**W-shaped mesogens and variations of their molecular structure**

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**1. Synthesis**

1.1. Synthesis of the lengthening arms

The acids **1-3** have been obtained by the previously reported procedures. [S1-S3] The synthesis of the THP-protected acids **6a-c** and **8a-c** has been performed by utilizing the reported procedure [S4] (see Scheme S1). Alkylation of methyl 4-hydroxybenzoate (**4**) with ω-tetrahydropyranyloxy alkyl bromides in basic medium yielded the corresponding esters **5a-c** which were subsequently hydrolysedto provide the one-ring lengthening arms **6a-c**. To get analogous two-ring acids, compounds **6a-c** were esterified with4-hydroxybenzaldehyde in the presence of *N*,*N*´-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) catalysis. The intermediate formyl esters **7a-c** were oxidised with potassium permanganate in acetone to give rise to acids **8a-c** (**a** m=2, **b** m=4, **c** m=8). Synthesis of acid **6d** and **8d** is shown in ref. [S4]



Scheme S1 Synthesis of lengthening arms.

1.2. Synthesis of intermediates

To obtain the key monomeric units **14,15,20a-d,21a-c,22,23** (Scheme S2 and S3) possessing a free hydroxylic group in the terminal position for the final junction, we utilized hydroxy derivatives **9** and **10**, synthesis of whose was described in the previous papers. [S3,S5]. The compound **11** terminated with the perfluoroalkyl chain has been synthesised analogously by acylation of naphthalene-2,7-diol with acid **3**. Compounds **14,15** lacking a terminal alkyl chain have been obtained by acylation of **9** with acid chlorides of the corresponding acid **1** and **2** to yield intermediate **12** and **13**, resp. The protecting benzyl group was then removed by catalytic hydrogenation on Pd/C to release the terminal hydroxyl phenyl residue (Scheme S2).

Esterification of compounds **9-11** with the THP-protected acids **6a-d** and **8a-d** was performed in a *N,N*´-dicyclohexylcarbodiimide (DCC) mediated reaction in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP) (Scheme S3) to give rise to intermediates **16a-d,17a-c,18,19**. The THP-protecting group was finally removed in a standard *p*-toluenesulfonic acid catalysed hydrolysis to get compounds **20a-d, 21a-c, 22,23**. Compounds **17d** and **21d** were taken from ref. [S4]



Scheme S2 Synthesis of intermediates **14,15**.



Scheme S3 Synthesis of intermediate monomers **20a-d,21a-c,22,23**.

1.3. Synthesis of dimers

Compounds **14, 15, 20a-d, 21a-d, 2,23** represent „monomeric“ compounds terminated with a hydroxylic group at one end. Thus, their esterification reaction with a difunctional bent-core unit acid dichloride, such as isophthaloyl chloride (**1,3Ph**), phthaloyl chloride (**1,2Ph**) and thiophene-2,5-dicarbonyl chloride (**Th**) results in connection of two monomers, creation of the inner bend of about 120°, 60° and 148°, and formation of the studied dimers **Ia-e**, **IIa-i**, and **IIIa-c**, resp. (Scheme 4 and 5). Hydrosilylation of **IIf** with 1,1,1,3,3-pentamethyl-1,3-disiloxane and 1,1,1,3,3,5,5-henptamethyl-1,3,5,trisiloxane was performed with Karstedt´s catalyst to yield terminal silylated dimers **IIg**,**IIh**, resp.



Scheme S4 Synthesis of dimers of series **I** and **II**.



Scheme S5 Synthesis of dimers **IIg**,**IIh** and **III**.

**2. Experimental**

The structures of the intermediates and the products were confirmed by proton (1H) and carbon (13C) nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform and dimethylsulfoxide (DMSO-d6) were used as solvents and signals of the solvents served as internal standards, *J* values are given in Hz. Purity of all final compounds was verified by high performance liquid chromatography (HPLC) analysis (Luna Silica 5 μm, 150 × 4.6 mm) and found >99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm).

**2.1. General method of acylation with acid chlorides**

To a mixture of acid **1** and **2**,**3** resp. (1 mmol) and oxalyl chloride (0.42 ml, 5 mmol) in dry dichloromethane (50 ml), a drop of DMF was added and the mixture was stirred at 25 °C for 18 h in an inert argon atmosphere and then evaporated. The residue was dissolved in toluene (10 ml). and added to a pre-heated solution (50 °C) of naphthol **9** (0.60 mmol), resp., and DMAP (0.9 mmol) in toluene (15 ml). The reaction mixture was stirred at 110 °C for 1 h, cooled to room temperature, and decomposed with water (40 ml). The organic layer was separated and the aqueous layer was washed with chloroform (3 × 40 ml). The combined organic solution was dried with anhydrous magnesium sulphate and the solvent was evaporated. The crude product was purified by column chromatography (chloroform/methanol 99/1).

***7-(4-Benzyloxybenzoyloxy)naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (12)***. Yield 98%), m.p. 150 °C. 1H NMR (CDCl3): 0.89 (t, 3 H, *J=*6.6, CH3), 1.27-1.51 (m, 18 H, (CH2)9), 1.83 (m, 2 H, CH2CH2O), 4.06 (t, 2 H, *J=*6.6, CH2O), 5.18 (s, 2 H, PhCH2O), 6.99 (d, 2 H, *J=*8.8), 7.09 (d, 2 H, *J=*8.8), 7.34-7.48 (m, 9 H), 7.68 (m, 2 H), 7.93 (d, 1 H, *J=*8.8), 7.94 (d, 1 H, *J=*8.8), 8.16 (d, 2 H, *J=*8.8), 8.21 (d, 2 H, *J=*8.8), 8.33 (d, 2 H, *J=*8.5). 13C NMR (CDCl3): 165.2 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.4 (C), 155.7 (C), 149.7 (C), 149.5 (C), 136.3 (C), 134.7 (C), 132.7 (4 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 129.0 (2 × CH), 128.5 (CH), 127.8 (2 × CH), 127.0 (C), 122.4 (2 × CH), 122.2 (C), 121.7 (CH), 121.3 (CH), 121.2 (C), 118.9 (CH), 118.8 (CH), 115.0 (2 × CH), 114.7 (2 × CH), 70.4 (CH2), 68.6 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 23.0 (CH2), 14.4 (CH3). Elemental analysis: for C50H50O8 (778.95): calculated C 77.10, H 6.47; found C 77.01, H 6.36%.

***7-[4-(4-Benzyloxybenzoyloxy)benzoyloxy]naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)-benzoate (13)***. Yield 92%, m.p. 169 °C. 1H NMR (CDCl3):0.89 (t, 3 H, *J=*6.6, CH3), 1.27-1.49 (m, 18 H, (CH2)9), 1.83 (m, 2 H, CH2CH2O), 4.06 (t, 2 H, *J=*6.4, CH2O), 5.18 (s, 2 H, PhCH2O), 7.00 (d, 2 H, *J=*8.8), 7.09 (d, 2 H, *J=*9.1), 7.37-7.47 (m, 11 H), 7.70 (d, 2 H, *J=*2.1), 7.95 (d, 2 H, *J=*8.8), 8.17 (d, 2 H, *J=*9.1), 8.18 (d, 2 H, *J=*9.1), 8.34 (d, 4 H, *J=*8.5). 13C NMR (CDCl3): 164.8 (C), 164.6 (C), 164.5 (C), 164.1 (C), 163.5 (C), 155.7 (C), 155.6 (C), 149.5 (2 × C), 136.2 (C), 134.6 (2 × C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 129.0 (2 × CH), 128.6 (CH), 127.8 (2 × CH), 127.1 (C), 127.0 (C), 122.4 (4 × CH), 121.7 (C), 121.5 (2 × CH), 121.1 (C), 118.9 (2 x CH), 115.1 (2 × CH), 114.7 (2 × CH), 70.5 (CH2), 68.6 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 23.0 (CH2), 14.4 (CH3). Elemental analysis: for C57H54O10 (899.06): calculated C 76.15, H 6.05; found C 76.08, H 6.00%.

***7-Hydroxynaphthalen-2-yl 4-[4-(9,9,10,10,11,11,12,12,12-nonafluordodecyloxy)-benzoyloxy]benzoate (11)***

In the silmilar way, the crude acid chloride (4.25 mmol) of acid **3** was dissolved in dry dichloromethane (5 ml) and added to a solution of naphthalene-2,7-diol (2.7 g, 17 mmol) and triethylamine (0.7 ml, 5.1 mmol) in a mixture of dichloromethane (110 ml) and acetone (30 ml). After stirring at 50 °C for 6 h and work up, the crude product was purified by column chromatography (chloroform/methanol 99/1) and crystallisation from toluene. Yield 2.30 g (70%) of naphthol **11**, m.p. 176-177.5 °C. 1H NMR (CDCl3): 1.40-1.62 (m, 10 H, (CH2)5), 1.84 (m, 2 H, CH2CH2O), 2.06 (m, 2 H, CH2CF2), 4.06 (t, 2 H, *J=*6.4, CH2O), 5.25 (s, 1 H, OH), 6.99 (d, 2 H, *J=*9.1), 7.05-7.10 (m, 2 H), 7.19 (dd, 1 H, *J=*8.8, *J=*2.3), 7.39 (d, 2 H, *J=*8.5), 7.50 (d, 1 H, *J=*2.1), 7.75 (d, 1 H, *J=*8.8), 7.81 (d, 1 H, *J=*8.8), 8.17 (d, 2 H, *J=*8.8), 8.32 (d, 2 H, *J=*8.5).13C NMR (CDCl3): 165.0 (C), 164.6 (C), 164.0 (C), 155.6 (C), 154.3 (C), 149.5 (C), 135.4 (C), 132.7 (2 × CH), 132.1 (2 × CH), 130.0 (CH), 129.6 (CH), 127.2 (2 × C), 122.4 (2 × CH), 121.2 (C), 119.0 (CH), 117.9 (CH), 117.5 (CH), 114.6 (2 × CH), 109.6 (CH), 68.5 (CH2), 31.0 (CH2), 29.4 (CH2), 29.3 (2 × CH2), 29.2 (CH2), 26.2 (CH2), 20.3 (CH2). 19F NMR (CDCl3): 81.4 (m, 3 F, CF3), 115.0 (m, 2 F, CF2), 124.9 (m, 2 F, CF2), 126.5 (m, 2 F, CF2). Elemental analysis: for C37H33F9O5 (728.66): calculated C 60.99, H 4.56; found C 60.86, H 4.48%.

**2.2. General procedure for the alkylation**

To a mixture of methyl 4-hydroxybenzoate (**4**) (1.8 g, 12 mmol) and freshly fused potassium carbonate (1.5 g, 11 mmol) in dry DMF (15 ml) was added the corresponding THPO-alkyl bromide (10 mmol) and the mixture was stirred at 60-75 °C for 25 h in an inert argon atmosphere. After cooling to room temperature the mixture was diluted with water (40 ml), extracted with toluene (3 x 10 ml) and the combined organic solution was dried with anhydrous MgSO4. The solvent was evaporated and the crude product was purified by column chromatography (hexane/ethyl acetate 6/1 and toluene/*tert*-butyl methyl ether 30/1, resp.).

***Methyl 4-[4-(tetrahydro-2H-pyran-2-yloxy)butoxy]benzoate (5b)****.* Yield 90%, colourless liquid. 1H NMR (CDCl3): 1.54-1.93 (m, 10 H, 5 × CH2), 3.49 (m, 2 H, CH2O), 3.84 (m, 5 H, CH2O, OCH3), 4.05 (t, 2 H, *J=*6.3, CH2O), 4.59 (m, 1 H, OCHO), 6.90 (d, 2 H, *J=*8.8), 7.97 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 167.0 (C), 163.1 (C), 131.7 (2 × CH), 122.5 (C), 114.2 (2 × CH), 99.1 (CH), 68.0 (CH2), 67.2 (CH2), 62.5 (CH2), 52.0 (CH3), 31.0 (CH2), 26.5 (CH2), 26.3 (CH2), 25.7 (CH2), 19.8 (CH2). Elemental analysis: for C17H24O5 (308.38): calculated C 66.21, H 7.84; found C 66.06, H 7.86%.

***Methyl******4-[8-(tetrahydro-2H-pyran-2-yloxy)octyloxy]benzoate (5c)***. Yield 96%, colourless liquid. 1H NMR (CDCl3): 1.35-1.70 (m, 16 H, 8 × CH2), 1.79 (m, 2 H, CH2CH2O), 3.38 (m, 1 H, CH2O), 3.49 (m, 1 H, CH2O), 3.73 (m, 1 H, CH2O), 3.87 (m, 4 H), 3.99 (t, 2 H, *J=*6.4, CH2O), 4.56 (m, 1 H, OCHO), 6.89 (d, 2 H, *J=*9.1), 7.97 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 167.2 (C), 163.2 (C), 131.8 (2 × CH), 122.5 (C), 114.3 (2 × CH), 99.1 (CH), 68.4 (CH2), 67.9 (CH2), 62.6 (CH2), 52.1 (CH3), 31.0 (CH2), 29.9 (CH2), 29.6 (CH2), 29.5 (CH2), 29.3 (CH2), 26.4 (CH2), 26.1 (CH2), 25.7 (CH2), 19.9 (CH2). Elemental analysis: for C21H32O5 (364.49): calculated C 69.20, H 8.85; found C 69.08, H 8.80%.

**2.3. General procedure for the hydrolysis**

To a solution of ester **5a-c** (10 mmol) in methanol (80 ml), a solution of sodium hydroxide (2.4 g, 60 mmol) in water (40 ml) was added. The reaction mixture was stirred at 90-100 °C for 3 h, cooled to room temperature and diluted with icy water (300 ml). After acidification with hydrochloric acid to pH=5-7, the precipitate was filtered off, washed with water (3 × 20 ml), dried at reduced pressure and crystallised from toluene.

***4-[2-(Tetrahydro-2H-pyran-2-yloxy)ethoxy]benzoic acid (6a)***. Yield 91%, m.p. 113.5-114.5 °C. 1H NMR spectrum is in agreement with ref.[S6] 13C NMR (CDCl3): 172.1 (C), 163.6 (C), 132.5 (2 × CH), 122.0 (C), 114.6 (2 × CH), 99.3 (CH), 67.8 (CH2), 65.9 (CH2), 62.4 (CH2), 30.7 (CH2), 25.6 (CH2), 19.5 (CH2).

***4-[4-(Tetrahydro-2H-pyran-2-yloxy)butoxy]benzoic acid (6b)***. Yield 93%, m.p. 107-109 °C. 1H NMR (CDCl3): 1.53-1.95 (m, 10 H, (CH2)5), 3.49 (m, 2 H, CH2O), 3.84 (m, 2 H, CH2O), 4.07 (t, 2 H, *J=*6,3, CH2O), 4.60 (m, 1 H, OCHO), 6.93 (d, 2 H, *J=*9.1), 8.04 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 172.0 (C), 163.7 (C), 132.5 (2 × CH), 121.8 (C), 114.4 (2 × CH), 99.1 (CH), 68.2 (CH2), 67.3 (CH2), 62.6 (CH2), 30.9 (CH2), 26.5 (CH2), 26.3 (CH2), 25.7 (CH2), 19.8 (CH2). Elemental analysis: for C16H22O5 (294.35): calculated C 65.29, H 7.53; found C 65.16, H 7.48%.

***4-[8-(Tetrahydro-2H-pyran-2-yloxy)octyloxy]benzoic acid (6c)***. Yield 99%, m.p. 80 °C. 1H NMR (CDCl3): 1.36-1.84 (m, 18 H, 9 × CH2), 3.39 (m, 1 H, CH2O), 3.50 (m, 1 H, CH2O), 3.76 (m, 1 H, CH2O), 3.87 (m, 1 H, CH2O), 4.00 (t, 2 H, *J=*6.3, CH2O), 4.58 (m, 1 H, OCHO), 6.90 (d, 2 H, *J=*8.5), 8.02 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 172.2 (C), 163.8 (C), 132.5 (2 × CH), 121.8 (C), 114.4 (2 × CH), 99.2 (CH), 68.3 (CH2), 67.9 (CH2), 62.6 (CH2), 31.0 (CH2), 30.0 (CH2), 29.6 (CH2), 29.5 (CH2), 29.3 (CH2), 26.4 (CH2), 26.2 (CH2), 25.7 (CH2), 19.9 (CH2). Elemental analysis: for C20H30O5 (350.46): calculated C 68.55, H 8.63; found C 68.41, H 8.55%.

**2.4. General procedure for the acylation by DCC coupling**

A mixture of 4-hydroxybenzaldehyde (1 mmol), acid **6a-c** (1.3 mmol), DCC (1.6 mmol) and DMAP (10 mg) in dry dichloromethane (60 ml) was stirred at room temperature for 20 h in an inert argon atmosphere. The reaction mixture was diluted with water (15 ml), layers were separated and the aqueous layer was washed with dichloromethane (2 x 10 ml). The combined organic solution was dried with anhydrous MgSO4. After evaporation, the crude product was purified by column chromatography (silica gel, toluene/tert-butyl methyl ether 8/1, 20/1 or 30/1).

***4-Formylphenyl******4-[2-(tetrahydro-2H-pyran-2-yloxy)ethoxy]benzoate (7a)***. Yield 82%, m.p. 53-55 °C. 1H NMR (CDCl3): 1.53-1.85 (m, 6 H, 3 × CH2), 3.53 (m, 1 H, CH2O), 3.86 (m, 2 H, CH2O), 4.10 (m, 1 H, CH2O), 4.24 (m, 2 H, CH2O), 4.71 (m, 1 H, OCHO), 7.02 (d, 2 H, *J=*9.1), 7.39 (d, 2 H, *J=*8.5), 7.95 (d, 2 H, *J=*8.8), 8.13 (d, 2 H, *J=*9.1), 10.00 (s, 1 H, CHO). 13C NMR (CDCl3): 191.2 (CHO), 164.4 (C), 163.8 (C), 156.1 (C), 134.1 (C), 132.6 (2 × CH), 131.5 (2 × CH), 122.8 (2 × CH), 121.4 (C), 114.9 (2 × CH), 99.3 (CH), 68.0 (CH2), 65.8 (CH2), 62.5 (CH2), 30.7 (CH2), 25.6 (CH2), 19.6 (CH2). Elemental analysis: for C21H22O6 (370.41): calculated C 68.10, H 5.99; found C 68.29, H 6.04%.

***4-Formylphenyl******4-[4-(tetrahydro-2H-pyran-2-yloxy)butoxy]benzoate (7b)***. Yield 78%, m.p. 51-53 °C. 1H NMR (CDCl3): 1.55-1.95 (m, 10 H, 5 × CH2), 3.50 (m, 2 H, CH2O), 3.85 (m, 2 H, CH2O), 4.10 (t, 2 H, *J=*6.3, CH2O), 4.61 (m, 1 H, OCHO), 6.98 (d, 2 H, *J=*8.8), 7.40 (d, 2 H, *J=*8.8), 7.97 (d, 2 H, *J=*8.5), 8.14 (d, 2 H, *J=*8.8), 10.02 (s, 1 H, CHO). 13C NMR (CDCl3): 191.2 (CHO), 164.4 (C), 164.0 (C), 156.1 (C), 134.1 (C), 132.7 (2 × CH), 131.5 (2 × CH), 122.8 (2 × CH), 121.1 (C), 114.7 (2 × CH), 99.2 (CH), 68.3 (CH2), 67.2 (CH2), 62.7 (CH2), 31.0 (CH2), 26.5 (CH2), 26.3 (CH2), 25.7 (CH2), 19.9 (CH2). Elemental analysis: for C23H26O6 (398.46): calculated C 69.33, H 6.58; found C 69.20, H 6.44%.

***4-Formylphenyl******4-[8-(tetrahydro-2H-pyran-2-yloxy)octyloxy]benzoate (7c)***. Yield 80%, m.p. 56-58 °C. 1H NMR (CDCl3): 1.37-1.84 (m, 18 H, 9 × CH2), 3.39 (m, 1 H, CH2O), 3.50 (m, 1 H, CH2O), 3.74 (m, 1 H, CH2O), 3.87 (m, 1 H, CH2O), 4.04 (t, 2 H, *J=*6.6, CH2O), 4.57 (m, 1 H, OCHO), 6.98 (d, 2 H, *J=*9.1), 7.40 (d, 2 H, *J=*8.8), 7.96 (d, 2 H, *J=*8.8), 8.13 (d, 2 H, *J=*9.1), 10.01 (s, 1 H, CHO). 13C NMR spectrum (CDCl3): 191.2 (CHO), 164.4 (C), 164.0 (C), 156.1 (C), 134.1 (C), 132.6 (2 × CH), 131.4 (2 × CH), 122.2 (2 × CH), 121.0 (C), 114.6 (2 × CH), 99.1 (CH), 68.6 (CH2), 67.8 (CH2), 62.6 (CH2), 31.0 (CH2), 29.9 (CH2), 29.6 (CH2), 29.5 (CH2), 29.3 (CH2), 26.4 (CH2), 26.1 (CH2), 25.7 (CH2), 20.0 (CH2). Elemental analysis: for C27H34O6 (454.57): calculated C 71.34, H 7.54; found C 71.19, H 7.30%.

In the same way, DCC coupling of hydroxy derivatives **9-11** with acids **6a-d,8a-d** yielded the THP protected monomers **16a-d,17a-c,18,19**.

***7-{4-[2-(Tetrahydro-2H-pyran-2-yloxy)ethoxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyl-oxybenzoyloxy)benzoate (16a)***. Yield 90%, m.p. 123-128 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.7, CH3), 1.27-1.85 (m, 26 H, 13 × CH2), 3.55 (m, 1 H, CH2O), 3.88 (m, 2 H, CH2O), 4.03-4.15 (m, 2 H, CH2O), 4.26 (m, 2 H, CH2O), 4.73 (m, 1 H, OCHO), 6.99 (d, 2 H, *J=*9.1), 7.04 (d, 2 H, *J=*9.1), 7.35-7.41 (m, 4 H), 7.68 (s, 2 H), 7.93 (d, 1 H, *J=*8.8), 7.94 (d, 1 H, *J=*9.1), 8.16 (d, 2 H, *J=*9.1), 8.20 (d, 2 H, *J=*9.1), 8.33 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 165.2 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.6 (C), 155.7 (C), 149.7 (C), 149,4 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 122.0 (C), 121.7 (CH), 121.3 (CH), 121.2 (C), 118.9 (CH), 118.8 (CH), 114.8 (2 × CH), 114.7 (2 × CH), 99.3 (CH), 68.6 (CH2), 67.9 (CH2), 65.9 (CH2), 62.5 (CH2), 32.2 (CH2), 30.7 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 25.6 (CH2), 22.9 (CH2), 19.6 (CH2), 14.4 (CH3). Elemental analysis: for C50H56O10 (817.00): calculated C 73.51, H 6.91; found C 73.38, H 6.88%.

***7-{4-[4-(Tetrahydro-2H-pyran-2-yloxy)butoxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyl-oxybenzoyloxy)benzoate (16b)***. Yield 93%, m.p. 125-129 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.6, CH3), 1.27-1.60 (m, 20 H, 10 × CH2), 1.74-1.95 (m, 10 H, 5 × CH2CH2O), 3.50 (m, 2 H, CH2O), 3.86 (m, 2 H, CH2O), 4.06 (t, 2 H, *J=*6.4, CH2O), 4.11 (t, 2 H, *J=*6.3, CH2O), 4.61 (m, 1 H, OCHO), 6.99 (d, 2 H, *J=*9.1), 7.00 (d, 2 H, *J=*8.8), 7.35-7.41 (m, 4 H), 7.68 (s, 2 H), 7.93 (d, 1 H, *J=*9.1), 7.94 (d, 1 H, *J=*9.1), 8.16 (d, 2 H, *J=*8.8), 8.19 (d, 2 H, *J=*8.8), 8.33 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 165.2 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.8 (C), 155.7 (C), 149.7 (C), 149.4 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 121.7 (C), 121.7 (CH), 121.3 (CH), 121.2 (C), 118.9 (CH), 118.8 (CH), 114.7 (2 × CH), 114.6 (2 × CH), 99.2 (CH), 68.6 (CH2), 68.3 (CH2), 67.3 (CH2), 62.7 (CH2), 32.2 (CH2), 31.0 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.5 (CH2), 26.4 (CH2), 26.2 (CH2), 25.7 (CH2), 22.9 (CH2), 19.9 (CH2), 14.4 (CH3). Elemental analysis: for C52H60O10 (845.05): calculated C 73.91, H 7.16; found C 73.86, H 7.11%.

***7-{4-[8-(Tetrahydro-2H-pyran-2-yloxy)octyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyl-oxybenzoyloxy)benzoate (16c)***. Yield 94%, m.p. 108.5-110.5 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.4, CH3),1.27-1.61 (m, 32 H, 16 × CH2),1.83 (m, 6 H, 3 × CH2CH2O),3.39 (m, 1 H, CH2O),3.50 (m, 1 H, CH2O),3.75 (m, 1 H, CH2O),3.86 (m, 1 H, CH2O),4.05 (t, 4 H, *J=*6.4, CH2O),4.58 (m, 1 H, OCHO),6.99 (d, 4 H, *J=*8.5),7.35-7.40 (m, 4 H), 7.67 (s, 2 H), 7.93 (d, 2 H, *J=*8.8), 8.16 (d, 2 H, *J=*8.5), 8.19 (d, 2 H, *J=*8.5), 8.32 (d, 2 H, *J=*7.9).13C NMR (CDCl3): 165.3 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.9 (C), 155.7 (C), 149.7 (C), 149.4 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 121.7 (CH), 121.6 (C), 121.3 (CH), 121.1 (C), 118.9 (CH), 118.8 (CH), 114.7 (2 × CH), 114.6 (2 × CH),99.1 (CH),68.6 (CH2), 68.5 (CH2), 67.9 (CH2), 62.7 (CH2),32.2 (CH2), 31.0 (CH2), 30.0 (CH2), 29.9 (2 × CH2), 29.8 (4 × CH2), 29.6 (2 × CH2), 29.5 (CH2), 29.3 (2 × CH2), 26.4 (CH2), 26.2 (CH2), 25.7 (CH2), 22.9 (CH2), 20.0 (CH2), 14.4 (CH3). Elemental analysis: for C56H68O10 (901.16): calculated C 74.64, H 7.61; found C 74.55, H 7.50%.

***7-{4-[12-(Tetrahydro-2H-pyran-2-yloxy)dodecyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (16d)***. Yield 86%, m.p. 107.5-109.5 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.7, CH3), 1.27-1.71 (m, 40 H, 20 × CH2), 1.83 (m, 6 H, 3 × CH2CH2O), 3.38 (m, 1 H, CH2O), 3.50 (m, 1 H, CH2O), 3.73 (m, 1 H, CH2O), 3.88 (m, 1 H, CH2O), 4.06 (t, 4 H, *J=*6.6, CH2O), 4.58 (m, 1 H, OCHO), 6.99 (d, 4 H, *J=*8.8), 7.35-7.41 (m, 4 H), 7.68 (s, 2 H), 7.93 (d, 1 H, *J=*8.8), 7.94 (d, 1 H, *J=*8.8), 8.16 (d, 2 H, *J=*8.5), 8.19 (d, 2 H, *J=*8.8), 8.33 (d, 2 H, *J=*8.5). 13C NMR (CDCl3): 165.2 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.9 (C), 155.7 (C), 149.7 (C), 149.4 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.5 (CH), 127.0 (C), 122.4 (2 × CH), 121.7 (CH), 121.6 (C), 121.3 (CH), 121.2 (C), 118.9 (CH), 118.8 (CH), 114.7 (2 × CH), 114.6 (2 × CH), 99.1 (CH), 68.6 (2 × CH2), 67.9 (CH2), 62.6 (CH2), 32.2 (CH2), 31.0 (CH2), 30.0 (CH2), 29.9 (4 × CH2), 29.8 (5 × CH2), 29.7 (2 × CH2), 29.6 (2 × CH2), 29.3 (2 × CH2), 26.5 (CH2), 26.2 (CH2), 25.8 (CH2), 22.9 (CH2), 20.0 (CH2), 14.4 (CH3). Elemental analysis: for C60H76O10 (957.27): calculated C 75.28, H 8.00; found C 75.12, H 7.96%.

***7-(4-{4-[2-(Tetrahydro-2H-pyran-2-yloxy)ethoxy]benzoyloxy}benzoyloxy)naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (17a)***. Yield 87%, m.p. 141.5-143 °C. 1H NMR (CDCl3): 0.89 (t, 3 H, *J=*6.7, CH3), 1.28-1.85 (m, 26 H, 13 × CH2), 3.55 (m, 1 H, CH2O), 3.88 (m, 2 H, CH2O), 4.05-4.15 (m, 3 H, CH2O), 4.26 (m, 2 H, CH2O), 4.73 (m, 1 H, OCHO), 6.99 (d, 2 H, *J=*8.8), 7.04 (d, 2 H, *J=*9.1), 7.36-7,41 (m, 6 H), 7.70 (d, 2 H, *J=*2.1), 7.94 (d, 2 H, *J=*9.1), 8.16 (d, 2 H, *J=*9.1), 8.17 (d, 2 H, *J=*9.1), 8.33 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (C), 164.5 (C), 164.1 (C), 163.8 (C), 155.7 (2 × C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (C), 121.5 (2 × CH), 121.1 (C), 118.9 (2 × CH), 114.8 (2 × CH), 114.7 (2 × CH), 99.4 (CH), 68.6 (CH2), 67.9 (CH2), 65.9 (CH2), 62.5 (CH2), 32.2 (CH2), 30.7 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 25.6 (CH2), 23.0 (CH2), 19.6 (CH2), 14.4 (CH3). Elemental analysis: for C57H60O12 (937.11): calculated C 73.06, H 6.45; found C 72.96, H 6.31%.

***7-(4-{4-[4-(Tetrahydro-2H-pyran-2-yloxy)butoxy]benzoyloxy}benzoyloxy)naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (17b)***. Yield 89%, m.p. 134.5-140 °C. 1H NMR (CDCl3): 0.89 (t, 3 H, *J=*6.7, CH3), 1.28-1.61 (m, 22 H, 11 × CH2), 1.73-1.97 (m, 8 H, 4 × CH2CH2O), 3.50 (m, 2 H, CH2O), 3.86 (m, 2 H, CH2O), 4.05 (t, 2 H, *J=*6.6, CH2O), 4.10 (t, 2 H, *J=*6.4, CH2O), 4.61 (m, 1 H, OCHO), 6.99 (d, 4 H, *J=*9.1), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.4), 7.94 (d, 2 H, *J=*8.8), 8.16 (d, 4 H, *J=*8.8), 8,33 (d, 4 H, *J=*8.5). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (2 × C), 164.1 (C), 164.0 (C), 155.7 (2 × C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.2 (C), 121.1 (C), 118.9 (2 × CH), 114.7 (4 × CH), 99.2 (CH), 68.6 (CH2), 68.3 (CH2), 67.3 (CH2), 62.7 (CH2), 32.2 (CH2), 31.0 (CH2), 29.9 (2 × CH2), 29.8 2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.5 (CH2), 26.4 (CH2), 26.2 (CH2), 25.7 (CH2), 23.0 (CH2), 19.9 (CH2), 14.4 (CH3). Elemental analysis: for C59H64O12 (965.16): calculated C 73.42, H 6.68; found C 76.33, H 6.59%.

***7-(4-{4-[8-(Tetrahydro-2H-pyran-2-yloxy)octyloxy]benzoyloxy}benzoyloxy)naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (17c)***. Yield 87%, m.p. 143-145.5 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.6, CH3), 1.27-1.61 (m, 34 H, 17 × CH2), 1.83 (m, 4 H, 2 × CH2CH2O), 3.39 (m, 1 H, CH2O), 3.51 (m, 1 H, CH2O), 3.75 (m, 1 H, CH2O), 3.88 (m, 1 H, CH2O), 4.06 (t, 4 H, *J=*6.4, CH2O), 4.58 (m, 1 H, OCHO), 6.99 (d, 4 H, *J=*9.1), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.3), 7.95 (d, 2 H, *J=*9.1), 8.16 (d, 4 H, *J=*8.8), 8.33 (d, 4 H, *J=*8.5). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (2 × C), 164.0 (2 × C), 155.7 (2 × C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.1 (2 × C), 118.9 (2 × CH), 114.6 (4 × CH), 99.2 (CH), 68.6 (2 × CH2), 67.9 (CH2), 62.7 (CH2), 32.2 (CH2), 31.0 (CH2), 30.0 (CH2), 29.9 (4 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.5 (CH2), 29.3 (2 x CH2), 26.4 (CH2), 26.2 (2 ×x CH2), 25.7 (CH2), 23.0 (CH2), 20.0 (CH2), 14.4 (CH3). Elemental analysis: for C63H72O12 (1021.27): calculated C 74.09, H 7.11; found C 73.94, H 7.08%.

***7-(4-{4-[12-(Tetrahydro-2H-pyran-2-yloxy)dodecyloxy]benzoyloxy}benzoyloxy)naphthalen-2-yl 4-(4-undec-10-enyloxybenzoyloxy)benzoate (18)***. Yield 68%, m.p. 142-144 °C. 1H NMR (CDCl3): 1.29-1.61 (m, 36 H, 18 × CH2), 1.83 (m, 4 H, 2 × CH2CH2O), 2.05 (m, 2 H, CH2), 3.38 (m, 1 H, CH2O), 3.50 (m, 1 H, CH2O), 3.73 (m, 1 H, CH2O), 3.88 (m, 1 H, CH2O), 4.06 (t, 4 H, *J=*6.6, 2 × CH2O), 4.58 (m, 1 H, OCHO), 4.98 (m, 2 H, CH2=CH), 5.82 (m, 1 H, CH2=CH), 6.99 (d, 4 H, *J=*9.1), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.3), 7.95 (d, 2 H, *J=*8.8), 8.16 (d, 4 H, *J=*9.1), 8.33 (d, 4 H, *J=*8.5). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 155.7 (2 × C), 149.5 (2 × C), 139.4 (CH), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.2 (2 × C), 118.9 (2 × CH), 114.7 (4 × CH), 114.4 (CH2), 99.1 (CH), 68.6 (2 × CH2), 67.9 (CH2), 62.6 (CH2), 34.0 (CH2), 31.0 (CH2), 30.0 (CH2), 29.8 (4 × CH2), 29.7 (3 × CH2), 29.6 (2 × CH2), 29.3 (3 × CH2), 29.2 (CH2), 26.5 (CH2), 26.2 (2 x CH2), 25.8 (CH2), 20.0 (CH2). Elemental analysis: for C66H76O12 (1061.33): calculated C 74.69, H 7.22; found C 74.52, H 7.19%.

***7-(4-{4-[12-(Tetrahydro-2H-pyran-2-yloxy)dodecyloxy]benzoyloxy}benzoyloxy)naphthalen-2-yl 4-[4-(9,9,10,10,11,11,12,12,12-nonafluordodecyloxy)benzoyloxy]benzoate (19)***. Yield 87%, m.p. 159-164 °C. 1H NMR (CDCl3): 1.30-1.82 (m, 38 H, 19 × CH2), 2.06 (m, 2 H, CH2CF2), 3.39 (m, 1 H, CH2O), 3.51 (m, 1 H, CH2O), 3.75 (m, 1 H, CH2O), 3.88 (m, 1 H, CH2O), 4.03 (t, 4 H, *J=*6.4, 2 × CH2O), 4.59 (m, 1 H, OCHO), 6.98 (d, 4 H, *J=*8.5), 7.38 (m, 6 H), 7.69 (d, 2 H, *J=*2.3), 7.91 (d, 2 H, *J=*8.8), 8.16 (d, 4 H, *J=*8.8), 8.31 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 164.7 (2 × C), 164.5 (2 × C), 164.1 (C), 164.0 (C), 155.7 (2 x C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.8 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.2 (C), 121.1 (C), 118.8 (2 × CH), 114.6 (4 × CH), 99.1 (CH), 68.6 (CH2), 68.5 (CH2), 67.9 (CH2), 62.6 (CH2), 31.1 (CH2), 30.0 (CH2), 29.8 (4 × CH2), 29.7 (CH2), 29.6 (CH2), 29.4 (CH2), 29.3 (3 × CH2), 29.2 (2 × CH2), 26.5 (CH2), 26.2 (CH2), 26.1 (CH2), 25.8 (CH2), 20.3 (CH2), 20.0 (CH2). 19F NMR (CDCl3): 81.4 (m, 3 F, CF3), 115.0 (m, 2 F, CF2), 124.9 (m, 2 F, CF2), 126.5 (m, 2 F, CF2). Elemental analysis: for C67H71F9O12 (1239.29): calculated C 64.94, H 5.77; found C 64.78, H 5.60%.

**2.5. General method for the oxidation by KMnO4**

A solution of aldehyde **7a-c** (1 mmol) in acetone (15 ml) was cooled to 0 °C and potassium permanganate (1.1 mmol) was added portion wise under stirring within 10 min. The mixture was stirred at 0 °C for 2 h and at room temperature for 0.5 h and the excess of reagent was removed by addition of isopropanol (0.3 ml). The mixture was acidified with acetic acid, filtered, the solid was washed with ethyl acetate (50 ml), and the combined filtrate was evaporated to dryness. The product was purified by column chromatography (toluene/acetone 1/1) and crystallisation from toluene or ethanol.

***4-{4-[2-(Tetrahydro-2H-pyran-2-yloxy)ethoxy]benzoyloxy}benzoic acid (8a)***. Yield 38%, m.p. 157-159 °C. 1H NMR (CDCl3): 1.56-1.83 (m, 6 H, 3 × CH2), 3.54 (m, 1 H, CH2O), 3.88 (m, 2 H, CH2O), 4.10 (m, 1 H, CH2O), 4.26 (s, 2 H, CH2O), 4.73 (s, 1 H, OCHO), 7.02 (d, 2 H, *J=*8.8), 7.32 (d, 2 H, *J=*8.5), 8.14 (d, 2 H, *J=*9.1), 8.18 (d, 2 H, *J=*8.5). 13C NMR (CDCl3): 171.3 (C), 164.5 (C), 163.7 (C), 155.6 (C), 132.6 (2 × CH), 132.1 (2 × CH), 127.1 (C), 122.2 (2 × CH), 121.6 (C), 114.8 (2 × CH), 99.3 (CH), 67.9 (CH2), 65.9 (CH2), 62.5 (CH2), 30.7 (CH2), 25.6 (CH2), 19.6 (CH2). Elemental analysis: for C21H22O7 (386.41): calculated C 65.28, H 5.74; found C 65.22, H 5.62%.

***4-{4-[4-(Tetrahydro-2H-pyran-2-yloxy)butoxy]benzoyloxy}benzoic acid (8b)***. Yield 72%, m.p. 160-161 °C. 1H NMR (CDCl3): 1.55-1.63 (m, 4 H, (CH2)2), 1.73-1.85 (m, 4 H, 2 × CH2CH2O), 1.93 (m, 2 H, CH2CH2O), 3.50 (m, 2 H, CH2O), 3.85 (m, 2 H, CH2O), 4.10 (t, 2 H, *J=*6.4, CH2O), 4.62 (s, 1 H, OCHO), 6.98 (d, 2 H, *J=*9.1), 7.33 (d, 2 H, *J=*8.8), 8.14 (d, 2 H, *J=*9.1), 8.19 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 171.3 (C), 164.6 (C), 163.9 (C), 155.7 (C), 132.7 (2 × CH), 132.1 (2 × CH), 127.0 (C), 122.2 (2 × CH), 121.2 (C), 114.6 (2 × CH), 99.2 (CH), 68.3 (CH2), 67.3 (CH2), 62.6 (CH2), 31.0 (CH2), 26.5 (CH2), 26.3 (CH2), 25.7 (CH2), 19.8 (CH2). Elemental analysis: for C23H26O7 (414.46): calculated C 66.65, H 6.32; found C 66.49, H 6.19%.

***4-{4-[8-(Tetrahydro-2H-pyran-2-yloxy)octyloxy]benzoyloxy}benzoic acid (8c)***. Yield 79%, m.p. 110 °C. 1H NMR (CDCl3): 1.38-1.85 (m, 18 H, 9 × CH2), 3.39 (m, 1 H, CH2O), 3.51 (m, 1 H, CH2O), 3.74 (m, 1 H, CH2O), 3.88 (m, 1 H, CH2O), 4.00 (t, 2 H, *J=*6.6, CH2O), 4.58 (m, 1 H, OCHO), 6.98 (d, 2 H, *J=*9.1), 7.33 (d, 2 H, *J=*8.8), 8.14 (d, 2 H, *J=*8.8), 8.18 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 171.3 (C), 164.6 (C), 164.0 (C), 155.7 (C), 132.7 (2 × CH), 132.1 (2 × CH), 126.9 (C), 122.2 (2 × CH), 121.2 (C), 114.6 (2 × CH), 99.1 (CH), 68.6 (CH2), 67.9 (CH2), 62.6 (CH2), 31.0 (CH2), 29.9 (CH2), 29.6 (CH2), 29.5 (CH2), 29.3 (CH2), 26.4 (CH2), 26.2 (CH2), 25.7 (CH2), 19.9 (CH2). Elemental analysis: for C27H34O7 (470.57): calculated C 68.92, H 7.28; found C 68.80, H 7.23%.

**2.6. General procedure for THP-deprotection**

To a mixture of compounds **16a-d,17a-c,18,19** (1 mmol) in a mixture of dichloromethane (60 ml) and methanol (30 ml), a catalytic amount of freshly fused *p*-toluenesulfonic acid (TsOH) was added and the mixture was stirred at room temperature for 24 h. The solvent was evaporated, the residue was dissolved in chloroform (50 ml) and washed with a saturated aq. solution of sodium bicarbonate (20 ml). The organic layer was dried with anhydrous magnesium sulphate and evaporated. The crude product was purified by column chromatography (chloroform/methanol 99/1) and crystallisation from toluene.

***7-[4-(2-Hydroxyethoxy)benzoyloxy]naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (20a)***. Yield 93%, m.p. 153 °C. 1H NMR (CDCl3): 0.89 (t, 3 H, *J=*6.7, CH3), 1.28-1.48 (m, 18 H, (CH2)9), 1.83 (m, 2 H, CH2CH2O), 2.14 (m, 1 H, OH), 4.01 (m, 2 H, CH2O), 4.05 (t, 2 H, *J=*6.6, CH2O), 4.17 (t, 2 H, *J=*6.4, OCH2), 6.99 (d, 2 H, *J=*9.1), 7.02 (d, 2 H, *J=*9.1), 7.35-7.41 (m, 4 H), 7.68 (s, 2 H), 7.92 (d, 1 H, *J=*8.8), 7.93 (d, 1 H, *J=*9.1), 8.16 (d, 2 H, *J=*9.1), 8.20 (d, 2 H, *J=*8.8), 8.32 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 165.1 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.3 (C), 155.7 (C), 149.7 (C), 149.5 (C), 134.7 (C), 132.7 (4 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 122.3 (C), 121.6 (CH), 121.4 (CH), 121.1 (C), 118.9 (CH), 118.8 (CH), 114.7 (2 × CH), 114.6 (2 × CH), 69.7 (CH2), 68.6 (CH2), 61.5 (CH2), 32.2 (CH2), 29.9 (2 x CH2), 29.8 (2 x CH2), 29.6 (2 x CH2), 29.3 (CH2), 26.2 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C45H48O9 (732.88): calculated C 73.75, H 6.60; found C 73.58, H 6.63%.

***7-[4-(4-Hydroxybutoxy)benzoyloxy]naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (20b)***. Yield 90%, m.p. 145 °C. 1H NMR (CDCl3): 0.89 (t, 3 H, *J=*6.5, CH3), 1.28-1.48 (m, 18 H, (CH2)9), 1.80 (m, 4 H, 2 × CH2CH2O), 1.92 (m, 2 H, CH2CH2O), 3.73 (t, 2 H, *J=*6.3, CH2O), 4.05 (t, 2 H, *J=*6.6, CH2O), 4.09 (t, 2 H, *J=*6.3, CH2O), 6.99 (d, 4 H, *J=*8.8), 7.35-7.41 (m, 4 H), 7.68 (m, 2 H), 7.92 (d, 1 H, *J=*9.1), 7.93 (d, 1 H, *J=*9.1), 8.16 (d, 2 H, *J=*9.1), 8.19 (d, 2 H, *J=*8.8), 8.33 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 165.2 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.6 (C), 155.7 (C), 149.7 (C), 149.5 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 121.8 (C), 121.7 (CH), 121.3 (CH), 121.1 (C), 118.9 (CH), 118.8 (CH), 114.7 (2 × CH), 114.6 (2 × CH), 68.6 (CH2), 68.3 (CH2), 62.7 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.5 (CH2), 29.3 (CH2), 26.2 (CH2), 25.9 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C47H52O9 (760.93): calculated C 74.19, H 6.89; found C 74.06, H 6.86%.

***7-[4-(8-Hydroxyoctyloxy)benzoyloxy]naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (20c)***. Yield 96%, m.p. 138 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.4, CH3), 1.27-1.48 (m, 26 H, 13 × CH2), 1.58 (m, 2 H, CH2CH2O), 1.83 (m, 4 H, 2 × CH2CH2O), 3.65 (t, 2 H, *J=*6.4, CH2OH), 4.05 (t, 4 H, *J=*6.4, 2 × CH2O),6.99 (d, 4 H, *J=*8.8), 7.35-7.41 (m, 4 H), 7.68 (s, 2 H), 7.93 (d, 2 H, *J=*9.1), 8.16 (d, 2 H, *J=*8.8), 8.19 (d, 2 H, *J=*8.8), 8.32 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 165.3 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.8 (C), 155.7 (C), 149.7 (C), 149.4 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 121.7 (CH), 121.6 (C), 121.3 (CH), 121.1 (C), 118.9 (CH), 118.8 (CH), 114.7 (2 × CH), 114.6 (2 × CH), 68.6 (CH2), 68.5 (CH2), 63.3 (CH2), 33.0 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 25.9 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C51H60O9 (817.04): calculated C 74.97, H 7.40; found C 74.82, H 7.43%.

***7-[4-(12-Hydroxydodecyloxy)benzoyloxy]naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)-benzoate (20d)***. Yield 96%, m.p. 120 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.4, CH3), 1.27-1.59 (m, 36 H, 18 × CH2), 1.83 (m, 4 H, 2 × CH2CH2O), 3.64 (t, 2 H, *J=*6.4, CH2O), 4.05 (t, 4 H, *J=*6.6, 2 × CH2O), 6.99 (d, 4 H, *J=*8.5), 7.35-7.41 (m, 4 H), 7.68 (s, 2 H), 7.93 (d, 2 H, *J=*9.0), 8.16 (d, 2 H, *J=*8.2), 8.19 (d, 2 H, *J=*8.5), 8.33 (d, 2 H, *J=*8.5). 13C NMR (CDCl3): 165.3 (C), 164.8 (C), 164.6 (C), 164.1 (C), 163.9 (C), 155.7 (C), 149.7 (C), 149.4 (C), 134.7 (C), 132.7 (2 × CH), 132.6 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.6 (2 × CH), 127.0 (C), 122.4 (2 × CH), 121.7 (CH), 121.7 (C), 121.3 (CH), 121.2 (C), 118.9 (2 × CH), 114.7 (2 × CH), 114.6 (2 × CH), 68.6 (2 × CH2), 63.3 (CH2), 33.0 (CH2), 32.2 (CH2), 29.8 (6 × CH2), 29.7 (2 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 26.0 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C55H68O9 (873.15): calculated C 75.66, H 7.85; found C 75.49, H 7.79%.

***7-{4-[4-(2-Hydroxyethoxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (21a)***. Yield 95%, m.p. 138 °C. Iso 190 N 185 B1 123 Cr. 1H NMR (CDCl3): 0.89 (t, 3 H, *J=*6.7, CH3), 1.28-1.48 (m, 18 H, (CH2)9), 1.83 (m, 2 H, CH2CH2O), 2.18 (bs, 1 H, OH), 3.99-4.07 (m, 4 H, 2 × CH2O), 4.16 (t, 2 H, *J=*4.6, CH2O), 6.99 (d, 2 H, *J=*8.8), 7.01 (d, 2 H, *J=*8.8), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.1), 7.94 (d, 2 H, *J=*8.8), 8.16 (d, 2 H, *J=*9.1), 8.17 (d, 2 H, *J=*8.9), 8.32 (d, 4 H, *J=*8.2). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (C), 164.5 (C), 164.1 (C), 163.5 (C), 155.7 (C), 155.6 (C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.1 (C), 127.0 (C), 122.4 (4 × CH), 121.9 (C), 121.5 (2 × CH), 121.1 (C), 118.9 (2 × CH), 114.7 (4 × CH), 69.7 (CH2), 68.6 (CH2), 61.4 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 23.0 (CH2), 14.4 (CH3). Elemental analysis: for C52H52O10 (836.99): calculated C 74.62, H 6.26; found C 74.50, H 6.16%.

***7-{4-[4-(4-Hydroxybutoxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (21b)***. Yield 93%, m.p. 144 °C. Iso 177 B1 118 Cr. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.7, CH3), 1.27-1.51 (m, 18 H, (CH2)9), 1.80 (m, 4 H, 2 × CH2CH2O), 1.94 (m, 2 H, CH2CH2O), 3.76 (m, 2 H, CH2OH), 4.06 (t, 2 H, *J=*6.4, CH2O), 4.12 (t, 2 H, *J=*6.3, CH2O), 6.99 (d, 2 H, *J=*9.1), 7.00 (d, 2 H, *J=*9.1), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.3), 7.95 (d, 2 H, *J=*9.1), 8.16 (d, 2 H, *J=*9.1), 8.17 (d, 2 H, *J=*8.8), 8.33 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (C), 164.5 (C), 164.1 (C), 163.8 (C), 155.7 (2 × C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.3 (C), 121.1 (C), 118.9 (2 x CH), 114.7 (4 × CH), 68.6 (CH2), 68.3 (CH2), 62.7 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.5 (CH2), 29.3 (CH2), 26.2 (CH2), 25.9 (CH2), 23.0 (CH2), 14.4 (CH3). Elemental analysis: for C54H56O10 (865.04): calculated C 74.98, H 6.53; found C 74.83, H 6.40%.

***7-{4-[4-(8-Hydroxyoctyloxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyloxy-benzoyloxy)benzoate (21c)***. Yield 94%, m.p. 149 °C. Iso 157 N 155 B1 123 Cr. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.6, CH3), 1.27-1.54 (m, 28 H, 14 × CH2), 1.83 (m, 4 H, 2 × CH2CH2O), 3.66 (t, 2 H, *J=*6.6, CH2OH), 4.06 (t, 4 H, *J=*6.4, 2 × CH2O), 6.99 (d, 4 H, *J=*8.8), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.3), 7.95 (d, 2 H, *J=*8.8), 8.16 (d, 4 H, *J=*8.8), 8.33 (d, 4 H, *J=*8.5). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 155.7 (2 × C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.1 (2 × C), 118.9 (2 × CH), 114.7 (4 × CH), 68.6 (2 × CH2), 63.3 (CH2), 33.0 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 25.9 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C58H64O10 (921.15): calculated C 75.63, H 7.00; found C 75.55, H 6.92%.

***7-{4-[4-(12-Hydroxydodecyloxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-(4-undec-10-enyloxybenzoyloxy)benzoate (22)***. Yield 94%, m.p. 136 °C. Iso 149 N 143 B1 119 Cr. 1H NMR (CDCl3): 1.30-1.56 (m, 28 H, 14 × CH2), 1.82 (m, 4 H, 2 × CH2CH2O), 2.05 (m, 2 H, CH2), 3.63 (t, 2 H, *J=*6.4, CH2OH), 4.04 (t, 4 H, *J=*6.6, 2 × CH2O), 4.98 (m, 2 H, CH2=CH), 5.82 (m, 1 H, CH2=CH), 6.99 (d, 4 H, *J=*9.1), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.1), 7.94 (d, 2 H, *J=*9.1), 8.16 (d, 4 H, *J=*9.1), 8.32 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 155.7 (2 × C), 149.5 (2 × C), 139.4 (CH), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.8 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.1 (2 × C), 118.9 (2 × CH), 114.7 (4 × CH), 114.4 (CH2), 68.6 (2 × CH2), 63.3 (CH2), 34.1 (CH2), 33.0 (CH2), 30.0 (CH2), 29.8 (5 × CH2), 29.7 (2 × CH2), 29.6 (CH2), 29.4 (2 × CH2), 29.3 (2 × CH2), 29.2 (CH2), 26.2 (2 × CH2), 26.0 (CH2). Elemental analysis: for C62H72O10 (977.26): calculated C 76.20, H 7.43; found C 76.19, H 7.37%.

***7-{4-[4-(12-Hydroxydodecyloxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-[4-(9,9,10,10,11,11,12,12,12-nonafluordodecyloxy)benzoyloxy]benzoate (23)***. Yield 97%, m.p. 148 °C. Iso 167 B7 130 Cr. 1H NMR (CDCl3): 1.30-1.61 (m, 28 H, 14 × CH2), 1.83 (m, 4 H, 2 × CH2CH2O), 2.07 (m, 2 H, CH2CF2), 3.64 (t, 2 H, *J=*6.6, CH2OH), 4.05 (t, 4 H, *J=*6.3, 2 × CH2O), 6.99 (d, 4 H, *J=*9.1), 7.37-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.1), 7.95 (d, 2 H, *J=*9.1), 8.17 (d, 4 H, *J=*9.1), 8.33 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 164.8 (2 × C), 164.6 (2 × C), 164.1 (C), 164.0 (C), 155.7 (2 × C), 149.5 (2 × C), 134.6 (C), 132.7 (4 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 127.0 (2 × C), 122.4 (4 × CH), 121.5 (2 × CH), 121.2 (C), 121.1 (C), 118.9 (2 × CH), 114.6 (4 × CH), 68.6 (CH2), 68.5 (CH2), 63.3 (CH2), 33.0 (CH2), 29.8 (6 × CH2), 29.7 (CH2), 29.6 (CH2), 29.4 (2 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 26.0 (CH2), 20.3 (CH2). 19F NMR (CDCl3): 81.4 (m, 3 F, CF3), 115.0 (m, 2 F, CF2), 124.9 (m, 2 F, CF2), 126.5 (m, 2 F, CF2). Elemental analysis: for C62H63F9O10 (1139.17): calculated C 65.37, H 5.57; found C 65.21, H 5.41%.

**2.7. General procedure for the hydrogenolysis of benzyl protecting group**

To a solution of compounds **12** and **13** (1 mmol) in ethyl acetate (100 ml) and ethanol (20 ml), 10% Pd/C (0.1 wt%) was added. The slurry was stirred in an hydrogen atmosphere at room temperature for 32 h, after dilution with chloroform (60 ml) the catalyst was filtered off and the filtrate was evaporated. The product **14** and **15**, resp., was purified by column chromatography (chloroform/methanol 99/1).

***7-(4-Hydroxybenzoyloxy)naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (14)***. Yield 89%, m.p. 194 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.7, CH3), 1.27-1.48 (m, 18 H, (CH2)9), 1.83 (m, 2 H, CH2CH2O), 4.06 (t, 2 H, *J=*6.6, CH2O), 5.59 (s, 1 H, OH), 6.87 (d, 2 H, *J=*8.8), 6.99 (d, 2 H, *J=*9.1), 7.33-7.41 (m, 4 H), 7.66 (m, 2 H), 7.91 (d, 1 H, *J=*8.8), 7.93 (d, 1 H, *J=*9.4), 8.10 (d, 2 H, *J=*8.8), 8.16 (d, 2 H, *J=*9.1), 8.33 (d, 2 H, *J=*8.8). 13C NMR (CDCl3): 165.1 (C), 164.9 (C), 164.6 (C), 164.1 (C), 160.5 (C), 155.7 (C), 149.6 (C), 149.4 (C), 134.6 (C), 132.9 (2 × CH), 132.7 (2 × CH), 132.1 (2 × CH), 129.8 (C), 129.7 (CH), 129.6 (CH), 127.0 (C), 122.4 (2 × CH), 122.3 (C), 121.6 (CH), 121.3 (CH), 121.1 (C), 118.8 (2 × CH), 115.7 (2 × CH), 114.7 (2 × CH), 68.6 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C43H44O8 (688.83): calculated C 74.98, H 6.44; found C 74.85, H 6.52%.

***7-[4-(4-Hydroxybenzoyloxy)benzoyloxy]naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)-benzoate (15)***. Yield 90%, m.p. 204 °C. 1H NMR (CDCl3): 0.88 (t, 3 H, *J=*6.7, CH3), 1.27-1.52 (m, 18 H, (CH2)9), 1.83 (m, 2 H, CH2CH2O), 4.06 (t, 2 H, *J=*6.4, CH2O), 5.38 (s, 1 H, OH), 6.93 (d, 2 H, *J=*8.8), 6.99 (d, 2 H, *J=*8.8), 7.36-7.41 (m, 6 H), 7.70 (d, 2 H, *J=*2.3), 7.95 (d, 2 H, *J=*9.4), 8.14 (d, 2 H, *J=*8.2), 8.16 (d, 2 H, *J=*8.5), 8.33 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 165.1 (C), 164.9 (C), 164.8 (C), 164.6 (C), 164.1 (C), 160.8 (C), 155.7 (C), 155.6 (C), 149.5 (2 × C), 134.6 (C), 133.0 (2 × CH), 132.7 (2 × CH), 132.1 (4 × CH), 129.9 (C), 129.7 (2 × CH), 128.8 (C), 127.1 (C), 127.0 (C), 122.4 (4 × CH), 121.5 (2 × CH), 121.1 (C), 118.9 (2 × CH), 115.8 (2 × CH), 114.7 (2 × CH), 68.6 (CH2), 32.2 (CH2), 29.9 (2 × CH2), 29.8 (2 × CH2), 29.6 (2 × CH2), 29.3 (CH2), 26.2 (CH2), 22.9 (CH2), 14.4 (CH3). Elemental analysis: for C50H48O10 (808.53): calculated C 74.24, H 5.98; found C 74.11, H 5.81%.

**2.8. General synthesis of dimers**

Isophthaloyl chloride (**1,3Ph**), phthaloyl chloride (**1,2Ph**), and thiophene-2,5-dicarbonyl dichoride (**Th**) (1 mmol) was added to a solution of alcohol **14,15,20a-d,21a-d,22,23** (2 mmol), resp., and DMAP (2 mmol) in dichloromethane (100 ml). The reaction mixture was stirred at 50 °C for 6 h in an argon atmosphere. After cooling, the mixture was worked-up as in the general procedure **4**. The crude dimers were purified by column chromatography (chloroform/methanol 99/1 ev. chloroform/acetone 98/2) and crystallisation from a toluene/acetone (1:3) mixture.

***Bis(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}phenyl) isophthalate (Ia)***. Yield 54%, m.p. 230 °C. 1H NMR (CDCl3): 0.88 (t, 6 H, *J=*6.4, 2 × CH3), 1.27-1.51 (m, 36 H, 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 4.06 (t, 4 H, *J=*6.6, 2 × CH2O), 6.99 (d, 4 H, *J=*9.1), 7.40 (m, 8 H), 7.46 (d, 4 H, *J=*8.8), 7.71 (s, 4 H), 7.76 (dd, 1 H, *J=*7.9, *J=*7.6), 7.96 (d, 4 H, *J=*9.1), 8.16 (d, 4 H, *J=*9.1), 8.34 (d, 4 H, *J=*8.8), 8.36 (d, 4 H, *J=*8.8), 8.53 (dd, 2 H, *J=*7.8, *J=*1.6), 9.08 (s, 1 H). Elemental analysis: for C94H90O18 (1507.75): calculated C 74.88, H 6.02; found C 74.79, H 5.91%.

***Bis[2-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}phenoxy)-ethyl] isophthalate (Ib)***. Yield 44%, m.p. 152 °C. 1H NMR (CDCl3): 0.89 (t, 6 H, *J=*6.7, 2 × CH3), 1.27-1.48 (m, 36 H, 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 4.05 (t, 4 H, *J=*6.6, 2 × CH2O), 4.43 (t, 4 H, *J=*4.5, 2 × CH2O), 4.76 (t, 4 H, *J=*4.7, 2 × CH2O), 6.99 (d, 4 H, *J=*9.1), 7.05 (d, 4 H, *J=*8.8), 7.33-7.40 (m, 8 H), 7.57 (dd, 1 H, *J=*7.9), 7.67 (d, 4 H, *J=*2.1), 7.91 (d, 2 H, *J=*9.1), 7.92 (d, 2 H, *J=*9.1), 8.16 (d, 4 H, *J=*8.8), 8.21 (d, 4 H, *J=*9.1), 8.28 (dd, 2 H, *J=*7.9, *J* =1.8), 8.32 (d, 4 H, *J=*8.5), 8.74 (dd, 1 H, *J*=1.5, *J*=1.8). 13C NMR (CDCl3): 165.8 (2 × C), 165.1 (2 × C), 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 163.1 (2 × C), 155.7 (2 × C), 149.6 (2 × C), 149.4 (2 × C), 134.6 (2 × C), 134.5 (2 × CH), 132.7 (8 × CH), 132.1 (4 × CH), 131.3 (CH), 130.5 (2 × C), 129.8 (2 × C), 129.7 (2 × CH), 129.6 (2 × CH), 129.0 (CH), 127.0 (2 × C), 122.5 (2 × C), 122.4 (4 × CH), 121.6 (2 × CH), 121.4 (2 × CH), 121.2 (2 × C), 118.8 (4 × CH), 114.7 (4 × CH), 114.6 (4 × CH), 68.6 (2 × CH2), 66.3 (2 × CH2), 63.7 (2 × CH2), 32.2 (2 × CH2), 29.9 (4 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C98H98O20 (1595.86): calculated C 73.76, H 6.19; found C 73.66, H 6.23%.

***Bis[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}phenoxy)-butyl] isophthalate (Ic)***. Yield 39%, m.p. 131 °C. 1H NMR (CDCl3): 0.89 (t, 6 H, *J=*6.7, 2 × CH3), 1.27-1.48 (m, 36 H, 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 2.03 (m, 8 H, 2 × CH2CH2O), 4.05 (t, 4 H, *J=*6.6, 2 × CH2O), 4.14 (m, 4 H, 2 × CH2O), 4.47 (m, 4 H, 2 × CH2O), 6.99 (d, 8 H, *J=*8.5), 7.34-7.40 (m, 8 H), 7.54 (dd, 1 H, *J=*7.8), 7.67 (m, 4 H), 7.91 (d, 2 H, *J=*9.1), 7.92 (d, 2 H, *J=*9.1), 8.16 (d, 4 H, *J=*9.1), 8.18 (d, 4 H, *J=*9.1), 8.24 (dd, 2 H, *J*=7.6, *J*=1.8), 8.32 (d, 4 H, *J=*8.9), 8.70 (dd, 1 H, *J*=1.5, *J*=1.8). 13C NMR (CDCl3): 166.0 (2 × C), 165.2 (2 × C), 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 163.5 (2 x C), 155.7 (2 × C), 149.7 (2 × C), 149.4 (2 × C), 134.7 (2 × C), 134.0 (2 × CH), 132.7 (4 × CH), 132.6 (4 × CH), 132.1 (4 × CH), 131.0 (2 × C), 130.9 (CH), 129.8 (2 × C), 129.7 (2 × CH), 129.6 (2 × CH), 128.9 (CH), 127.0 (2 × C), 122.4 (4 × CH), 121.9 (2 × C), 121.7 (2 × CH), 121.3 (2 × CH), 121.2 (2 × C), 118.8 (4 × CH), 114.7 (4 × CH), 114.5 (4 × CH), 68.6 (2 × CH2), 67.8 (2 × CH2), 65.2 (2 × CH2), 32.2 (2 × CH2), 29.9 (4 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 26.1 (2 × CH2), 25.7 (2 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C102H106O20 (1651.97): calculated C 74.16, H 6.47; found C 74.04, H 6.50%.

***Bis[8-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}phenoxy)-octyl] isophthalate (Id)***. Yield 58 %, m.p. 129 °C. 1H NMR (CDCl3): 0.88 (t, 6 H, *J=*6.7, 2 × CH3), 1.27-1.50 (m, 52 H, 26 × CH2), 1.82 (m, 12 H, 6 × CH2CH2O), 4.05 (t, 8 H, *J=*6.4, 4 × CH2O), 4.36 (t, 4 H, *J=*6.7, 2 × CH2O), 6.98 (d, 4 H, *J=*9.1), 6.99 (d, 4 H, *J=*9.1), 7.34-7.40 (m, 8 H), 7.53 (dd, 1 H, *J=*7.8), 7.67 (m, 4 H), 7.92 (d, 2 H, *J=*9.1), 7.93 (d, 2 H, *J=*9.1), 8.16 (d, 4 H, *J=*8.8), 8.18 (d, 4 H, *J=*8.8), 8.23 (dd, 2 H, *J*=7.9, *J*=1.8), 8.32 (d, 4 H, *J=*8.8), 8.70 (dd, 1 H, *J*=1.5, *J*=1.8). 13C NMR (CDCl3): 166.1 (2 × C), 165.2 (2 × C), 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 163.8 (2 × C), 155.7 (2 × C), 149.7 (2 × C), 149.4 (2 × C), 134.7 (2 × C), 133.9 (2 × CH), 132.7 (4 × CH), 132.6 (4 × CH), 132.1 (4 × CH), 131.1 (2 × C), 130.9 (CH), 129.8 (2 × C), 129.7 (2 × CH), 129.6 (2 × CH), 128.8 (CH), 127.0 (2 × C), 122.4 (4 × CH), 121.7 (2 × CH), 121.7 (2 × C), 121.3 (2 × CH), 121.1 (2 × C), 118.9 (2 × CH), 118.8 (2 × CH), 114.6 (4 × CH), 114.5 (4 × CH), 68.6 (2 × CH2), 68.5 (2 × CH2), 65.7 (2 × CH2), 32.2 (2 × CH2), 29.9 (6 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.5 (2 × CH2), 29.4 (4 × CH2), 29.3 (2 × CH2), 28.9 (2 × CH2), 26.2 (4 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C110H122O20 (1764.19): calculated C 74.89, H 6.97; found C 74.81, H 6.90%.

***Bis[12-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxy)dodecyl] isophthalate (Ie)***. Yield 60%, m.p. 107 °C. 1H NMR (CDCl3): 0.88 (t, 6 H, *J=*6.7, 2 × CH3), 1.27-1.53 (m, 68 H, 34 × CH2), 1.81 (m, 12 H, 6 × CH2CH2O), 4.05 (t, 8 H, *J=*6.6, 4 × CH2O), 4.34 (t, 4 H, *J=*6.7, 2 × CH2O), 6.99 (d, 8 H, *J=*9.1), 7.34-7.40 (m, 8 H), 7.53 (dd, 1 H, *J=*7.9), 7.67 (m, 4 H), 7.92 (d, 2 H, *J=*9.1), 7.93 (d, 2 H, *J=*8.8), 8.16 (d, 4 H, *J=*8.8), 8.18 (d, 4 H, *J=*8.8), 8.22 (dd, 2 H, *J*=7.9, *J*=1.8), 8.33 (d, 4 H, *J=*8.5), 8.69 (dd, 1 H, *J*=1.5, *J*=1.8). 13C NMR (CDCl3): 166.1 (2 × C), 165.2 (2 × C), 164.8 (2 × C), 164.6 (2 × C), 164.1 (2 × C), 163.9 (2 × C), 155.7 (2 × C), 149.7 (2 × C), 149.4 (2 × C), 134.7 (2 × C), 133.9 (2 × CH), 132.7 (4 × CH), 132.6 (4 × CH), 132.1 (4 × CH), 131.2 (2 × C), 130.9 (CH), 129.8 (2 × C), 129.7 (2 × CH), 129.6 (2 × CH), 128.8 (CH), 127.0 (2 × C), 122.4 (4 × CH), 121.7 (2 × CH), 121.7 (2 × C), 121.3 (2 × CH), 121.2 (2 × C), 118.8 (4 × CH), 114.7 (4 × CH), 114.6 (4 × CH), 68.6 (4 × CH2), 65.7 (2 × CH2), 32.2 (2 × CH2), 29.9 (6 × CH2), 29.8 (8 × CH2), 29.6 (6 × CH2), 29.5 (6 × CH2), 29.4 (4 × CH2), 28.9 (2 × CH2), 26.2 (4 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C118H138O20 (1876.40): calculated C 75.53, H 7.41; found C 75.43, H 7.46%.

***Bis[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}phenoxy-carbonyl)phenyl] isophthalate (IIa)***. Yield 29%, m.p. 230 °C. 1H NMR (CDCl3): 0.88 (t, 6 H, *J=*6.6, 2 × CH3), 1.27-1.48 (m, 36 H, 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 4.06 (t, 4 H, *J=*6.6, 2 × CH2O), 6.99 (d, 4 H, *J=*8.8), 7.37-7.48 (m, 16 H), 7.71 (s, 4 H), 7.77 (dd, 1 H, *J=*7.6), 7.96 (d, 4 H, *J=*8.8), 8.16 (d, 4 H, *J=*8.8), 8.32-8.38 (m, 12 H), 8.53 (d, 2 H, *J=*9.1), 9.07 (s, 1 H). Elemental analysis: for C108H98O22 (1747.97): calculated C 74.21, H 5.65; found C 74.12, H 5.60%.

***Bis{2-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]ethyl} isophthalate (IIb)***. Yield 43%, m.p. 193 °C. 1H NMR (CDCl3): 0.89 (t, 6 H, *J=*6.6, 2 × CH3), 1.28-1.49 (m, 36 H, 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 4.05 (t, 4 H, *J=*6.4, 2 × CH2O), 4.41 (t, 4 H, *J=*4.5, 2 × CH2O), 4.75 (t, 4 H, *J=*4.4, 2 × CH2O), 6.99 (d, 4 H, *J=*8.8), 7.04 (d, 4 H, *J=*9.1), 7.36-7.41 (m, 12 H), 7.56 (dd, 1 H, *J=*7.8), 7.69 (s, 4 H), 7.93 (d, 4 H, *J=*8.8), 8.16 (d, 4 H, *J=*8.8), 8.18 (d, 4 H, *J=*8.8), 8.26-8.34 (m, 10 H), 8.75 (s, 1 H). 13C NMR (CDCl3): 165.8 (2 × C), 164.8 (2 × C), 164.7 (2 × C), 164.6 (2 × C), 164.4 (2 × C), 164.1 (2 × C), 163.2 (2 × C), 155.7 (2 × C), 155.6 (2 × C), 149.5 (4 × C), 134.6 (2 × C), 134.5 (2 × CH), 132.8 (4 × CH), 132.7 (4 × CH), 132.1 (8 × CH), 131.3 (CH), 130.5 (2 × C), 129.8 (2 × C), 129.7 (4 × CH), 129.1 (CH), 127.1 (2 × C), 127.0 (2 × C), 122.4 (8 × CH), 122.0 (2 × C), 121.5 (4 × CH), 121.2 (2 × C), 118.9 (4 × CH), 114.8 (4 × CH), 114.7 (4 × CH), 68.6 (2 × CH2), 66.3 (2 × CH2), 63.6 (2 × CH2), 32.2 (2 × CH2), 29.9 (4 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 23.0 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C112H106O24 (1836.08): calculated C 73.27, H 5.82; found C 73.20, H 5.85%.

***Bis{4-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]butyl} isophthalate (IIc)***. Yield 31%, m.p. 177 °C. 1H NMR (CDCl3): 0.88 (t, 6 H, *J=*6.7, 2 × CH3), 1.27-1.48 (m, 36 H, 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 2.03 (m, 8 H, 4 × CH2CH2O), 4.05 (t, 4 H, *J=*6.6, 2 × CH2O), 4.15 (m, 4 H, 2 × CH2O), 4.47 (m, 4 H, 2 × CH2O), 6.99 (d, 8 H, *J=*8.8), 7.35-7.41 (m, 12 H), 7.54 (dd, 1 H, *J*=7.9, *J*=7.6), 7.69 (d, 4 H, *J=*2.3), 7.94 (d, 4 H, *J=*8.8), 8.15 (d, 4 H, *J=*8.8), 8.16 (d, 4 H, *J=*9.1), 8.24 (dd, 2 H, *J*=7.9, *J*=1.8), 8.33 (d, 8 H, *J=*8.8), 8.70 (dd, 1 H, *J*=1.8, *J*=1.5). 13C NMR (CDCl3): 166.0 (2 × C), 164.8 (4 × C), 164.6 (2 × C), 164.5 (2 × C), 164.1 (2 × C), 163.7 (2 × C), 155.7 (2 × C), 155.6 (2 × C), 149.5 (4 × C), 134.6 (2 × C), 134.1 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 131.0 (2 × C), 130.9 (CH), 129.8 (2 × C), 129.7 (4 × CH), 128.9 (CH), 127.1 (2 × C), 127.0 (2 × C), 122.4 (8 × CH), 121.5 (4 × CH), 121.4 (2 × C), 121.1 (2 × C), 118.9 (4 × CH), 114.7 (4 × CH), 114.6 (4 × CH), 68.6 (2 × CH2), 67.9 (2 × CH2), 65.2 (2 × CH2), 32.2 (2 × CH2), 29.9 (4 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 26.1 (2 × CH2), 25.7 (2 × CH2), 23.0 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C116H114O24 (1892.19): calculated C 73.63, H 6.07; found C 73.52, H 5.99%.

***Bis{8-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]octyl} isophthalate (IId)***. Yield 43%, m.p. 142 °C. 1H NMR (CDCl3): 0.89 (t, 6 H, *J=*6.7, 2 × CH3), 1.27-1.48 (m, 52 H, 26 × CH2), 1.82 (m, 12 H, 6 × CH2CH2O), 4.05 (t, 8 H, *J=*6.6, 4 × CH2O), 4.36 (t, 4 H, *J=*6.6, 2 × CH2O), 6.98 (d, 4 H, *J=*9.1), 6.99 (d, 4 H, *J=*9.1), 7.36-7.41 (m, 12 H), 7.54 (dd, 1 H, *J=*7.6), 7.70 (d, 4 H, *J=*2.3), 7.94 (d, 4 H, *J=*8.8), 8.16 (d, 8 H, *J=*8.8), 8.23 (dd, 2 H, *J*=7.9, *J*=1.8), 8.33 (d, 8 H, *J=*8.2), 8.70 (dd, 1 H, *J*=1.8, *J*=1.5). 13C NMR (CDCl3): 166.1 (2 × C), 164.8 (4 × C), 164.6 (4 × C), 164.1 (2 × C), 164.0 (2 × C), 155.7 (4 × C), 149.5 (4 × C), 134.6 (2 × C), 133.9 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 131.2 (2 × C), 130.9 (CH), 129.9 (2 × C), 129.7 (4 × CH), 128.8 (CH), 127.0 (4 × C), 122.4 (8 × CH), 121.5 (4 × CH), 121.2 (4 × C), 118.9 (4 × CH), 114.7 (8 × CH), 68.6 (2 × CH2), 68.5 (2 × CH2), 65.7 (2 × CH2), 32.2 (2 × CH2), 29.9 (6 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.5 (2 × CH2), 29.4 (2 × CH2), 29.3 (4 × CH2), 28.9 (2 × CH2), 26.2 (4 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C124H130O24 (2004.40): calculated C 74.31, H 6.54; found C 74.20, H 6.50%.

***Bis{12-[4-(4-{7-[4-(4-undec-10-enyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxy-carbonyl}phenoxycarbonyl)phenoxy]dodecyl} isophthalate (IIf)***. Yield 54%, m.p. 134 °C. 1H NMR (CDCl3): 1.31-1.48 (m, 56 H, 28 × CH2), 1.82 (m, 12 H, 6 × CH2CH2O), 2.05 (m, 4 H, 2 × CH2), 4.05 (t, 8 H, *J=*6.6, 4 × CH2O), 4.35 (t, 4 H, *J=*6.7, 2 × CH2O), 4.97 (m, 4 H, 2 × CH2=CH), 5.82 (m, 2 H, 2 × CH2=CH), 6.99 (d, 8 H, *J=*8.9), 7.36-7.41 (m, 12 H), 7.53 (dd, 1 H, *J*=7.8), 7.70 (d, 4 H, *J=*2.3), 7.95 (d, 4 H, *J=*8.8), 8.16 (d, 8 H, *J=*9.1), 8.23 (dd, 2 H, *J*=7.7, *J*=1.8), 8.33 (d, 8 H, *J=*8.2), 8.69 (dd, 1 H, *J*=1.6). 13C NMR (CDCl3): 166.1 (2 × C), 164.8 (4 × C), 164.6 (4 × C), 164.1 (4 × C), 155.7 (4 × C), 149.5 (4 × C), 139.4 (2 × CH), 134.6 (2 × C), 133.9 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 131.2 (2 × C), 130.9 (CH), 129.9 (2 × C), 129.7 (4 × CH), 128.8 (CH), 127.0 (4 × C), 122.4 (8 × CH), 121.5 (4 × CH), 121.2 (4 × C), 118.9 (4 × CH), 114.7 (8 × CH), 114.4 (2 × CH2), 68.6 (4 × CH2), 65.8 (2 × CH2), 34.1 (2 × CH2), 29.8 (8 × CH2), 29.7 (4 × CH2), 29.6 (4 × CH2), 29.5 (2 × CH2), 29.4 (4 × CH2), 29.3 (4 × CH2), 29.2 (2 × CH2), 28.9 (2 × CH2), 26.2 (4 × CH2). Elemental analysis: for C130H138O24 (2084.53): calculated C 74.91, H 6.67; found C 74.83, H 6.73%.

***Bis(12-{4-[4-(7-{4-[4-(9,9,10,10,11,11,12,12,12-nonafluordodecyloxy)benzoyloxy]-benzoyloxy}naphthalen-2-yloxycarbonyl)phenoxycarbonyl]phenoxy}dodecyl) isophthalate (IIi)***. Yield 51%, m.p. 136 °C. 1H NMR (CDCl3): 1.31-1.62 (m, 52 H, 26 × CH2), 1.82 (m, 12 H, 6 × CH2CH2O), 2.06 (m, 4 H, 2 × CH2CF2), 4.05 (t, 8 H, *J=*6.3, 4 × CH2O), 4.35 (t, 4 H, *J=*6.6, 2 × CH2O), 6.99 (d, 8 H, *J=*8.8), 7.36-7.41 (m, 12 H), 7.53 (dd, 1 H, *J*=7.8), 7.70 (m, 4 H), 7.94 (d, 4 H, *J=*8.8), 8.16 (d, 8 H, *J=*8.5), 8.23 (d, 2 H, *J=*7.6), 8.33 (d, 8 H, *J=*8.5), 8.69 (s, 1 H). 13C NMR (CDCl3): 166.1 (2 × C), 164.8 (4 × C), 164.6 (4 × C), 164.1 (2 × C), 164.0 (2 × C), 155.7 (4 × C), 149.5 (4 × C), 134.6 (2 × C), 133.9 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 131.2 (2 × C), 130.9 (CH), 129.9 (2 × C), 129.7 (4 × CH), 128.8 (CH), 127.0 (4 × C), 122.4 (8 × CH), 121.5 (4 × CH), 121.2 (4 × C), 118.9 (4 × CH), 114.6 (8 × CH), 68.6 (2 × CH2), 68.5 (2 × CH2), 65.7 (2 × CH2), 29.8 (10 × CH2), 29.6 (2 × CH2), 29.5 (2 × CH2), 29.4 (4 × CH2), 29.3 (8 × CH2), 28.9 (2 × CH2), 26.2 (4 × CH2), 26.1 (2 × CH2). 19F NMR (CDCl3): 81.4 (m, 6 F, 2 × CF3), 115.0 (m, 4 F, 2 × CF2), 124.9 (m, 4 F, 2 × CF2), 126.5 (m, 4 F, 2 × CF2). ). Elemental analysis: for C132H128F18O24 (2440.45): calculated C 64.97, H 5.29; found C 64.85, H 5.20%.

***Bis{2-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]ethyl} phthalate (IIIa)***. Yield 60%, m.p. 190 °C. 1H NMR (CDCl3): 0.89 (t, 6 H, *J=*6.6, 2 × CH3), 1.27-1.48 (m, 36 H, 2 2 × (CH2)9), 1.83 (m, 4 H, 2 × CH2CH2O), 4.05 (t, 4 H, *J=*6.6, 2 × CH2O), 4.36 (t, 4 H, *J=*4.7, 2 × CH2O), 4.70 (t, 4 H, *J=*4.7, 2 × CH2O), 6.99 (d, 4 H, *J=*8.8), 7.02 (d, 4 H, *J=*8.8), 7.35-7.40 (m, 12 H), 7.58 (m, 2 H), 7.67 (m, 4 H), 7.78 (m, 2 H), 7.91 (d, 2 H *J=*9.1), 7.92 (d, 2 H, *J=*8.8), 8.15 (d, 4 H, *J=*9.1), 8.16 (d, 4 H, *J=*8.8), 8.31 (d, 4 H, *J=*8.8), 8.32 (d, 4 H, *J=*8.8). 13C NMR (CDCl3): 167.5 (2 × C), 164.7 (4 × C), 164.6 (2 × C), 164.3 (2 × C), 164.1 (2 × C), 163.2 (2 × C), 155.7 (2 × C), 155.6 (2 × C), 149.5 (4 × C), 134.6 (2 × C), 132.7 (8 × CH), 132.1 (8 × CH), 131.9 (2 × C), 131.7 (2 × CH), 129.8 (2 × C), 129.7 (4 × CH), 129.3 (2 × CH), 127.1 (2 × C), 127.0 (2 × C), 122.4 (4 × CH), 122.3 (4 × CH), 122.0 (2 × C), 121.5 (4 × CH), 121.2 (2 × C), 118.8 (4 × CH), 114.7 (8 × CH), 68.6 (2 × CH2), 66.2 (2 × CH2), 63.8 (2 × CH2), 32.2 (2 × CH2), 29.9 (4 × CH2), 29.8 (4 × CH2), 29.6 (4 × CH2), 29.3 (2 × CH2), 26.2 (2 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C112H106O24 (1836.08): calculated C 73.27, H 5.82; found C 73.15, H 5.88%.

***Bis{12-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]dodecyl} phthalate (IIIb)***. Yield 17%, m.p. 131 °C. 1H NMR (CDCl3): 0.89 (t, 6 H, *J=*6.5, 2 × CH3), 1.27-1.48 (m, 68 H, 34 × CH2), 1.78 (m, 12 H, 6 × CH2CH2O), 4.05 (t, 8 H, *J=*6.4, 4 × CH2O), 4.30 (t, 4 H, *J=*6.7, 2 × CH2O), 6.99 (d, 8 H, *J=*8.8), 7.36-7.41 (m, 12 H), 7.53 (m, 2 H), 7.72 (m, 6 H), 7.94 (d, 4 H, *J=*9.1), 8.16 (d, 8 H, *J=*8.8), 8.33 (d, 8 H, *J=*8.5). 13C NMR (CDCl3): 168.0 (2 × C), 164.8 (4 × C), 164.6 (4 × C), 164.1 (4 × C), 155.7 (4 × C), 149.5 (4 × C), 134.6 (2 × C), 132.7 (8 × CH), 132.5 (2 × C), 132.1 (8 × CH), 131.2 (2 × CH), 129.9 (2 × C), 129.7 (4 x CH), 129.1 (2 × CH), 127.0 (4 × C), 122.4 (8 × CH), 121.5 (4 × CH), 121.1 (4 × C), 118.8 (4 × CH), 114.6 (8 × CH), 68.6 (4 × CH2), 66.1 (2 × CH2), 32.2 (2 × CH2), 29.9 (6 × CH2), 29.8 (12 × CH2), 29.6 (6 × CH2), 29.5 (2 × CH2), 29.3 (4 × CH2), 28.8 (2 × CH2), 26.2 (4 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C132H146O24 (2116.62): calculated C 74.91, H 6.95; found C 74.88, H 6.82%.

***Bis{12-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]dodecyl} thiophene-2,5-dicarboxylate (IIIc)***. Yield 43%, m.p. 134 °C. 1H NMR (CDCl3): 0.82 (t, 6 H, *J=*6.6, 2 × CH3), 1.21-1.41 (m, 68 H, 34 × CH2), 1.71 (m, 12 H, 6 × CH2CH2O), 3.98 (t, 8 H, *J=*6.4, 4 × CH2O), 4.24 (t, 4 H, *J=*6.7, 2 × CH2O), 6.92 (d, 8 H, *J=*8.8), 7.29-7.34 (m, 12 H), 7.63 (d, 4 H, *J=*2.1), 7.66 (s, 2 H), 7.87 (d, 4 H, *J=*9.1), 8.09 (d, 8 H, *J=*8.8), 8.26(d, 8 H, *J=*8.8). 13C NMR (CDCl3): 164.8 (4 × C), 164.6 (4 × C), 164.1 (4 × C), 162.0 (2 × C), 155.7 (4 × C), 149.5 (4 × C), 139.4 (2 × C), 134.6 (2 × C), 133.1 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 129.8 (2 × C), 129.7 (4 × CH), 127.0 (4 × C), 122.4 (8 × CH), 121.5 (4 × CH), 121.2 (4 × C), 118.8 (4 × CH), 114.7 (8 × CH), 68.6 (4 × CH2), 66.1 (2 × CH2), 32.2 (2 × CH2), 29.9 (6 × CH2), 29.8 (12 × CH2), 29.6 (6 × CH2), 29.5 (2 × CH2), 29.3 (4 × CH2), 28.8 (2 × CH2), 26.2 (4 × CH2), 22.9 (2 × CH2), 14.4 (2 × CH3). Elemental analysis: for C130H144O24S(2122.65): calculated C 73.56, H 6.84, S 1.51; found C 73.46, H 6.74, S 1.39%.

***Bis[12-(4-{4-[7-(4-{4-[11-(1,1,3,3,3-pentamethyldisiloxanyl)undecyloxy]benzoyloxy}-benzoyloxy)naphthalen-2-yloxycarbonyl]phenoxycarbonyl}phenoxy)dodecyl] isophthalate (IIg)***. Karstedt´s catalyst (1 drop) and 1,1,1,3,3-pentamethyltrisiloxane (44 mg, 0.3 mmol) were added to a heated solution (44 °C) of **IIf** (205 mg, 1 mmol) in dry toluene (30 ml) in an inert argon atmosphere. The reaction mixture was stirred at 44 °C for 24 h and evaporated. The residue was washed with hexane (2 × 15 ml) and methanol (2 × 15 ml) and filtered. The crude product was purified by column chromatography (chloroform/methanol/triethylamine 100/0.5/0.1) and crystallisation from a chloroform/acetone (1:8) mixture. Yield 100 mg (43%), m.p. 134 °C. 1H NMR (CDCl3): 0.04 (s, 12 H, 4 × CH3Si), 0.06 (s, 18 H, 6 × CH3Si), 0.51 (m, 4 H, 2 × CH2Si), 1.29-1.48 (m, 64 H, 32 × CH2), 1.82 (m, 12 H, 6 × CH2CH2O), 4.05 (t, 8 H, *J=*6.6, 4 × CH2O), 4.35 (t, 4 H, *J=*6.7, 2 × CH2O), 6.99 (d, 8 H, *J=*8.8), 7.36-7.41 (m, 12 H), 7.53 (dd, 1 H, *J*=7.8), 7.70 (d, 4 H, *J=*2.3), 7.94 (d, 4 H, *J=*9.1), 8.16 (d, 8 H, *J=*9.1), 8.22 (dd, 2 H, *J*=7.9, *J*=1.8), 8.33 (d, 8 H, *J=*8.8), 8.69 (dd, 1 H, *J*=1.5). 13C NMR (CDCl3): 166.1 (2 × C), 164.8 (4 × C), 164.5 (4 × C), 164.1 (4 × C), 155.7 (4 × C), 149.5 (4 × C),134.6 (2 × C), 133.9 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 131.2 (2 × C), 130.9 (CH), 129.8 (2 × C), 129.7 (4 × CH), 128.8 (CH), 127.0 (4 × C),122.4 (8 × CH), 121.5 (4 × CH), 121.2 (4 × C), 118.8 (4 × CH), 114.7 (8 × CH), 68.6 (4 × CH2), 65.7 (2 × CH2),33.6 (2 × CH2), 29.8 (10 × CH2), 29.6 (4 × CH2), 29.5 (2 × CH2), 29.3 (6 × CH2), 28.9 (2 × CH2), 27.0 (4 × CH2), 26.2 (6 × CH2), 23.5 (2 × CH2), 18.6 (2 × CH2), 2.2 (6 × CH3), 0.6 (4 × CH3). Elemental analysis: for C140H170O26Si4 (2381.24): calculated C 70.62, H 7.20; found C 70.51, H 7.26%.

***Bis[12-(4-{4-[7-(4-{4-[11-(1,1,3,3,5,5,5-heptamethyltrisiloxanyl)undecyloxy]benzoyloxy}-benzoyloxy)naphthalen-2-yloxycarbonyl]phenoxycarbonyl}phenoxy)dodecyl] isophthalate (IIh)***. Dimer **IIh** has been obtained as for **IIg**, yield 40%, m.p. 133 °C. 1H NMR (CDCl3): 0.03 (s, 18 H, 6 × CH3Si), 0.06 (s, 24 H, 8 × CH3Si), 0.50 (m, 4 H, 2 × CH2Si), 1.30-1.48 (m, 64 H, 32 × CH2), 1.82 (m, 12 H, 6 × CH2CH2O), 4.05 (t, 8 H, *J=*6.4, 4 × CH2O), 4.34 (t, 4 H, *J=*6.6, 2 × CH2O), 6.99 (d, 8 H, *J=*8.8), 7.36-7.41 (m, 12 H), 7.53 (dd, 1 H, *J*=7.6), 7.70 (d, 4 H, *J=*2.3), 7.95 (d, 4 H, *J=*9.1), 8.16 (d, 8 H, *J=*8.8), 8.22 (dd, 2 H, *J*=7.6, *J*=1.9), 8.33 (d, 8 H, *J=*8.8), 8.69 (dd, 1 H, *J*=1.9). 13C NMR (CDCl3): 166.1 (2 × C), 164.8 (4 × C), 164.5 (4 × C), 164.1 (4 × C), 155.7 (4 × C), 149.5 (4 × C),134.6 (2 × C), 133.9 (2 × CH), 132.7 (8 × CH), 132.1 (8 × CH), 131.2 (2 × C), 130.9 (CH), 129.8 (2 × C), 129.7 (4 × CH), 128.8 (CH), 127.0 (4 × C),122.4 (8 × CH), 121.5 (4 × CH), 121.2 (4 × C), 118.8 (4 × CH), 114.7 (8 × CH), 68.6 (4 × CH2), 65.7 (2 × CH2),33.6 (2 × CH2), 29.8 (10 × CH2), 29.6 (4 × CH2), 29.5 (2 × CH2), 29.3 (6 × CH2), 28.9 (2 × CH2), 27.0 (4 × CH2), 26.2 (6 × CH2), 23.5 (2 × CH2), 18.6 (2 × CH2), 2.8 (4 × CH3), 2.2 (6 × CH3), 0.6 (4 × CH3). Elemental analysis: for C144H182O28Si6 (2529.56): calculated C 68.38, H 7.25; found C 68.25, H 7.32%.

**2.9. Experimental methods and setup**

For all prepared compounds differential scanning calorimetry (DSC) measurements have been performed using Perkin-Elmer 7 calorimeter (Perkin Elmer, Shelton, CT, USA). Phase transition temperatures and corresponding enthalpies have been established. The values of temperature and enthalpy were calibrated on extrapolated onset values for melting points of water, indium and zinc. A small amount of compound (2-5 mg) was hermetically sealed in aluminium pans and inserted into the calorimeter chamber, which was filled in with a nitrogen atmosphere during measurements. Calorimetric measurements were taken on cooling/heating runs at a rate of 5 K min‒1.

Preliminary the transition temperatures and phases were identified from observation of textures under polarizing microscope Eclipse E600Pol (Nikon, Tokyo, Japan). Sample cells for texture observation and electro-optical studies were prepared from glasses with ITO transparent electrodes (5×5 mm2) separated by two mylar sheets, which were used to define the cell thickness. The cells were filled with studied materials in the isotropic phase by capillary action. Another type of cell (one-free-surface sample) was prepared by removing the upper glass (without any treatment) during the cooling from the isotropic phase. The Linkam LTS E350 heating/cooling stage with TMS 93 temperature programmer (Linkam, Tadworth, UK) was used and temperature was stabilized within ±0.1 K.

Electric field was applied using driving voltage from generator PM 5191 (Philips, Amsterdam, Netherlands), the signal was amplified and the maximum amplitude of about ±120 V. Tektronix DPO4034 digital oscilloscope (Tektronix, Oregon, US) was utilized to obtain information about the switching current profile vs. time.

Bruker Nanostar system (Bruker, Santa Barbara, CA, USA) with CuKα radiation (wavelength λ=1.5418 Å), Vantec 2000 area detector, MRI TCPU H heating stage) working in the transmission mode has been utilized for the small angle x-ray diffraction studies. X-ray diffraction patterns in wide angle range were collected using Bruker GADDS system (CuKα radiation, point beam collimator, Vantec 2000 area detector) equipped with modified Linkam heating stage. In both systems the temperature stability was 0.1 K. Powder samples for Nanostar system were prepared in thin-walled glass capillaries (1.5 mm diameter), partially oriented samples for experiments in reflection were prepared as droplets on heated surface.

**3. Mesomorphic properties**



Figure S1

DSC thermographs for selected compounds (a) **Id**, (b) **IId**, and (c) **IIg**. The second heating run is in red and the second cooling in blue colour. Phases are indicated.



Figure S2

Planar texture of **IIa** in the nematic phase at T= 200ºC. The width of the figure is about 250 m.

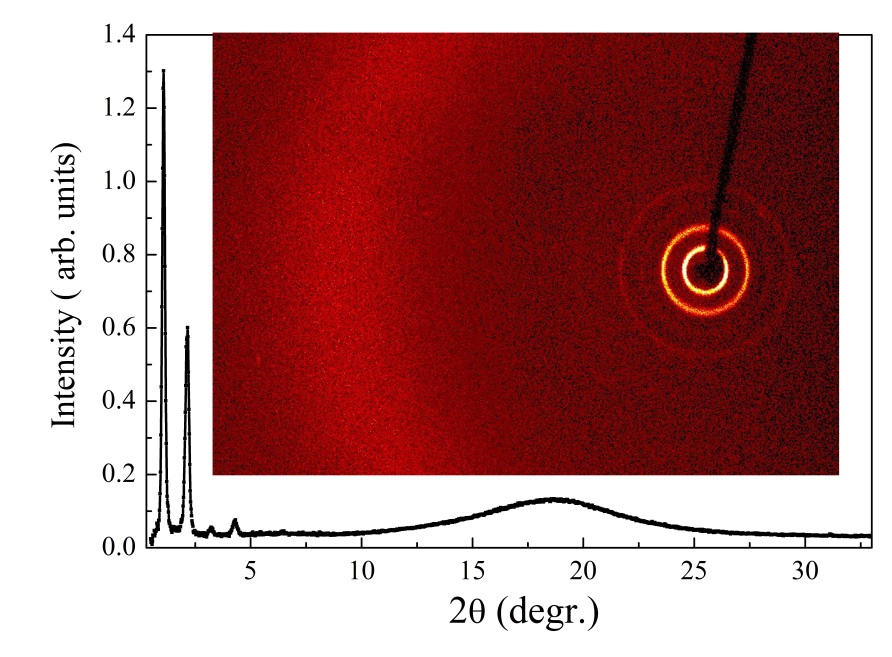


Figure S3

X-ray diffraction intensity profile versus the scattering angle for **IIi** at T=140 °C obtained by integration of 2D pattern (inset) over azimuthal angle.

1. **References**

# Neubert ME, Keast SS, Ezenyilimba MC, Greeer PB, Jones WC, Leonhardt D, Shenoudas. The Effect of carbonyl containing terminal chains on mesomorphic properties in 4,4′-disubstituted phenylbenzoates and thiobenzoates 8. Phenylbenzoates containing two carbonyl containing terminal chains. Mol Cryst Liq Cryst. 1993;237:4768.

1. Pintre IC, Serrano J L, Ros MB, Ortega J, Alonso I, Martínez-Perdiguero J, Folcia CL, Etxebarria J, Goc F, Amabilino DB, Puigmartí-Luis J, Gomar-Nadal E. TTF-based bent-core liquid crystals. Chem Commun. 2008;22:25232525.

# Kovářová A, Kozmík V, Svoboda J, Novotná V, Glogarová M, Pociecha D. Naphthalene-based bent-shaped liquid crystals with a semifluorinated terminal chain. Liq Cryst. 2012;39:755767.

## Horčic M, Svoboda J., Seidler A., Kozmík V, Novotná V, Pociecha D, Gorecka E. W-shaped liquid crystalline dimers. RSC Advances. 2016;6:41972-41981.

## Kozmík V, Kovářová A, Kuchař M, Svoboda J, Novotná V., Glogarová M, Kroupa J. Novel polymerizable bent‐shaped monomeric molecules. Liq Cryst. 2006;33:41-56.

1. Nakanishi S, Ueda M. Synthesis of novel glass-forming liquid crystals containing acrylic acid trimer core unit and mesogenic moiety, and their use in cholesteric reflection films. Polym J. 2007;39:252–258.