# Electronic supporting information

## Bent-core mesogens with an aromatic unit at the terminal position

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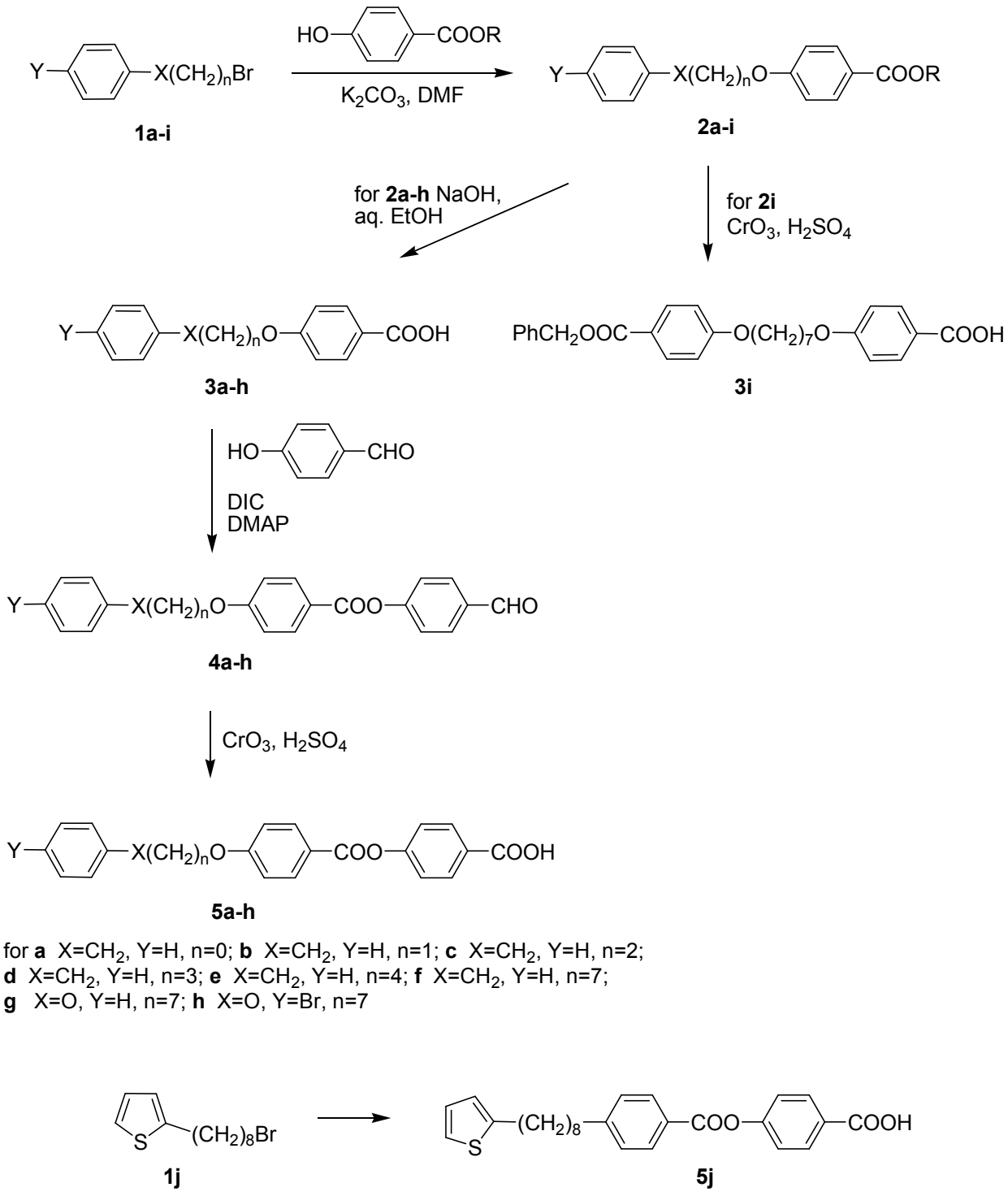
## Content



## 1. Synthesis of the lengthening arms

The aryl-terminated lengthening arms have been obtained by a multi-step procedure depicted in scheme S1. The starting arylalkyl bromides **1d-If** and **Ij** were prepared by the general methods of coupling the arylmagnesium bromides and thienyllithium, resp., with the corresponding dibromoalkanes [S1,S2]. the aryloxyalkyl bromides **1g-Ii** were obtained by alkylation of the corresponding substituted phenol with 1,7-dibromoheptane [S3,S4]. The methyl esters **2a-2h** have been obtained by a base catalysed alkylation of methyl 4-hydroxybenzoate (R=$CH_3$) and for **2i** by alkylation of benzyl 4-hydroxybenzoate (R=$CH_2Ph$) in *N,N*-dimethylformamide (DMF), resp. The formed esters **2a-2h** were subsequently hydrolysed to the corresponding acids **3a-3h** with sodium hydroxide in sq. ethanol**.** The formyl group (Y=CHO) of **2i** has been oxidized with the Jones reagent to yield acid **3i**. The acids **3a-3h** were coupled in the next step with 4-hydroxybenzaldehyde by the means of *N,N′*-diisopropylcarbodiimide (DIC) in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP) to provide formyl esters **4a-h**. Finally, oxidation of the

formyl group of **4a-h** was achieved with the Jones reagent yielded the series of lengthening arms **5a-5h**. The thiophene terminated acid **5j** has been obtained as for compounds **5a-5h** starting with **1j** through the corresponding intermediates **3j,4j** in the same way.



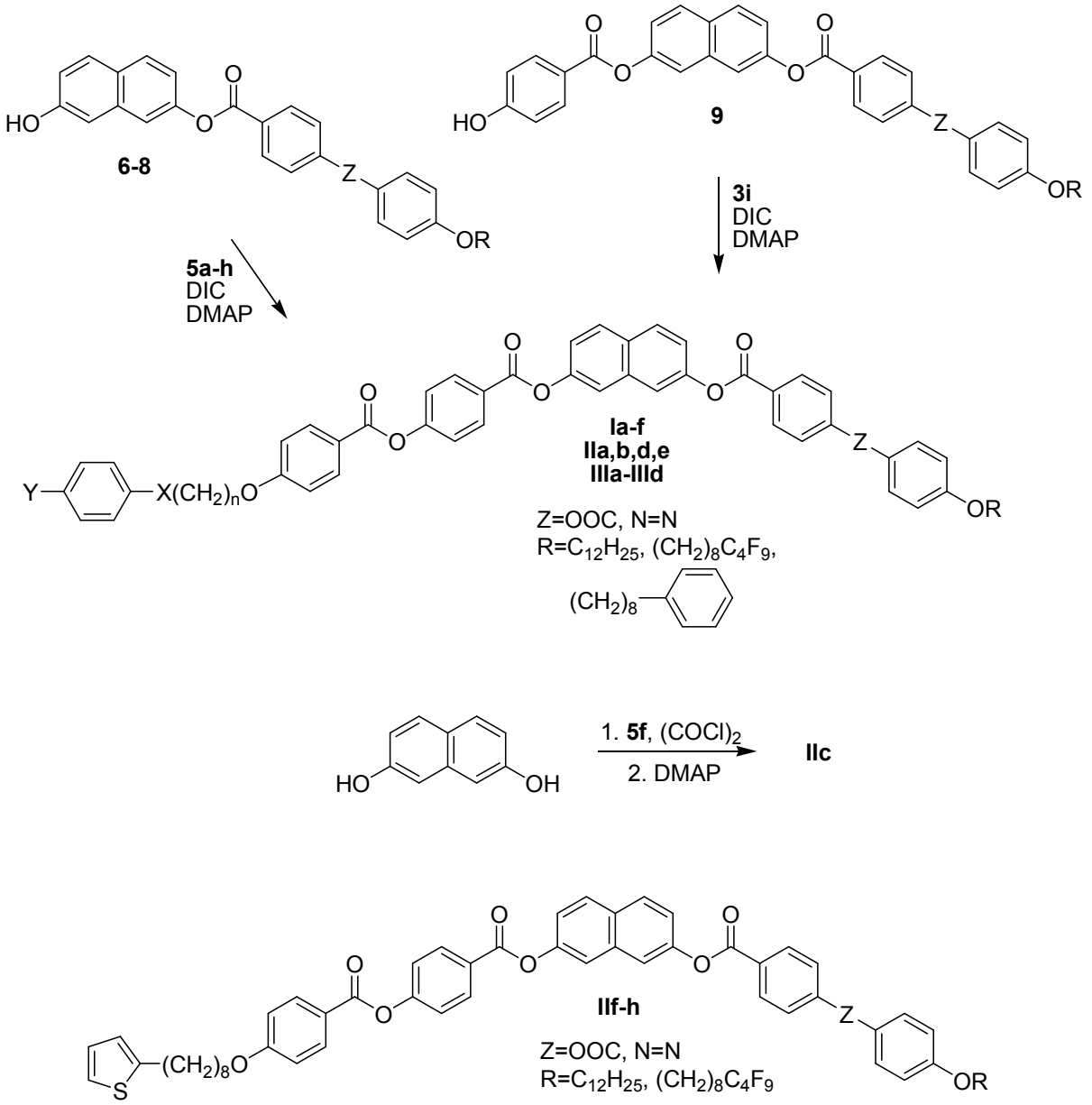

for **a** X=$CH_2$, Y=H, n=0; **b** X=$CH_2$, Y=H, n=1; **c** X=$CH_2$, Y=H, n=2;
**d** X=$CH_2$, Y=H, n=3; **e** X=$CH_2$, Y=H, n=4; **f** X=$CH_2$, Y=H, n=7;
**g** X=O, Y=H, n=7; **h** X=O, Y=Br, n=7




Scheme S1 Synthesis of the aryl-terminated lengthening arms **3i** and **5a-h, j**.

## 2. Synthesis of the target materials

The intermediate compounds **6-9** have already been utilized previously in the studies of naphthalene based bent-core materials [S5-S7]. With exception of **IIc** the non-symmetrical target compounds have been synthesised by acylation of naphthols **6-8** with acids **5a-j** in a diisopropylcarbodiimide (DIC) mediated coupling reaction catalysed with 4-dimethylaminopyridine (DMAP), phenol **9** was coupled with acid **3i** analogously, resp., (Scheme S2), to yield compounds **Ia-f,IIa-h,IIIa-c**. Finally, debenzylation of **IIIc** was achieved by catalytic hydrogenation on Pd/C to yield compound **IIId**. Compound **IIc** possessing a phenyl group in both the terminal chains was obtained by acylation of naphthalene-2,7-diol with acid chloride of acid **5f** in the presence of DMAP.




Scheme S2 Synthesis of the target compounds of series **I-III**.

## 3. Experimental

### Characterisation

Elemental analyses were carried out on Elementar vario EL III instrument. Structures of intermediates and products were confirmed by $^{1}H$ and $^{13}C$ NMR spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform, acetone-$d_6$, and methanol-$d_4$ were used as solvents, resp., and signals of the solvents served as internal standards. Chemical shifts are presented in ppm and *J* values in Hz. The purity of all final compounds was checked by high-performance liquid chromatography analysis (Luna Silica, 150 × 4.6 ID, 5μ column) to be ≥99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm).

The experimental summarizes new and modified procedures for the syntheses of new intermediate compounds and all target compounds as well as their spectral characterisation.

### 3.1 Synthesis of the lengthening arms

**2-(8-Bromooctyl)thiophene (1j)**

To a solution of thiophene (6.90 g; 82 mmol) in THF (70 ml) cooled to -78 °C, a 2.5 M solution of butyllithium in hexanes (28 ml, 70 mmol) was added drop wise during 15 min, the mixture was stirred at -30 °C for 30 min and cooled back to -78 °C. 1,8-Dibromooctane (19.0 g; 69.8 mmol) in THF (10 ml) was added, the cooling bath was removed and the mixture was stirred for 18 h in an argon atmosphere. Saturated aq. ammonium chloride solution (50 ml) was added and the mixture was diluted with ethyl acetate (150 ml) and water (50 ml). The aqueous layer was extracted with ethyl acetate (100 ml), the combined organic solution was washed with brine (50 ml) and dried with anhydrous magnesium sulphate. The solvent was evaporated and the product was obtained by distillation under reduced pressure. Yield 7.25 g (35%), b.p. 123-125 °C/27 Pa. $^{1}H$ NMR spectrum ($CDCl_3$, 300 MHz): 1.36 (m, 6 H, $(CH_2)_3$), 1.45 (m, 2 H, $CH_2$), 1.68 (m, 2 H, $CH_2$), 1.85 (q, 2 H, $CH_2$), 2.82 (t, 2 H, J=7.8, $CH_2$), 3.40 (t, 2 H, *J*=6.8, $CH_2$), 6.78 (dd, 1 H, H-4), 6.91 (dd, 1 H, *J*=5.0, H-3), 7.10 (dd, 1 H, *J*=5.0, H-5).
Elemental analysis: for $C_{12}H_{19}BrS$ (275.25): calculated C 52.36, H 6.96, Br 29.03; found C 52.30, H 6.82, Br 29.11%.

**Methyl-4-(4-phenylbutyloxy)benzoate (2d)**

A mixture of methyl 4-hydroxybenzoate (2.14 g; 14.1 mmol), 1-bromo-4-phenylbutane (**1d**) (3.00 g; 14.1 mmol), sodium iodide (0.25 g; 1.67 mmol), potassium carbonate (2.52 g; 18.2 mmol) and dry DMF (20 ml) was stirred and heated to 100 °C for 1 day. After cooling, water (300 ml) was added and the mixture was extracted with toluene (4 × 70 ml). The combined extracts were washed with water (70 ml), brine (70 ml) and dried with anhydrous magnesium sulphate. After evaporation, the product was purified by column chromatography (toluene) to yield 3.38 g (85%) of **2d**, m.p. 63-66°C. $^{1}H$ NMR spectrum ($CDCl_3$, 300 MHz): 1.74-1.90 (m, 4 H, $(CH_2)_2$), 2.70 (t, 2 H, *J*=7.0, $CH_2$), 3.88 (s, 3 H, $CH_3$), 4.02 (t, 2 H, *J*=6.2, $CH_2$); 6.89 (d, 2 H, *J*=9.1), 7.16-7.34 (m, 5 H, Ph), 7.98 (d, 2 H, *J*=9.1). $^{13}C$ NMR APT spectrum ($CDCl_3$, 100 MHz): 27.8 ($CH_2$), 28.7 ($CH_2$), 35.5 ($CH_2$), 51.8 ($CH_3$), 67.9 ($CH_2$), 114.0 (2 × CH), 122.37 (C), 125.9 (CH), 128.4 (4 × CH), 131.6 (2 × CH), 142.045 (C), 162.86 (C), 166.88 (C).

Elemental analysis: for $C_{18}H_{20}O_3$ (284.36): calculated C 76.03, H 7.09; found C 75.88, H 7.01%.

In the same way, esters **2a-c,e-j** were prepared.

**Methyl-4-(5-phenylpentyloxy)benzoate (2e).** $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.64-1.80 (m, 6 H, $(CH_2)_3$), 2.70 (t, 2 H, *J*=7.0, $CH_2$), 3.88 (s, 3 H, $CH_3$), 4.02 (t, 2 H, *J*=6.2, $CH_2$); 6.89 (d, 2 H, *J*=9.1), 7.16-7.34 (m, 5 H, Ph), 7.98 (d, 2 H, *J*=9.1). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 27.8 ($CH_2$), 28.7 ($CH_2$), 29.3 ($CH_2$), 35.5 ($CH_2$), 51.8 ($CH_3$), 68.0 ($CH_2$), 114.0 (2 × CH), 122.37 (C), 125.9 (CH), 128.4 (4 × CH), 131.6 (2 × CH), 142.045 (C), 162.86 (C), 166.88 (C).

**Methyl 4-(8-phenyloctyloxy)benzoate (2f).** Yield 82%, colourless oil. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.36 (m, 6 H, $(CH_2)_3$), 1.45 (m, 2 H, $CH_2$), 1.61 (m, 2 H, $CH_2$), 1.79 (m, 2 H, $CH_2$), 2.61 (t, 2 H, *J*=8.2, $CH_2$), 3.88 (s, 3 H, $OCH_3$), 4.00 (t, 2 H, *J*=6.5, $OCH_2$), 6.90 (d, 2 H, *J*=8.8), 7.17 (m, 3 H, Ar), 7.27 (m, 2 H, Ar), 7.97 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.2 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 29.5 ($CH_2$), 31.5 ($CH_2$), 36.0 ($CH_2$), 51.8 ($CH_3$), 68.2 ($CH_2$), 114.1 (2 × CH), 122.4 (C), 125.7 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 131.6 (2 × CH), 142.85 (C), 163.01 (C), 166.91 (C).

**Methyl 4-(7-phenoxyheptyloxy)benzoate (2g)**. Crystallisation from cyclohexane, yield 87%, m.p. 73-76°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.51 (m, 6 H, $(CH_2)_3$), 1.81 (m, 4 H, 2 × $CH_2$), 3.88 (s, 3 H, $OCH_3$), 3.96 (t, 2 H, *J*=6.4, $OCH_2$), 4.01 (t, 2 H, *J*=6.5, $OCH_2$), 6.90 (m, 4 H), 7.27 (m, 3 H, Ph), 7.98 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 51.8 ($CH_3$), 67.7 ($CH_2$), 68.1 ($CH_2$), 114.1 (2 × CH), 114.5 (2 × CH), 120.5 (CH), 122.3 (C), 129.4 (2 × CH), 131.6 (2 × CH), 159.1 (C), 162.9 (C), 166.9 (C).

**Methyl 4-(4-bromophenyloxy)heptyloxybenzoate (2h)**. Purification by column chromatography (toluene/ethyl acetate 95/5). Yield 65%, m.p. 63-67°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.38-1.55 (m, 6 H, $(CH_2)_3$), 1.72-1.85 (m, 4 H, 2 × $CH_2$), 3.88 (s, 3 H, $CH_3$), 3.91 (t, 2 H, *J*=7.0, $CH_2O$), 4.00 (t, 2 H, *J*=7.0, $CH_2O$), 6.76 (d, 2 H, *J*=9.0), 6.90 (d, 2 H, *J*=9.0), 7.35 (d, 2 H, *J*=8.6), 7.98 (d, 2 H, *J*=9.0). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 29.0-29.1 (4 × $CH_2$), 51.8 ($CH_3$), 68.1 (2 × $CH_2$), 112.6 (C), 114.0 (2 × CH), 116.3 (2 × CH), 122.4 (C), 131.6 (2 × CH), 132.2 (2 × CH), 158.2 (C), 162.9 (C), 166.9 (C).

**Benzyl 4-[7-(4-formylphenyloxy)heptyloxy]benzoate (2i).** Purification by column chromatography (toluene/ethyl acetate 100/5), yield 77%, m.p. 75-83°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.40-1.60 (m, 6 H, $(CH_2)_3$), 1.78-1.90 (m, 4 H, 2 × $CH_2$), 3.98-4.03 (m, 4 H, 2 × $CH_2O$), 5.33 (s, 2 H, $CH_2Ph$), 6.89 (d, 2 H, *J*=9.1), 6.98 (d, 2 H, *J*=8.8), 7.32-7.47 (m, 5 H, Ph), 7.82 (d, 2 H, *J*=8.8), 8.01 (d, 2 H, *J*=9.1), 9.87 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 29.0 (4 × $CH_2$), 66.4 ($CH_2$), 68.1 ($CH_2$), 68.3 ($CH_2$), 114.1 (2 × CH), 114.7 (2 × CH), 122.3 (C), 128.1 (3 × CH), 128.6 (2 × CH), 129.8 (C), 131.7 (2 × CH), 132.0 (2 × CH), 136.3 (C), 163.0 (C), 164.2 (C), 166.2 (C), 190.8 (CH).

**Methyl 4-(8-thiophen-2-yloctyloxy)benzoate (2j).** Yield 88% of a yellowish oil. $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 1.36 (m, 6 H, $(CH_2)_3$), 1.44 (m, 2 H, $CH_2$), 1.69 (m, 2 H, $CH_2$), 1.80 (m, 2 H, $CH_2$), 2.83 (t, 2 H, *J*=7.0, $CH_2$), 3.89 (s, 3 H, $OCH_3$), 4.00 (t, 2 H, *J*=6.4, $OCH_2$), 6.78 (m, 1 H, H-3 thiophene), 6.90 (d, 1 H, *J* =8.2), 6.91 (m, 1 H, H-4 thiophene),

7.11 (dd, 1 H, $^{3}J$=4.1, $^{4}J$=1.2, H-5 thiophene), 7.99 (d, , 2 H, $J$=9.2). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.2 (2 × $CH_2$), 29.9 ($CH_2$), 31.8 ($CH_2$), 51.8 ($CH_3$), 68.2 ($CH_2$), 114.1 (2 × CH), 122.3 (C), 122.8 (CH), 123.9 (CH), 126.6 (CH), 131.6 (2 × CH), 145.7 (C), 162.9 (C), 166.9 (C).

**4-(4-Phenylbutyloxy)benzoic acid (3d)**

A solution of sodium hydroxide (844 mg, 21.1 mmol) in water (20 ml) was added to a solution of ester **2d** (2.00 g, 7.03 mmol) in ethanol (44 ml) and the reaction mixture was stirred at reflux for 2 h. Ethanol was then evaporated, the residue diluted with water (20 ml) and acidified with conc. hydrochloric acid (8 ml). The deposited solid was filtered off, dried under reduced pressure and crystallised from toluene. 1.63 g (86%) of **3d** was isolated, m.p. 134-137°C. $^{1}$H NMR spectrum ($CDCl_3$, 300 MHz): 1.82 (m, 4 H, $(CH_2)_2$), 2.70 (t, 2 H, $J$=7.0, $CH_2$), 4.03 (t, 2 H, $J$=5.9, $CH_2$), 6.90 (d, 2 H, $J$=8.8), 7.15-7.34 (m, 5 H, Ph), 8.04 (d, 2 H, $J$=9.1). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 27.9 ($CH_2$), 28.8 ($CH_2$), 35.7 ($CH_2$), 68.4 ($CH_2$), 114.2 (2 × CH), 121.4 (C), 125.9 (CH), 128.4 (4 × CH), 132.3 (2 × CH), 142.0 (C), 163.6 (C), 172.0 (C). Elemental analysis: for $C_{17}H_{18}O_3$ (270.33): calculated C 75.53, H 6.71; found C 75.39, H 6.75%.

Analogously, acids **3a-c,e-j** have been obtained.

**4-(2-Phenylethyloxy)benzoic acid (3b)**. Crystallisation from ethanol, yield 81%, m.p. 170-172°C. $^{1}$H NMR spectrum ($CDCl_3$, 300 MHz): 3.13 (t, $J$=7.3, 2 H, $CH_2$), 4.24 (t, $J$=7.0, 2 H, $CH_2$), 6.93 (d, $J$=8.8, 2 H, Ar), 7.30 (m, 5 H, Ph), 8.04 (d, $J$=8.8, 2 H, Ar). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 35.6 ($CH_2$), 68.9 ($CH_2$), 114.2 (2 × CH), 121.6 (C), 126.7 (CH), 128.6 (2 × CH), 129.0 (2 × CH), 132.4 (2 × CH), 137.8 (C), 163.3 (C), 171.7 (C).

**4-(3-Phenylpropyloxy)benzoic acid (3c)**. Crystallization from ethanol, yield 89%, m.p. 171-173°C. $^{1}$H NMR spectrum ($CDCl_3$, 300 MHz): 2.14 (m, 2 H, $CH_2$), 2.83 (t, $J$=7.9, $CH_2$), 4.03 (t, $J$=6.5, $CH_2$), 6.93 (d, $J$=9.1, 2 H, Ar), 7.17-7.34 (m, 5 H, Ph), 8.05 (d, $J$=8.8, 2 H, Ar). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 30.6 ($CH_2$), 32.0 ($CH_2$), 67.1 ($CH_2$), 114.2 (2 × CH), 121.5 (C), 126.1 (CH), 128.5 (4 × CH), 132.4 (2 × CH), 141.2 (C), 163.5 (C), 171.8 (C).

**4-(4-Phenylpentyloxy)benzoic acid (3e).** Crystallisation from toluene, yield 79%, m.p. 172-243°C. $^{1}$H NMR spectrum ($CDCl_3$, 300 MHz): 1.52 (m, 2 H, $CH_2$), 1.71 (m, 2 H, $CH_2$), 1.85 (m, 2 H, $CH_2$), 2.65 (t, 2 H, $J$=7.6, $CH_2$), 4.02 (t, 2 H, $J$=6.5,$CH_2$), 6.92 (d, 2 H, $J$=9.1), 7.15-7.34 (m, 5 H, Ph), 8.05 (d, 2 H, $J$=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.6 ($CH_2$), 29.0 ($CH_2$), 31.2 ($CH_2$), 35.8 ($CH_2$), 68.1 ($CH_2$), 114.2 (2 × CH), 121.4 (C), 125.7 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 132.3 (2 × CH), 142.4 (C), 163.6 (C), 172.0 (C).

**4-(8-Phenyloctyloxy)benzoic acid (3f)**. Crystallisation from ethanol, yield 92%, m.p. 89-118°C. $^{1}$H NMR spectrum ($CDCl_3$, 400 MHz): 1.30-1.42 (m, 6 H, $(CH_2)_3$), 1.46 (m, 2 H, $CH_2$), 1.63 (m, 2 H, $CH_2$), 1.81 (m, 2 H, $CH_2$), 2.61 (t, 2 H, $J$=7.8, $CH_2$), 4.02 (t, 2 H, $J$=6.7, $CH_2$), 6.93 (d, 2 H, $J$=9.0), 7.18 (m, 3 H, Ph), 7.28 (m, 2 H, Ph), 8.06 (d, 2 H, $J$=9.0). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 29.3 ($CH_2$), 29.4 ($CH_2$), 31.5 ($CH_2$), 36.0 ($CH_2$), 68.3 ($CH_2$), 114.2 (2 × CH), 121.4 (C), 125.6 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 132.3 (2 × CH), 142.8 (C), 163.7 (C), 172.0 (C).

**4-(7-Phenoxyheptyloxy)benzoic acid (3g)**. Crystallisation from toluene, yield 92%, m.p. 129-131°C. $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 1.50 (m, 6 H, $(CH_2)_3$), 1.81 (m, 4 H, 2 × $CH_2$), 3.97 (t, 2 H, *J*=6.3, $CH_2$), 4.03 (t, 2 H, *J*=6.3, $CH_2$), 6.92 (m, 5 H), 7.28 (m, 2 H, Ph), 8.05 (d, 2 H, *J*=9.0). $^{13}$C NMR APT spectrum ($CDCl_3$, 400 MHz): 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 67.7 ($CH_2$), 68.2 ($CH_2$), 114.2 (2 × CH), 114.6 (2 × CH), 120.5 (CH), 121.4 (C), 129.4 (2 × CH), 132.3 (2 × CH), 159.1 (C), 163.7 (C), 171.2 (C).

**4-[7-(4-Bromophenoxy)heptyloxy]benzoic acid (3h)**. Crystallisation from ethanol, yield 94%, m.p. 161-164°C. $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 1.38-1.59 (m, 6 H, $(CH_2)_3$), 1.71-1.86 (m, 4 H, 2 × $CH_2$), 3.92 (t, 2 H, *J*=6.7, $OCH_2$), 4.03 (t, 2 H, *J*=6.3, $OCH_2$), 6.77 (d, 2 H, *J*=9.0), 6.92 (d, 2 H, *J*=8.6), 7.36 (d, 2 H, *J*=8.6), 8.04 (d, 2 H, *J*=8.6). $^{13}$C NMR APT spectrum (methanol-$d_4$, 100 MHz): 25.8 ($CH_2$), 28.9 (4 × $CH_2$), 68.1 ($CH_2$), 68.2 ($CH_2$), 112.1 (C), 114.7 (2 × CH), 117.2 (2 × CH), 123.2 (C), 131.8 (2 × CH), 132.5 (2 × CH), 158.4 (C), 162.7 (C), 167.5 (C).

**4-(8-Thiophen-2-yloctyloxy)benzoic acid (3j).** Crystallisation from toluene, yield 90%, m.p. 101-124°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.30-1.52 (m, 8 H, $(CH_2)_4$), 1.68 (m, 2 H, $CH_2$), 1.80 (m, 2 H, $CH_2$), 2.82 (t, 2 H, *J*=7.9, $CH_2$), 4.02 (t, 2 H, *J*=6.7, $CH_2$), 6.77 (dd, 1 H, $^3J$=3.4, $^4J$=1.2,H-3 thiophene), 6.91 (m, 1 H, H-4 thiophene), 6.92 (d, 2 H, *J*=8.8), 7.10 (dd, 1 H, $^3J$=5.3, $^4J$=1.2, H-4 thiophene). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.3 (2 × $CH_2$), 29.9 ($CH_2$), 31.8 ($CH_2$), 68.2 ($CH_2$), 114.2 (2 × CH), 121.4 (C), 122.8 (CH), 123.9 (CH), 126.7 (CH), 132.4 (2 × CH), 145.7 (C), 163.7 (C), 172.2 (C).

**4-Formylphenyl 4-(2-phenylethyloxy)benzoate (4b)**

To a solution of acid **3b** (3.85 g, 15.8 mmol) in dry dichloromethane (130 ml), 4-hydroxybenzaldehyde (2.91 g, 23.8 mmol), DIC (2.02 g, 16.0 mmol, 2.48 ml), and DMAP (350 mg) were added and the reaction mixture was stirred at room temperature for 2 days in an inert argon atmosphere. The solvent was then evaporated and the residue was purified by column chromatography (toluene). Yield 5.31 g (96%), m.p. 84-85°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 3.15 (t, 2 H, *J*=7.0, $CH_2$), 4.27 (t, 2 H, *J*=7.0, $CH_2$), 6.99 (d, 2 H, *J*=9.1), 7.22-7.36 (m, 5 H, Ph), 7.39 (d, 2 H, *J*=8.5), 7.96 (d, 2 H, *J*=8.5), 8.13 (d, 2 H, *J*=9.1), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 35.6 ($CH_2$), 69.0 ($CH_2$), 114.5 (2 × CH), 121.1 (C), 122.6 (2 × CH), 126.7 (CH), 128.6 (2 × CH), 129.0 (2 × CH), 131.2 (2 × CH), 132.5 (2 × CH), 133.9 (C), 137.7 (C), 155.9 (C), 163.5 (C), 164.2 (C), 191.0 (CHO). Elemental analysis: for $C_{22}H_{18}O_4$ (346.39): calculated C 76.29, H 5.24; found C 76.19, H 5.16%.

By the same procedure, intermediates **4a, 4c-4h** and **4j** have been obtained.

**4-Formylphenyl 4-(3-phenylpropyloxy)benzoate (4c)**. Purification by column chromatography (toluene/ethyl acetate 100/5), yield 93%, m.p. 110-113°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 2.16 (m, 2 H, $CH_2$), 2.84 (t, 2 H, *J*=7.9, $CH_2$), 4.06 (t, 2 H, *J*=6.2, $CH_2$), 6.98 (d, 2 H, *J*=8.8), 7.18-7.35 (m, 5 H, Ph), 7.40 (d, 2 H, *J*=8.5), 7.97 (d, 2 H, *J*=8.8), 8.14 (d, 2 H, *J*=8.8), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 30.6 ($CH_2$), 32.0 ($CH_2$), 67.2 ($CH_2$), 114.5 (2 × CH), 121.0 (C), 122.6 (2 × CH), 126.1 (CH), 128.5

(4 × CH), 131.2 (2 × CH), 132.5 (2 × CH), 133.9 (C), 141.1 (C), 155.9 (C), 163.7 (C), 164.2 (C), 191.0 (CH).

**4-Formylphenyl 4-(4-phenylbutyloxy)benzoate (4d)**. Purification by column chromatography (toluene), yield 97%, m.p. 61-64°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.85 (m, 4 H, $(CH_2)_2$), 2.71 (t, 2, *J*=7.0, $CH_2$), 4.07 (t, 2 H, *J*=6.2, $CH_2$), 6.97 (d, 2 H, *J*=8.8), 7.16-7.34 (m, 5 H, Ph), 7.40 (d, 2 H, *J*=8.5), 7.97 (d, 2 H, *J*=8.5), 8.14 (d, 2 H, *J*=8.8), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 27.7 ($CH_2$), 28.6 ($CH_2$), 35.5 ($CH_2$), 68.1 ($CH_2$), 114.4 (2 × CH), 120.9 (C), 122.6 (2 × CH), 125.9 (CH), 128.4 (4 × CH), 131.2 (2 × CH), 132.4 (2 × CH), 138.9 (C), 142.0 (C), 155.9 (C), 163.8 (C), 164.2 (C), 191.0 (CH).

**4-Formylphenyl 4-(5-phenylpentyloxy)benzoate (4e)**. Purification by column chromatography (toluene), yield 97%, m.p. 75-77 °C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.53 (m, 2 H, $CH_2$), 1.72 (m, 2 H, $CH_2$), 1.86 (m, 2 H, $CH_2$), 2.66 (t, 2 H, *J*=7.0, $CH_2$), 4.05 (t, 2 H, *J*=6.5, $CH_2$), 6.97 (d, 2 H, *J*=9.1), 7.15-7.34 (m, 5 H, Ph), 7.40 (d, 2 H, *J*=8.5), 7.97 (d, 2 H, *J*=8.8), 8.14 (d, 2 H, *J*=9.1, 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.6 ($CH_2$), 29.1 ($CH_2$), 31.2 ($CH_2$), 35.8 ($CH_2$), 68.2 ($CH_2$), 114.4 (2 × CH), 120.9 (C), 122.6 (2 × CH), 125.8 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 131.2 (2 × CH), 132.4 (2 × CH), 133.9 (C), 142.4 (C), 155.9 (C), 163.8 (C), 164.2 (C), 191.0 (CH).

**4-Formylphenyl 4-(8-phenyloctyloxy)benzoate (4f)**. Purification by column chromatography (toluene), yield 92%, m.p. 57-59°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.36 (m, 6 H, $(CH_2)_3$), 1.46 (m, 2 H, $CH_2$), 1.63 (m, 2 H, $CH_2$), 1.82 (m, 2 H, $CH_2$), 2.60 (t, 2 H, *J*=7.8, $CH_2$), 4.04 (t, 2 H, *J*=6.4, $CH_2$), 6.98 (d, 2 H, *J*=8.8), 7.19 (m, 3 H, Ph), 7.28 (m, 2 H, Ph), 7.40 (d, 2 H, *J*=8.5), 7.94 (d, 2 H, *J*=8.8), 8.14 (d, 2 H, *J*=9.0), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 29.3 ($CH_2$), 29.4 ($CH_2$), 31.5 ($CH_2$), 36.0 ($CH_2$), 68.4 ($CH_2$), 114.4 (2 × CH), 120.8 (C), 122.6 (2 × CH), 125.6 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 131.2 (2 × CH), 132.4 (2 × CH), 133.9 (C), 142.8 (C), 155.9 (C), 163.9 (C), 164.2 (C), 191.0 (CH).

**4-Formylphenyl 4-(7-phenyloxyheptyloxy)benzoate (4g)**. Purification by column chromatography (toluene/ethyl acetate 95/5), yield 98%, m.p. 86-88°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.52 (m, 6 H, $(CH_2)_3$), 1.82 (m, 4 H, 2 × $CH_2$), 3.97 (t, 2 H, *J*=6.7, $CH_2$), 4.06 (t, 2 H, *J*=6.5, $CH_2$), 6.91 (m, 3 H, Ph), 6.98 (d, 2 H, *J*=8.8), 7.28 (m, 2 H, Ph), 7.40 (d, 2 H, *J*=8.5), 7.97 (d, 2 H, *J*=8.5), 8.14 (d, 2 H, *J*=9.1), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 67.8 ($CH_2$), 68.3 ($CH_2$), 114.5 (2 × CH), 114.6 (2 × CH), 120.5 (CH), 120.9 (C), 122.6 (2 × CH), 129.4 (2 × CH), 131.2 (2 × CH), 132.4 (2 × CH), 134.0 (C), 156.0 (C), 159.1 (C), 163.9 (C), 164.2 (C), 190.8 (CH).

**4-Formylphenyl 4-[7-(4-bromophenyloxy)heptyloxy)benzoate (4h)**. Purification by column chromatography (toluene/ethyl acetate 95/5) and crystallisation from cyclohexane, yield 92%, m.p. 99-102°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.43-1.55 (m, 6 H, $(CH_2)_3$), 1.76-1.86 (m, 4 H, 2 × $CH_2$), 3.93 (t, 2 H, *J*=6.7, $CH_2O$), 4.06 (t, 2 H, *J*=6.3, $CH_2O$), 6.77 (d, 2 H, *J*=9.0), 6.98 (d, 2 H, *J*=9.0), 7.36 (d, 2 H, *J*=9.0), 7.40 (d, 2 H, *J*=8.2), 7.97 (d, 2 H, *J*=8.6), 8.14 (d, 2 H, *J*=9.0), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 29.0-29.1 (4 × $CH_2$), 68.1 ($CH_2$), 68.3 ($CH_2$), 112.6 (C), 114.4 (2 × CH),

116.3 (2 × CH), 120.9 (C), 122.6 (2 × CH), 131.2 (2 × CH), 132.2 (2 × CH), 132.4 (2 × CH), 133.9 (C), 155.9 (C), 158.2 (C), 163.8 (C), 164.2 (C).191.0 (CH).

**4-Formylphenyl 4-(8-thiophen-2-yloctyloxy)benzoate (4j)**. Purification by column chromatography (toluene), yield 96%, m.p. 50-53°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.33-1.58 (m, 8 H, $(CH_2)_4$, 1.69 (m, 2 H, $CH_2$), 1.83 (m, 2 H, $CH_2$), 2.83 (d, 2 H, *J*=7.3, $CH_2$), 4.05 (t, 2 H, *J*=6.4, $CH_2$), 6.78 (dd, 1 H, $^3J$=3.4, $^4J$=1.2, H-3 thiophene), 6.92 (dd, 1 H, $^3J$=5.1, $^3J$=3.2, H-4 thiophene), 6.98 (d, 2 H, *J*=9.1), 7.11 (dd, 1 H, $^3J$=5.0, $^4J$=1.2, H-5 thiophene), 7.40 (d, 2 H, *J*=8.5), 7.97 (d, 2 H, *J*=8.5), 8.14 (d, 2 H, *J*=9.1), 10.02 (s, 1 H, CHO). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.0 (2 × $CH_2$), 29.2 (2 × $CH_2$), 29.9 ($CH_2$), 31.7 ($CH_2$), 68.3 ($CH_2$), 114.4 (2 × CH), 120.8 (C), 122.6 (2 × CH), 122.7 (CH), 123.9 (CH), 126.6 (CH), 131.2 (2 × CH), 132.4 (2 × CH), 133.9 (C), 145.7 (C), 155.9 (C), 163.8 (C), 164.2 (C), 191.0 (CH).

**4-[4-(2-Phenylethyloxy)benzoyloxy]benzoic acid (5b)**

To a solution of aldehyde derivative **4b** (5.15 g, 14.88 mmol) in acetone (150 ml), Jones reagent (7.5 ml) was added drop wise and the reaction mixture was stirred at laboratory temperature until the starting aldehyde was fully oxidized (monitored using thin layer chromatography in toluene). The reaction mixture was then poured on ice (300 ml) and the crystalline product was filtered off. Crystallisation from ethanol afforded 4.90 g (91%) of acid **5b**, m.p. 184-220°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 3.15 (t, 2 H, *J*=7.3, $CH_2$), 4.27 (t, 2 H, *J*=7.0, $CH_2$), 6.99 (d, 2 H, *J*=8.8), 7.22-7.39 (m, 7 H), 8.14 (d, 2 H, *J*=9.1), 8.19 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 35.6 ($CH_2$), 69.0 ($CH_2$), 114.5 (2 × CH), 121.4 (C), 121.9 (2 × CH), 126.5 (C), 126.7 (CH), 128.6 (2 × CH), 128.9 (2 × CH), 131.8 (2 × CH), 132.4 (2 × CH), 137.7 (C), 155.5 (C), 163.5 (C), 164.2 (C), 171.4 (C). Elemental analysis: for $C_{22}H_{18}O_5$ (362.39): calculated C 72.92, H 5.01; found C 72.90, H 4.96%.

In the same way, acids **3i, 5a, 5c-5h** and **5j** have been synthesised.

**4-[7-(4-Benzyloxycarbonylphenyloxy)heptyloxy]benzoic acid (3i).** Crystallisation from toluene, yield 88 %, m.p. 130-135°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.40-1.62 (m, 6 H, $(CH_2)_3$), 1.78-1.90 (m, 4 H, 2 × $CH_2$), 4.02 (m, 4 H, 2 × $CH_2O$), 5.33 (s, 2 H, $CH_2Ph$), 6.89 (d, 2 H, *J*=8.7), 6.92 (d, 2 H, *J*=8.6), 7.30-7.47 (m, 5 H, Ph), 8.02 (d, 2 H, *J*=8.6), 8.04 (d, 2 H, *J*=8.7). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 29.0-29.1 (4 × $CH_2$), 66.4 ($CH_2$), 68.1 (2 × CH), 114.1 (2 × CH), 114.2 (2 × CH), 121.4 (C), 122.3 (C), 128.1 (3 × CH), 128.6 (2 × CH), 131.7 (2 × CH), 132.3 (2 × CH), 136.3 (C), 163.0 (C), 163.6 (C), 166.2 (C), 171.8 (C).

**4-[4-(3-Phenylpropyloxy)benzoyloxy]benzoic acid (5c)**. Crystallisation from ethanol, yield 98%, m.p. 184-220°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 2.16 (m, 2 H, $CH_2$), 2.84 (t, 2 H, *J*=7.0, $CH_2$), 4.06 (t, 2 H, *J*=6.2, $CH_2$), 6.99 (d, 2 H, *J*=8.8), 7.16-7.32 (m, 5 H, Ph), 7.34 (d, 2 H, *J*=8.8), 8.15 (d, 2 H, *J*=9.1), 8.2 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 30.6 ($CH_2$), 32.0 ($CH_2$), 67.2 ($CH_2$), 114.4 (2 × CH), 121.1 (C), 122.0 (2 × CH), 126.1 (CH), 126.6 (C), 128.5 (4 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 141.1 (C), 155.5 (C), 163.7 (C), 164.3 (C), 170. 6 (C).

**4-[4-(4-Phenylbutyloxy)benzoyloxy]benzoic acid (5d)**. Crystallisation from toluene, yield 94%, m.p. 162-226°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.86 (m, 4 H, $(CH_2)_2$), 2.71 (t, 2 H, *J*=6.7, $CH_2$), 4.06 (t, 2 H, *J*=6.6, $CH_2$), 6.97 (d, 2 H, *J*=9.1), 7.15-7.38 (m, 7 H), 8.14 (d, 2 H, *J*=8.8), 8.19 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 27.8 ($CH_2$), 28.7 ($CH_2$), 35.6 ($CH_2$), 68.1 ($CH_2$), 114.4 (2 × CH), 121.0 (C), 122.0 (2 × CH), 125.9 (CH), 126.7 (C), 128.4 (4 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 142.0 (C), 155.6 (C), 163.7 (C), 164.3 (C), 171.4 (C).

**4-[4-(5-Phenylpentyloxy)benzoyloxy]benzoic acid (5e)**. Crystallisation from toluene, yield 88%, m.p. 172-243°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.53 (m, 2 H, $CH_2$), 1.72 (m, 2 H, $CH_2$), 1.87 (m, 2 H, $CH_2$), 2.66 (t, 2 H, *J*=6.0, $CH_2$), 4.05 (t, 2 H, *J*=6.0, $CH_2$), 6.98 (d, 2 H, *J*=9.0), 7.15-7.31 (m, 5 H, Ph), 7.34 (d, 2 H, *J*= 9.0), 8.15 (d, 2 H, *J*=9.0), 8.19 (d, 2 H, *J*=9.1). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.6 ($CH_2$), 29.1 ($CH_2$), 31.2 ($CH_2$), 35.8 ($CH_2$), 68.2 ($CH_2$), 114.4 (2 × CH), 121.0 (C), 122.0 (2 × CH), 125.8 (CH), 126.6 (C), 128.3 (2 × CH), 128.4 (2 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 142.4 (C), 155.5 (C), 163.7 (C), 164.3 (C), 170.9 (C).

**4-[4-(8-Phenyloctyloxy)benzoyloxy]benzoic acid (5f)**. Crystallisation from ethanol, yield 82%, m.p.120-210°C. $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 1.30-1.42 (m, 6 H, $(CH_2)_3$), 1.48 (m, 2 H, $CH_2$), 1.64 (m, 2 H, $CH_2$), 1.83 (m, 2 H, $CH_2$), 2.62 (t, 2 H, *J*=8.4, $CH_2$), 4.05 (t, 2 H, *J*=6.4, $CH_2$), 6.98 (d, 2 H, *J*=9.2), 7.18 (m, 3 H, Ph), 7.28 (m, 2 H, Ph), 7.35 (d, 2 H, *J*=8.8), 8.15 (d, 2 H, *J*=9.2), 8.21 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 29.3 ($CH_2$), 29.4 ($CH_2$), 31.5 ($CH_2$), 36.0 ($CH_2$), 68.3 ($CH_2$), 114.4 (2 × CH), 121.0 (C), 122.0 (2 × CH), 125.6 (CH), 126.6 (C), 128.2 (2 × CH), 128.4 (2 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 142.8 (C), 155.6 (C), 163.8 (C), 164.3 (C), 171.3 (C).

**4-[4-(7-Phenyloxyheptyloxy)benzoyloxy]benzoic acid (5g)**. Crystallisation from toluene, yield 89%, m.p. 154-222°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.49 (m, 6 H, $(CH_2)_3$), 1.83 (m, 4 H, 2 × $CH_2$), 3.97 (t, 2 H, *J*=6.5, $CH_2$), 4.06 (t, 2 H, *J*=6.7, $CH_2$), 6.93 (m, 5 H, Ph), 7.32 (m, 4 H), 8.15 (d, 2 H, *J*=9.1), 8.19 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.2 ($CH_2$), 67.7 ($CH_2$), 68.2 ($CH_2$), 114.4 (2 × CH), 114.5 (2 × CH), 120.5 (CH), 121.0 (C), 122.0 (2 × CH), 126.6 (C), 129.4 (2 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 155.5 (C), 159.1 (C), 163.8 (C), 164.3 (C), 171.0 (C).

**4-{4-[7-(4-Bromophenyloxy)heptyloxy)benzoyloxy}benzoic acid (5h)**. Crystallisation from toluene, yield 93%, m.p. 165-241°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.40-1.62 (m, 6 H, $(CH_2)_3$), 1.50-1.70 (m, 4 H, 2 × $CH_2$), 3.93 (t, 2 H, *J*=6.4, $CH_2O$), 4.06 (t, 2 H, *J*=6.5, $CH_2O$), 6.77 (d, 2 H, *J*=9.1), 6.98 (d, 2 H, *J*=8.8), 7.33 (d, 2 H, *J*=8.8), 7.36 (d, 2 H, *J*=8.8), 8.14 (d, 2 H, *J*=8.8), 8.17 (d, 2 H, *J*=8.5). $^{13}$C NMR APT spectrum ($CDCl_3$(locked)/MeOH-$d_4$, 100 MHz): 29.8 ($CH_2$), 32.8-32.9 (4 × $CH_2$), 72.0 ($CH_2$), 72.2 ($CH_2$), 116.5 (C), 118.3 (2 × CH), 120.2 (2 × CH), 124.8 (C), 125.6 (2 × CH), 131.8 (C), 135.3 (2 × CH), 136.1 (2 × CH), 136.3 (2 × CH), 158.6 (C), 162.0 (C), 167.7 (C), 168.6 (C), 172.0 (C).

**4-[4-(8-Thiophen-2-yloctyloxy)benzoyloxy]benzoic acid (5j)**. Crystallisation from toluene, yield 72%, m.p. 117-228°C. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.28-1.55 (m, 8 H, $(CH_2)_4$), 1.69 (m, 2 H, $CH_2$), 1.82 (m, 2 H, $CH_2$), 2.83 (t, 2 H, *J*=7.9, $CH_2$), 4.04 (t, 2 H, *J*=6.4, $CH_2$), 6.78 (dd, 1 H, $^3J$=3.2, $^4J$=1.2, H-3 thiophene), 6.92 (dd, 1 H, $^3J$=5.0, $^3J$=3.2, H-4

thiophene), 6.98 (d, 2 H, *J*=8.8), 7.11 (dd, 1 H, $^{3}J$=5.1, $^{4}J$=1.2, H-5 thiophene), 7.33 (d, 2 H, *J*=8.8), 8.14 (d, 2 H, *J*=8.8), 8.19 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 400 MHz): 25.9 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.2 (2 × $CH_2$), 29.9 ($CH_2$), 31.7 ($CH_2$), 68.3 ($CH_2$), 114.4 (2 × CH), 121.0 (C), 122.0 (2 × CH), 122.8 (CH), 123.9 (CH), 126.6 (C), 126.6 (CH), 131.9 (2 × CH), 132.4 (2 × CH), 145.7 (C), 155.5 (C), 163.8 (C), 164.3 (C), 171.1 (C).

### 3.2 Synthesis of the target materials

**7-[4-(4-Benzyloxy)benzoyloxy]benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)-benzoate (Ia, X=$CH_2$, n=0)**

Diisopropylcarbodiimide (DIC) (87.0 mg, 0.69 mmol, 0.11 ml) was added to a mixture of acid **5a** (240 mg, 0.69 mmol), phenol **6** (200 mg, 0.57 mmol) and DMAP (40 mg) in dry dichloromethane (40 ml) in an inert argon atmosphere. After stirring overnight, the solvent was evaporated and the residue was separated by column chromatography (toluene/ethyl acetate 95/5), the fraction containing the product were collected evaporated and crystallised from ethyl acetate to provide 233 mg (45%) of **IIa**. $^{1}$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=6.5, $CH_3$), 1.17-1.85 (m, 20 H, $(CH_2)_{10}$), 4.06 (t, 2 H, *J*=6.7, $OCH_2$), 5.18 (s, 2 H, $PhCH_2O$), 6.99 (d, 2 H, *J*=9.1), 7.09 (d, 2 H, *J*=8.5), 7.25-7.50 (m, 11 H), 7.70 (s, 2 H), 7.95 (d, 2 H, *J*=8.8), 8.16 (d, 2 H, *J*=8.2), 8.18 (d, 2 H, *J*=8.5), 8.33 (d, 4 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.8 ($CH_2$), 26.0 ($CH_2$), 27.1 ($CH_2$), 29.1($CH_2$), 29.4 ($CH_2$), 29.6 ($CH_2$), 29.7 ($CH_2$), 29.7 (2 × $CH_2$), 32.0 ($CH_2$), 68.5 ($CH_2$), 70.3 ($CH_2$), 114.5 (2 × CH), 114.9 (2 × CH), 118.7 (2 × CH), 121 (C), 121.3 (2 × CH), 121.5 (C), 122.2 (4 × CH), 126.9 (2 × C), 127.6 (2 × CH), 128.4 (CH), 128.8 (2 × CH), 129.5 (2 × CH), 129.7 (C), 131.9 (4 × CH), 132.5 (4 × CH), 134.5 (C), 136.1 (C), 149.3 (2 × C), 155.5 (2 × C), 163.4 (C), 163.9 (C), 164.4 (2 × C), 164.6 (2 × C). Elemental analysis: for $C_{57}H_{54}O_{10}$ (899.06): calculated C 76.15, H 6.05; found C 76.02, H 5.99%.

**7-{4-[4-(2-Phenylethyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (Ib, X=$CH_2$, n=1)**

By the reaction of acid **5b** (239 mg, 0.66 mmol), hydroxy derivative **6** (250 mg, 0.44 mmol), DMAP (25 mg) and DIC (83 mg, 0.66 mmol, 0.10 ml), 267 mg (66%) of **IIb** was isolated after column chromatography (toluene/*tert*-butyl methyl ether 30/1) and crystallisation from ethyl acetate. $^{1}$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=6.4, $CH_3$), 1.25-1.62 (m, 18 H, $(CH_2)_9$), 1.83 (m, 2 H, $CH_2$), 3.16 (t, 2 H, *J*=6.7, $CH_2$), 4.06 (t, 2 H, *J*=6.2, $OCH_2$), 4.28 (t, 2 H, *J*=7.0, $OCH_2$), 7.00 (d, 4 H, *J*=8.8), 7.28-7.45 (m, 11 H), 7.70 (s, 2 H), 7.95 (d, 2 H, *J*=9.1), 8.16 (d, 4 H, *J*=8.8), 8.33 (d, 4 H, *J*=8.2). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 26.0 ($CH_2$), 29.1 ($CH_2$), 29.4 ($CH_2$), 29.6 (4 × $CH_2$), 29.7 ($CH_2$), 31.9 ($CH_2$), 35.6 ($CH_2$), 68.4 ($CH_2$), 69.0 ($CH_2$), 114.4 (2 × CH), 114.5 (2 × CH), 118.6 (2 × CH), 120.9 (2 × C), 121.2 (2 × CH), 122.1 (4 × CH), 126.7 (CH), 126.8 (2 × C), 128.6 (2 × CH), 129.0 (2 × CH), 129.4 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 137.7 (C), 149.3 (2 × C), 155.4 (C), 155.5 (C), 163.4 (C), 163.8 (C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{58}H_{56}O_{10}$ (913.09): calculated C 76.30, H 6.18; found C 76.32, H 6.11%.

**7-{4-[4-(3-Phenylpropyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (Ic, X=$CH_2$, n=2)**

Material **IIc** was prepared analogously from carboxylic acid **5c** (248 mg, 0.66 mmol), hydroxy derivative **6** (250 mg, 0.44 mmol), DMAP (25 mg) and DIC (83 mg, 0.66 mmol, 0.10 ml). Product was purified by column chromatography (toluene/ethyl acetate 95/5) and multiple crystallisation from ethyl acetate, yield 284 mg (70%). $^1$H NMR spectrum ($CDCl_3$, 300 Hz): 0.88 (t, 3 H, *J*=6.7, $CH_3$), 1.20-1.58 (m, 20 H, 10 × $CH_2$), 1.83 (m, 2 H, $CH_2$), 2.85 (t, 2 H, *J*=7.9, $CH_2$), 4.06 (m, 4 H, 2 × $OCH_2$), 6.99 (d, 4 H, *J*=8.8), 7.18-7.35 (m, 5 H, Ph), 7.36-7.43 (m, 6 H), 7.70 (d, 2 H, *J*=2.1), 7.95 (d, 2 H, *J*=9.1), 8.16 (d, 4 H, *J*=8.5), 8.33 (d, 4 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.2 ($CH_3$), 22.7 ($CH_2$), 26.0 ($CH_2$), 29.1 ($CH_2$), 29.4 (2 × $CH_2$), 29.6 (2 × $CH_2$), 29.7 (2 × $CH_2$), 30.6 ($CH_2$), 31.9 ($CH_2$), 32.0 ($CH_2$), 67.2 ($CH_2$), 68.4 ($CH_2$), 114.4 (2 × CH), 114.5 (2 × CH), 118.6 (2 × CH), 120.9 (C), 121.1 (C), 121.2 (2 × CH), 122.2 (4 × CH), 126.1 (CH), 126.8 (2 × C), 128.5 (4 × CH), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (2 × CH), 132.5 (2 × CH), 134.4 (C), 141.2 (C), 149.3 (2 × C), 155.5 (2 × C), 163.7 (C), 163.8 (C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{59}H_{58}O_{10}$ (927.11): calculated C 76.44, H 6.31; found C 76.33, H 6.29%.

**7-{4-[4-(4-Phenylbutyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (Id, X=$CH_2$, n=3)**

In the same manner, reaction of acid **5d** (257 mg, 0.66 mmol), hydroxy derivative **6** (250 mg, 0.44 mmol), DMAP (25 mg) and DIC (83 mg, 0.66 mmol, 0.10 ml) yielded after column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone 369 mg (89%) of **IId**. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J* =6.7, $CH_3$), 1.17-1.57 (m, 18 H, 9 × $CH_2$), 1.83 (m, 6 H, 3 × $CH_2$), 2.72 (t, 2 H, *J*=7.0, $CH_2$), 4.06 (t, 4 H, *J*=6.7, 2 × $CH_2$), 6.98 (d, 2 H, *J*=9.1), 6.99 (d, 2 H, *J*=8.8), 7.18-7.34 (m, 5 H, Ph), 7.39 (m, 6 H), 7.70 (d, 2 H, *J*=2.1), 7.95 (d, 2 H, *J*=8.5), 8.16 (d, 4 H, *J*=9.1), 8.33 (d, 4 H, *J*=8.5). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 26.0 ($CH_2$), 27.8 ($CH_2$), 28.7 ($CH_2$), 29.1 ($CH_2$), 29.4 (2 × $CH_2$), 29.6 (2 × $CH_2$), 29.7 (2 × $CH_2$), 31.9 ($CH_2$), 35.5 ($CH_2$), 68.1 ($CH_2$), 68.4 ($CH_2$), 114.4 (4 × CH), 118.6 (2 × CH), 120.9 (C), 121.0 (C), 121.2 (2 × CH), 122.2 (4 × CH), 125.9 (CH), 126.8 (2 × C), 128.4 (4 × CH), 129.4 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 142.0 (C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{60}H_{60}O_{10}$ (941.14): calculated C 76.57, H 6.43; found C 76.46, H 6.36%.

**7-{4-[4-(5-Phenylpentyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (Ie, X=$CH_2$, n=4)**

Compound **IIe** was prepared analogously from acid **5e** (267 mg, 0.66 mmol), hydroxy derivative **6** (250 mg, 0.44 mmol), DMAP (25 mg) and DIC (83 mg, 0.66 mmol, 0.10 ml). The product was purified by column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone, yield 392 mg (93%). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.89 (t, 3 H, *J*=7.0, $CH_3$), 1.25-1.65 (m, 20 H, 10 × $CH_2$), 1.72 (m, 2 H, $CH_2$), 1.88 (m, 4 H, 2 × $CH_2$), 2.67 (t, 2 H, *J*=7.6, $CH_2$), 4.06 (t, 4 H, *J*=6.4, 2 × $OCH_2$), 6.98 (d, 2 H, *J*=9.1), 6.99 (d, 2 H, *J*=8.8), 7.18-7.34 (m, 5 H, Ph), 7.39 (m, 6 H), 7.70 (d, 2 H, *J* =2.1), 7.95 (d, 2 H, *J*=9.1), 8.16 (d, 4 H, *J*=9.1), 8.34 (d, 4 H, *J*=9.1). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.2

($CH_3$), 22.7 ($CH_2$), 25.7 ($CH_2$), 26.0 ($CH_2$), 29.0 ($CH_2$), 29.1 ($CH_2$), 29.4 (2 × $CH_2$), 29.6 (2 × $CH_2$), 29.7 (2 × $CH_2$), 31.2 ($CH_2$), 31.9 ($CH_2$), 35.8 ($CH_2$), 68.2 ($CH_2$), 68.4 ($CH_2$), 114.4 (4 × CH), 118.6 (2 × CH), 121 (2 × C), 121.3 (2 × CH), 122.2 (4 × CH), 125.8 (CH), 126.8 (2 × C), 128.3 (2 × CH), 128.4 (2 × CH), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 142.4 (C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{61}H_{62}O_{10}$ (955.17): calculated C 76.71, H 6.54; found C 76.63, H 6.55%.

**7-{4-[4-(8-Phenyloctyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (If, X=$CH_2$, n=7)**

Diisopropylcarbodiimide (DIC) (44 mg, 0.35 mmol, 0.05 ml) was added to a mixture of acid **5f** (157 mg, 0.352 mmol), hydroxy derivative **6** (200 mg, 0.35 mmol), and DMAP (8 mg) in dry dichloromethane (20 ml) in an inert argon atmosphere. After stirring overnight at room temperature, the solvent was evaporated and the residue was purified by column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone to yield 273 mg (93 %) of **Ia**. $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 0.93 (t, 3 H, *J*=6.7, $CH_3$), 1.43-1.55 (m, 26 H, 13 × $CH_2$), 1.66 (m, 2 H, $CH_2$), 1.84 (m, 4 H, 2 × $CH_2$), 2.64 (t, 2 H, *J*=7.8, $CH_2$), 4.05 (m, 4 H, 2 × $CH_2$), 7.00 (d, 4 H, *J*=8.6), 7.21 (m, 3 H, Ph), 7.30 (m, 2 H, Ph), 7.41 (m, 6 H), 7.72 (s, 2 H), 7.94 (d, 2 H, *J*=9.0), 8.61 (d, 4 H, *J*=8.2), 8.34 (d, 4 H, *J*=8.6). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 25.9 ($CH_2$), 29.1 (2 × $CH_2$), 29.2 (2 × $CH_2$), 29.3 ($CH_2$), 29.4 ($CH_2$), 29.5 ($CH_2$), 29.6 (3 × $CH_2$), 29.7 (2 × $CH_2$), 31.4 ($CH_2$), 31.9 ($CH_2$), 35.9 ($CH_2$), 68.4 (2 × $CH_2$), 114.4 (4 × CH), 118.6 (2 × CH), 121.0 (2 × C), 121.2 (2 × CH), 122.1 (4 × CH), 125.6 (CH), 126.8 (2 × C), 128.2 (2 × CH), 128.4 (2 × CH), 129.4 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 142.8 (C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{64}H_{68}O_{10}$ (997.25): calculated C 77.08, H 6.87; found C 76.94, H 6.84%.

**7-[4-(4-Benzyloxy)benzoyloxy]benzoyloxynaphtalen-2-yl 4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate (IIa, X=$CH_2$, n=0)**

Compound **Ih** was prepared as for from acid **5a** (140 mg, 0.40 mmol), phenol **7** (250 mg, 0.34 mmol), DMAP (25 mg) and DIC (51 mg, 0.40 mmol, 0.06 ml). Purification by column chromatography (toluene/ethyl acetate 95/5), and crystallisation from ethyl acetate, yield 302 mg (85 %). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.25-1.70 (m, 10 H, $(CH_2)_5$), 1.82 (m, 2 H, $CH_2$), 2.04 (m, 2 H, $CH_2$), 4.06 (t, 2 H, *J*=6.4, $CH_2O$), 5.18 (s, 2 H, $CH_2O$), 6.99 (d, 2 H, *J*=9.4), 7.09 (d, 2 H, *J*=9.1), 7.34-7.48 (m, 11 H), 7.70 (d, 2 H, *J*=2.1), 7.95 (d, 2 H, *J*=8.8), 8.16 (d, 2 H, *J*=8.8), 8.18 (d, 2 H, *J*=8.8), 8.33 (d, 4 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 29.0-29.1 (6 × $CH_2$), 68.3 ($CH_2$), 70.2 ($CH_2$), 114.4 (2 × CH), 114.8 (2 × CH), 118.6 (2 × CH), 121.0 (C), 121.2 (2 × CH), 121.5 (C), 122.1 (2 × CH), 122.2 (2 × CH), 126.8 (2 × C), 127.5 (2 × CH), 128.3 (CH), 128.7 (2 × CH), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (2 × CH), 132.5 (2 × CH), 134.4 (C), 136.0 (C), 149.3 (2 × C), 155.4 (C), 155.5 (C), 163.3 (C), 163.8 (C), 164.2 (C), 164.3 (C), 164.5 (2 × C). Elemental analysis: for $C_{57}H_{45}F_9O_{10}$ (1060.97): calculated C 64.53, H 4.28; found C 64.44, H 4.09%.

**7-[4-(4-Benzyloxy)benzoyloxy]benzoyloxynaphtalen-2-yl 4-(4-dodecyloxyphenylazo)-benzoate (IIb, X=$CH_2$, n=0)**

Material **Ii** was prepared from acid **5a** (157 mg, 0.45 mmol), phenol **8** (250 mg, 0.45 mmol), DMAP (20 mg) and DIC (57 mg, 0.45 mmol, 0.07 ml). Purification by column chromatography (chloroform) and crystallisation from toluene, yield 288 mg (72%). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=6.7, $CH_3$), 1.21-1.52 (m, 18 H, $(CH_2)_9$), 1.84 (m, 2 H, $CH_2$), 4.07 (t, 2 H, *J*=6.4, $CH_2O$), 5.18 (s, 2 H, $OCH_2$), 7.03 (d, 2 H, *J*=9.1), 7.09 (d, 2 H, *J*=8.8), 7.35-7.49 (m, 9 H), 7.72 (dd, 2 H, $^3J$=6.0, $^4J$=1.8), 7.96 (d, 2 H, *J*=8.8), 7.97 (d, 2 H, *J*=9.0), 8.00 (d, 2 H, *J*=8.4), 8.18 (d, 2 H, *J*=9.1), 8.34 (d, 2 H, *J*=8.5), 8.39 (d, 2 H, *J*=8.5). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 26.0 ($CH_2$), 29.2-29.7 (7 × $CH_2$), 31.9 ($CH_2$), 68.5 ($CH_2$), 70.2 ($CH_2$), 114.8 (4 × CH), 118.6 (2 × CH), 121.2 (2 × CH), 121.5 (C), 122.1 (2 × CH), 122.6 (2 × CH), 125.3 (2 × CH), 126.8 (C), 127.5 (2 × CH), 128.3 (CH), 128.7 (2 × CH), 129.5 (2 × CH), 129.6 (C), 130.3 (C), 131.3 (2 × CH), 131.9 (2 × CH), 132.5 (2 × CH), 134.4 (C), 136.0 (C), 146.9 (C), 149.3 (2 × C), 155.4 (C), 155.9 (C), 162.5 (C), 163.3 (C), 164.2 (C), 164.5 (C), 164.8 (C). Elemental analysis: for $C_{56}H_{54}N_2O_8$ (883.06): calculated C 76.17, H 6.16, N 3.17; found C 76.08, H 6.09, N 3.10%.

**7-{4-[4-(8-Phenyloctyl)oxy]benzoyloxy}benzoyloxynaphtalen-2-yl 4-[4-(8-phenyloctyl-oxy)benzoyloxy]benzoate (IIc)**

To a mixture of naphthalene-2,7-diol (431 mg, 2.69 mmol) in toluene, solution of acid chloride of acid **5f** (1.34 mmol) in toluene (6 ml) and DMAP (164 mg, 1.34 mmol) were added. The mixture was then stirred and heated to boiling for 6 h. After cooling, the mixture was poured into 2% aq. HCl (100 ml). The layers were separated and the aqueous layer was extracted with toluene (3 × 70 ml). The combined organic solution was washed with water (70 ml), brine (70 ml), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the product purified by column chromatography (toluene/ethyl acetate 95/5) to yield 117 mg (9%) of **Ib**. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.30-1.70 (m, 20 H, 10 × $CH_2$), 1.82 (m, 4 H, 2 × $CH_2$), 2.61 (t, 4 H, *J*=7.9, 2 × $CH_2$), 4.05 (t, 4 H, *J*=6.5, 2 × $CH_2$), 6.99 (d, 4 H, *J*=8.8), 7.18 (m, 6 H, Ph), 7.27 (m, 4 H, Ph), 7.38 (dd, 2 H, $^3J$=8.9, $^4J$=2.6), 7.39 (d, 4 H, *J*=8.8), 7.70 (d, 2 H, *J*=2.1), 7.95 (d, 2 H, *J*=8.8), 8.16 (d, 4 H, *J*=9.1), 8.33 (d, 4 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 26.0 (2 × $CH_2$), 29.1 (2 × $CH_2$), 29.2 (2 × $CH_2$), 29.3 (2 × $CH_2$), 29.4 (2 × $CH_2$), 31.5 (2 × $CH_2$), 36.0 (2 × $CH_2$), 68.3 (2 × $CH_2$), 114.4 (4 × CH), 118.6 (2 × CH), 121.0 (2 × C), 121.2 (2 × CH), 122.2 (4 × CH), 125.6 (2 × CH), 126.8 (2 × C), 128.2 (4 × CH), 128.4 (4 × CH), 129.4 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 142.8 (2 × C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{66}H_{64}O_{10}$ (1017.24): calculated C 77.93, H 6.34; found C 77.85, H 6.24%.

**7-{4-[8-(5-Phenyloctyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate (IId, X=$CH_2$, n=7)**

Compound **Ic** was prepared by the reaction of acid **5f** (120 mg, 0.27 mmol), hydroxy derivative **7** (200 mg, 0.27 mmol), DMAP (5 mg) and DIC (34 mg, 0.27 mmol, 0.04 ml).

Purification by column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone, yield 193 mg (62%). $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 1.30-1.57 (m, 16 H, 8 × $CH_2$), 1.63 (m, 4 H, 2 × $CH_2$), 1.84 (m, 4 H, 2 × $CH_2$), 2.07 (m, 2 H, $CH_2$), 2.62 (t, 2 H, *J*=7.8, $CH_2$), 4.06 (m, 4 H, 2 × $CH_2$), 6.99 (d, 2 H, *J*=9.0), 7.0 (d, 2 H, *J*=8.6), 7.19 (m, 3 H, Ph), 7.29 (m, 2 H, Ph), 7.40 (m, 6 H), 6.46 (d, 2 H, *J*=2.4), 7.95 (d, 2 H, *J*=9.0), 8.17 (d, 4 H, *J*=9.0), 8.34 (d, 4 H, *J*=8.6). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0 (2 × $CH_2$), 29.1 (3 × $CH_2$), 29.2 (2 × $CH_2$), 29.3 ($CH_2$), 29.4 ($CH_2$), 30.8 ($CH_2$), 31.5 ($CH_2$), 36.0 ($CH_2$), 68.3 ($CH_2$), 68.4 ($CH_2$), 114.4 (4 × CH), 118.6 (4 × CH), 120.9 (C), 121.0 (C), 121.2 (2 × CH), 122.2 (2 × CH), 125.6 (CH), 126.8 (2 × C), 128.2 (2 × CH), 128.4 (2 × CH), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 142.8 (C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{64}H_{59}F_9O_{10}$ (1159.16): calculated C 66.32, H 5.13; found C 66.25, H 4.89%.

**7-{4-[4-(8-Phenyloctyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-phenylazo)benzoate (IIe, X=$CH_2$, n=7)**

Coupling of acid **5f** (162 mg, 0.362 mmol) with hydroxy derivative **8** (200 mg, 0.36 mmol) in the presence of DMAP (5 mg) and DIC (46 mg, 0.36 mmol, 0.06 ml) yielded the product, which was purified by column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone, yield 312 mg (88%). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=7.0, $CH_3$), 1.43-1.53 (m, 26 H, 13 × $CH_2$), 1.63 (m, 2 H, $CH_2$), 1.82 (m, 4 H, 2 × $CH_2$), 2.61 (t, 2 H, *J*=7.9, $CH_2$), 4.05 (m, 4 H, 2 × $CH_2$), 6.99 (d, 2 H, *J*=8.8), 7.03 (d, 2 H, *J*=9.4), 7.18 (m, 3 H, Ph), 7.27 (m, 2 H, Ph), 7.40 (m, 4 H), 7.71 (d, 1 H, *J*=2.1), 7.73 (d, 1 H, *J*=2.4), 7.96 (d, 2 H, *J*=8.5), 7.97 (d, 2 H, *J*=9.1), 8.00 (d, 2 H, *J*=8.8), 8.16 (d, 2 H, *J*=9.1), 8.33 (d, 2 H, *J*=8.8), 8.39 (d, 2 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 26.0 (2 × $CH_2$), 29.1 ($CH_2$), 29.2 (2 × $CH_2$), 29.3 ($CH_2$), 29.4 (2 × $CH_2$), 29.6 (2 × $CH_2$), 29.7 (3 × $CH_2$), 31.5 ($CH_2$), 31.9 ($CH_2$), 36.0 ($CH_2$), 68.3 ($CH_2$), 68.5 ($CH_2$), 114.4 (2 × CH), 114.8 (2 × CH), 118.6 (2 × CH), 121(C), 121.3 (2 × CH), 122.2 (2 × CH), 122.6 (2 × CH), 125.3 (2 × CH), 125.6 (CH), 126.8 (C), 128.2 (2 × CH), 128.4 (2 × CH), 129.5 (2 × CH), 129.6 (C), 130.3 (C), 131.3 (2 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 134.4 (C), 142.8 (C), 146.9 (C), 149.3 (2 × C), 155.5 (C), 155.9 (C), 162.5 (C), 163.8 (C), 164.3 (C), 164.5 (C), 164.8 (C). Elemental analysis: for $C_{63}H_{68}N_2O_8$ (981.25): calculated C 77.12, H 6.99, N 2.85; found C 77.03, H 6.87, N 2.87%.

**7-{4-[4-(8-Thiophen-2-yloctyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyl-oxybenzoyloxy)benzoate (IIf)**

Acid **5j** (159 mg, 0.35 mmol) was coupled with hydroxy derivative **6** (200 mg, 0.35 mmol) in the presence of DMAP (20 mg) and DIC (44 mg, 0.35 mmol, 0.06 ml). The product was isolated as for **Ia**, yield 230 mg (65%). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=6.7, $CH_3$), 1.22-1.58 (m, 26 H, 13 × $CH_2$), 1.69 (m, 2 H, $CH_2$), 1.83 (m, 4 H, 2 × $CH_2$), 2.83 (t, 2 H, *J*=7.0, $CH_2$), 4.04 (t, 4 H, *J*=6.4, 2 × $CH_2$), 6.78 (dd, 1 H, $^3J$=3.5, $^4J$=1.2, H-3 thiophene), 6.92 (dd, 1 H, $^3J$=5.1, $^3J$=3.2, H-4 thiophene), 6.99 (d, 4 H, *J*=8.5), 7.11 (dd, 1 H, $^3J$=5.3, $^4J$=1.2, H-5 thiophene), 7.39 (m, 6 H), 7.70 (d, 2 H, *J*=2.1), 7.95 (d, 2 H, *J*=9.1), 8.16 (d, 4 H, *J*=8.8), 8.33 (d, 4 H, *J*=9.1). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.2 ($CH_3$), 22.7 ($CH_2$), 26.0 (2 × $CH_2$), 29.0-29.9 (12 × $CH_2$), 31.8 ($CH_2$), 31.9 ($CH_2$), 68.3 ($CH_2$),

68.4 ($CH_2$), 114.4 (4 × CH), 118.6 (2 × CH), 121.0 (2 × C), 121.2 (2 × C), 122.2 (4 × CH), 122.8 (CH), 123.9 (CH), 126.7 (CH), 126.8 (2 × C), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 145.7 (C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{62}H_{66}O_{10}S$ (1003.28): calculated C 74.23, H 6.63, S 3.20; found C 74.16, H 6.56, S 3.14%.

**7-{4-[4-(8-Thiophen-2-yloctyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate (IIg)**

Compound **If** was obtained analogously by the reaction of acid **5j** (150 mg, 0.33 mmol) and hydroxy derivative **7** (370 mg, 0.50 mmol), DMAP (15 mg) and DIC (63 mg, 0.50 mmol, 0.08 ml). The product was purified by column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone, yield 277 mg (72%). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 1.25-1.88 (m, 8 H), 2.04 (m, 2 H, $CH_2$), 2.83 (t, 2 H, $J$=7.0, $CH_2$), 4.06 (m, 4 H, 2 × $CH_2O$), 6.78 (dd, 1 H, $^3J$=3.4, $^4J$=1.2, H-3 thiophene), 6.92 (dd, 1 H, $^3J$=5.0, $^3J$=3.2, H-4 thiophene), 6.99 (d, 4 H, $J$=8.8), 7.11 (dd, 1 H, $^3J$=5.2, $^4J$=1.2, H-5 thiophene), 7.39 (m, 6 H), 7.70 (d, 2 H, $J$=2.1), 7.95 (d, 2 H, $J$=7.9), 8.17 (d, 4 H, $J$=8.5), 8.34 (d, 4 H, $J$=8.5). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 25.9 (2 × $CH_2$), 29.0-29.2 (10 × $CH_2$), 29.9 ($CH_2$), 31.8 ($CH_2$), 68.3 (2 × $CH_2$), 114.4 (4 × CH), 118.6 (2 × CH), 131 (2 × C), 121.2 (2 × CH), 122.2 (4 × CH), 122.8 (CH), 123.9 (CH), 126.7 (CH), 126.8 (2 × C), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 145.7 (C), 149.3 (2 × C), 155.5 (2 × C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{62}H_{57}F_9O_{10}S$ (1165.19): calculated C 63.91, H 4.93, S 2.75; found C 63.90, H 4.81, S 2.55%.

**7-{4-[4-(8-Thiophen-2-yloctyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyl-oxyphenylazo)benzoate (IIh)**

Analogous reaction of acid **5j** (100 mg, 0.22 mmol) with hydroxy derivative **8** (183 mg, 0.33 mmol), DMAP (10 mg) and DIC (42 mg, 0.33 mmol, 0.05 ml) yielded after column chromatography (toluene/ethyl acetate 95/5) and crystallisation from toluene 134 mg (61%) of compound **Ig**. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, $J$=7.0, $CH_3$), 1.20-1.77 (m, 28 H, 14 × $CH_2$), 1.83 (m, 4 H, 2 × $CH_2$), 2.83 (t, 2 H, $J$=7.3, $CH_2$), 2.83 (m, 4 H, 2 × $CH_2$), 6.78 (dd, 1 H, $^3J$=3.2, $^4J$=1.2, H-3 thiophene), 6.92 (dd, 1 H, $^3J$=5.0, $^3J$=3.4, H-4 thiophene), 6.99 (d, 2 H, $J$=9.1), 7.03 (d, 2 H, $J$=9.1), 7.11 (dd, 1 H, $^3J$=5.3, $^4J$=1.2, H-5 thiophene), 7.40 (m, 4 H), 7.71 (d, 1 H, $J$=2.3r), 7.73 (d, 1 H, $J$=2.1), 7.97 (m, 6 H), 8.16 (d, 2 H, $J$=8.8), 8.33 (d, 2 H, $J$=8.8), 8.39 (d, 2 H, $J$=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0-29.9 (12 × $CH_2$), 31.7 ($CH_2$), 31.9 ($CH_2$), 68.3 ($CH_2$), 68.5 ($CH_2$), 114.4 (2 × CH), 114.8 (2 × CH), 118.6 (2 × CH), 121.0 (C), 121.2 (2 × CH), 122.2 (2 × CH), 122.6 (2 × CH), 122.8 (CH), 123.9 (CH), 125.3 (2 × CH), 126.6 (CH), 126.8 (C), 129.5 (2 × CH), 129.6 (C), 130.3 (C), 131.3 (2 × CH), 131.9 (2 × CH), 132.4 (2 × CH), 134.4 (C), 146.9 (C), 149.3 (2 × C), 155.5 (C), 155.9 (C), 156.7 (C), 162.5 (C), 163.8 (C), 164.3 (C), 164.5 (C), 164.8 (C). Elemental analysis: for $C_{61}H_{66}N_2O_8S$ (987.28): calculated C 74.21, H 6.74, N 2.84 S 3.25; found C 74.11, H 6.61, N 2.76, S 3.20%.

**7-{4-[4-(7-Phenyloxyheptyloxy)]benzoyloxy}benzoyloxynaphtalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (IIIa, X=O, n=7)**

Compound **IIIa** was prepared as for **Ia** from acid **5g** (296 mg, 0.66 mmol), hydroxy derivative **6** (250 mg, 0.44 mmol), DMAP (25 mg) and DIC (83 mg, 0.66 mmol, 0.10 ml). Product was purified by column chromatography (toluene/ethyl acetate 95/5) and crystallisations from acetone to yield 334 mg (76%) of **IIIa**. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=7.0, $CH_3$), 1.18-1.57 (m, 24 H, 12 × $CH_2$), 1.83 (m, 6 H, 3 × $CH_2$), 3.96 (t, 2 H, *J*=6.5, $CH_2$), 4.06 (m, 4 H, 2 × $CH_2$), 6.91 (m, 3 H, Ph), 6.99 (d, 4 H, *J*=9.1), 7.30 (m, 2 H, Ph), 7.38 (dd, 2 H, $^3J$=8.6, $^4J$=2.3), 7.40 (d, 4 H, *J*=8.8), 7.70 (d, 2 H, *J* =2.4), 7.95 (d, 2 H, *J*=9.1), 8.16 (d, 4 H, *J*=8.8), 8.33 (d, 4 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 25.9 ($CH_2$), 26.0 (2 × $CH_2$), 29.0-29.7 (10 × $CH_2$), 31.8 ($CH_2$), 67.7 ($CH_2$), 68.3 ($CH_2$), 68.4 ($CH_2$), 114.4 (4 × CH), 114.5 (2 × CH), 118.6 (2 × CH), 120.5 (3 × CH), 121.0 (3 × C), 122.2 (4 × CH), 126.8 (2 × C), 129.4 (4 × CH), 129.6 (C), 131.9 (4 × CH), 132.4 (4 × CH), 134.4 (C), 149.3 (2 × C), 155.5 (C), 159.1 (C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{63}H_{66}O_{11}$ (999.22): calculated C 75.73, H 6.66; found C 75.60, H 6.59%.

**7-(4-{4-[7-(4-Bromophenyloxy)heptyloxy]}benzoyloxy)benzoyloxynaphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (IIIb)**

By the same method, reaction of acid **5h** (300 mg, 0.57 mmol), hydroxy derivative **6** (388 mg, 0.68 mmol), DMAP (40 mg) and DIC (72 mg, 0.57 mmol, 0.09 ml) yield after column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone 383 mg (62%) of **IIIb**. $^1$H NMR spectrum ($CDCl_3$, 400 MHz): 0.89 (t, 3 H, *J*=7.0, $CH_3$), 1.22-1.58 (m, 24 H, 12 × $CH_2$), 1.76-1.88 (m, 6 H, 3 × $CH_2$), 3.93 (t, 2 H, *J*=6.3, $CH_2O$), 4.04-4.08 (m, 4 H, 2 × $CH_2O$), 6.77 (d, 2 H, *J*=9.0), 6.99 (d, 2 H, *J*=8.6), 6.99 (d, 2 H, *J*=9.0), 7.34-7.42 (m, 8 H), 7.70 (d, 2 H, *J*=2.0), 7.95 (d, 2 H, *J*=9.0), 8.16 (d, 4 H, *J*=8.6), 8.33 (d, 4 H, *J*=8.6). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 26.0 (2 × $CH_2$), 29.0-29.7 (11 × $CH_2$), 31.9 ($CH_2$), 68.1 ($CH_2$), 68.3 ($CH_2$), 68.4 ($CH_2$), 112.6 (C), 114.4 (4 × CH), 116.3 (2 × CH), 118.6 (2 × CH), 120.9 (C), 121.0 ( 2 xC), 121.2 (2 × CH), 122.2 (4 × CH), 126.8 (2 × C), 129.5 (2 × CH), 129.6 (C), 131.9 (4 × CH), 132.2 (2 × CH), 132.4 (4 × CH), 134.4 (C), 149.3 (2 × C), 155.5 (C), 158.2 (C), 163.8 (2 × C), 164.3 (2 × C), 164.5 ( 2 × C). Elemental analysis: for $C_{63}H_{65}BrO_{11}$ (1078.12): calculated C 70.19, H 6.08, Br 7.41; found C 70.05, H 6.06, Br 7.40%.

**7-[4-(4-{7-[4-Benzyloxycarbonyl)phenyloxy]heptyloxy})benzoyloxy]benzoyloxy-naphtalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (IIIc)**

In the same way, coupling of acid **3i** (161 mg, 0.35 mmol) with 7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-yl 4-hydroxybenzoate **9** (200 mg, 0.29 mmol) in the presence of DMAP (20 mg) and DIC (44 mg, 0.35 mmol, 0.05 ml) yielded after column chromatography (toluene/ethyl acetate 95/5) and crystallisation from acetone 298 mg (91%) of compound **IIIc**. $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=7.0, $CH_3$), 1.18-1.54 (m, 26 H, 13 × $CH_2$), 1.80-1.86 (m, 4 H, 2 × $CH_2$), 3.99-4.09 (m, 6 H, 3 × $CH_2O$), 5.33 (s, 2 H, $CH_2O$), 6.90 (d, 2 H, *J*=8.8), 6.99 (d, 2 H, *J*=9.1), 6.99 (d, 2 H, *J*=8.8), 7.32-7.47 (m, 11 H), 7.70 (d, 2 H, *J*=2.4), 7.95 (d, 2 H, *J*=8.8), 8.02 (d, 2 H, *J*=9.1), 8.16 (d, 4 H, *J*=9.1), 8.33 (d, 4 H, *J*=8.5). $^{13}$C NMR APT spectrum ($CDCl_3$, 100 MHz): 14.1 ($CH_3$), 22.7 ($CH_2$), 25.9 ($CH_2$), 26.0 ($CH_2$), 29.0-29.7 (11 × $CH_2$), 31.9 ($CH_2$), 66.4 ($CH_2$), 68.1 ($CH_2$),

68.3 ($CH_2$), 68.4 ($CH_2$), 114.1 (4 × CH), 114.4 (4 × CH), 118.6 (2 × CH), 120.9 (C), 121.0 (C), 121.2 (2 × CH), 122.1 (4 × CH), 122.3 (2 × C), 126.8 (2 × C), 128.1 (3 × CH), 128.6 (2 × CH), 129.4 (2 × CH), 129.6 (C), 131.7 (2 × CH), 131.9 (4 × CH), 132.4 (2 × CH), 134.4 (C), 136.0 (C), 149.3 (2 × C), 155.5 (2 × C), 163.0 (C), 163.8 (2 × C), 164.3 (2 × C), 164.5 (2 × C). Elemental analysis: for $C_{71}H_{72}O_{13}$ (1133.36): calculated C 75.24, H 6.40; found C 75.10, H 6.31%.

**4-{7-[4-(4-{7-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-yloxycarbonyl}-phenyloxycarbonyl)phenyloxy]heptyloxy}benzoic acid (IIId)**

A suspension of benzyl ester **IIIc** (250 mg, 0.22 mmol) and 10% Pd/C (25 mg) in a mixture of toluene and ethyl acetate (100 ml, 1/1) was stirred in a hydrogen atmosphere. When the starting benzyl ester disappeared (checked using thin layer chromatography), the catalyst was filtered off together with the formed product **IIId**. The product was extracted with a chloroform/methanol mixture (90/10) (5 × 10 ml), the extracts were evaporated and the product was crystallised from toluene. Yield 186 mg (81%). $^1$H NMR spectrum ($CDCl_3$, 300 MHz): 0.88 (t, 3 H, *J*=7.0, $CH_3$), 1.15-1.60 (m, 26 H, 13 × $CH_2$), 1.75-1.90 (m, 4 H, 2 × $CH_2$), 4.01-4.08 (m, 6 H, 3 × $CH_2O$), 6.92 (d, 2 H, *J*=9.0), 6.99 (d, 4 H, *J*=8.8), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J*=1.8), 7.95 (d, 2 H, *J*=8.8), 8.04 (d, 2 H, *J*=8.8), 8.16 (d, 4 H, *J*=8.8), 8.33 (d, 4 H, *J*=8.8). $^{13}$C NMR APT spectrum ($CDCl_3$(locked)/$CH_3OH$-$d_4$, 100 MHz): 17.8 ($CH_3$), 29.8-33.5 (15 × $CH_2$), 72.0 ($CH_2$), 72.3 (2 × $CH_2$), 117.9 (2 × CH), 118.4 (4 × CH), 122.4 (2 × CH), 124.6 (2 × C), 125.1 (2 × CH), 126.1 (4 × CH), 130.6 (3 × C), 133.4 (2 × CH), 133.6 (C), 135.7 (6 × CH), 136.3 (4 × CH), 138.3 (C), 153.1 (2 × C), 159.4 (2 × C), 166.9 (C), 167.8 (2 × C), 168.6 (4 × C), 172.7 (C). Elemental analysis: for $C_{64}H_{66}O_{13}$ (1043.23): calculated C 73.69, H 6.38; found C 73.55, H 6.30%.

### 3.3 Measurement methods and set-up

The phase transition temperatures and corresponding enthalpies are determined by differential scanning calorimetry (DSC) using Pyris Diamond Perkin-Elmer 7 calorimeter. The samples of about 2-5 mg are hermetically sealed in aluminium pans, inserted into calorimeter and inflated by a nitrogen atmosphere during measurements. Temperature and enthalpy change value were calibrated on extrapolated onset temperatures and enthalpy changes of melting points of water, indium and zinc. Calorimetric measurements are performed on cooling/heating runs at a rate of 5 K/min.

At first, phases are identified according the textures and their changes when observing the samples under the polarizing optical microscope Nikon Eclipse E600Pol. The cells for texture observation and electro-optical studies are prepared from glasses with evaporated ITO transparent electrodes (25 mm$^2$) separated by mylar sheets, which define the cell thickness (usually of about 2-3 μm). Cells are filled with studied compounds in the isotropic phase by capillary action. The Linkam LTS E350 heating/cooling stage with TMS 93 temperature programmer is used for the temperature control and the stabilization of temperature is within ±0.1 K.

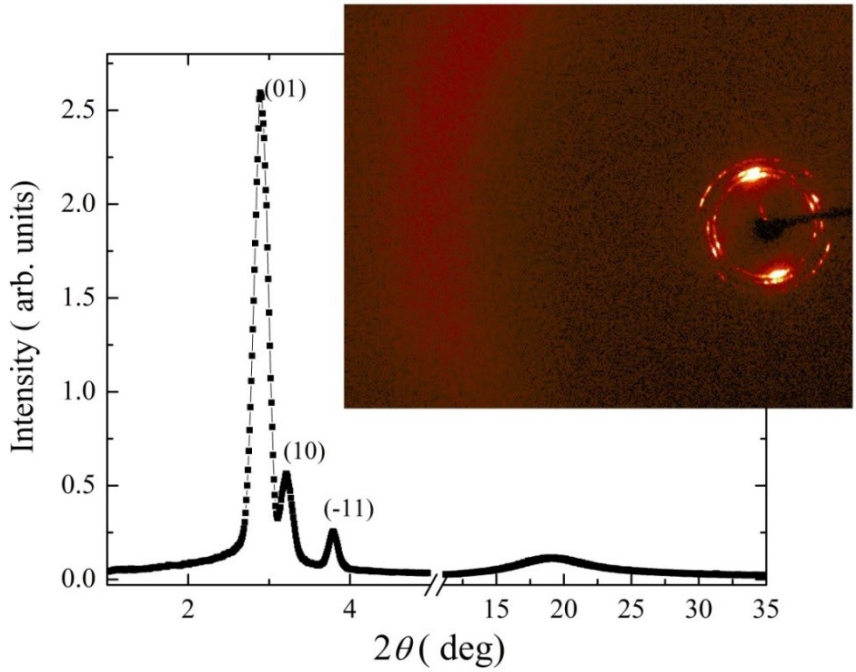
Switching studies are performed using driving voltage from an Agilent generator 33210A accompanied by a linear amplifier FLC Electronics A600. Memory oscilloscope Tektronix TDC70 allows to record profiles of the switching current vs. time.

Phase identification is proved by the X-ray diffraction studies. These measurements are performed using Bruker Nanostar system (CuKα radiation, cross-coupled Goebel mirrors, three-pinhole collimation system, Vantec 2000 area detector, MRI TCPU H heating stage) working in transmission mode and Bruker GADDS system (CuKα radiation, Goebel mirror, point collimator, Vantec 2000 area detector, modified Linkam heating stage) working in reflection mode. In both systems the temperature stability was 0.1 K. Powder samples (for Nanostar) have been put into thin-walled glass capillaries (1.5 mm diameter). Partially oriented samples for experiments in reflection for GADDS system are prepared as droplets on heated surface.

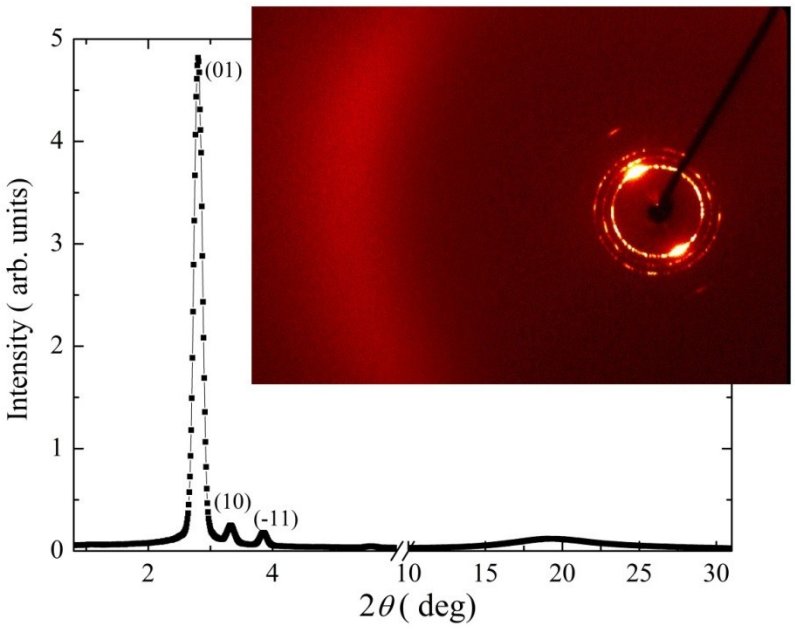
AFM measurements were performed using Bruker Dimension Icon microscope, working in scan assist mode for material-air surface at room temperature. Cantilevers with a low spring constant, $k = 0.4\ Nm^{-1}$ were used, for which the resonant frequency was in a range of 70-80 kHz.

# 4. Mesomorphic properties

a)

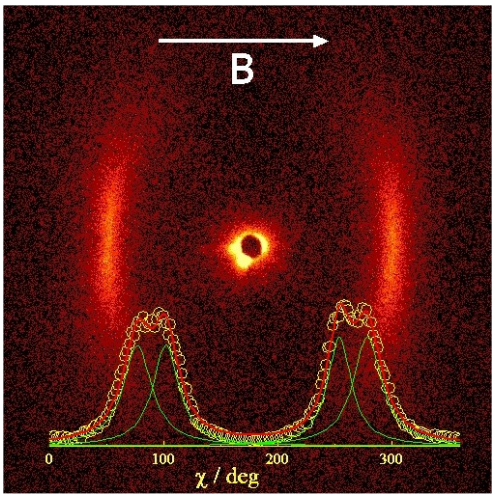



b)




Figs. S1

The x-ray intensity versus corresponding scattering angle, $\theta$, in the $B_{1Rev}$ phase for a) **Ic** at the temperature T=150ºC and b) **Id** at T=135ºC. In the inset (upper right corner), 2-dimensional x-ray pattern is placed, which was detected at the corresponding temperature.




Figs. S2

2D xrd pattern obtained in nematic phase of compound **IIIb** aligned in nematic field, at T = 140 °C, showing weakly cybotactic character of the nematic phase. Azimuthal dependence of diffracted intensity could be de-convoluted into four distinct signals, the splitting angle is ~24 deg.

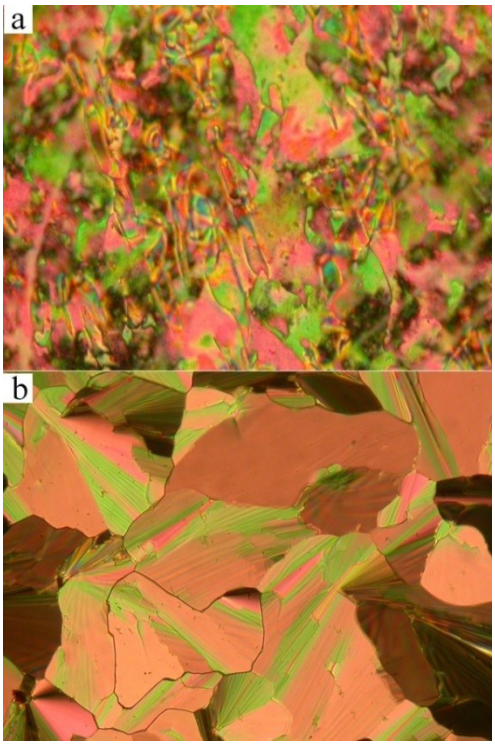



Fig. S3

Texture of **IIa** in a) the nematic phase at T=192°C and b) in the columnar $B_{1Rev}$ phase at T=184°C. The width of the figure corresponds to 300 μm.

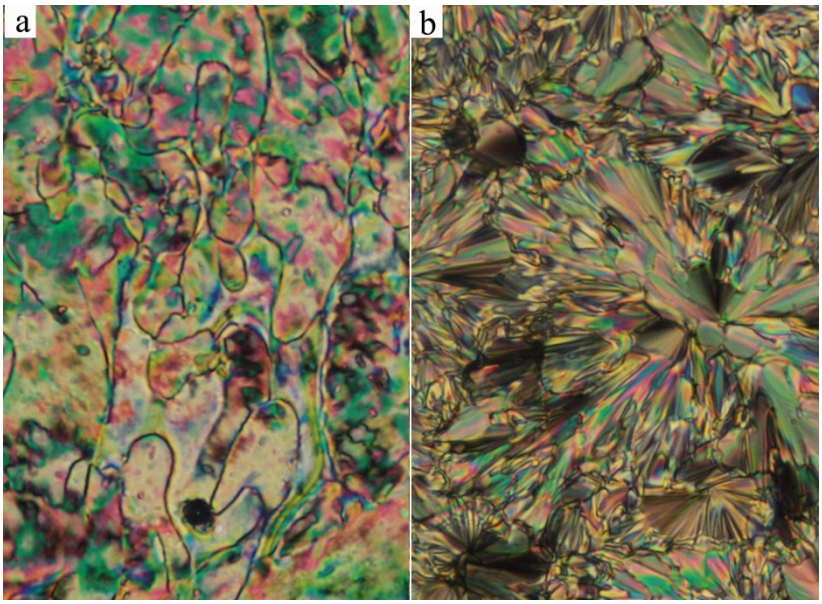
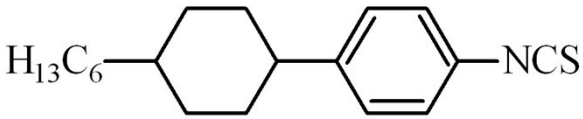



Fig. S4
Texture of **IIIb** in a) the nematic phase at T=150°C and b) in the columnar $B_{1Rev}$ phase at T=120°C. The width of every figure corresponds to 250 μm.




6CHBT
m.p. below RT
N 43.1 Iso

Fig. S5
Molecular structure of nematogenic compound 6CHBT. Material was provided by Military University of technology, Warsaw, Poland

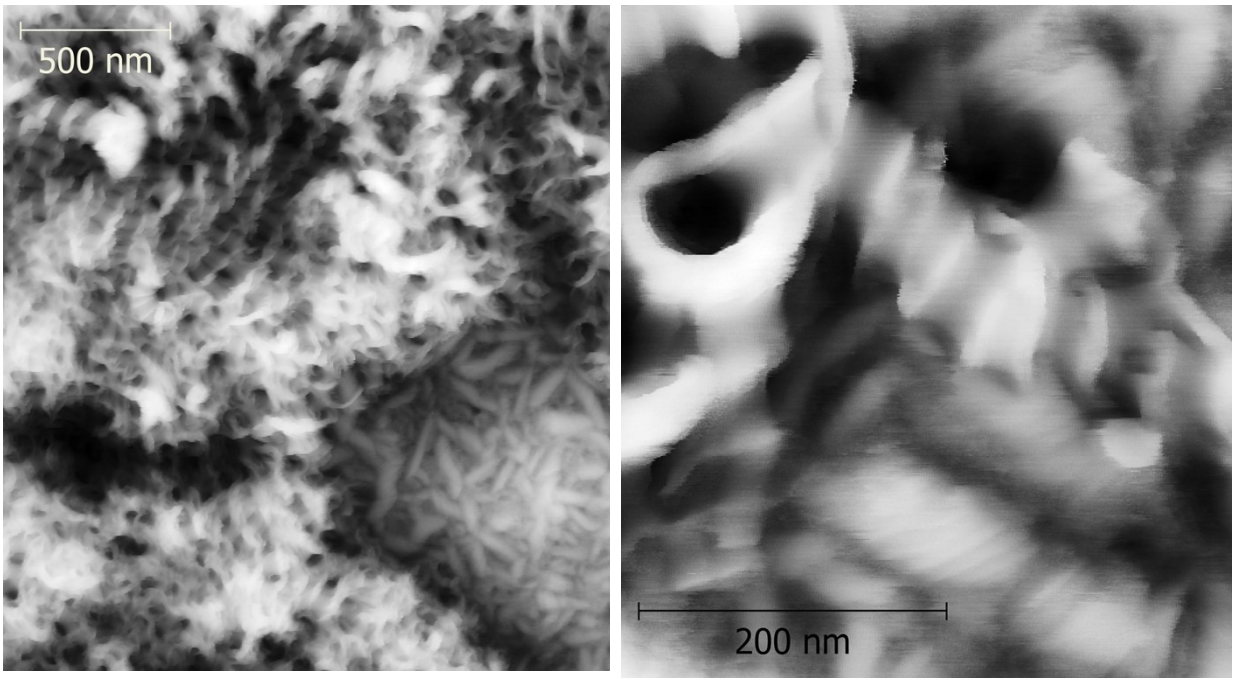



Fig. S6
AFM images taken for a contact cell filled with pure compound **If** and its mixture with nematogen 6CHB, showing the change of the DC phase morphology upon doping with rod-like molecules: toroidal-like objects are replaced with irregular sponge and twisted ribbons.

# 5. References

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