

## Novel bent-shaped liquid crystals with a thiophene ring in the outer position

Václav Kozmík<sup>1</sup>, Petr Polášek<sup>1</sup>, Arnošt Seidler<sup>1</sup>, Michal Kohout<sup>1</sup>, Jiří Svoboda\*<sup>1</sup>, Vladimíra Novotná<sup>2</sup>, Milada Glogarová<sup>2</sup>, Damian Pociecha<sup>3</sup>

<sup>1</sup>Department of Organic Chemistry, Institute of Chemical Technology, CZ-166 28 Prague 6, Czech Republic

<sup>2</sup>Institute of Physics, Academy of Science of the Czech Republic, Na Slovance 2, CZ-182 21 Prague 9, Czech Republic

<sup>3</sup>Laboratory of Dielectrics and Magnetics, Chemistry Department, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland

### General

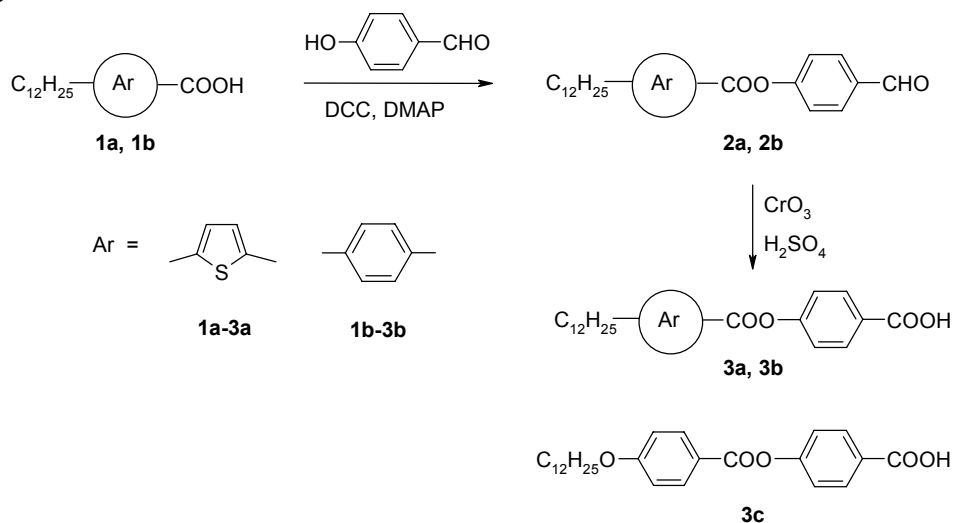
<sup>1</sup>H NMR spectra were recorded on Varian Gemini 300 HC instrument at 300 MHz. Deuteriochloroform was used as solvent and signals of the solvent served as internal standard, chemical shifts ( $\delta_{\text{H}}$ ) are given in ppm,  $J$  values are given in Hz).

Elemental analyses were carried out on a Perkin-Elmer 2400. Column chromatography was carried out using Merck Kieselgel 60 (60-100  $\mu\text{m}$ ). The purity of all final compounds were checked by HPLC analysis (Tessek C18 25x4.5 RP column) and were found >99.8%. The molecular structure and size was evaluated using HyperChem software.

X-ray studies were performed with D8-Discover Bruker system, CuK $\alpha$  radiation was used. The signal intensities were registered with linear Vantec detector.

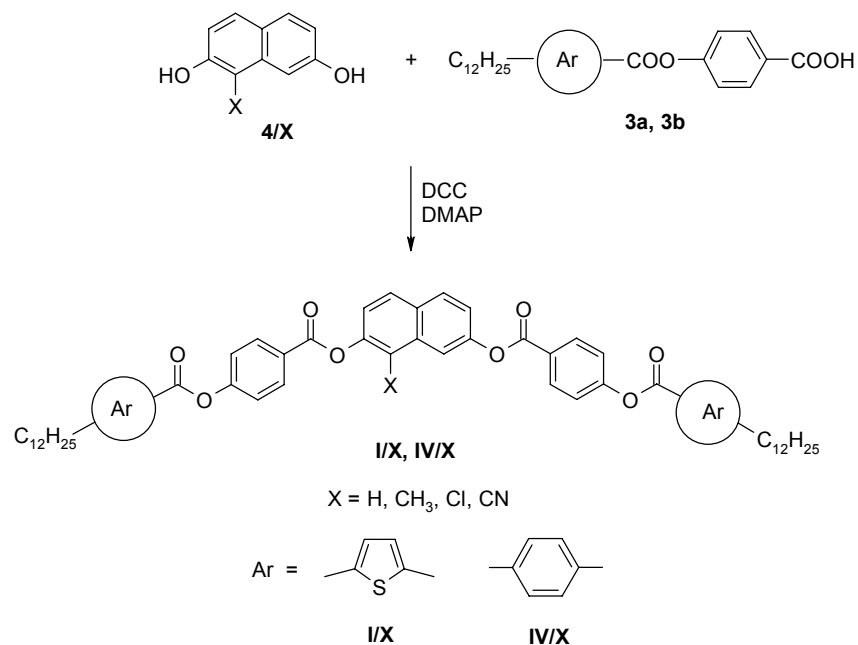
### Synthesis and characterization of intermediates 1-7 and target materials I-V

The 5-dodecylthiophene-2-carboxylic acid (**1a**) and 4-dodecylbenzoic acid (**1b**) were obtained by known methods.<sup>S1,S2</sup> Both acids were esterified with 4-hydroxybenzaldehyde in the presence of DCC and catalytic amount of DMAP (scheme 1) and the formed formyl ester **2a** and **2b** were oxidized with a solution of chromium(VI) oxide in diluted sulfuric acid (Jones reagent) to the acids **3a** and **3b**. Synthesis of the dodecyloxy substituted acid **3c** was described previously<sup>S3</sup>.



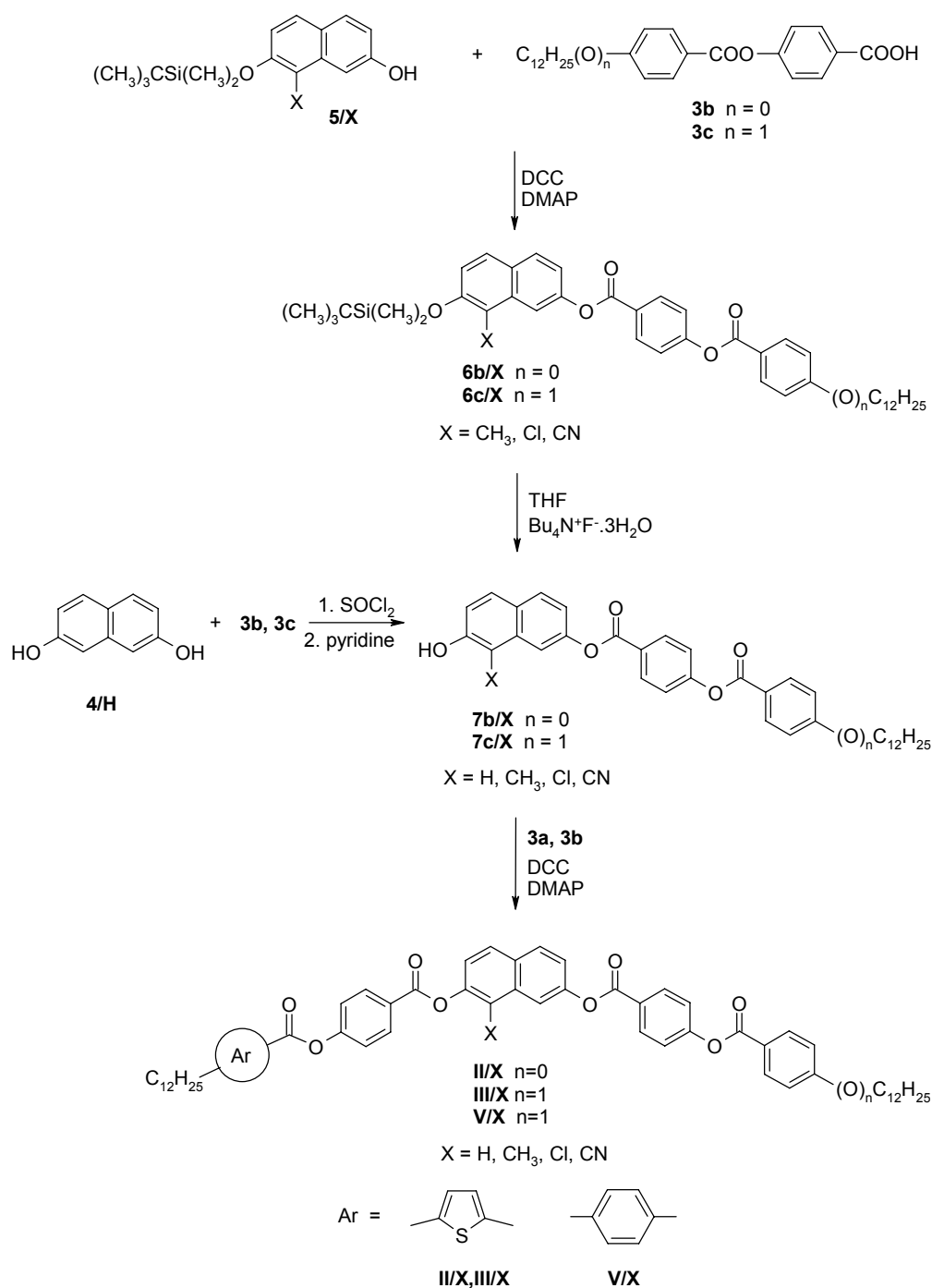
Scheme 1

Symmetrical materials **I** and **IV** with identical lengthening arms were obtained by acylation of the unprotected naphthalene-2,7-diol **4/X** ( $X = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}$ ) by a DCC mediated coupling<sup>S4</sup> with an excess of acid **3a** and **3b** ( $\text{Ar} = 2,5\text{-thienylene}, 1,4\text{-phenylene}$ ) (Scheme 2).



Scheme 2

Synthesis of the materials **II**, **III**, and **V** started with the *tert*-butyldimethylsilyl protected naphthalene-2,7-diol **5/X**<sup>S5,S6</sup> ( $X = \text{CH}_3, \text{Cl}, \text{CN}$ ), which was first coupled with the corresponding acid **3b**, **3c** in the presence of DCC and DMAP (Scheme 3). The protecting silyl group in the intermediate **6b/X**, **6c/X** ( $n=0,1$ ) was then removed by the means of tetrabutylammonium fluoride to form the hydroxy derivative **7b/X**, **7c/X** ( $X = \text{CH}_3, \text{Cl}, \text{CN}, n = 0,1$ ). The non-substituted hydroxy derivatives **7b/H** and **7c/H** (scheme 4) were obtained by a direct acylation of excessive naphthalene-2,7-diol (**4/H**) with chlorides of acids **3b** and **3c**. Finally, the second lengthening arms was introduced by a DCC mediated acylation of the formed hydroxy derivatives **7b/X**, **7c/X** ( $X = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}$ ) with acid **3a**, **3b**, resp.



Scheme 3

#### (4-Formylphenyl) 5-dodecylthiophene-2-carboxylate (**2a**)

To a mixture of acid **1a** (5.24 g; 17.7 mmol), 4-hydroxybenzaldehyde (2.27 g; 18.6 mmol) and DMAP (113 mg) in dry dichloromethane (150 ml), DCC (4.75 g; 23 mmol) was added and the mixture was stirred at room temperature in argon atmosphere for 12 h. The deposited solid was filtered and washed with dichloromethane (2x30 ml). The filtrate was evaporated and the residue crystallized from hexane. Yield: 5.27 g (74%) of **2a**, m.p. 47-48 °C.  $^1\text{H}$  NMR: 0.88 t (3 H,  $J=6.7$  Hz,  $\text{CH}_3$ ), 1.30 (m, 18 H,  $(\text{CH}_2)_9$ ); 1.72 m, 2 H,  $\text{CH}_2$ ), 2.88 (t, 2 H,  $J=7.7$  Hz,  $\text{CH}_2$ ), 6.89 (d, 1 H,  $J=3.8$  Hz), 7.40 (d, 2 H,  $J=8.8$  Hz), 7.82 (d, 1 H), 7.96 (d, 2 H),

10.00 (s, 1 H, CHO) ppm. Elemental analysis: for  $C_{24}H_{32}O_3S$  (400.58), calculated C 71.96, H 8.05; found C 71.87, H 7.99%.

By the same way, reaction of acid **1b** (6.3 g; 21.8 mmol) with 4-hydroxybenzaldehyde (2.88 g; 23.6 mmol) afforded after crystallization from hexane 7.3 g (85%) of aldehyde **2b**, m.p. 60-61 °C.  $^1H$  NMR: 0.88 (t, 3 H,  $J=6.7$  Hz,  $CH_3$ ), 1.40 (m, 18 H,  $(CH_2)_9$ ), 1.65 (m, 2 H,  $CH_2$ ), 2.70 (t, 2 H,  $J=7.6$  Hz,  $CH_2$ ), 7.32 (d, 2 H,  $J=8.2$  Hz), 7.40 (d, 2 H,  $J=8.5$  Hz), 7.96 (d, 2 H), 8.12 (d, 2 H), 10.05 (s, 1 H, CHO) ppm. Elemental analysis: for  $C_{26}H_{34}O_3$  (394.56), calculated C 79.15, H 8.69; found C 79.01, H 8.47%.

#### 4-(5-Dodecylthiophene-2-carbonyloxy)benzoic acid (**3a**)

To a solution of **2a** (3.61 g; 9 mmol) in acetone (200 ml), the Jones reagent (9.0 ml) was added dropwise during 10 min. When the starting compound disappeared, the mixture was diluted with water (1000 ml) and stirred for 30 min. The solid was filtered, washed with water and dried. Crystallization from ethyl acetate yielded 3.69 g (98 %) of acid **3a**, m.p. 149-151 °C.  $^1H$  NMR: 0.86 (t, 3 H,  $J=6.6$  Hz,  $CH_3$ ), 1.26 (m, 18 H,  $(CH_2)_9$ ), 1.70 (m, 2 H,  $CH_2$ ), 2.86 (t, 2 H,  $J=7.7$  Hz,  $CH_2$ ), 6.88 (d, 1 H,  $J=3.8$  Hz), 7.34 (d, 2 H,  $J=8.8$  Hz), 7.83 (d, 1 H), 8.17 (d, 2 H) ppm. Elemental analysis: for  $C_{24}H_{32}O_4S$  (416.58), calculated C 69.20, H 7.74; found C 69.14, H 7.69%.

In the same way, aldehyde **2b** (5.6 g; 14.2 mmol) was oxidized to yield 5.33 g (91 %) of acid **3b**, m.p. 142-222 °C (ethyl acetate).  $^1H$  NMR: 1.88 (t, 3 H,  $J=6.6$  Hz,  $CH_3$ ), 1.26 (m, 18 H,  $(CH_2)_9$ ), 1.64 (m, 2 H,  $CH_2$ ), 2.70 (t, 2 H,  $J=7.6$  Hz,  $CH_2$ ), 7.32 (d, 2 H), 7.35 (d, 2 H), 8.12 (d, 2 H,  $J=8.5$  Hz), 8.18 (d, 2 H). Elemental analysis: for  $C_{26}H_{34}O_4$  (410.56), calculated C 76.06, H 8.35; found C 75.81, H 8.44%.

#### Naphthalene-2,7-diyl bis(4-(5-dodecylthiophene-2-carbonyloxy)benzoate) (**I/H**)

A mixture of acid **3a** (651 mg; 1.56 mmol), naphthalene-2,7-diol (**4/H**) (125 mg; 0.78 mmol), DMAP (15 mg), and DCC (402 mg; 1.95 mmol) in dry dichloromethane (50 ml) was stirred at room temperature in argon atmosphere for 24 h, filtered and the solid washed with dichloromethane (2x10 ml). The filtrate was evaporated and the crude product purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether 12/1) and crystallized from an acetone/ethyl acetate mixture. Yield 0.50 g (67 %) of **I/H**.  $^1H$  NMR: 0.88 (t, 6 H,  $J=6.7$  Hz,  $2 \times CH_3$ ), 1.30 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.74 (m, 4 H,  $2 \times CH_2$ ), 2.88 (t, 4 H,  $J=7.6$  Hz,  $2 \times CH_2$ ), 6.88 (d, 2 H,  $J=3.9$  Hz), 7.38 (m, 6 H), 7.70 (d, 2 H,  $J=2.2$  Hz), 7.86 (d, 2 H), 7.95 (d, 2 H,  $J=9.0$  Hz), 8.32 (d, 4 H,  $J=8.8$  Hz) ppm. Elemental analysis: for  $C_{58}H_{68}O_8S_2$  (957.31), calculated C 72.77, H 7.16; found C 72.62, H 7.01%.

Following materials were obtained in the same way:

**(1-Methylnaphthalene-2,7-diyl) bis(4-(5-dodecylthiophene-2-carbonyloxy)benzoate) (I/CH<sub>3</sub>)**.  $^1H$  NMR: 0.88 (t, 6 H,  $J=6.7$  Hz,  $2 \times CH_3$ ), 1.30 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.74 (m, 4 H,  $2 \times CH_2$ ), 2.54 (s, 3 H,  $CH_3$ ), 2.88 (t, 4 H,  $J=7.6$  Hz,  $2 \times CH_2$ ), 6.89 (d, 2 H,  $J=3.5$  Hz), 7.31 (d, 1 H,  $J=8.8$  Hz), 7.40 (m, 5 H), 7.81 (d, 1 H,  $J=9.0$  Hz), 7.86 (m, 3 H), 7.5 (d, 1 H,  $J=8.8$  Hz), 8.34 (m, 4 H) ppm. Elemental analysis: for  $C_{59}H_{70}O_8S_2$  (971.34), calculated C 72.96, H 7.26; found C 72.88, H 7.20%.

**(1-Chloronaphthalen-2,7-diyl) bis(4-(5-dodecylthiophene-2-carbonyloxy)benzoate) (I/Cl)**.  $^1H$  NMR: 0.88 (t, 6 H,  $J=6.7$  Hz,  $2 \times CH_3$ ), 1.30 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.74 (m, 4 H,  $2 \times CH_2$ ), 2.88 (t, 4 H,  $J=7.6$  Hz,  $2 \times CH_2$ ), 6.89 (d, 2 H,  $J=3.8$  Hz), 7.44 (m, 6 H), 7.86 (dd, 2 H,  $^3J=9.0$  Hz,  $^4J=2.3$  Hz), 7.88 (d, 1 H,  $J=9.0$  Hz), 7.98 (d, 1 H), 8.14 (d, 1 H,  $^4J=2.3$  Hz), 8.35 (m, 4 H) ppm. Elemental analysis: for  $C_{58}H_{67}ClO_8S_2$  (991.76), calculated C 70.24, H 6.81; found C 70.11, H 6.79%.

**(1-Cyanonaphthalene-2,7-diyl) bis(4-(5-dodecylthiophene-2-carbonyloxy)benzoate) (I/CN)**.  $^1H$  NMR: 0.88 (t, 6 H,  $J=6.6$  Hz,  $2 \times CH_3$ ), 1.30 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.74 (m, 4 H,

2 × CH<sub>2</sub>), 2.88 (t, 4 H, *J*=7.6 Hz, 2 × CH<sub>2</sub>), 6.89 (d, 2 H *J*=3.8 Hz), 7.43 (m, 4 H), 7.56 (dd, 1 H, *J*=2.3 Hz), 7.60 (d, 1 H, *J*=8.8 Hz), 7.86 (d, 2 H), 8.04 (d, 1 H, *J*=9.1 Hz), 8.08 (d, 1 H, *J*=2.3 Hz), 8.18 (d, 1 H, *J*=9.1), 8.33 (d, 2 H), 8.37 (d, 2 H) ppm. Elemental analysis: for C<sub>59</sub>H<sub>67</sub>NO<sub>8</sub>S<sub>2</sub> (982.32), calculated C 72.14, H 6.87, N 1.43; found C 72.07, H 6.75, N 1.29%.

**Naphthalene-2,7-diyl bis(4-(4-dodecylbenzoyloxy)benzoate (IV/H).** <sup>1</sup>H NMR: 0.88 (t, 6 H, *J*=6.6 Hz, 2 × CH<sub>3</sub>), 1.30 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.64 (m, 4 H, 2 × CH<sub>2</sub>), 2.88 (t, 4 H, *J*=7.8 Hz, CH<sub>2</sub>), 7.36 (m, 10 H), 7.70 (d, 2 H, *J*=2.0 Hz), 7.95 (d, 2 H, *J*=8.8), 8.14 (d, 4 H, *J*=8.2 Hz), 8.34 (d, 4 H, *J*=8.5 Hz) ppm. Elemental analysis: for C<sub>62</sub>H<sub>72</sub>O<sub>8</sub> (945.26), calculated C 78.78, H 7.68; found C 78.66, H 7.54%.

**(1-Methylnaphthalene-2,7-diyl) bis(4-(4-dodecylbenzoyloxy)benzoate) (IV/CH<sub>3</sub>).** <sup>1</sup>H NMR: 0.88 (t, 6 H, *J*=6.6 Hz, 2 × CH<sub>3</sub>), 1.30 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.64 (m, 4 H, 2 × CH<sub>2</sub>), 2.53 (s, 3 H, CH<sub>3</sub>), 2.70 (t, 4 H, *J*=7.5 Hz, 2 × CH<sub>2</sub>), 7.30 (d, 1 H), 7.34 (d, 2 H, *J*=8.5 Hz), 7.42 (m, 3 H), 7.82 (d, 1 H, *J*=9.0 Hz), 7.86 (d, 1 H, *J*=2.0 Hz), 7.95 (d, 1 H, *J*=8.8 Hz), 8.14 (d, 2 H), 8.34 (d, 1 H), 8.37 (d, 1 H) ppm. Elemental analysis: for C<sub>63</sub>H<sub>74</sub>O<sub>8</sub> (959.29), calculated C 78.88, H 7.78; found C 78.74, H 7.69%.

**(1-Chloronaphthalene-2,7-diyl) bis(4-(4-dodecylbenzoyloxy)benzoate) (IV/Cl).** <sup>1</sup>H NMR: 0.88 (t, 6 H, *J*=6.6 Hz, 2 × CH<sub>3</sub>), 1.28 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.64 (m, 4 H, 2 × CH<sub>2</sub>), 2.70 (t, 4 H, *J*=7.5 Hz, 2 × CH<sub>2</sub>), 7.34 (d, 4 H, *J*=8.5 Hz), 7.45 (m, 6 H), 7.89 (d, 1 H, *J*=9.1 Hz), 7.98 (d, 1 H, *J*=9.1 Hz), 8.14 (m, 5 H), 8.36 (m, 4 H) ppm. Elemental analysis: for C<sub>62</sub>H<sub>71</sub>ClO<sub>8</sub> (979.71), calculated C 76.01, H 7.30; found C 75.94, H 7.15%.

**(1-Cyanonaphthalene-2,7-diyl) bis(4-(4-dodecylbenzoyloxy)benzoate) (IV/CN).** <sup>1</sup>H NMR: 0.88 (t, 6 H, *J*=6.6 Hz, 2 × CH<sub>3</sub>), 1.28 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.66 (m, 4 H, 2 × CH<sub>2</sub>), 2.70 (t, 4 H, *J*=7.5 Hz, 2 × CH<sub>2</sub>), 7.34 (d, 4 H, *J*=8.5 Hz), 7.42 (m, 4 H), 7.56 (dd, 1 H, <sup>3</sup>*J*=8.8 Hz, <sup>4</sup>*J*=2.3 Hz), 7.60 (d, 1 H, *J*=9.1 Hz), 8.05 (d, 1 H, *J*=9.1 Hz), 8.08 (d, 1 H, *J*=2.3 Hz), 8.14 (d, 4 H), 8.19 (d, 1 H, *J*=9.1 Hz), 8.34 (d, 2 H, *J*=8.2 Hz), 8.39 (d, 2 H, *J*=8.2 Hz) ppm. Elemental analysis: for C<sub>63</sub>H<sub>71</sub>NO<sub>8</sub> (970.27), calculated C 77.99, H 7.38, N 1.44; found C 77.79, H 7.41, N 1.34%.

#### **(7-(*tert*-Butyldimethylsilyloxy)-8-methylnaphthalen-2-yloxy) 4-(4-dodecylbenzoyloxy)-benzoate (6b/CH<sub>3</sub>)**

A mixture of acid **3b** (427 mg; 1.04 mmol), diol **5/CH<sub>3</sub>** (300 mg; 1.04 mmol), DMAP (15 mg), and DCC (389 mg; 1.9 mmol) in dry dichloromethane (50 ml) was stirred at room temperature in argon atmosphere for 24 h, filtered and the solid washed with dichloromethane (2×10 ml). The filtrate was evaporated and the crude product purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether 12/1). 398 mg (56 %) of **6b/CH<sub>3</sub>** was obtained, m.p. 101-103 °C. <sup>1</sup>H NMR: 0.22 (s, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.88 (t, 3 H, *J*=6.6 Hz, CH<sub>3</sub>), 1.14 (s, 9 H, C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (m, 18 H, (CH<sub>2</sub>)<sub>9</sub>), 1.64 (m, 2 H, CH<sub>2</sub>), 2.48 (s, 3 H, CH<sub>3</sub>), 2.70 (t, 2 H, *J*=7.6 Hz, CH<sub>2</sub>), 7.06 (d, 1 H, *J*=8.8 Hz), 7.21 (dd, 1 H, <sup>3</sup>*J*=8.8 Hz, <sup>4</sup>*J*=2.1 Hz), 7.34 (d, 2 H, *J*=8.5 Hz), 7.40 (d, 2 H), 7.62 (d, 1 H, *J*=9.1 Hz), 7.71 (d, 1 H), 7.82 (d, 1 H, *J*=8.8 Hz); 8.13 (d, 2 H), 8.34 (d, 2 H) ppm. Elemental analysis: for C<sub>43</sub>H<sub>56</sub>O<sub>5</sub>Si (681.01), calculated C 75.84, H 8.29; found C 75.61, H 8.24%.

Compound **6b/Cl** (m.p. 99-101 °C), **6b/CN** (m.p. 127-129 °C), **6c/CH<sub>3</sub>** (m.p. 102-104 °C), **6c/Cl** (m.p. 104-106 °C), and **6c/CN** (m.p. 135-137 °C) were prepared in the same way.

#### **(7-Hydroxynaphthalen-2-yloxy) 4-(4-dodecylbenzoyloxy)benzoate (7b/H)**

A mixture of acid **3b** (150 mg; 0.37 mmol), thionyl chloride (0.11 ml; 1.46 mmol), pyridine (0.12 ml; 1.5 mmol), and toluene (30 ml) was heated to boiling for 3 h and then evaporated. The crude acid chloride was dissolved in dry dichloromethane (20 ml) and the solution added dropwise during 15 min to a mixture of **4/H** (175 mg; 1.1 mmol) and pyridine (0.6 ml) in dichloromethane (30 ml). After stirring at room temperature for 48 h, water (50 ml) was added,

the organic layer was separated and the aqueous layer was washed with dichloromethane (3x20 ml). The combined organic solution was washed with brine and dried with anhydrous magnesium sulphate. The solvent was evaporated and the residue purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether 12/1). 144 mg (72 %) of **6a** was isolated, m.p. 141-142 °C. <sup>1</sup>H NMR: 0.88 (t, 3 H, *J*=6.7 Hz, CH<sub>3</sub>), 1.25 (m, 18 H, (CH<sub>2</sub>)<sub>9</sub>), 1.65 (m, 2 H, CH<sub>2</sub>), 2.70 (t, 2 H, *J*=7.6, CH<sub>2</sub>), 5.12 (s, 1 H, OH), 7.08 (dd, 1 H, <sup>3</sup>*J*=8.5 Hz, <sup>4</sup>*J*=2.4 Hz), 7.12 (d, 1 H), 7.20 (dd, 1 H, <sup>3</sup>*J*=8.8 Hz, <sup>4</sup>*J*=2.1 Hz), 7.34 (d, 2 H), 7.38 (d, 2 H), 7.52 (d, 1 H, *J*=2.1 Hz), 7.76 d, 1 H, *J*=8.5 Hz), 7.82 (d, 1 H, *J*=8.8 Hz), 8.14 (d, 2 H), 8.32 (d, 2 H) ppm. Elemental analysis: for C<sub>36</sub>H<sub>40</sub>O<sub>5</sub> (552.72), calculated C 78.23, H 7.29; found C 78.14, H 7.33%.

#### **(7-Hydroxy-8-methylnaphthalen-2-yloxy) 4-(4-dodecylbenzoyloxy)benzoate (7b/CH<sub>3</sub>)**

To a solution of **7b/CH<sub>3</sub>** (383 mg; 0.56 mmol) in THF (30 ml) and water (2 ml), tetrabutylammonium-fluoride trihydrate (44 mg; 0.14 mmol) was added and the mixture was stirred at room temperature for 1 h, diluted with water (50 ml) and washed with ethyl acetate (3x30 ml). The organic solution was washed with water (30 ml) and dried with anhydrous magnesium sulphate. The residue after evaporation was purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether 12/1). Yield 282 mg (89 %) of **7b/CH<sub>3</sub>**, m.p. 154-155 °C. <sup>1</sup>H NMR: 0.88 (t, 3 H, *J*=6.7 Hz, CH<sub>3</sub>), 1.30 (m, 18 H, (CH<sub>2</sub>)<sub>9</sub>), 1.65 (m, 2 H, CH<sub>2</sub>), 2.50 (s, 3 H, CH<sub>3</sub>), 2.70 (t, 2 H, CH<sub>2</sub>), 4.80 (s, 1 H, OH), 7.06 (d, *J*=8.5 Hz, 1 H), 7.21 (dd, 1 H, <sup>3</sup>*J*=8.8 Hz, <sup>4</sup>*J*=2.1 Hz), 7.34 (d, 2 H), 7.40 (d, 2 H, *J*=8.8 Hz), 7.64 (d, 1 H, *J*=9.1 Hz), 7.72 (d, 1 H, *J*=2.1), 7.82 (d, 1 H), 8.14 (d, 2 H), 8.34 (d, 2 H) ppm. Elemental analysis: for C<sub>37</sub>H<sub>42</sub>O<sub>5</sub> (566.74), calculated C 78.42, H 7.47; found C 78.21, H 7.36%.

Compound **7b/Cl** (m.p. 136-138 °C), **7b/CN**, (m.p. 203-204 °C), **7c/CH<sub>3</sub>** (m.p. 146-148 °C), **7c/Cl** (m.p. 138-139 °C), and **7c/CN** (m.p. 186-188 °C) were prepared in the same way.

#### **4-[(7-(4-(4-Dodecylbenzoyloxy)benzoyloxy)naphthalen-2-yloxy)carbonyl]phenyl 5-dodecylthiophene-2-carboxylate (II/H)**

Compound **II/H** was obtained as for **I/H** by acylation of **7b/H** (67 mg; 0.12 mmol) with acid **3a** (51 mg; 0.12 mmol) in the presence of DCC (85 mg; 0.41 mmol) and catalytic amount of DMAP (15 mg). After column chromatography (silica gel, toluene/*tert*-butyl methyl ether 12/1) and crystallization from an acetone/ethyl acetate mixture 10/1, 102 mg (89 %) of **II/H** was obtained. <sup>1</sup>H NMR: 0.86 (t, 6 H, *J*=6.7 Hz, 2 × CH<sub>3</sub>), 1.28 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.70 (m, 4 H, 2 × CH<sub>2</sub>), 2.70 (t, 2 H, CH<sub>2</sub>), 2.88 (t, 2 H, CH<sub>2</sub>), 6.88 (d, 1 H, *J*=3.8 Hz), 7.34 (d, 2 H, *J*=8.5 Hz), 7.38 (m, 6 H), 7.70 (d, 2 H, *J*=2.3 Hz), 7.85 (d, 1 H), 7.75 (d, 2 H, *J*=8.8 Hz), 8.14 (d, 2 H), 8.32 (d, 2 H), 8.35 (d, 2 H) ppm. Elemental analysis: for C<sub>60</sub>H<sub>70</sub>O<sub>8</sub>S (951.29), calculated C 75.76, H 7.42; found C 75.59, H 7.38%.

By the same way compounds of the series **II/X**, **III/X**, and **V/X** were obtained.

**4-[(7-(4-(4-Dodecylbenzoyloxy)benzoyloxy)-1-methylnaphthalen-2-yloxy)carbonyl]-phenyl 5-dodecylthiophene-2-carboxylate (II/CH<sub>3</sub>)**. <sup>1</sup>H NMR: 0.86 (t, 6 H, *J*=6.7 Hz, 2 × CH<sub>3</sub>), 1.28 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.70 (m, 4 H, 2 × CH<sub>2</sub>), 2.52 (s, 3 H, CH<sub>3</sub>), 2.70 (t, 2 H, CH<sub>2</sub>), 2.88 (t, 2 H, CH<sub>2</sub>), 6.88 (d, 1 H, *J*=3.8 Hz), 7.28 (d, 1 H, *J*=9.1 Hz), 7.34 (d, 2 H, *J*=8.5 Hz), 7.49 (m, 4 H), 7.81 (d, 1 H, *J*=8.8 Hz), 7.86 (d, 2 H), 7.94 (d, 2 H, *J*=9.1), 8.20 (d, 2 H, *J*=8.5 Hz), 8.35 (d, 4 H) ppm. Elemental analysis: for C<sub>61</sub>H<sub>72</sub>O<sub>8</sub>S (965.31), calculated C 75.90, H 7.52; found C 75.88, H 7.41%.

**4-[(1-Chloro-7-(4-(4-dodecylbenzoyloxy)benzoyloxy)naphthalen-2-yloxy)carbonyl]-phenyl 5-dodecylthiophene-2-carboxylate (II/Cl)**. <sup>1</sup>H NMR: 0.86 (t, 6 H, *J*=6.7 Hz, 2 × CH<sub>3</sub>), 1.28 (m, 36 H, 2 × (CH<sub>2</sub>)<sub>9</sub>), 1.70 (m, 4 H, 2 × CH<sub>2</sub>), 2.70 (t, 2 H, CH<sub>2</sub>), 2.88 (t, 2 H, CH<sub>2</sub>), 6.88 (d, 1 H, *J*=3.8 Hz), 7.34 (d, 2 H, *J*=8.2 Hz), 7.44 (m, 6 H), 7.86 (d, 1 H), 7.88 (d,

1 H,  $J=8.8$  Hz), 7.98 (d, 1 H,  $J=8.8$  Hz), 8.13 (m, 3 H), 8.34 (d, 2 H), 8.37 (d, 2 H) ppm. Elemental analysis: for  $C_{60}H_{69}ClO_8S$  (985.73), calculated C 73.11, H 7.06; found C 72.93, H 7.02%.

**4-[(7-(4-(4-Dodecylbenzoyloxy)benzoyloxy)-1-cyanonaphthalen-2-yloxy)carbonyl]phenyl 5-dodecylthiophene-2-carboxylate (II/CN).**  $^1H$  NMR: 0.86 (t, 6 H,  $J=6.7$  Hz,  $2 \times CH_3$ ), 1.28 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.70 (m, 4 H,  $2 \times CH_2$ ), 2.70 (t, 2 H,  $CH_2$ ), 2.88 (t, 2 H,  $CH_2$ ), 6.88 (d, 1 H,  $J=3.8$  Hz), 7.34 (d, 2 H,  $J=8.5$  Hz), 7.42 (m, 4 H), 7.56 (dd, 1 H,  $^3J=8.8$  Hz,  $^4J=2.1$  Hz), 7.59 (d, 1 H,  $J=9.1$  Hz), 7.86 (d, 1 H), 8.04 (d, 1 H,  $J=8.8$ ), 8.08 (d, 1 H,  $J=2.1$  Hz), 8.14 (d, 2 H), 8.18 (d, 1 H), 8.34 (d, 2 H), 8.38 (d, 2 H) ppm. Elemental analysis: for  $C_{61}H_{69}NO_8S$  (976.30), calculated C 75.05, H 7.12, N 1.43; found C 74.92, H 6.95, N 1.41%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)naphthalen-2-yloxy)carbonyl]phenyl 5-dodecylthiophene-2-carboxylate (III/H).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.20 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.80 (m, 4 H,  $2 \times CH_2$ ), 2.88 (t, 6 H,  $J=7.7$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.6$  Hz,  $CH_2$ ), 6.89 (d, 1 H,  $J=3.8$  Hz), 6.99 (d, 2 H,  $J=8.8$  Hz), 7.40 (m, 6 H), 7.70 (d, 2 H,  $J=1.8$  Hz), 7.86 (d, 1 H,  $J=3.8$  Hz), 7.95 (d, 2 H,  $J=8.8$  Hz), 8.26 (d, 2 H,  $J=8.8$  Hz), 8.33 (dd, 4 H,  $J=2.6$  Hz) ppm. Elemental analysis: for  $C_{60}H_{70}O_9S$  (967.29), calculated C 74.50, H 7.29; found C 74.54, H 7.21%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-1-methylnaphthalen-2-yloxy)carbonyl]phenyl 5-dodecylthiophene-2-carboxylate (III/CH<sub>3</sub>).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.20 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.70 (m, 4 H,  $2 \times CH_2$ ), 2.42 (s, 3 H,  $CH_3$ ), 2.88 (t, 2 H,  $J=7.6$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.4$  Hz,  $OCH_2$ ), 6.89 (d, 1 H,  $J=3.8$  Hz), 6.99 (d, 2 H,  $J=8.8$  Hz), 7.31 (d, 1 H,  $J=9.1$  Hz), 7.40 (m, 5 H), 7.82 (d, 1 H,  $J=8.8$  Hz), 7.86 (d, 2 H,  $J=3.2$  Hz), 7.96 (d, 1 H,  $J=8.8$  Hz), 8.16 (d, 2 H,  $J=9.1$  Hz), 8.33 (dd, 4 H,  $J=2.0$  Hz) ppm. Elemental analysis: for  $C_{61}H_{72}O_9S$  (981.31), calculated C 74.66, H 7.40; found C 74.58, H 7.30%.

**4-[(1-Chloro-7-(4-(4-dodecyloxybenzoyloxy)benzoyloxy)naphthalen-2-yloxy)carbonyl]phenyl 5-dodecylthiophene-2-carboxylate (III/Cl).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.20 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.78 (m, 4 H,  $2 \times CH_2$ ), 2.88 (t, 2 H,  $J=7.5$  Hz,  $CH_2$ ), 4.04 (t, 2 H,  $J=6.4$  Hz,  $OCH_2$ ), 6.88 (d, 1 H,  $J=3.8$  Hz), 6.98 (d, 2 H,  $J=8.8$  Hz), 7.42 (m, 5 H), 7.86 (d, 1 H,  $J=3.8$  Hz), 7.88 (d, 1 H,  $J=8.8$  Hz), 7.98 (d, 2 H,  $J=9.1$  Hz), 8.16 (m, 3 H), 8.36 (m, 4 H) ppm. Elemental analysis: for  $C_{60}H_{69}ClO_9S$  (1001.73), calculated C 71.94, H 6.94; found C 71.77, H 6.90%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-1-cyanonaphthalen-2-yloxy)carbonyl]phenyl 5-dodecylthiophene-2-carboxylate (III/CN).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.20 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.76 (m, 2 H,  $CH_2$ ), 1.82 (m, 2 H,  $CH_2$ ), 2.88 (t, 2 H,  $J=7.8$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.6$  Hz,  $OCH_2$ ), 6.88 (d, 1 H,  $J=3.8$  Hz), 7.00 (d, 2 H,  $J=8.5$  Hz), 7.41 (d, 2 H,  $J=8.8$  Hz), 7.43 (d, 2 H,  $J=8.8$  Hz), 7.56 (dd, 1 H,  $^3J=8.8$  Hz,  $^4J=2.3$  Hz), 7.60 (d, 1 H), 7.82 (d, 1 H), 8.04 (d, 1 H), 8.08 (d, 1 H,  $^4J=2.3$  Hz), 8.18 (m, 2 H), 8.33 (m, 2 H) ppm. Elemental analysis: for  $C_{61}H_{69}NO_9S$  (992.30), calculated C 73.84, H 7.01, N 1.41; found C 73.79, H 6.90, N 1.28%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)naphthalen-2-yloxy)carbonyl]phenyl 4-dodecylbenzoate (V/H).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.15 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.76 (m, 2 H,  $CH_2$ ), 1.82 (m, 2 H,  $CH_2$ ), 2.70 (t, 2 H,  $J=7.8$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.6$  Hz,  $OCH_2$ ), 6.98 (d, 2 H,  $J=8.5$  Hz), 7.37 (m, 8 H), 7.70 (d, 2 H,  $J=2.1$  Hz), 7.95 (d, 2 H,  $J=8.8$  Hz), 8.15 (t, 4 H,  $J=8.6$  Hz), 8.34 (dd, 4 H,  $J=2.1$  Hz) ppm. Elemental analysis: for  $C_{62}H_{72}O_9$  (961.26), calculated C 77.47, H 7.55; found C 77.39, H 7.48%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-1-methylnaphthalen-2-yloxy)carbonyl]phenyl 4-dodecylbenzoate (V/CH<sub>3</sub>).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.15 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.66 (m, 2 H,  $CH_2$ ), 1.83 (m, 2 H,  $CH_2$ ), 2.72 (t, 2 H,  $J=7.5$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.6$  Hz,  $OCH_2$ ), 6.98 (d, 2 H,  $J=9.1$  Hz), 7.38 (m, 8 H), 7.82 (d, 1 H,  $J=8.8$  Hz), 7.87 (s, 1

H), 7.95 (d, 1 H,  $J=9.1$  Hz), 8.15 (t, 4 H,  $J=8.2$  Hz), 8.36 (m, 4 H) ppm. Elemental analysis: for  $C_{63}H_{74}O_9$  (975.29), calculated C 77.59, H 7.65; found C 77.43, H 7.58%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-1-chloronaphthalen-2-yloxy)carbonyl]-phenyl 4-dodecylbenzoate (V/Cl).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.25 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.66 (m, 2 H,  $CH_2$ ), 1.83 (m, 2 H,  $CH_2$ ), 2.72 (t, 2 H,  $J=7.5$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.4$  Hz,  $OCH_2$ ), 6.98 (d, 2 H,  $J=8.8$  Hz), 7.34 (d, 2 H,  $J=8.2$  Hz), 7.44 (m, 7 H), 7.88 (d, 1 H,  $J=9.1$  Hz), 7.98 (d, 1 H,  $J=8.8$  Hz), 8.15 (m, 4 H), 8.34 (d, 2 H,  $J=8.8$  Hz), 8.38 (d, 2 H,  $J=8.8$  Hz) ppm. Elemental analysis: for  $C_{62}H_{71}ClO_9$  (995.70), calculated C 74.79, H 7.19; found C 74.65, H 7.13%.

**4-[(7-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-1-cyanonaphthalen-2-yloxy)carbonyl]-phenyl 4-dodecylbenzoate (V/CN).**  $^1H$  NMR: 0.90 (t, 6 H,  $2 \times CH_3$ ), 1.15 (m, 36 H,  $2 \times (CH_2)_9$ ), 1.65 (m, 2 H,  $CH_2$ ), 1.82 (m, 2 H,  $CH_2$ ), 2.70 (t, 2 H,  $J=7.6$  Hz,  $CH_2$ ), 4.06 (t, 2 H,  $J=6.4$  Hz,  $OCH_2$ ), 7.00 (d, 2 H,  $J=8.8$  Hz), 7.34 (d, 2 H,  $J=8.0$  Hz), 7.20 (m, 4 H), 7.56 (dd, 1 H,  $J=2.1$  Hz), 7.60 (d, 1 H,  $J=9.4$  Hz), 8.04 (d, 1 H,  $J=8.8$  Hz), 8.08 (d, 1 H,  $J=2.1$  Hz), 8.16 (m, 5 H), 8.34 (d, 2 H,  $J=8.5$  Hz), 8.39 (d, 2 H,  $J=8.5$  Hz) ppm. Elemental analysis: for  $C_{63}H_{71}NO_9$  (986.27), calculated C 76.72, H 7.26, N 1.42; found C 76.48, H 7.12, N 1.41%.

## Experimental results

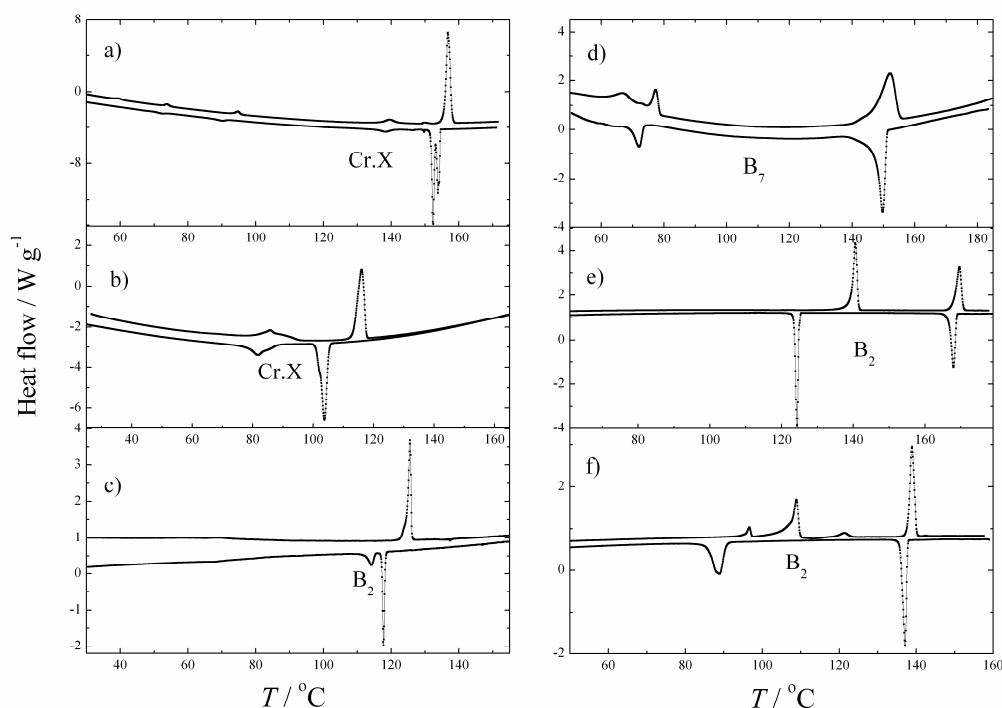


Figure ESI 1

DSC plots for a) I/H, b) I/Cl, c) II/Cl, d) III/CN, e) V/H and f) V/Cl. The upper and lower curves show the second heating and cooling runs, resp. The slopes are adjusted for convenience, phases are indicated.



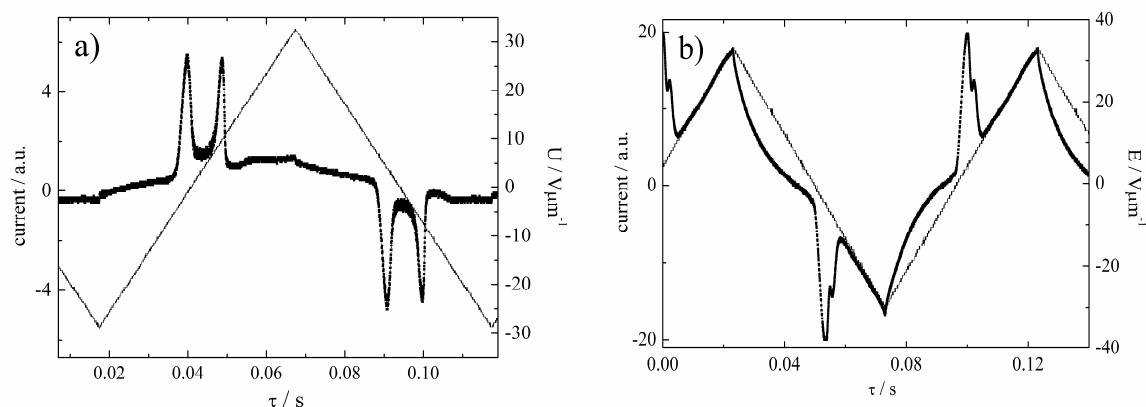


Figure ESI 2

The switching current profile under a triangular ac electric field in the  $B_2$  phase for a)  $\text{II}/\text{CH}_3$  at  $T=120^\circ\text{C}$  and b)  $\text{V}/\text{H}$  at  $T=135^\circ\text{C}$ , both measurements are at frequency of 10 Hz.

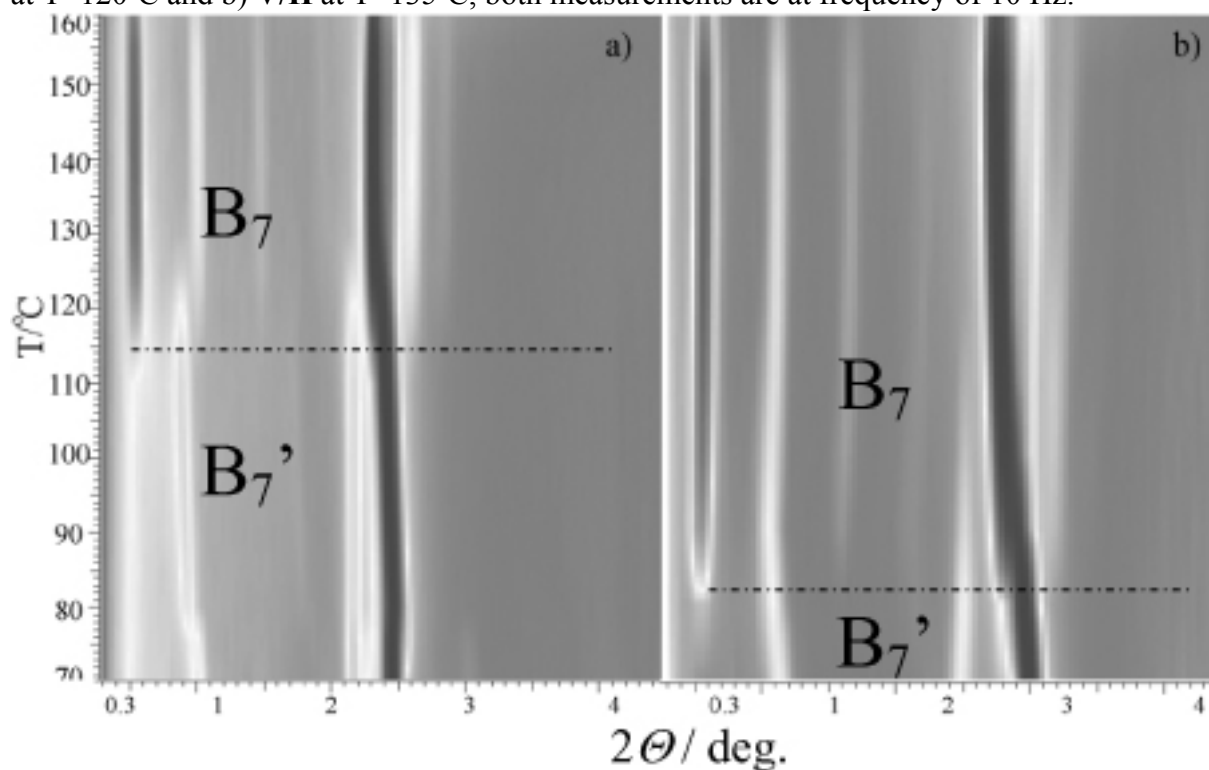


Figure ESI 2

Temperature evolution of x-ray signals for homologues a)  $\text{IV}/\text{CN}$  and b)  $\text{V}/\text{CN}$  taken on cooling from the isotropic phase. Darkness of spot is proportional to the signal intensity.

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