measure the frequency dispersion of the complex permittivity,  $\epsilon^*$ . The frequency sweeps in a frequency range of 1 Hz  $\div$  1 MHz were detected at a temperature stabilized within  $\pm 0.1$  K. The data were analysed by the Cole-Cole formula, which was modified to eliminate the low frequency contribution from d.c. conductivity,  $\sigma$ , and the high frequency contribution due to the resistance of the ITO electrodes, respectively:

$$\epsilon^* - \epsilon_\infty = \frac{\Delta\epsilon}{1 + (jf / f_r)^{(1-\alpha)}} - i\left(\frac{\sigma}{2\pi\epsilon_0 f^n} + Af^m\right) \quad (1),$$

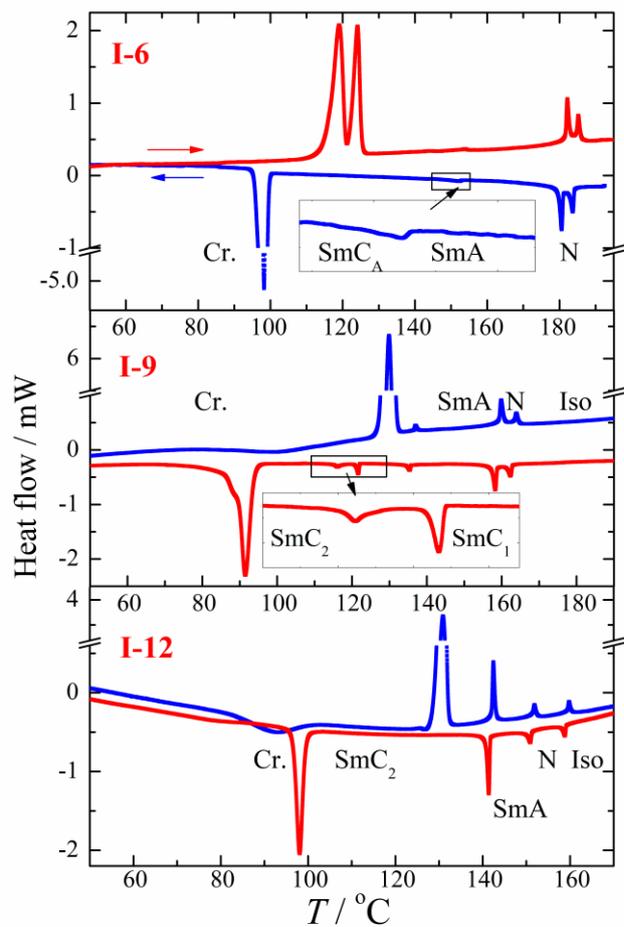
where  $f_r$  is the relaxation frequency,  $\Delta\epsilon$  is the dielectric strength,  $\alpha$  is the distribution parameter of relaxation,  $\epsilon_0$  is the permittivity of vacuum,  $\epsilon_\infty$  is the high frequency permittivity and  $n$ ,  $m$ ,  $A$  are the fitting parameters. We fitted the measured values of the real,  $\epsilon'$ , and imaginary,  $\epsilon''$ , parts of permittivity  $\epsilon^*(f) = \epsilon' - i\epsilon''$  simultaneously to formula (1) to obtain information about  $f_r$  and  $\Delta\epsilon$ .

### 3. Mesomorphic properties

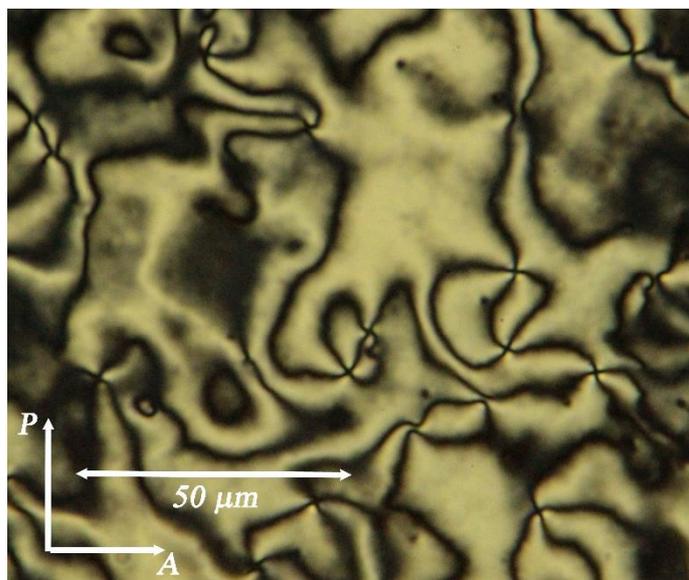
We synthesised a homologue series with rigid naphthalene-based molecular core prolonged in one arm via a flexible alkoxy linker, which is terminated by the outer phenyl ring substituted in para position by a nitro group. We designated new homologues as **I-n** and *n* number varied from 4 to 12, describing the number of carbons in the flexible connecting linker. We studied all homologues by various experimental techniques. First, we established the phase transition temperatures based on the observations under a polarizing microscope (POM) and performed DSC measurements. The phase transition temperatures and corresponding enthalpy values are summarized in Table S1. The phase transitions were clearly distinguishable during DSC measurements and three DSC thermographs are shown in Figure S1. The only exception is the SmC<sub>1</sub>- SmC<sub>2</sub> phase transitions, which were detected based on the textural changes and birefringence measurements. We found that lengthening of the alkoxy chain (*n*= 4-12) in the flexible linker resulted in a gradual decrease of transition temperatures. With the exception for the materials with the shorter alkyl chains (**I-4** and **I-5**), all compounds exhibit a nematic phase below the isotropic fluid (Iso) during the cooling process. The richest mesomorphism is observed for **I-9**, for which the N-SmA phase sequence and several smectic phases have been detected on cooling the samples.

Table S1 DSC measurements results: the melting points, m.p., taken on the second heating, the phase transition temperatures,  $T_{tr}$ , and the crystallization temperature,  $T_{cr}$ , subsequently on the second cooling from the isotropic phase, are in °C, and corresponding enthalpy changes,  $\Delta H$ , are in kJ/mol, in brackets at the corresponding temperature. The symbol \* means that the temperature was established from x-ray measurements and a corresponding peak was not detectable from DSC data.

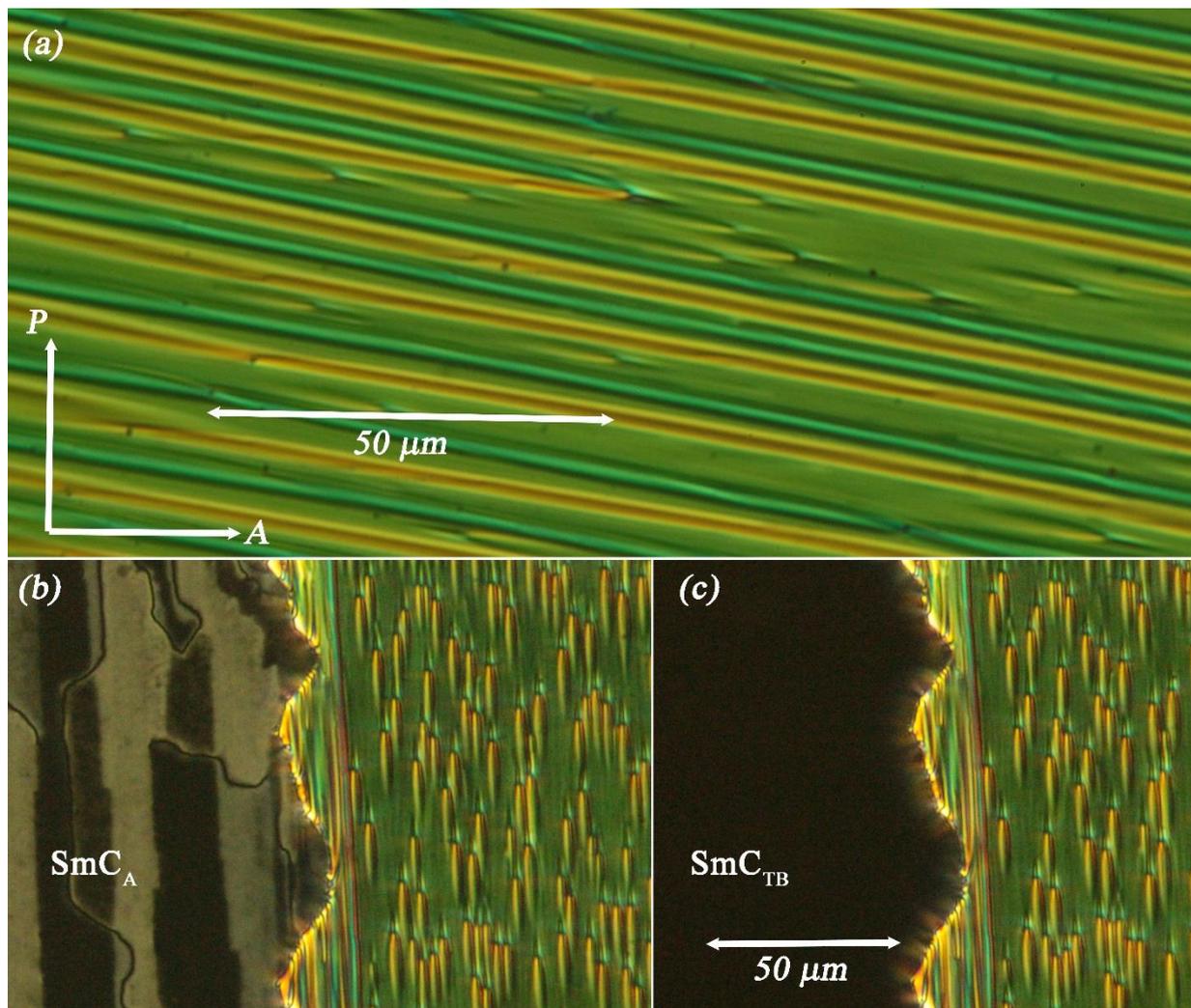
|             | m.p.<br>[ $\Delta H$ ] | $T_{cr}$<br>[ $\Delta H$ ] |                         | $T_{tr}$<br>[ $\Delta H$ ] |                        | $T_{tr}$<br>[ $\Delta H$ ] |            | $T_A$<br>[ $\Delta H$ ] |          | $T_{iso}$<br>[ $\Delta H$ ] |
|-------------|------------------------|----------------------------|-------------------------|----------------------------|-------------------------|----------------------------|-------------------------|----------------------------|-------------------------|----------------------------|------------------------|----------------------------|------------|-------------------------|----------|-----------------------------|
| <b>I-4</b>  | 148<br>[+30.5]         | 128<br>[-30.6]             | –                       | –                          | –                       | –                          |                         |                            | <b>SmC<sub>A</sub></b>  | 164<br>[-0.89]             | –                      | –                          | <b>SmA</b> | 198<br>[-2.7]           | –        | –                           |
| <b>I-5</b>  | 130<br>[+20.0]         | 102<br>[-27.1]             | –                       | –                          | –                       | –                          |                         |                            | <b>SmC<sub>A</sub></b>  | 156<br>[-0.60]             | –                      | –                          | <b>SmA</b> | 167<br>[-2.5]           | –        | –                           |
| <b>I-6</b>  | 121<br>[+22.5]         | 98<br>[-21.1]              | –                       | –                          | –                       | –                          |                         |                            | <b>SmC<sub>A</sub></b>  | 153<br>[-0.17]             | –                      | –                          | <b>SmA</b> | 181<br>[-0.79]          | <b>N</b> | 184<br>[-0.99]              |
| <b>I-7</b>  | 113<br>[+23.5]         | 88<br>[-18.9]              | <b>SmC<sub>TB</sub></b> | 132<br>[-0.03]             | –                       | –                          |                         |                            | <b>SmC<sub>A</sub></b>  | 146<br>[-0.04]             | –                      | –                          | <b>SmA</b> | 162<br>[-1.16]          | <b>N</b> | 165<br>[-0.31]              |
| <b>I-8</b>  | 130<br>[+54.7]         | 105<br>[-46.8]             | <b>SmC<sub>TB</sub></b> | 118<br>[-0.01]             | –                       | –                          |                         |                            | <b>SmC<sub>A</sub></b>  | 140<br>[-1.25]             | –                      | –                          | <b>SmA</b> | 168<br>[-0.50]          | <b>N</b> | 173<br>[-0.67]              |
| <b>I-9</b>  | 127<br>[+45.4]         | 93<br>[-19.5]              | <b>SmC<sub>2</sub></b>  | 116<br>[-0.14]             | <b>SmC<sub>2</sub>'</b> | 118<br>[*]                 | <b>SmC<sub>1</sub>'</b> | 122<br>[-0.35]             | <b>SmC<sub>1</sub>'</b> | 135<br>[-0.25]             | <b>SmC<sub>1</sub></b> | 136<br>[*]                 | <b>SmA</b> | 158<br>[-2.7]           | <b>N</b> | 162<br>[-0.51]              |
| <b>I-10</b> | 122<br>[+36.1]         | 100<br>[-25.9]             | <b>SmC<sub>2</sub></b>  | 123<br>[*]                 |                         |                            |                         |                            | <b>SmC<sub>1</sub></b>  | 131<br>[-0.51]             |                        |                            | <b>SmA</b> | 159<br>[-0.72]          | <b>N</b> | 166<br>[-0.36]              |
| <b>I-11</b> | 131<br>[+27.1]         | 109<br>[-21.7]             | <b>SmC<sub>2</sub></b>  | 142<br>[*]                 |                         |                            | –                       | –                          | <b>SmC<sub>1</sub></b>  | 143<br>[-2.63]             | –                      | –                          | <b>SmA</b> | 153<br>[-1.46]          | <b>N</b> | 158<br>[-0.63]              |
| <b>I-12</b> | 129<br>[+35.2]         | 98<br>[-31.7]              | <b>SmC<sub>2</sub></b>  | 142<br>[-3.01]             | –                       | –                          | –                       | –                          |                         |                            | –                      | –                          | <b>SmA</b> | 151<br>[-0.55]          | <b>N</b> | 159<br>[-1.08]              |



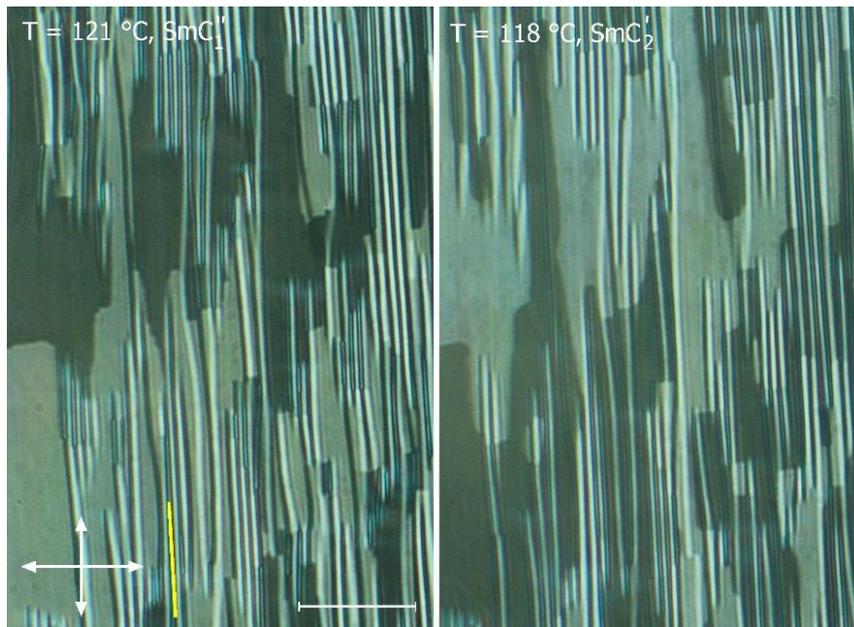
**Figure S1.** DSC thermographs for homologues a) I-6, b) I-9 and c) I-12.



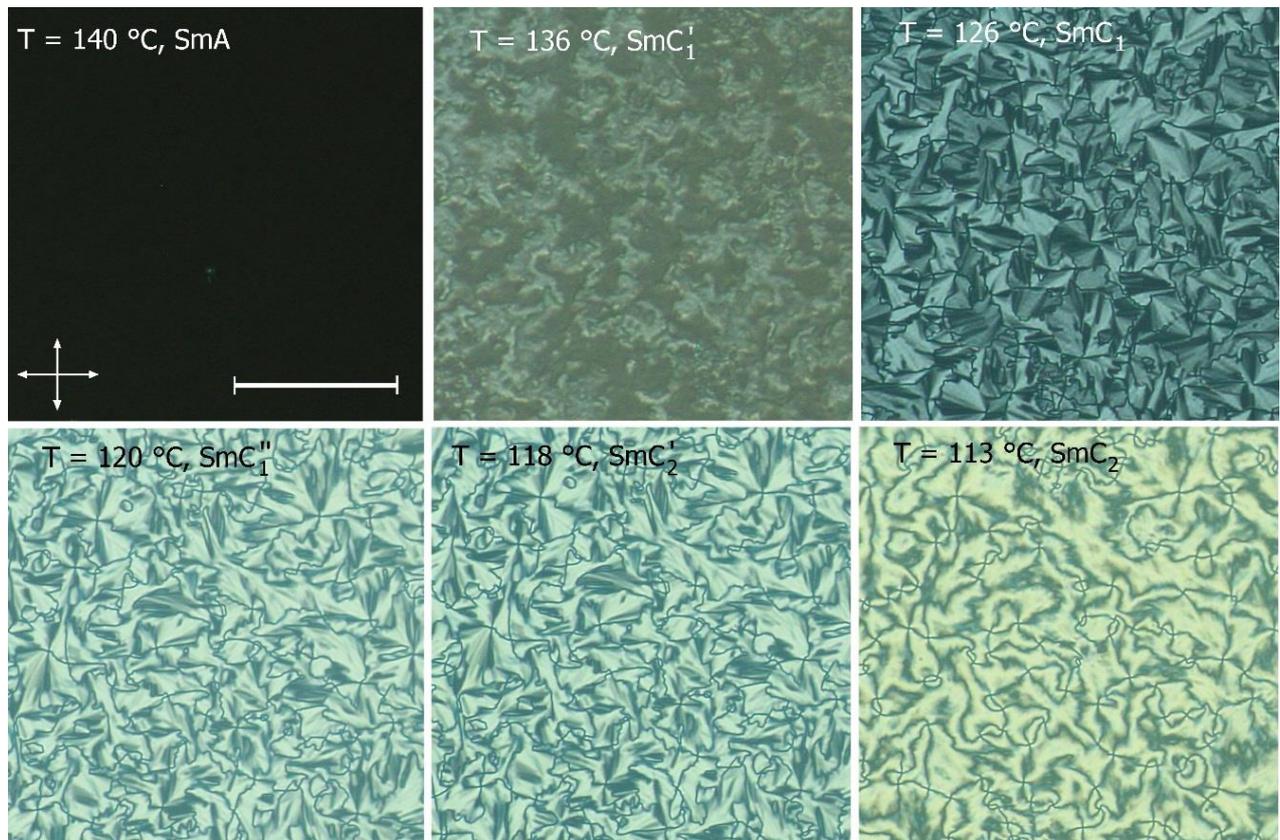
**Figure S2.** Texture for I-6 in the  $\text{SmC}_A$  phase in a 5- $\mu\text{m}$  HT cell.



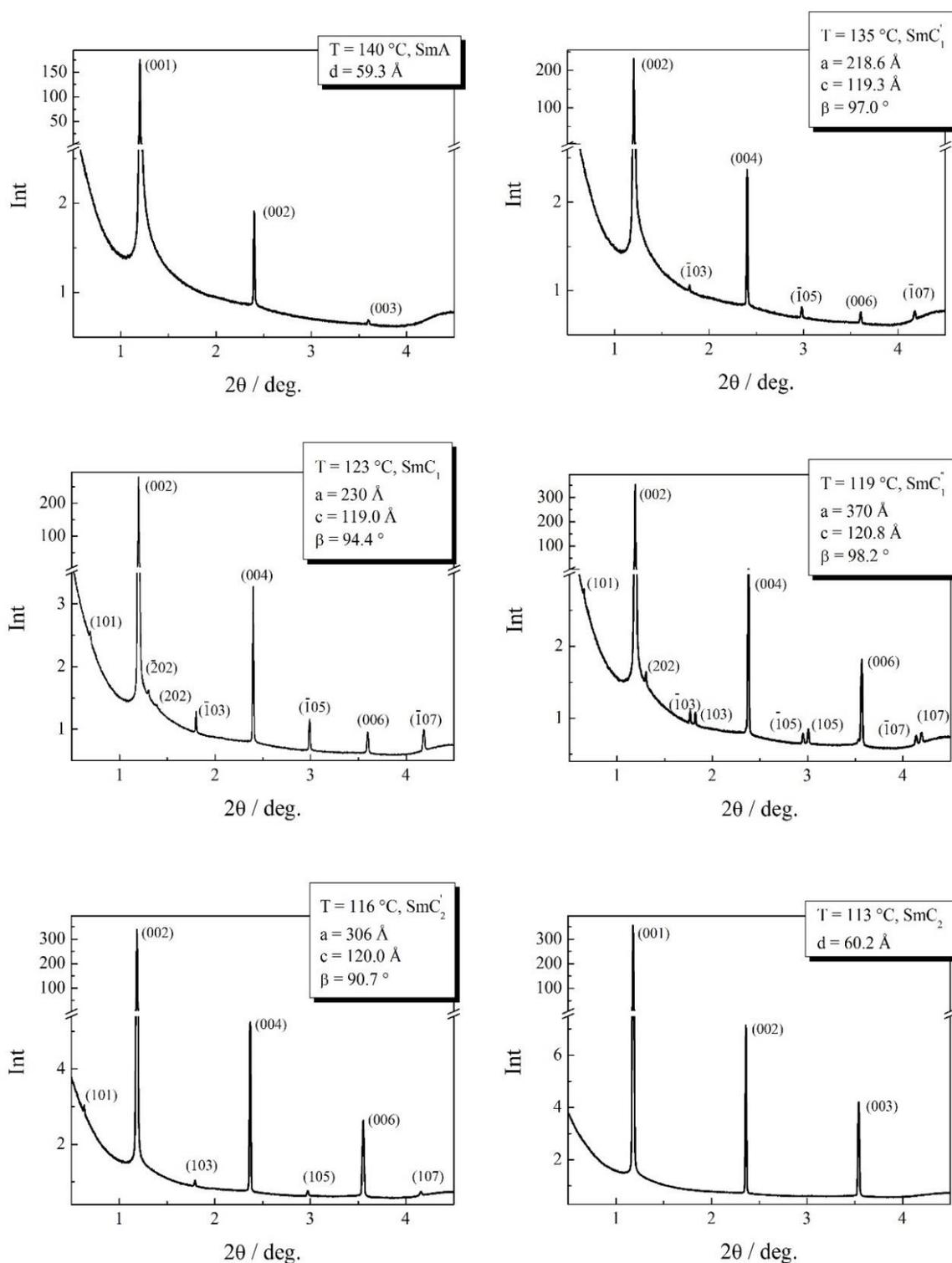
**Figure S3.** Polarised microscopy textures for **I-8** in a 5- $\mu\text{m}$  HG cell: (a) in the SmA phase, (b) in the SmC<sub>A</sub> and (c) SmC<sub>TB</sub> phase at a boarder with no alignment layer (right part of the figures) that corresponds to a homeotropic alignment.



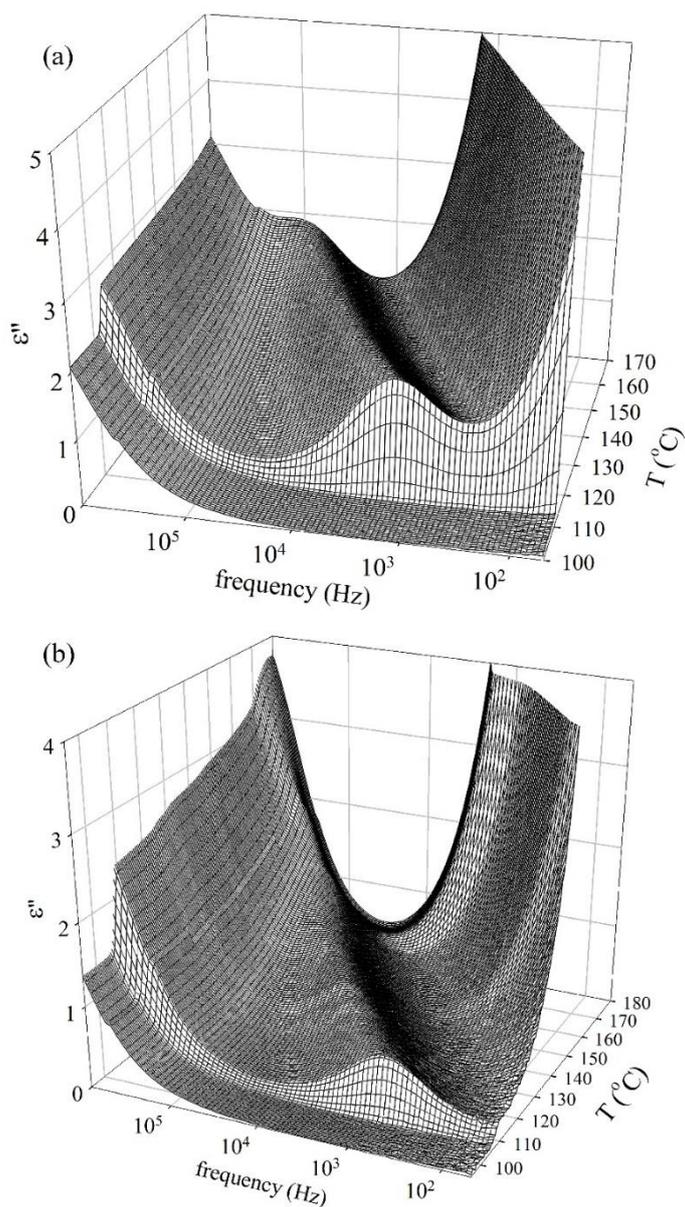
**Figure S4.** Optical textures observed for the homologue **I-9** in a 1.5- $\mu\text{m}$ -thick cell with planar anchoring, showing the inversion of the apparent tilt direction in tilted domains, which accompanies the transition between the  $\text{SmC}_1$  and  $\text{SmC}_2$  phases. The arrows mark the orientation of the crossed polarizers, a yellow line presents the rubbing direction being slightly inclined from polarizer direction, a scale bar corresponds to 100  $\mu\text{m}$ .



**Figure S5.** Optical textures observed in a 10- $\mu\text{m}$ -thick cell with homeotropic anchoring in the consecutive smectic phases formed by the homologue **I-9**. Arrows mark the orientation of the crossed polarizers, a scale bar corresponds to 100  $\mu\text{m}$ .



**Figure S6.** Small angle X-ray diffractograms recorded in the smectic phases formed by **I-9** compound. The signal intensity is given in arbitrary units. Note that only in the SmA and SmC<sub>2</sub> phases the structure is simple lamellar (as evidenced by all the signals being commensurate), in all other phases the structure is additionally modulated along the layers, resulting in 2D crystallographic lattices. Indexation of the diffraction signals was done assuming oblique unit cells, with parameters given on each panel.



**Figure S7.** 3-Dimensional graph of the imaginary part of permittivity versus temperature and frequency for homologues (a) **I-5** and (a) **I-9**. Dielectric spectroscopy has been performed in 5- $\mu\text{m}$  HT cell.

### References

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