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Electronic supporting information

W-shaped liquid crystalline dimers

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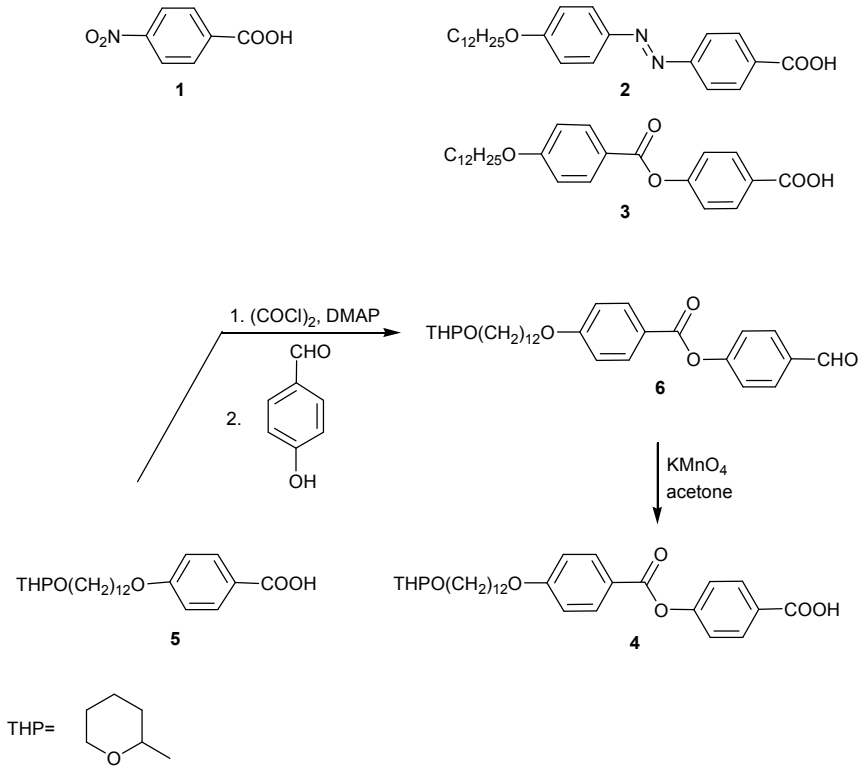
Content

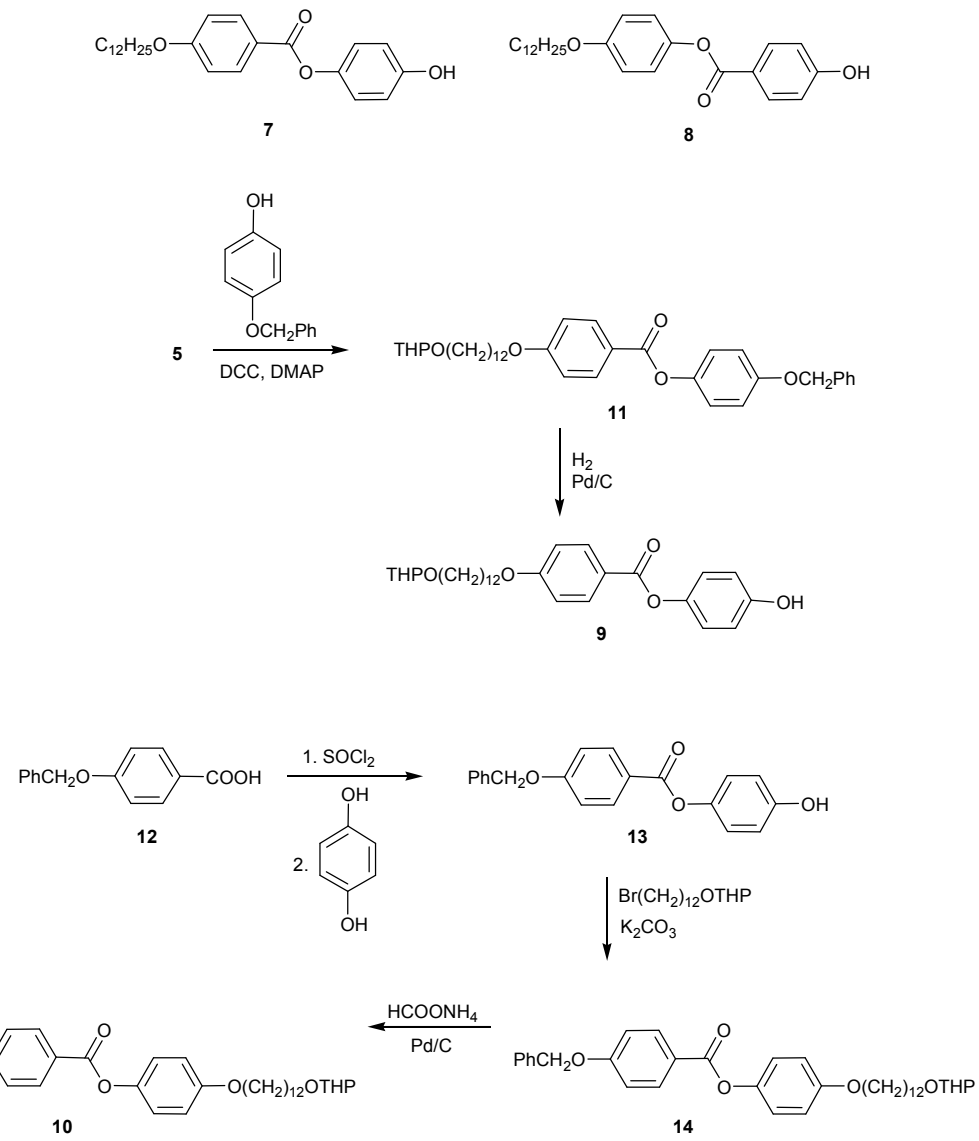
1. Synthesis of the lengthening arms

p-Nitrobenzoic acid (**1**) was a commercial product. Acids **2**,**3** (Scheme S1) were prepared by the known procedures[S1,S2]. In the first step of synthesis of the THP-protected acid **4** (Scheme S1), *p*-hydroxybenzaldehyde was acylated with acid chloride of the acid **5**[S3] and the intermediate formyl ester **6** was subsequently oxidized with potassium permanganate in acetone to yield compound **4**.



Scheme S1 Structures of acids **1-3** and synthesis of acid **4**.

Phenols **7**,**8** were obtained according to ref.[S4] Synthesis of the THP-protected phenols **9**,**10** is summarized in Scheme S2. In the two-step synthesis of phenol **9**, acid **5** was coupled with 4-benzyloxyphenol[S5] by the means of *N*,*N*′-dicyclohexylcarbodiimide (DCC) in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP), and the protecting benzyl group ($PhCH_2$) in the formed ester **11** (yield 61%) was removed by catalytic hydrogenation to give rise to phenol **9** (yield 89%). In the synthesis of phenol **10**, acid **12**[S6] was first transformed to the corresponding acid chloride, which monoacylated hydroquinone to yield ester **13**[S7] (yield 69%), hydroxyl group of which was then alkylated with 12-(tetrahydropyranyloxy)dodecyl bromide[S8] to yield ester **14** (yield 79%). Final catalytic transfer-hydrogenation removed the protecting benzyl group to afford phenol **10** (yield 99%).



Scheme S2 Structure of phenols **7**,**8** and synthesis of phenols **9**,**10**.

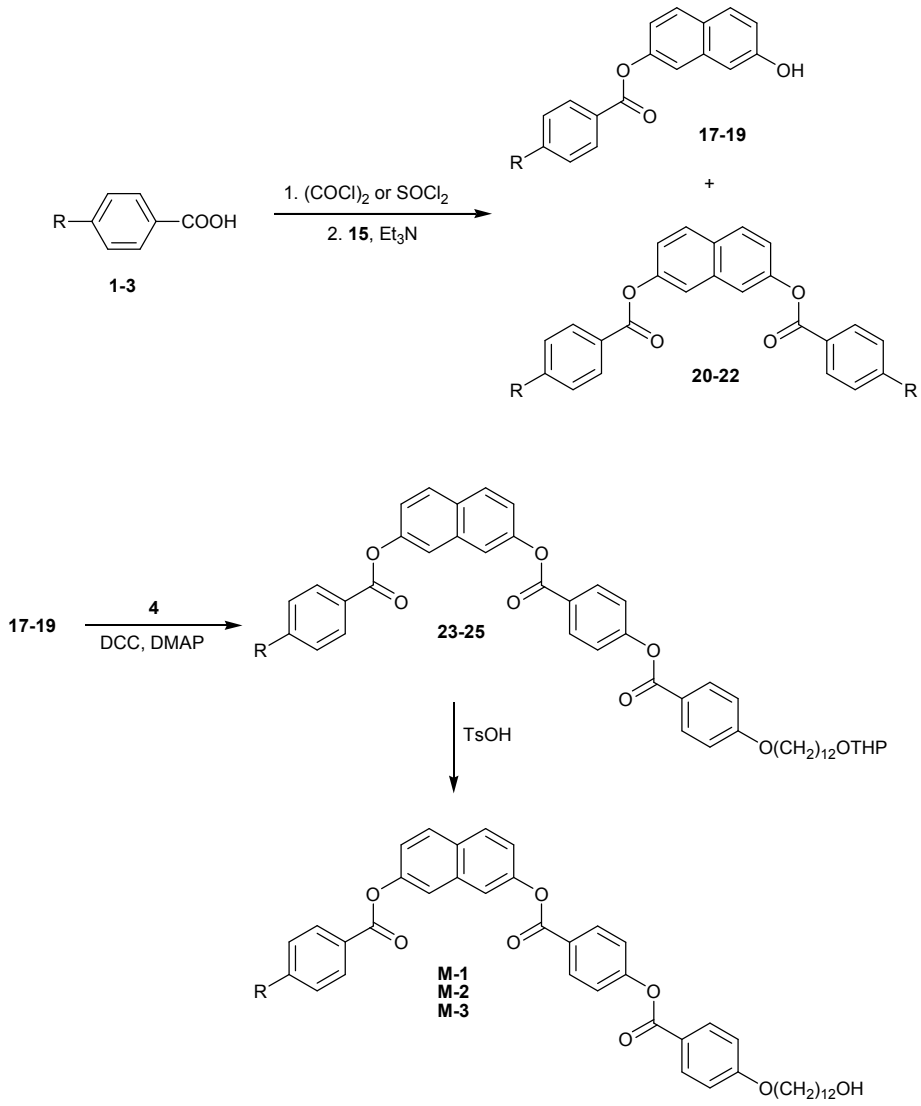
2. Synthesis of monomers

The molecular structures of monomers represent a type of non-symmetrical bent-core liquid crystals with a terminal hydroxyl group in one of the lengthening arms. Therefore, it is necessary to join the lengthening arms to the central unit successively in two separate reaction steps. Further, protection of one of the central unit functionalities is required. For this purpose, we utilized naphthalene-2,7-diol (**15**) and 7-benzyloxynaphthalene-2-carboxylic acid (**16**)[S2,S9] central cores, resp.

2.1 Monomers M-1 to M-3 with naphthalene-2,7-diol central unit

Monoacylated intermediates **17-19**, which enable a non-symmetrical substitution of the central unit, have been prepared by the same way. First, naphthalenediol **15** was acylated with freshly prepared acid chlorides of acids **1-3** (Scheme S3). The excess of the diol **15**

guaranteed the preferential monoacylation of the central unit (Scheme S3) and subst. naphthols **17-19** were isolated in 69%, 55%, and 72% yield, resp. In addition, the corresponding bis-acyl derivatives **20-22** were also obtained in a low yield (7%[S10], 1 %, and 9%[S11], resp.).



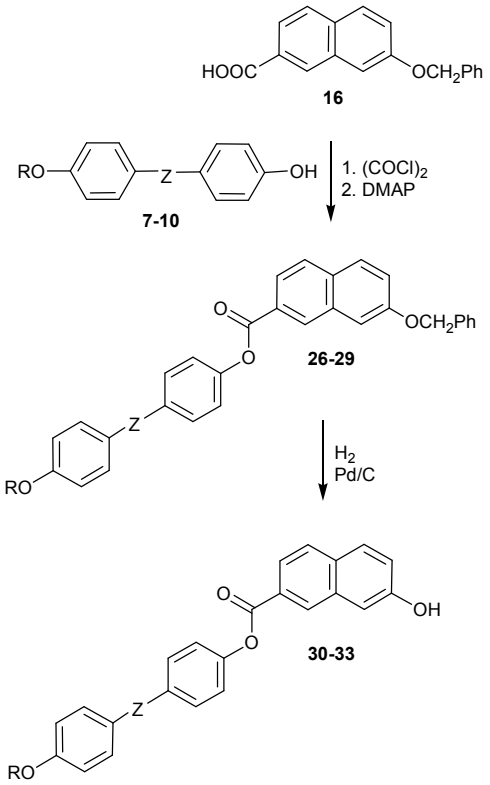
For **1**,**17**,**20**,**23**,**M-1** R=NO_2; **2**,**18**,**21**,**24**,**M-2** R=4-$C_{12}H_{25}$OPhN=N;
3,**19**,**22**,**25**,**M-3** R=4-$C_{12}H_{25}$OPhCOO

Scheme S3 Synthesis of the monomers **M-1** to **M-3**.

Introduction of the second arms was achieved by acylation of the naphthols **17-19** with acid **4** in a DCC mediated coupling (Scheme S3) to afford compounds **23-25** (yield 60%, 34%, and 99%, resp.). Deprotection of the terminal THP protecting group was accomplished at standard conditions utilizing *p*-toluenesulphonic acid (TsOH) catalysis to yield liquid crystalline monomers **M-1** to **M-3** with the terminal hydroxyl group (yield 91%, 84%, and 95%, resp.).

2.2 Monomers M-4 to M-7 with 7-hydroxynaphthalene-2-carboxylic acid central unit

Monomers with this central unit have been synthesised by gradual joining the lengthening arms to the central unit **16** (Scheme S4). First, the phenol arms **7-10** were acylated with acid chloride of acid **16** in the presence of DMAP to yield esters **26-29** (yield 98%, 75%, 99%, and 84%, resp.). In the second step, the benzylic protecting group was removed by hydrogenolysis to release the hydroxyl group for introduction of the second arm. The yield of the corresponding naphthols **30-33** amounted to 66%, 57%, 66%, and 61%, resp.

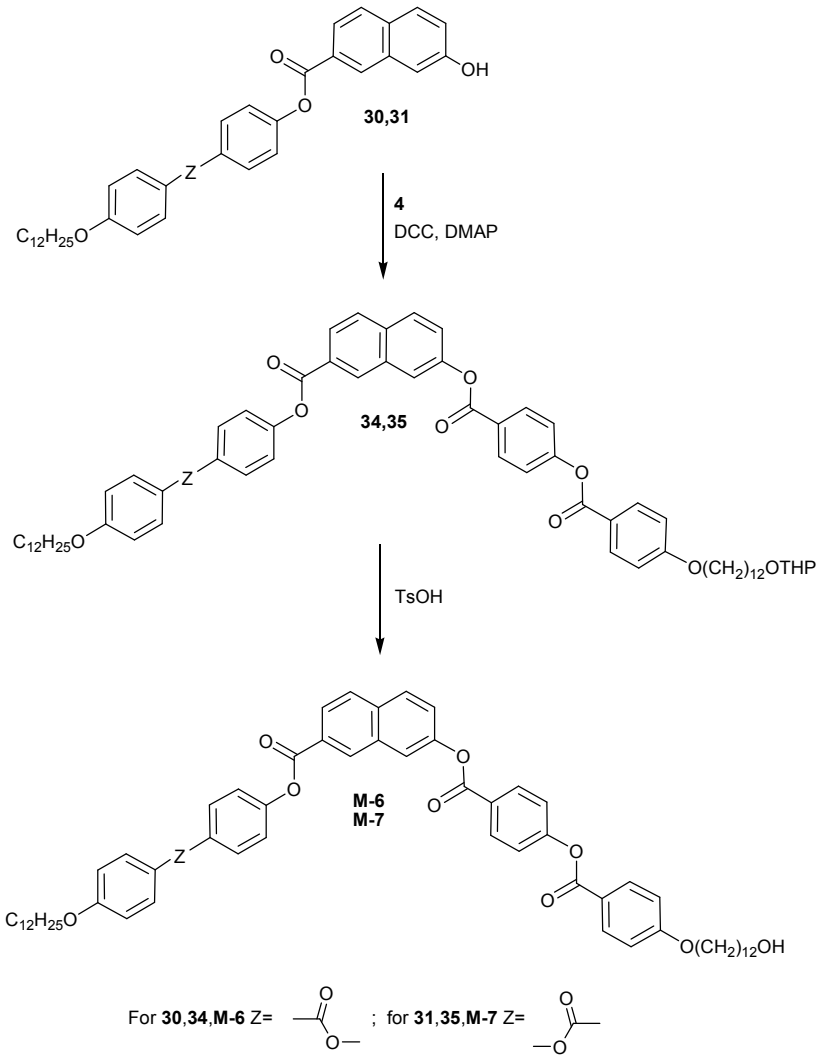


For **7**,**8**,**26**,**27**,**30**,**31** R=$C_{12}H_{25}$; for **9**,**10**,**28**,**29**,**32**,**33** R=THPO$(CH_2)_{12}$;

for **7**,**9**,**26**,**28**,**30**,**32** Z=  ; for **8**,**10**,**27**,**29**,**31**,**33** Z= 

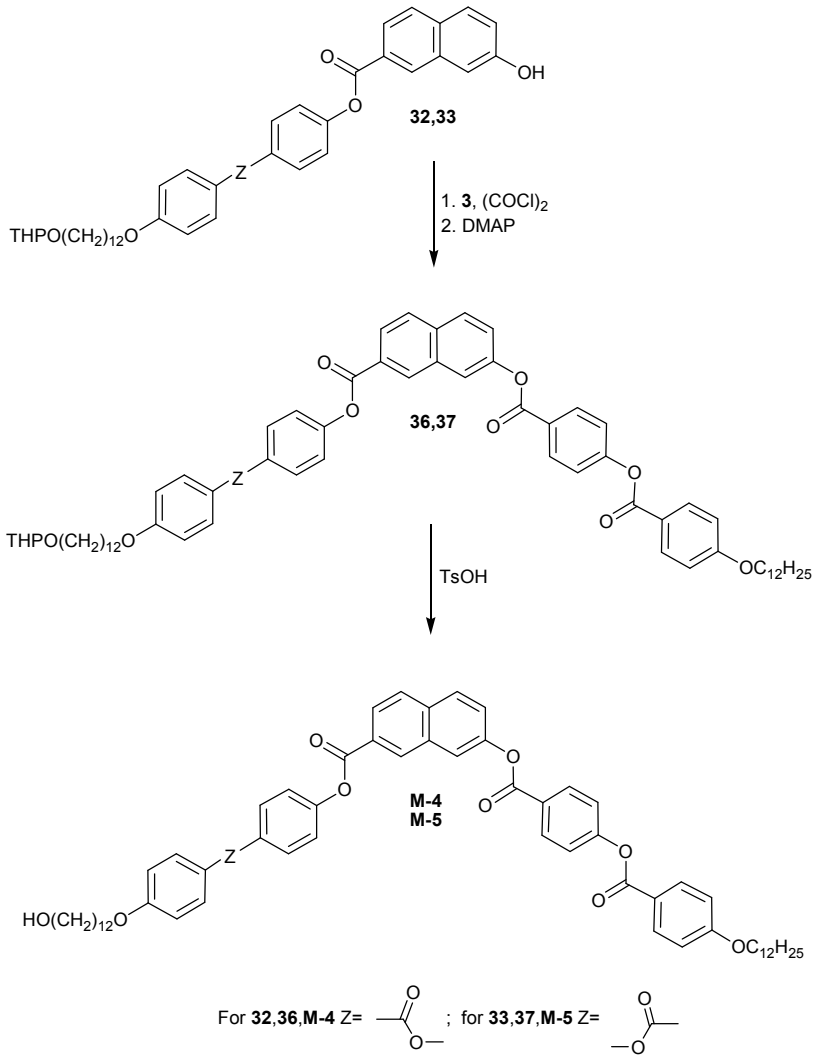
Scheme S4 Synthesis of the intermediate naphthols **30-33**.

Naphthols **30**,**31** were acylated with acid **4** as above to get the protected derivatives **34** (yield 73%) and **35** (yield 60%). Final deprotection of the THP-group left monomers **M-6** (yield 92%) and **M-7** (yield 92%), resp., see Scheme S5.



Scheme S5 Synthesis of monomers **M-6**,**M-7**.

On the other hand, naphthols **32, 33** were acylated with acid chloride of acid **3** to yield the bent materials **36**,**37** (yield 89% and 87%, resp.) (Scheme S6). The final monomers **M-4** (yield 93%) and **M-5** (yield 88%) were obtained by the means of TsOH analogously.

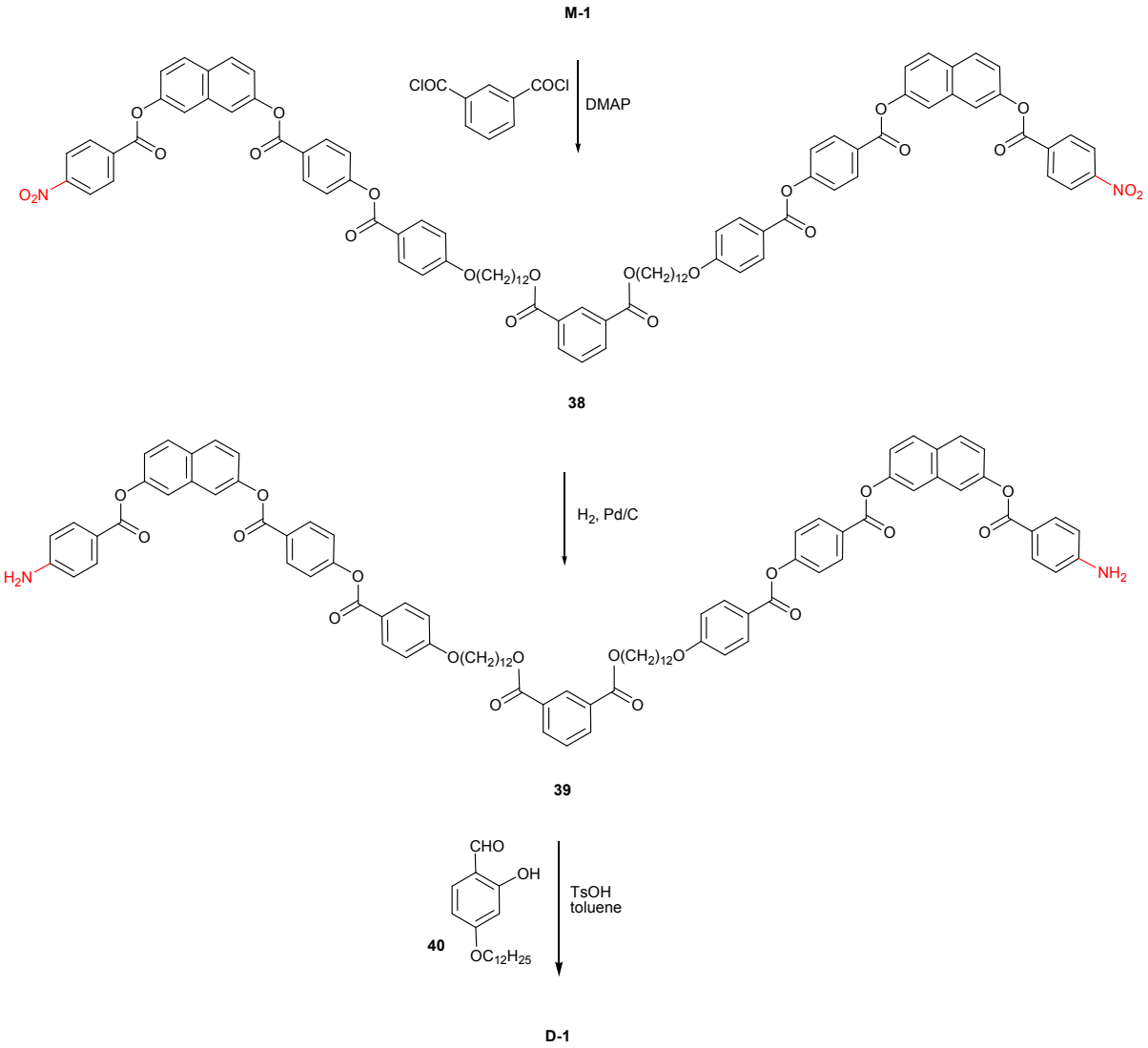


Scheme S6 Synthesis of monomers **M-4**,**M-5**.

3. Synthesis of dimers

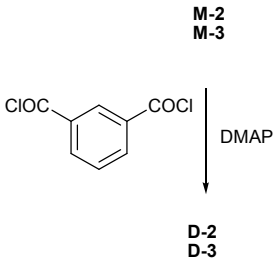
3.1 Dimers derived from naphthalene-2,7-diol

The final synthesis of dimer **D-1** is shown in Scheme S7. The hydroxyl group of the intermediate monomer **M-1** was acylated with with isophthaloyl chloride in the presence of DMAP to the compound **38** in 63% yield. The nitro groups of **38** were then reduced by Pd-catalysed hydrogenation to yield diamine **39** (yield 28%) which was finally condensed with 4-dodecyloxy-2-hydroxybenzaldehyde (**40**)[S12] to yield dimer **D-1** (yield 35%) possessing imino linkages in the outer arms.



Scheme S7 Synthesis of dimer **D-1**.

Dimers **D-2** and **D-3** were obtained by acylation of the terminal hydroxyl group of monomers **M-2** and **M-3** with isophthaloyl chloride as above, yield 45% and 33%, resp., see Scheme S8.



Scheme S8 Synthesis of dimers **D-2**,**D-3**.

3.2 Dimers with the 7-hydroxynaphthalene-2-carboxylic acid central unit

Connection of monomers **M-4** to **M-7** was performed analogously as for monomers **M-2**,**M-3** to yield dimers **D-4** to **D-7** (yield 47%, 25%, 35%, and 43%, resp.).

4. Experimental

Characterization

The structures of the intermediates and the products were confirmed by proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform ($CDCl_3$) and dimethylsulfoxide (DMSO-d_6) 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). The HR-MS of monomers and dimers has been performed on spectrometer LTQ Orbitrap Velos, hybrid ion-trap-orbitrap (Thermo Scientific), positive electrospray.

4.1 General procedure for the preparation of acid chlorides

A. Oxalyl chloride method.

To a mixture of acid **2**,**3**,**16** (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. To remove the traces of oxalyl chloride, the residue was dissolved in dry toluene (10 ml) and re-evaporated.

B. Thionyl chloride method.

Thionyl chloride (0.36 ml; 5 mmol) was added to a slurry of acid **1**,**12** in dry toluene (5 ml) and the mixture was stirred at 100 °C for 4 h in an inert argon atmosphere and then evaporated to dryness.

4.2 General procedure for preparation of monoacyl derivatives 13,17-19

The acid chloride (1 mmol) was dissolved in dry dichloromethane (5 ml) and added to a solution of naphthalene-2,7-diol (**15**) and hydroquinone (4 mmol), resp., and triethylamine (1.2 mmol) in a dichloromethane (10 ml)/acetone (1 ml) mixture. The reaction mixture was stirred at 50 °C for 6 h in an argon atmosphere, cooled to room temperature, and diluted with water (10 ml). The organic layer was separated and the aqueous layer was washed with dichloromethane (2 × 5 ml). The combined organic solution was washed with brine (7 ml) and dried with anhydrous $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography (chloroform/methanol, 99/1) and crystallisation from toluene.

4.3 General procedure for the acylation by DCC coupling

A mixture of alcohol **17-19**,**30**,**31** (1 mmol), acid **4**,**5** (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 × 10 ml). The combined organic solution was dried with anhydrous $MgSO_4$. After evaporation, the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 20/1).

4.4 General procedure for the acylation with acid chlorides

The acid chloride (1.2 mmol) was dissolved in dry dichloromethane (10 ml) and the solution was added to a mixture of alcohol **7-10**,**32**,**33** (1 mmol) and DMAP (1.2 mmol) in dichloromethane (60 ml). After stirring at 50 °C for 3 h in an argon atmosphere, the mixture was worked-up as for compounds prepared by general procedure **2**. The crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 20/1).

4.5 General procedure for the THP-deprotection

To a mixture of compounds **23-25**,**34-37** (1 mmol) in dichloromethane (60 ml) and methanol (30 ml), a catalytic amount of freshly fused p-toluenesulfonic acid was added and the mixture was stirred at room temperature for 24 h. The solvent was evaporated, and the residue was dissolved in chloroform (50 ml) and washed with a saturated aq. solution of sodium hydrogen carbonate (20 ml). The organic layer was dried with anhydrous $MgSO_4$. After evaporation, the crude product was purified by column chromatography (chloroform/methanol, 99/1) and crystallisation from toluene.

4.6 General procedure for the hydrogenolysis of benzyl protecting group and nitro group

To a mixture of compounds **11**,**26-29**,**38** (1 mmol) in ethyl acetate (100 ml) and ethanol (10 ml) (**11** in acetone, resp.), 10% Pd/C (0.1 wt%) was added. The slurry was stirred in a hydrogen atmosphere at room temperature for 48 h, the catalyst was filtered off and the filtrate was evaporated. Column chromatography (chloroform/methanol, 99/1) and crystallisation from toluene yielded the product.

4.7 General synthesis of the W-shaped dimers

Isophthaloyl chloride (1 mmol) was added to a solution of alcohol **M-2** to **M-7** (2 mmol) 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 reaction mixture was worked-up according the general procedure **4**. The dimers were purified by column chromatography (chloroform/methanol, 99/1) and crystallisation from a toluene/acetone (1/3) mixture.

4.8 Synthesis of the lengthening arms

4-Formylphenyl 4-[12-(tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoate (6)

Oxalyl chloride (11.3 g; 88.7 mmol) was added slowly to a mixture of acid **5** (32.8 g; 80.7 mmol) and DMAP (21.7 g; 177 mmol) in dry dichloromethane (250 ml). The reaction mixture was stirred at room temperature for 24 h in an inert argon atmosphere. Then another portion of DMAP (9.86 g; 80.7 mmol) was added, followed by 4-hydroxybenzaldehyde (11.8 g; 96.8 mmol). The mixture was heated and stirred at 50 °C for 3 h. After cooling, it was diluted with cold water (150 ml), the organic layer was separated and the aqueous layer was washed with dichloromethane (2 × 70 ml). The combined organic solution was dried with anhydrous $MgSO_4$, the solvent was evaporated and the crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether, 20/1). Yield 39.3 g (95%) of **6**, m.p. 52-54.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.27-1.86 (m, 26 H, $(CH_2)_{13}$); 3.39 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.74 (m, 1 H, CH_2O); 3.87 (m, 1 H, CH_2O); 4.05 (t, 2 H, J = 6.7, CH_2O); 4.57 (m, 1 H, OCHO); 6.98 (d, 2 H, J = 9.1); 7.40 (d, 2 H, J = 8.5); 7.96 (d, 2 H, J = 8.8); 8.14 (d, 2 H, J = 8.8); 10.02 (s, 1 H, CHO). ^{13}C NMR spectrum ($CDCl_3$): 191.2 (CHO); 164.5 (C); 164.1 (C); 156.2 (C); 134.1 (C); 132.7 (2 × CH); 131.5 (2 × CH); 122.9 (2 × CH); 121.0 (C); 114.7 (2 × CH); 99.1 (CH); 68.6 (CH_2); 67.9 (CH_2); 62.6 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.8 (3 × CH_2); 29.7 (2 × CH_2); 29.6 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.7 (CH_2); 20.0 (CH_2). Elemental analysis: for $C_{31}H_{42}O_6$ (510.68) calcd C 72.91, H 8.29; found C 72.80, H 8.19%.

4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}benzoic acid (4)

The solution of aldehyde **6** (22.8 g; 44.6 mmol) in acetone (450 ml) was cooled at 0 °C and potassium permanganate (7.8 g; 49.1 mmol) was added portion wise during 0.5 h. The reaction mixture was stirred for 3 h at 0 °C and 1 h at room temperature, and decomposed by addition of propan-2-ol (15 ml). After 1 h stirring, the mixture was acidified with acetic acid, evaporated to dryness and eluted with hot ethanol (20 × 200 ml). The combined filtrates were evaporated and acid **4** was purified by crystallisation from toluene. Yield 11.9 g (51%), m.p. 108-109 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.25-1.85 (m, 26 H, $(CH_2)_{13}$); 3.38 (m, 1 H, CH_2O); 3.52 (m, 1 H, CH_2O); 3.76 (m, 1 H, CH_2O); 3.85 (m, 1 H, CH_2O); 4.06 (t, 2 H, J = 6.7, CH_2O); 4.57 (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). ^{13}C NMR spectrum ($CDCl_3$): 171.3 (C); 164.6 (C); 164,0 (C); 155.8 (C); 132.6 (2 × CH); 132.1 (2 × CH); 126.8 (C); 122.2 (2 × CH); 121.2 (C); 114.6 (2 × CH); 99.1 (CH); 68.6 (CH_2); 68.0 (CH_2); 62.6 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.8 (3 × CH_2); 29.7 (2 × CH_2); 29.6 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.7 (CH_2); 19.9 (CH_2). Elemental analysis: for $C_{31}H_{42}O_7$ (526.68) calcd C 70.70, H 8.04; found C 70.66, H 8.01%.

4-Benzyloxyphenyl 4-[12-(tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoate (11)

Compound **11** was prepared by the general procedure **4.3**, yield 61%, m.p. 78-81 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.28-1.84 (m, 26 H, $(CH_2)_{13}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.87 (m, 1 H, CH_2O); 4.03 (t, 2 H, J = 6.4, CH_2O); 4.57 (m, 1 H, OCHO); 5.07 (s, 2 H, CH_2O); 6.96 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 9.1); 7.11 (d, 2 H, J = 9.4); 7.32-7.45 (m, 5 H); 8.12 (d, 2 H, J = 9.1). ^{13}C NMR spectrum ($CDCl_3$): 165.5 (C); 163.7 (C); 156.6 (C); 145.0 (C); 137.1 (C); 132.5 (2 × CH); 128.9 (2 × CH); 128.3 (CH); 127.7 (2 × CH); 122.8 (2 × CH); 121.9 (C); 115.7 (2 × CH); 114.5 (2 × CH); 99.1 (CH); 70.6 (CH_2); 68.5 (CH_2); 67.9 (CH_2); 62.6 (CH_2); 31.1 (CH_2); 30.0 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6

(CH_2); 29.4 (CH_2); 26.5 (CH_2); 26.3 (CH_2); 25.8 (CH_2); 20.0 (CH_2). Elemental analysis: for $C_{37}H_{48}O_6$ (588.79) calcd C 75.48, H 8.22; found C 75.36, H 8.19%.

4-Hydroxyphenyl 4-[12-(tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoate (9)

Compound **9** was prepared by the general procedure **4.6**, yield 89%, m.p. 82-84 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.29-1.87 (m, 26 H, $(CH_2)_{13}$); 3.39 (m, 1 H, CH_2O); 3.51 (m, 1 H, CH_2O); 3.74 (m, 1 H, CH_2O); 3.89 (m, 1 H, CH_2O); 4.04 (t, 2 H, J = 6.4, CH_2O); 4.59 (m, 1 H, OCHO); 6.82 (d, 2 H, J = 8.8); 6.96 (d, 2 H, J = 8.5); 7.04 (d, 2 H, J = 8.8); 8.13 (d, 2 H, J = 8.5). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (C); 163.8 (C); 154.0 (C); 144.4 (C); 132.5 (2 × CH); 122.8 (2 × CH); 121.7 (C); 116.4 (2 × CH); 114.5 (2 × CH); 99.2 (CH); 68.6 (CH_2); 68.1 (CH_2); 62.7 (CH_2); 31.0 (CH_2); 29.9 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.7 (CH_2); 19.9 (CH_2). Elemental analysis: for $C_{30}H_{42}O_6$ (498.67) calcd C 72.76, H 8.49; found C 72.80, H 8.44%.

4-Hydroxyphenyl 4-benzyloxybenzoate (13)

Compound **13** was prepared by the general procedure **4.2**, yield 69%, m.p. 202-204 °C, m.p.[S7] 210 °C.

4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]phenyl 4-benzyloxybenzoate (14)

The mixture of 12-tetrahydropyranyloxydodecyl bromide (6.9 g; 20 mmol), phenol **13** (5.8 g; 18 mmol) and dry potassium carbonate (3 g; 21.6 mmol) in dry DMF (60 ml) was heated at 80 °C for 12 h in an argon atmosphere. After cooling, the reaction mixture was diluted with water (300 ml), extracted with toluene (3 × 100 ml), and the combined organic solution was dried with anhydrous $MgSO_4$. After evaporation, the crude product was purified by column chromatography (chloroform). Yield 8.3 g (79%) of **14**, m.p. 79-81 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.28-1.85 (m, 26 H, $(CH_2)_{13}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.87 (m, 1 H, CH_2O); 3.95 (t, 2 H, J = 6.6, CH_2O); 4.58 (m, 1 H, OCHO); 5.16 (s, 2 H, CH_2O); 6.92 (d, 2 H, J = 9.1); 7.07 (m, 4 H); 7.36-7.43 (m, 5 H); 8.15 (d, 2 H, J = 8.8). ^{13}C NMR spectrum ($CDCl_3$): 165.5 (C); 163.2 (C); 157.0 (C); 144.5 (C); 136.4 (C); 132.5 (2 × CH); 129.0 (2 × CH); 128.5 (CH); 127.7 (2 × CH); 122.7 (2 × CH); 122.4 (C); 115.3 (2 × CH); 114.9 (2 × CH); 99.1 (CH); 70.4 (CH_2); 68.6 (CH_2); 67.9 (CH_2); 62.6 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.5 (CH_2); 26.5 (CH_2); 26.3 (CH_2); 25.8 (CH_2); 20.0 (CH_2). Elemental analysis: for $C_{37}H_{48}O_6$ (588.79) calcd C 75.48, H 8.22; found C 75.40, H 8.16%.

4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]phenyl 4-hydroxybenzoate (10)

To a solution of benzyl ether **14** (8.3 g; 14.1 mmol) and ammonium formate (8.9 g; 141 mmol) in dry acetone (150 ml) was added 10% Pd/C (830 mg), and the mixture was stirred at 70 °C for 10 h. After cooling to room temperature, it was filtered, evaporated, the residue was dissolved in chloroform (100 ml) and diluted with water (60 ml). Layers were separated, the aqueous layer was washed with chloroform (2 × 30 ml), and the combined organic solution was dried with anhydrous $MgSO_4$. The solvent was evaporated, the crude product was purified by column chromatography (chloroform/methanol, 99/1) and crystallised from a hexane/toluene (2/1) mixture. Yield 7.0 g (99%) of **10**, m.p. 78-81 °C. ^{1}H NMR spectrum

($CDCl_3$): 1.25-1.82 (m, 26 H, $(CH_2)_{13}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.88 (m, 1 H, CH_2O); 3.95 (t, 2 H, J = 6.6, CH_2O); 4.58 (m, 1 H, OCHO); 6.91 (d, 4 H, J = 9.1); 7.09 (d, 2 H, J = 9.1); 8.10 (d, 2 H, J = 8.8). ^{13}C NMR spectrum ($CDCl_3$): 165.9 (C); 161.8 (C); 157.0 (C); 144.5 (C); 132.7 (2 × CH); 122.7 (2 × CH); 121.3 (C); 115.8 (2 × CH); 115.3 (2 × CH); 99.2 (CH); 68.7 (CH_2); 68.1 (CH_2); 62.7 (CH_2); 31.0 (CH_2); 29.9 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.5 (CH_2); 26.4 (CH_2); 26.3 (CH_2); 25.7 (CH_2); 19.9 (CH_2). Elemental analysis: for $C_{30}H_{42}O_6$ (498.67) calcd C 72.76, H 8.49; found C 72.66, H 8.48%.

4.9 Synthesis of monomers

4.9.1 Monomers M-1 to M-3 with naphthalene-2,7-diol central unit

7-Hydroxynaphthalen-2-yl 4-nitrobenzoate (17)
Naphthol **17** was prepared by the general procedure **4.2**, yield 69% of a yellowish solid, m.p. 213-217 °C. ^{1}H NMR spectrum ($CDCl_3$): 5.12 (s, 1 H, OH); 7.10-7.22 (m, 3 H); 7.55 (d, 1 H, J = 2.4); 7.79 (d, 1 H, J = 8.8); 7.85 (d, 1 H, J = 9.0); 8.42 (m, 4 H). ^{13}C NMR spectrum (DMSO-d_6): 164.0 (C); 156.9 (C); 151.2 (C); 149.2 (C); 135.8 (C); 135.2 (C); 131.9 (2 × CH); 130.1 (CH); 129.9 (CH); 126.6 (C); 124.7 (2 × CH); 119.4 (CH); 118.4 (CH); 117.6 (CH); 109.3 (CH). Elemental analysis: for $C_{17}H_{11}NO_5$ (309.28) calcd C 66.02, H 3.58, N 4.53; found C 65.88, H 3.62, N 4.41%.
As a by-product, derivative **20** was also isolated, yield 7%, m.p. 247-248 °C, m.p.[S10] 238 °C.

(*E*)-7-Hydroxynaphthalen-2-yl 4-(4-dodecyloxyphenyldiazenyl)benzoate (18)
Naphthol **18** was prepared by the general procedure **4.2**, yield 55% of orange solid, m.p. 177-181 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 3 H, J = 6.6, CH_3); 1.20-1.57 (m, 18 H, $(CH_2)_9$); 1.83 (m, 2 H, $\underline{CH_2}CH_2O$); 4.07 (t, 2 H, J = 6.6, CH_2O); 5.08 (s, 1 H, OH); 7.04 (d, 2 H, J = 8.8); 7.12 (dd, 1 H, ^3J = 8.8, ^4J = 2.4); 7.16 (d, 1 H, J = 2.4); 7.24 (dd, 1 H, ^3J = 8.8, ^4J = 2.2); 7.57 (d, 1 H, J = 2.2); 7.80 (d, 1 H, J = 8.8); 7.85 (d, 1 H, J = 8.8); 7.98 (d, 2 H, J = 9.1); 8.00 (d, 2 H, J = 8.5); 8.38 (d, 2 H, J = 8.5). ^{13}C NMR spectrum (DMSO-d_6): 164.9 (C); 163.0 (C); 156.8 (C); 155.9 (C); 149.5 (C); 147.0 (C); 135.9 (C); 131.8 (2 × CH); 131.0 (C); 130.0 (CH); 129.8 (CH); 126.6 (C); 125.8 (2 × CH); 123.2 (2 × CH); 119.3 (CH); 118.6 (CH); 117.6 (CH); 115.9 (2 × CH); 109.4 (CH); 68.9 (CH_2); 31.9 (CH_2); 29.7 (2 × CH_2); 29.6 (2 × CH_2); 29.4 (2 × CH_2); 29.2 (CH_2); 26.1 (CH_2); 22.7 (CH_2); 14.5 (CH_3). Elemental analysis: for $C_{35}H_{40}N_2O_4$ (552.72) calcd C 76.06, H 7.29, N 5.07; found C 75.89, H 7.66, N 4.99%.
By chromatographic separation, derivative **21** (yield 1%) was also isolated, m.p. 200 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 6 H, J = 6.7, 2 × CH_3); 1.20-1.55 (m, 36 H, $(CH_2)_{18}$); 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$); 4.06 (t, 4 H, J = 6.4, 2 × CH_2O); 7.03 (d, 4 H, J = 9.1); 7.41 (dd, 2 H, J_1 = 8.8, J_2 = 2.2); 7.73 (d, 2 H, J = 2.2); 7.96 (d, 2 H, J = 8.8); 7.97 (d, 4 H, J = 9.1); 8.00 (d, 4 H, J = 8.8); 8.39 (d, 4 H, J = 8.8). ^{13}C NMR spectrum ($CDCl_3$): 164.7 (2 × C); 162.7 (2 × C); 156.2 (2 × C); 149.7 (2 × C); 147.2 (2 × C); 134.6 (C); 131.5 (4 × CH); 130.7 (2 × C); 129.8 (2 × CH); 129.4 (C); 125.6 (4 × CH); 122.8 (4 × CH); 121.2 (2 × CH); 118.6 (2 × CH); 115.1 (4 × CH); 68.7 (2 × CH_2); 32.2 (2 × CH_2); 29.8 (8 × CH_2); 29.6 (4 × CH_2); 29.4 (2 ×

CH_2); 26.2 (2 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3). Elemental analysis: for $C_{60}H_{72}N_4O_6$ (945.27) calcd C 76.24, H 7.68, N 5.93; found C 76.16, H 7.59, N 5.85%.

7-Hydroxynaphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (19)

Naphthol **19** was prepared by the general procedure **4.2**, yield 72%, m.p. 148-152 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.6, CH_3); 1.27-1.48 (m, 18 H, $(CH_2)_9$); 1.83 (m, 2 H, $\underline{CH_2}CH_2O$); 4.06 (t, 2 H, J = 6.6, CH_2O); 5.05 (s, 1 H, OH); 6.99 (d, 2 H, J = 8.8); 7.08-7.13 (m, 2 H); 7.20 (dd, 1 H, ^3J = 8.8, ^4J = 2.1); 7.39 (d, 2 H, J = 8.5); 7.52 (d, 1 H, J = 2.3); 7.77 (d, 1 H, J = 8.8); 7.82 (d, 1 H, J = 8.8); 8.16 (d, 2 H, J = 8.8); 8.32 (d, 2 H, J = 8.5). ^{13}C NMR spectrum ($CDCl_3$): 165.0 (C); 164.6 (C); 164.1 (C); 155.6 (C); 164.3 (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); 121.1 (C); 119.1 (CH); 117.9 (CH); 117.5 (CH); 114.7 (2 × CH); 109.6 (CH); 68.6 (CH_2); 32.2 (CH_2); 29.9 (2 × CH_2); 29.8 (2 × CH_2); 29.6 (2 × CH_2); 29.3 (CH_2); 26.2 (CH_2); 22.9 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.98, H 7.03%.

As a by-product, the known compound **22** (yield 9%) was obtained, m.p. 133-135.5 °C, m.p.[S13] 135 °C.

7-(4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}benzoyloxy)-naphthalen-2-yl 4-nitrobenzoate (23)

Compound **23** was prepared by the general procedure **4.3**, yield 60%, white solid, m.p. 140-142.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.29-1.85 (m, 26 H, $(CH_2)_{13}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.87 (m, 1 H, CH_2O); 4.06 (t, 2 H, J = 6.6, CH_2O); 4.58 (m, 1 H, OCHO); 6.99 (d, 2 H, J = 9.1); 7.36-7.42 (m, 4 H); 7.71 (s, 2 H); 7.97 (d, 2 H, J = 7.3); 8.16 (d, 2 H, J = 9.1); 8.33 (d, 2 H, J = 8.5); 8.42 (m, 4 H). ^{13}C NMR spectrum ($CDCl_3$): 164.8 (C); 164.6 (C); 164.1 (C); 163.6 (C); 155.8 (C); 151.2 (C); 149.7 (C); 149.1 (C); 135.1 (C); 134.6 (C); 132.7 (2 × CH); 132.1 (2 × CH); 131.6 (2 × CH); 130.0 (C); 129.9 (CH); 129.8 (CH); 126.9 (C); 124.0 (2 × CH); 122.4 (2 × CH); 121.8 (CH); 121.1 (C); 120.9 (CH); 118.9 (CH); 118.7 (CH); 114.7 (2 × CH); 99.1 (CH); 68.6 (CH_2); 67.9 (CH_2); 62.6 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.7 (CH_2); 20.0 (CH_2). Elemental analysis: for $C_{48}H_{51}NO_{11}$ (817.94) calcd C 70.49, H 6.28, N 1.71; found C 70.40, H 6.22, N 1.64%.

(*E*)-7-(4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}benzoyloxy)-naphthalen-2-yl 4-(4-dodecyloxyphenyldiazenyl)benzoate (24)

Compound **24** was prepared by the general procedure **4.3**, yield 34%, orange solid, m.p. 151-153 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.85 (m, 46 H, $(CH_2)_{23}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.87 (m, 1 H, CH_2O); 4.05 (t, 2 H, J = 6.6, CH_2O); 4.06 (t, 2 H, J = 6.4, CH_2O); 4.58 (m, 1 H, OCHO); 6.99 (d, 2 H, J = 8.8); 7.03 (d, 2 H, J = 9.1); 7.37-7.42 (m, 4 H); 7.70 (d, 1 H, J = 2.1); 7.72 (d, 1 H, J = 2.1); 7.95 (d, 2 H, J = 8.8); 7.97 (d, 2 H, J = 8.8); 7.99 (d, 2 H, J = 8.8); 8.16 (d, 2 H, J = 8.8); 8.33 (d, 2 H, J = 8.8); 8.38 (d, 2 H, J = 8.8). ^{13}C NMR spectrum ($CDCl_3$): 165.1 (C); 164.8 (C); 164.6 (C); 164.1 (C); 162.7 (C); 156.1 (C); 155.7 (C); 149.5 (2 × C); 147.1 (C); 134.7 (C);

132.7 (2 × CH); 132.1 (2 × CH); 131.5 (2 × CH); 130.6 (C); 129.9 (C); 129.7 (2 × CH); 127.0 (C); 125.6 (2 × CH); 122.8 (2 × CH); 122.4 (2 × CH); 121.5 (2 × CH); 121.2 (C); 118.9 (2 × CH); 115.1 (2 × CH); 114.7 (2 × CH); 99.1 (CH); 68.7 (CH_2); 68.6 (CH_2); 67.9 (CH_2); 62.6 (CH_2); 32.2 (CH_2); 31.0 (CH_2); 30.0 (2 × CH_2); 29.9 (3 × CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.4 (CH_2); 29.3 (CH_2); 27.5 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.7 (CH_2); 22.9 (CH_2); 20.0 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{68}H_{80}N_2O_{10}$ (1061.38) calcd C 74.69, H 7.60, N 2.64; found C 74.60, H 7.55, N 2.58%.

7-(4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}benzoyloxy)-naphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (25)

Compound **25** was prepared by the general procedure **4.3**, yield 99%, m.p. 147-149 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3H, J = 6.7, CH_3); 1.27-1.87 (m, 46 H, $(CH_2)_{23}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.87 (m, 1 H, CH_2O); 4.06 (t, 4 H, J = 6.6, 2 × CH_2O); 4.58 (m, 1 H, OCHO); 6.99 (d, 4 H, J = 8.8); 7.40 (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); 8.33 (d, 4 H, J = 8.8). ^{13}C NMR spectrum ($CDCl_3$): 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); 121.2 (2 × C); 118.8 (2 × CH); 114.7 (4 × CH); 99.1 (CH); 68.6 (2 × CH_2); 67.9 (CH_2); 62.6 (CH_2); 32.2 (CH_2); 31.0 (2 x CH_2); 30.0 (CH_2); 29.9 (CH_2); 29.8 (6 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.3 (2 × CH_2); 26.5 (CH_2); 26.2 (2 × CH_2); 25.8 (CH_2); 22.9 (CH_2); 20.0 (2 × CH_2); 14.4 (CH_3). Elemental analysis: for $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.98, H 7.03%.

7-{4-[4-(12-Hydroxydodecyloxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-nitro-benzoate (M-1)

Monomer **M-1** was prepared by the general procedure **4.5**, yield 91%, m.p. 145 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.30-1.59 (m, 18 H, $(CH_2)_9$); 1.83 (m, 2 H, $\underline{CH_2}CH_2O$); 3.64 (m, 2 H, CH_2OH); 4.06 (t, 2 H, J = 6.6, CH_2O); 6.99 (d, 2 H, J = 8.8); 7.36-7.42 (m, 4 H); 7.72 (s, 2 H); 7.97 (dd, 2 H, ^3J = 9.1, ^4J = 1.8); 8.16 (d, 2 H, J = 8.8); 8.33 (d, 2 H, J = 8.8); 8.42 (m, 4 H). ^{13}C NMR spectrum ($CDCl_3$): 164.8 (C); 164.6 (C); 164.1 (C); 163.6 (C); 155.8 (C); 151.2 (C); 149.7 (C); 149.1 (C); 135.1 (C); 134.6 (C); 132.7 (2 × CH); 132.1 (2 × CH); 131.6 (2 × CH); 130.0 (C); 129.9 (CH); 129.8 (CH); 126.9 (C); 124.0 (2 × CH); 122.4 (2 × CH); 121.8 (CH); 121.1 (C); 120.9 (CH); 118.9 (CH); 118.7 (CH); 114.7 (2 × CH); 68.6 (CH_2); 63.3 (CH_2); 33.0 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.3 (CH_2); 26.2 (CH_2); 26.0 (CH_2). Elemental analysis: for $C_{43}H_{43}NO_{10}$ (733.82) calcd C 70.38, H 5.91, N 1.91; found C 70.26, H 5.84, N 1.85%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{43}H_{43}NO_{10}Na$ 756.2785; found 756.2779.

(*E*)-7-{4-[4-(12-Hydroxydodecyloxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyloxyphenyldiazenyl)benzoate (M-2)

Monomer **M-2** was obtained by the general procedure **4.5**, yield 84%, orange solid, m.p. 165 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.61 (m, 38 H, $(CH_2)_{19}$); 1.83 (m, 4 H, $\underline{CH_2}CH_2O$); 3.64 (m, 2 H, CH_2OH); 4.05 (t, 2 H, J = 6.6, CH_2O); 4.06 (t, 2 H, J = 6.7, CH_2O); 6.99 (d, 2 H, J = 9.1); 7.03 (d, 2 H, J = 9.1); 7.38-7.42 (m, 4 H); 7.71 (d, 1 H, J

= 2.4); 7.73 (d, 1 H, *J* = 2.1); 7.96 (d, 2 H, *J* = 8.8); 7.97 (d, 2 H, *J* = 9.1); 7.99 (d, 2 H, *J* = 8.8); 8.16 (d, 2 H, *J* = 9.1); 8.33 (d, 2 H, *J* = 8.8); 8.38 (d, 2 H, *J* = 9.1). ^{13}C NMR spectrum ($CDCl_3$): 165.0 (C); 164.8 (C); 164.6 (C); 164.1 (C); 162.7 (C); 156.1 (C); 155.7 (C); 149.5 (2 × C); 147.1 (C); 134.6 (C); 132.7 (2 × CH); 132.1 (2 × CH); 131.5 (2 × CH); 130.5 (C); 129.8 (C); 129.7 (2 × CH); 127.0 (C); 125.6 (2 × CH); 122.8 (2 × CH); 122.4 (2 × CH); 121.5 (2 × CH); 121.2 (C); 118.9 (2 × CH); 115.1 (2 × CH); 114.7 (2 × CH); 68.7 (2 × CH_2); 65.8 (CH_2); 32.2 (CH_2); 31.0 (CH_2); 29.9 (2 × CH_2); 29.8 (7 × CH_2); 29.6 (4 × CH_2); 29.4 (CH_2); 29.3 (CH_2); 26.2 (2 × CH_2); 22.9 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{61}H_{72}N_2O_9$ (977.26) calcd C 74.97, H 7.43, N 2.87; found C 74.86, H 7.33, N 2.81%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{61}H_{72}N_2O_9Na$ 999.5136; found 999.5130.

7-{4-[4-(12-Hydroxydodecyloxy)benzoyloxy]benzoyloxy}naphthalen-2-yl 4-(4-dodecyl-oxybenzoyloxy)benzoate (M-3)

Monomer **M-3** was synthesised by the general procedure **4.5**, yield 95%, m.p. 128 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 3 H, *J* = 6.7, CH_3); 1.28-1.56 (m, 36 H, $(CH_2)_{18}$); 1.83 (m, 4 H, 2 x $\underline{CH_2}CH_2O$); 3.63 (m, 2 H, CH_2OH); 4.05 (t, 4 H, *J* = 6.4, 2 x CH_2O); 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* = 8.8); 8.33 (d, 4 H, *J* = 8.8). ^{13}C NMR spectrum ($CDCl_3$): 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); 121.2 (2 × C); 118.8 (2 × CH); 114.7 (4 × CH); 68.6 (2 × CH_2); 63.3 (CH_2); 33.0 (CH_2); 32.2 (CH_2); 29.9 (2 x CH_2); 29.8 (6 × CH_2); 29.7 (2 × CH_2); 29.6 (2 × CH_2); 29.3 (2 × CH_2); 26.2 (2 × CH_2); 26.0 (CH_2); 22.9 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{62}H_{72}O_{11}$ (993.26) calcd C 74.97, H 7.31; found C 74.90, H 7.35%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{62}H_{72}O_{11}Na$ 1015.4972; found 1015.4967.

4.9.2 Monomers M-4 to M-7 with 7-hydroxynaphthalene-2-carboxylic acid central unit

4-(4-Dodecyloxybenzoyloxy)phenyl 7-benzyloxynaphthalene-2-carboxylate (26)

The derivative **26** was prepared by the general procedure **4.4** with acid chloride of acid **16** (procedure **4.1A**), yield 98%, m.p. 131-134.5 °C, m.p.[S2] 128 °C.

In the same way, further intermediates have been prepared.

4-(4-Dodecyloxyphenoxycarbonyl)phenyl 7-benzyloxynaphthalene-2-carboxylate (27). Yield 75%, m.p. 180-183 °C, m.p.[S9] 177-179 °C.

4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}phenyl 7-benzyloxy-naphthalene-2-carboxylate (28). Yield 99%, m.p. 103-107.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.30-1.86 (m, 26 H, $(CH_2)_{13}$); 3.40 (m, 1 H, CH_2O); 3.51 (m, 1 H, CH_2O); 3.75 (m, 1 H, CH_2O); 3.89 (m, 1 H, CH_2O); 4.04 (t, 2 H, *J* = 6.6, CH_2O); 4.59 (m, 1 H, OCHO); 5.21 (s, 2 H, CH_2O); 6.98 (d, 2 H, *J* = 8.8); 7.31 (d, 4 H, *J* = 2.6); 7.36-7.53 (m, 7 H); 7.83 (d, 1 H, *J* = 8.8); 7.87 (d, 1 H, *J* = 8.8); 8.07 (dd, 1 H, ^3J = 8.5, ^4J = 1.8); 8.16 (d, 2 H, *J* = 8.8); 8.67 (d, 1 H, *J* = 1.5). ^{13}C NMR spectrum ($CDCl_3$): 165.6 (C); 165.1 (C); 163.9 (C); 157.6 (C);

148.8 (C); 148.6 (C); 136.7 (C); 134.0 (C); 132.6 (2 × CH); 131.8 (C); 130.9 (CH); 129.6 (CH); 128.9 (2 × CH); 128.4 (2 × CH); 127.8 (2 × CH); 127.3 (C); 123.7 (CH); 123.0 (2 × CH); 122.9 (2 × CH); 122.3 (CH); 121.6 (C); 114.6 (2 × CH); 108.5 (CH); 99.1 (CH); 70.4 (CH_2); 68.6 (CH_2); 68.0 (CH_2); 62.6 (CH_2); 31.1 (CH_2); 30.0 (CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (CH_2); 29.4 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.8 (CH_2); 20.0 (CH_2). Elemental analysis: for $C_{48}H_{54}O_8$ (758.96) calcd C 75.96, H 7.17; found C 75.88, H 7.09%.

4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]phenoxycarbonyl}phenyl 7-benzyloxynaphthalene-2-carboxylate (29). Yield 84%, m.p. 171-173.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.31-1.84 (m, 26 H, $(CH_2)_{13}$); 3.41 (m, 1 H, CH_2O); 3.52 (m, 1 H, CH_2O); 3.76 (m, 1 H, CH_2O); 3.90 (m, 1 H, CH_2O); 3.96 (t, 2 H, J = 6.4, CH_2O); 4.60 (m, 1 H, OCHO); 5.21 (s, 2 H, CH_2O); 6.95 (d, 2 H, J = 9.1); 7.14 (d, 2 H, J = 8.8); 7.35-7.46 (m, 7 H); 7.51 (m, 2 H); 7.83 (d, 1 H, J = 8.8); 7.88 (d, 1 H, J = 8.8); 8.07 (dd, 1 H, ^3J = 8.5, ^4J = 1.5); 8.30 (d, 2 H, J = 8.8); 8.68 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.1 (C); 165.0 (C); 157.7 (C); 157.2 (C); 155.4 (C); 144.4 (C); 136.7 (C); 134.0 (C); 132.1 (2 × CH); 131.9 (C); 131.1 (CH); 129.6 (CH); 129.0 (2 × CH); 128.5 (2 × CH); 127.8 (2 × CH); 127.5 (C); 126.9 (C); 123.6 (CH); 122.6 (2 × CH); 122.5 (CH); 122.3 (2 × CH); 115.4 (2 × CH); 108.5 (CH); 99.1 (CH); 70.4 (CH_2); 68.7 (CH_2); 68.0 (CH_2); 62.6 (CH_2); 31.1 (CH_2); 30.0 (CH_2); 29.9 (4 × CH_2); 29.8 (CH_2); 29.7 (CH_2); 29.5 (CH_2); 26.5 (CH_2); 26.3 (CH_2); 25.8 (CH_2); 20.0 (CH_2). Elemental analysis: for $C_{48}H_{54}O_8$ (758.96) calcd C 75.96, H 7.17; found C 75.86, H 7.11%.

4-(4-Dodecyloxybenzoyloxy)phenyl 7-hydroxynaphthalene-2-carboxylate (30)
Naphthol **30** was prepared by the general procedure **4.6**, yield 66%, m.p. 174-176 °C, m.p.[S2] 171 °C.

Analogously, following derivatives were obtained.

4-(4-Dodecyloxyphenoxycarbonyl)phenyl 7-hydroxynaphthalene-2-carboxylate (31). Yield 57%, m.p. 153-156 °C, m.p.[S9] 154.5-155.5 °C.

4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}phenyl 7-hydroxy-naphthalene-2-carboxylate (32). Yield 66%, white solid, m.p. 123-126.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.28-1.84 (m, 26 H, $(CH_2)_{13}$); 3.41 (m, 1 H, CH_2O); 3.53 (m, 1 H, CH_2O); 3.76 (m, 1 H, CH_2O); 3.90 (m, 1 H, CH_2O); 4.04 (t, 2 H, J = 6.6, CH_2O); 4.61 (m, 1 H, OCHO); 6.21 (s, 1 H, OH); 6.98 (d, 2 H, J = 8.8); 7.22-7.30 (m, 6 H); 7.81 (d, 1 H, J = 8.5); 7.86 (d, 1 H, J = 8.5); 8.02 (dd, 1 H, ^3J = 8.5, ^4J = 1.6); 8.15 (d, 2 H, J = 9.1); 8.58 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.8 (C); 165.3 (C); 163.9 (C); 154.8 (C); 148.8 (C); 148.6 (C); 134.0 (C); 132.6 (2 × CH); 131.4 (C); 130.6 (CH); 129.9 (CH); 128.5 (CH); 127.2 (C); 123.3 (CH); 123.0 (2 × CH); 122.9 (2 × CH); 121.5 (C); 121.1 (CH); 114.6 (2 × CH); 111.0 (CH); 99.2 (CH); 68.6 (CH_2); 68.1 (CH_2); 62.7 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.8 (4 × CH_2); 29.1 (CH_2); 29.6 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.2 (CH_2); 25.1 (CH_2); 19.9 (CH_2). Elemental analysis: for $C_{41}H_{48}O_8$ (668.83) calcd C 73.63 H 7.23; found C 73.52, H 7.25%.

4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]phenoxycarbonyl}phenyl 7-hydroxynaphthalene-2-carboxylate (33). Yield 61%, m.p. 113-115 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.27-1.85 (m, 26 H, $(CH_2)_{13}$); 3.43 (m, 1 H, CH_2O); 3.56 (m, 1 H, CH_2O); 3.78 (m, 1 H, CH_2O); 3.93 (m, 3 H, CH_2O); 4.64 (m, 1 H, OCHO); 6.93 (d, 2 H, J = 9.1); 6.96 (s, 1 H); 7.12 (d, 2 H, J = 8.8); 7.24 (m, 1 H); 7.41 (d, 2 H, J = 8.8); 7.79 (d, 1 H, J = 8.8); 7.86 (d, 1 H, J = 8.8); 8.02 (dd, 1 H, ^3J = 8.5, ^4J = 1.7); 8.29 (d, 2 H, J = 8.8); 8.59 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.4 (C); 165.3 (C); 157.2 (C); 155.5 (C); 155.2 (C); 144.4 (C); 134.1 (C); 132.1 (2 × CH); 131.4 (C); 130.8 (CH); 129.8 (CH); 128.6 (CH); 127.4 (C); 126.7 (C); 123.1 (CH); 122.6 (2 × CH); 122.2 (2 × CH); 121.5 (CH); 115.4 (2 × CH); 111.0 (CH); 99.3 (CH); 68.7 (CH_2); 68.2 (CH_2); 62.8 (CH_2); 31.1 (CH_2); 30.0 (CH_2); 29.8 (4 × CH_2); 29.7 (2 × CH_2); 29.5 (CH_2); 26.5 (CH_2); 26.3 (CH_2); 25.7 (CH_2); 19.9 (CH_2). Elemental analysis: for $C_{41}H_{48}O_8$ (668.83) calcd C 73.63 H 7.23; found C 73.50, H 7.17%.

4-(4-Dodecyloxybenzoyloxy)phenyl 7-(4-{4-[12-(tetrahydro-2*H*-pyran-2-yloxy)dodecyl-oxy]benzoyloxy}benzoyloxy)naphthalene-2-carboxylate (34)

Compound **34** was prepared by the general procedure **3**, yield 73%, m.p. 125-128 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.83 (m, 46 H, $(CH_2)_{23}$); 3.39 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.74 (m, 1 H, CH_2O); 3.88 (m, 1 H, CH_2O); 4.05 (t, 2 H, J = 6.6, CH_2O); 4.06 (t, 2 H, J = 6.6, CH_2O); 4.58 (m, 1 H, OCHO); 6.98 (d, 2 H, J = 9.0); 7.00 (d, 2 H, J = 9.0); 7.32 (m, 4 H); 7.41 (d, 2 H, J = 8.8); 7.54 (dd, 1 H, ^3J = 8.9, ^4J = 2.3); 7.88 (d, 1 H, J = 2.2); 8.00 (d, 2 H, J = 8.6); 8.16 (d, 2 H, J = 8.9); 8.17 (d, 2 H, J = 8.9); 8.22 (dd, 1 H, ^3J = 8.6, ^4J = 1.7); 8.34 (d, 2 H, J = 8.8); 8.79 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.3 (C); 165.1 (C); 164.7 (C); 164.5 (C); 164.1 (C); 163.9 (C); 155.8 (C); 149.5 (C); 148.9 (C); 148.5 (C); 134.1 (C); 133.2 (C); 132.7 (2 × CH); 132.6 (2 × CH); 132.1 (2 × CH); 131.8 (CH); 129.7 (CH); 128.6 (CH); 127.6 (C); 126.8 (C); 125.7 (CH); 124.4 (CH); 123.0 (2 × CH); 122.8 (2 × CH); 122.5 (2 × CH); 121.6 (C); 121.2 (C); 120.5 (CH); 114.7 (2 × CH); 114.6 (2 × CH); 99.1 (CH); 68.6 (2 × CH_2); 67.9 (CH_2); 62.6 (CH_2); 32.2 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.9 (5 × CH_2); 29.8 (4 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.3 (2 × CH_2); 26.5 (CH_2); 26.2 (2 × CH_2); 25.8 (CH_2); 22.9 (CH_2); 20.0 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.93, H 7.01%.

Analogously compound **35** was synthesised.

4-(4-Dodecyloxyphenoxycarbonyl)phenyl 7-(4-{4-[12-(tetrahydro-2*H*-pyran-2-yloxy)-dodecyloxy]benzoyloxy}benzoyloxy)naphthalene-2-carboxylate (35). Yield 60%, m.p. 128-131 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.83 (m, 46 H, $(CH_2)_{23}$); 3.39 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.74 (m, 1 H, CH_2O); 3.88 (m, 1 H, CH_2O); 3.97 (t, 2 H, J = 6.4, CH_2O); 4.06 (t, 2 H, J = 6.6, CH_2O); 4.58 (m, 1 H, OCHO); 6.94 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 9.0); 7.13 (d, 2 H, J = 9.1); 7.43 (m, 4 H); 7.55 (dd, 1 H, ^3J = 8.8, ^4J = 2.3); 7.88 (d, 1 H, J = 2.1); 8.02 (d, 2 H, J = 8.8); 8.17 (d, 2 H, J = 9.0); 8.22 (dd, 1 H, ^3J = 8.6, ^4J = 1.7); 8.33 (m, 4 H); 8.80 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 160.3 (C); 160.1 (C); 160.0 (C); 159.8 (C); 159.3 (C); 152.4 (C); 151.1 (C); 150.6 (C); 144.8 (C); 139.6 (C); 129.5 (C); 128.5 (C); 127.9 (2 × CH); 127.4 (2 × CH); 127.3 (2 × CH); 127.2 (CH); 125.0 (CH); 124.0 (CH); 122.8 (C); 122.5 (C); 122.0 (C); 120.9 (CH); 119.8 (CH); 117.8 (2 ×

CH); 117.7 (2 × CH); 117.5 (2 × CH); 116.3 (C); 115.8 (CH); 110.6 (2 x CH); 109.9 (2 × CH); 94.4 (CH); 63.9 (2 × CH_2); 63.2 (CH_2); 57.9 (CH_2); 27.4 (CH_2); 26.3 (CH_2); 25.3 (CH_2); 25.1 (9 × CH_2); 24.9 (4 × CH_2); 24.8 (CH_2); 24.6 (CH_2); 21.7 (CH_2); 21.5 (2 × CH_2); 21.0 (CH_2); 18.2 (CH_2); 15.2 (CH_3). Elemental analysis: for $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.93, H 6.98%.

4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]benzoyloxy}phenyl 7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-carboxylate (36)

Utilizing the acid chloride of acid **3** (procedure **4.1A**), the derivative **36** was prepared by the general procedure **4**, yield 89%, m.p. 145-148.5 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.85 (m, 46 H, $(CH_2)_{23}$); 3.38 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.88 (m, 1 H, CH_2O); 4.05 (t, 2 H, J = 6.4, CH_2O); 4.06 (t, 2 H, J = 6.4, CH_2O); 4.58 (m, 1 H, OCHO); 6.98 (d, 2 H, J = 8.8); 7.00 (d, 2 H, J = 8.8); 7.32 (m, 4 H); 7.41 (d, 2 H, J = 8.8); 7.54 (dd, 1 H, ^3J = 8.8, ^4J = 2.1); 7.88 (d, 1 H, J = 2.1); 8.00 (d, 2 H, J = 8.5); 8.16 (d, 2 H, J = 8.8); 8.17 (d, 2 H, J = 8.8); 8.22 (dd, 1 H, ^3J = 8.8, ^4J = 1.5); 8.34 (d, 2 H, J = 8.5); 8.79 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.2 (C); 165.0 (C); 164.7 (C); 164.5 (C); 164.1 (C); 163.8 (C); 155.8 (C); 149.5 (C); 148.9 (C); 148.5 (C); 134.1 (C); 133.2 (C); 132.7 (2 × CH); 132.6 (2 × CH); 132.1 (2 × CH); 131.8 (CH); 129.7 (CH); 128.6 (CH); 127.6 (C); 126.8 (C); 125.7 (CH); 124.4 (CH); 123.0 (2 × CH); 122.8 (2 × CH); 122.5 (2 × CH); 121.6 (C); 121.2 (C); 120.5 (CH); 114.7 (2 × CH); 114.6 (2 × CH); 99.1 (CH); 68.6 (2 × CH_2); 67.9 (CH_2); 62.6 (CH_2); 32.2 (CH_2); 31.1 (CH_2); 30.0 (CH_2); 29.9 (4 × CH_2); 29.8 (5 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.4 (2 × CH_2); 26.5 (CH_2); 26.2 (2 × CH_2); 25.8 (CH_2); 23.0 (CH_2); 20.0 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.91, H 7.07%.

In the same way, **4-{4-[12-(Tetrahydro-2*H*-pyran-2-yloxy)dodecyloxy]phenoxycarbonyl}-phenyl 7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalene-2-carboxylate (37)** was prepared, yield 87%, m.p. 123-127 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 3 H, J = 6.7, CH_3); 1.27-1.86 (m, 46 H, $(CH_2)_{23}$); 3.39 (m, 1 H, CH_2O); 3.50 (m, 1 H, CH_2O); 3.73 (m, 1 H, CH_2O); 3.88 (m, 1 H, CH_2O); 3.96 (t, 2 H, J = 6.6, CH_2O); 4.06 (t, 2 H, J = 6.4, CH_2O); 4.58 (m, 1 H, OCHO); 6.94 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 9.1); 7.13 (d, 2 H, J = 9.1); 7.42 (m, 4H); 7.55 (dd, 1 H, ^3J = 8.8, ^4J = 2.3); 7.88 (d, 1 H, J = 2.1); 8.01 (d, 2 H, J = 8.8); 8.17 (d, 2 H, J = 8.8); 8.22 (dd, 1 H, ^3J = 8.5, ^4J = 1.7); 8.33 (m, 4 H); 8.80 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.0 (C); 164.8 (C); 164.7 (C); 164.6 (C); 164.1 (C); 157.2 (C); 155.8 (C); 155.3 (C); 149.6 (C); 144.4 (C); 134.2 (C); 133.2 (C); 132.7 (2 × CH); 132.2 (2 × CH); 132.1 (2 × CH); 132.0 (CH); 129.7 (CH); 128.7 (CH); 127.6 (C); 127.3 (C); 126.8 (C); 125.6 (CH); 124.6 (CH); 122.6 (2 × CH); 122.5 (2 × CH); 122.3 (2 × CH); 121.1 (C); 120.5 (CH); 115.4 (2 × CH); 114.7 (2 × CH); 99.1 (CH); 68.6 (2 × CH_2); 67.9 (CH_2); 62.6 (CH_2); 32.2 (CH_2); 31.0 (CH_2); 30.0 (CH_2); 29.9 (3 × CH_2); 29.8 (6 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.5 (CH_2); 29.3 (CH_2); 26.5 (CH_2); 26.3 (CH_2); 26.2 (CH_2); 25.8 (CH_2); 22.9 (CH_2); 20.0 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{36}H_{40}O_6$ (568.72) calcd C 76.03, H 7.09; found C 75.92, H 6.96%.

4-[4-(12-Hydroxydodecyloxy)benzoyloxy]phenyl 7-[4-(4-dodecyloxybenzoyloxy)benzoyl-oxy]naphthalene-2-carboxylate (M-4)

Monomer **M-4** was prepared by the general procedure **4.5**, yield 93%, white solid, m.p. 170 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 3 H, J = 6.7, CH_3); 1.27-1.57 (m, 36 H, $(CH_2)_{18}$); 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$); 3.64 (m, 2 H, CH_2OH); 4.05 (t, 2 H, J = 6.4, CH_2O); 4.06 (t, 2 H, J = 6.6, CH_2O); 6.98 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 9.1); 7.32 (m, 4 H); 7.41 (d, 2 H, J = 8.8); 7.54 (dd, 1 H, ^3J = 8.8, ^4J = 2.1); 7.88 (d, 1 H, J = 2.1); 8.00 (d, 2 H, J = 8.8); 8.16 (d, 2 H, J = 9.1); 8.17 (d, 2 H, J = 8.8); 8.22 (dd, 1 H, ^3J = 8.5, ^4J = 1.5); 8.34 (d, 2 H, J = 8.5); 8.79 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.3 (C); 165.1 (C); 164.7 (C); 164.6 (C); 164.1 (C); 163.9 (C); 155.8 (C); 149.5 (C); 148.9 (C); 148.5 (C); 134.1 (C); 133.3 (C); 132.7 (2 × CH); 132.6 (2 × CH); 132.2 (2 × CH); 131.8 (CH); 129.7 (CH); 128.6 (CH); 127.7 (C); 126.8 (C); 125.7 (CH); 124.4 (CH); 123.0 (2 × CH); 122.8 (2 × CH); 122.5 (2 x CH); 121.6 (C); 121.1 (C); 120.5 (CH); 114.7 (2 × CH); 114.6 (2 × CH); 68.6 (2 × CH_2); 63.3 (CH_2); 33.0 (CH_2); 32.2 (CH_2); 29.9 (4 × CH_2); 29.8 (5 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.3 (2 × CH_2); 26.2 (2 × CH_2); 26.0 (CH_2); 22.9 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{62}H_{72}O_{11}$ (993.26) calcd C 74.97, H 7.31; found C 74.88, H 7.26%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{62}H_{72}O_{11}Na$ 1015.4972; found 1015.4967.

Monomers **M-5 to M-7** were prepared analogously.

4-[4-(12-Hydroxydodecyloxy)phenoxycarbonyl]phenyl 7-[4-(4-dodecyloxybenzoyloxy)-benzoyloxy]naphthalene-2-carboxylate (M-5). Yield 88%, white solid, m.p. 152 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 3 H, J = 6.7, CH_3); 1.27-1.61 (m, 36 H, $(CH_2)_{18}$); 1.81 (m, 4 H, 2 × $\underline{CH_2}CH_2O$); 3.64 (t, 2 H, J = 6.6, CH_2OH); 3.97 (t, 2 H, J = 6.4, CH_2O); 4.06 (t, 2 H, J = 6.7, CH_2O); 6.94 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 9.1); 7.13 (d, 2 H, J = 9.1); 7.43 (m, 4 H); 7.55 (dd, 1 H, ^3J = 8.8, ^4J = 2.4); 7.89 (d, 1 H, J = 2.1); 8.02 (d, 2 H, J = 8.8); 8.17 (d, 2 H, J = 9.1); 8.22 (dd, 1 H, ^3J = 8.8, ^4J = 1.7); 8.33 (m, 4 H); 8.81 (s, 1 H). Elemental analysis: for $C_{62}H_{72}O_{11}$ (993.26) calcd C 74.97, H 7.31; found C 74.85, H 7.29%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{62}H_{72}O_{11}Na$ 1015.4972; found 1015.4967.

4-(4-Dodecyloxybenzoyloxy)phenyl 7-{4-[4-(12-hydroxydodecyloxy)benzoyloxy]benzoyl-oxy}naphthalene-2-carboxylate (M-6). Yield 92%, white solid, m.p. 155 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.59 (m, 36 H, $(CH_2)_{18}$); 1.83 (m, 4 H, 2 × $\underline{CH_2}CH_2O$); 3.64 (t, 2 H, J = 6.4, CH_2OH); 4.05 (t, 2 H, J = 6.6, CH_2O); 4.06 (t, 2 H, J = 6.4, CH_2O); 6.98 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 8.8); 7.32 (m, 4 H); 7.41 (d, 2 H, J = 8.8); 7.54 (dd, 1 H, ^3J = 8.8, ^4J = 2.3); 7.88 (d, 1 H, J = 2.1); 8.00 (d, 2 H, J = 8.5); 8.16 (d, 2 H, J = 9.1); 8.17 (d, 2 H, J = 8.8); 8.22 (dd, 1 H, ^3J = 8.5, ^4J = 1.8); 8.34 (d, 2 H, J = 9.1); 8.79 (s, 1 H). ^{13}C NMR spectrum ($CDCl_3$): 165.3 (C); 165.1 (C); 164.7 (C); 164.6 (C); 164.1 (C); 163.9 (C); 155.8 (C); 149.5 (C); 148.9 (C); 148.5 (C); 134.1 (C); 133.2 (C); 132.7 (2 x CH); 132.6 (2 × CH); 132.2 (2 × CH); 131.8 (CH); 129.7 (CH); 128.6 (CH); 127.7 (C); 126.8 (C); 125.7 (CH); 124.4 (CH); 123.0 (2 × CH); 122.8 (2 × CH); 122.5 (2 × CH); 121.6 (C); 121.1 (C); 120.5 (CH); 114.7 (2 × CH); 114.6 (2 × CH); 68.6 (2 × CH_2); 63.3 (CH_2); 33.0 (CH_2); 32.2 (CH_2); 29.9 (CH_2); 29.8 (7 × CH_2); 29.7 (CH_2); 29.6 (2 × CH_2); 29.3 (2 × CH_2); 28.0 (CH_2);

26.2 (2 × CH_2); 26.0 (CH_2); 22.9 (CH_2); 14.4 (CH_3). Elemental analysis: for $C_{62}H_{72}O_{11}$ (993.26) calcd C 74.97, H 7.31; found C 74.83, H 7.38%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{62}H_{72}O_{11}Na$ 1015.4972; found 1015.4967.

4-(4-Dodecyloxyphenoxycarbonyl)phenyl 7-{4-[4-(12-hydroxydodecyloxy)benzoyloxy]-benzoyloxy}naphthalene-2-carboxylate (M-7). Yield 92%, white solid, m.p. 139 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 3 H, J = 6.7, CH_3); 1.27-1.57 (m, 36 H, $(CH_2)_{18}$); 1.81 (m, 4 H, 2 × $\underline{CH_2}CH_2O$); 3.65 (m, 2 H, CH_2OH); 3.97 (t, 2 H, J = 6.6, CH_2O); 4.06 (t, 2 H, J = 6.4, CH_2O); 6.94 (d, 2 H, J = 9.1); 7.00 (d, 2 H, J = 8.8); 7.13 (d, 2 H, J = 9.1); 7.43 (m, 4 H); 7.55 (dd, 1 H, J_1 = 8.6, J_2 = 2.2); 7.89 (d, 1 H, J = 2.1); 8.02 (d, 2 H, J = 8.8); 8.17 (d, 2 H, J = 8.8); 8.22 (dd, 1 H, J_1 = 8.6, J_2 = 1.6); 8.33 (m, 4 H); 8.81 (s, 1 H). Elemental analysis: for $C_{62}H_{72}O_{11}$ (993.26) calcd C 74.97, H 7.31; found C 74.91, H 7.25%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{62}H_{72}O_{11}Na$ 1015.4972; found 1015.4967.

4.10 Synthesis of dimers

4.10.1 Dimers derived from naphthalene-2,7-diol

Bis[12-(4-{4-[7-(4-nitrobenzoyloxy)naphthalen-2-yloxycarbonyl]phenoxycarbonyl}-phenoxy)dodecyl] isophthalate (38)
Compound **38** was prepared by the general procedure **4.7**, yield 63%, m.p. 157-159 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.31-1.48 (m, 32 H, $(CH_2)_{16}$); 1.80 (m, 8 H, 4 × $\underline{CH_2}CH_2O$); 4.05 (t, 4 H, J = 6.6, 2 × CH_2O); 4.34 (t, 4 H, J = 6.6, 2 × CH_2O); 6.98 (d, 4 H, J = 9.1); 7.36-7.42 (m, 8 H); 7.53 (dd, 1 H, ^3J = 7.9, ^4J = 7.6); 7.71 (s, 4 H); 7.96 (dd, 4 H, ^3J = 9.1, ^4J = 2.1); 8.15 (d, 4 H, J = 9.1); 8.22 (dd, 2 H, ^3J = 7.6, ^4J = 1.7); 8.32 (d, 4 H, J = 8.8); 8.41 (m, 8 H); 8.69 (dd, 1 H, J = 1.8). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (2 × C); 164.7 (2 × C); 164.6 (2 × C); 164.1 (2 × C); 163.6 (2 × C); 155.7 (2 × C); 151.2 (2 × C); 149.7 (2 × C); 149.1 (2 × C); 135.1 (2 × C); 134.6 (2 × C); 133.9 (2 × CH); 132.7 (4 × CH); 132.1 (4 × CH); 131.6 (4 × CH); 131.2 (2 × C); 130.9 (CH); 130.0 (2 × C); 129.9 (2 × CH); 129.7 (2 × CH); 128.8 (CH); 126.9 (2 × C); 124.0 (4 × CH); 122.4 (4 × CH); 121.8 (2 × CH); 121.1 (2 × C); 120.9 (2 × CH); 118.9 (2 × CH); 118.7 (2 × CH); 114.7 (4 × CH); 68.6 (2 × CH_2); 65.7 (2 × CH_2); 29.8 (8 × CH_2); 29.6 (2 × CH_2); 29.5 (2 × CH_2); 29.3 (2 × CH_2); 28.9 (2 × CH_2); 26.2 (4 × CH_2). Elemental analysis: for $C_{94}H_{88}N_2O_{22}$ (1597.75) calcd C 70.66, H 5.55, N 1.75; found C 70.54, H 5.50, N 1.68%.

Bis[12-(4-{4-[7-(4-aminobenzoyloxy)naphthalen-2-yloxycarbonyl]phenoxycarbonyl}-phenoxy)dodecyl] isophthalate (39)
Compound **39** was prepared by the general procedure **4.6**, yield 28% of a light green solid, m.p. 162-165 °C. ^{1}H NMR spectrum ($CDCl_3$): 1.31-1.47 (m, 32 H, $(CH_2)_{16}$); 1.80 (m, 8 H, 4 × $\underline{CH_2}CH_2O$); 4.04 (t, 4 H, J = 6.6, 2 × CH_2O); 4.17 (s, 4 H, 2 × NH_2); 4.34 (t, 4 H, J = 6.7, 2 × CH_2O); 6.71 (d, 4 H, J = 8.8); 6.98 (d, 4 H, J = 9.1); 7.33-7.40 (m, 8 H); 7.53 (dd, 1 H, ^3J =

7.9, ^4J = 7.6); 7.65 (m, 4 H); 7.91 (dd, 4 H, ^3J = 8.8, ^4J = 3.1); 8.05 (d, 4 H, J = 8.5); 8.15 (d, 4 H, J = 9.1); 8.22 (dd, 2 H, ^3J = 7.9, ^4J =1.7); 8.32 (d, 4 H, J = 8.8); 8.69 (dd, 1 H, J = 1.8, J = 1.2). ^{13}C NMR spectrum ($CDCl_3$): 166.2 (2 × C); 165.5 (2 × C); 164.8 (2 × C); 164.6 (2 × C); 164.0 (2 × C); 155.7 (2 × C); 151.8 (2 × C); 149.9 (2 × C); 149.4 (2 × C); 134.7 (2 × C); 133.9 (2 × CH); 132.7 (8 × CH); 132.1 (4 × CH); 131.2 (2 × C); 130.9 (CH); 129.7 (2 × C); 129.7 (2 × CH); 129.5 (2 × CH); 128.8 (CH); 127.0 (2 × C); 122.4 (4 × CH); 121.8 (2 × CH); 121.2 (2 × CH); 121.1 (2 × C); 118.9 (2 × CH); 118.8 (2 × C); 118.8 (2 × CH); 114.6 (4 × CH); 114.1 (4 × CH); 68.6 (2 × CH_2); 65.8 (2 × CH_2); 29.8 (8 × CH_2); 29.6 (2 × CH_2); 29.5 (2 × CH_2); 29.3 (2 × CH_2); 28.9 (2 × CH_2); 26.2 (4 × CH_2). Elemental analysis: for $C_{94}H_{92}N_2O_{18}$ (1537.78) calcd C 73.42, H 6.03, N 1.82; found C 73.30, H 6.11, N 1.75%.

(*E*)-Bis{12-[4-(4-{7-[4-(4-dodecyloxy-2-hydroxybenzylideneamino)benzoyloxy]-naphthalen-2-yloxycarbonyl}phenoxycarbonyl)phenoxy]dodecyl} isophthalate (D-1)

To a mixture of derivative **39** (90 mg; 0.06 mmol) and aldehyde **40** (43 mg; 0.14 mmol) in dry toluene (50 ml), a catalytic amount (10 mg) of *p*-toluenesulfonic acid was added. The reaction mixture was stirred at 120 °C for 6 h and water formed was removed by azeotropic distillation. After cooling the reaction mixture was evaporated and the crude product was purified by column chromatography (chloroform/acetone, 98/2) and crystallised from a mixture of toluene and acetone (1/3). Yield 43 mg (35%), yellow solid, m.p. 112 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 6 H, J = 6.6, 2 × CH_3); 1.27-1.45 (m, 68 H, $(CH_2)_{34}$); 1.80 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 4.03 (m, 8 H, 4 × CH_2O); 4.34 (t, 4 H, J = 6.6, 2 × CH_2O); 6.51 (m, 4 H); 6.98 (d, 4 H, J = 8.5); 7.31 (d, 2 H, J = 9.7); 7.38 (m, 12 H); 7.53 (dd, 1 H, ^3J = 7.9, ^3J = 7.6); 7.69 (s, 4 H); 7.94 (d, 4 H, J = 9.1); 8.15 (d, 4 H, J = 8.5); 8.23 (dd, 2 H, ^3J = 7.5, ^4J = 1.5); 8.31 (m, 8 H); 8.58 (s, 2 H, 2 × CH=N); 8.69 (s, 1 H); 13.4 (s, 2 H, 2 × OH). ^{13}C NMR spectrum ($CDCl_3$): 166.2 (2 × C); 165.1 (2 × C); 164.8 (2 × C); 164.6 (2 × C); 164.5 (2 × C); 164.3 (2 × C); 164.1 (2 × C); 163.3 (2 × CH); 155.7 (2 × C); 153.6 (2 × C); 149.6 (2 × C); 149.5 (2 × C); 134.7 (2 × C); 134.3 (2 × CH); 133.9 (2 × CH); 132.7 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 131.2 (2 × C); 130.9 (CH); 129.8 (2 × C); 129.7 (4 × CH); 128.8 (CH); 127.2 (2 × C); 127.0 (2 × C); 122.4 (4 × CH); 121.5 (4 × CH); 121.2 (2 × C); 118.8 (4 × CH); 114.6 (4 × CH); 113.0 (2 × C); 108.4 (2 × CH); 101.8 (2 × CH); 68.6 (4 × CH_2); 65.7 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (2 × CH_2); 29.8 (16 × CH_2); 29.6 (4 × CH_2); 29.5 (2 × CH_2); 29.3 (2 × CH_2); 28.9 (2 × CH_2); 26.2 (8 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3). Elemental analysis: for $C_{132}H_{148}N_2O_{22}$ (2114.65) calcd C 74.98, H 7.05, N 1.32; found C 74.86, H 7.11, N 1.26%. HRMS (ESI-LTQ) m/z: $[M + H]^+$ calcd for $C_{132}H_{149}N_2O_{22}$ 2115.0636; found 2115.0630.

(*E*)-Bis{12-[4-(4-{7-[4-(4-dodecyloxyphenyldiazenyl)benzoyloxy]naphthalen-2-yloxy-carbonyl}phenoxycarbonyl)phenoxy]dodecyl} isophthalate (D-2)

Dimer **D-2** was prepared by the general procedure **4.7**, yield 45%, m.p. 149 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 6 H, J = 6.6, 2 × CH_3); 1.27-1.48 (m, 68 H, $(CH_2)_{34}$); 1.81 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 4.05 (m, 8 H, 4 × CH_2O); 4.34 (t, 4 H, J = 6.6, 2 × CH_2O); 6.98 (d, 4 H, J = 8.8); 7.03 (d, 4 H, J = 9.1); 7.37-7.42 (m, 8 H); 7.53 (dd, 1 H, ^3J = 7.9, ^3J = 7.6); 7.70 (d, 2 H, J = 2.1); 7.72 (d, 2 H, J = 2.1); 7.95 (d, 4 H, J = 8.2); 7.97 (d, 4 H, J = 8.8); 7.99 (d, 4 H, J = 8.2); 8.16 (d, 4 H, J = 8.8); 8.22 (dd, 2 H, ^3J = 7.9, ^4J = 1.7); 8.33 (d, 4 H, J = 8.8); 8.38 (d,

4 H, *J* = 8.5); 8.68 (dd, 1 H, *J* = 1.8). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (2 × C); 165.0 (2 × C); 164.8 (2 × C); 164.6 (2 × C); 164.1 (2 × C); 162.7 (2 × C); 156.1 (2 × C); 155.7 (2 × C); 149.5 (4 × C); 147.1 (2 × C); 134.6 (2 × C); 133.9 (2 × CH); 132.7 (4 × CH); 132.1 (4 × CH); 131.5 (4 × CH); 131.2 (2 × C); 130.9 (CH); 130.5 (2 × C); 129.8 (2 × C); 129.7 (4 × CH); 128.8 (CH); 127.0 (2 × C); 125.6 (4 × CH); 122.8 (4 × CH); 122.4 (4 × CH); 121.5 (4 × CH); 121.2 (2 × C); 118.9 (4 × CH); 115.1 (4 × CH); 114.6 (4 × CH); 68.7 (2 × CH_2); 68.6 (2 × CH_2); 65.7 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (6 × CH_2); 29.8 (14 × CH_2); 29.6 (4 × CH_2); 29.5 (2 × CH_2); 29.4 (2 × CH_2); 29.3 (2 × CH_2); 28.9 (2 × CH_2); 26.3 (4 × CH_2); 23.0 (2 × CH_2); 14.4 (2 × CH_3). Elemental analysis: $C_{130}H_{146}N_4O_{20}$ (2084.63) calcd C 74.90, H 7.06, N 2.69; found C 74.82, H 7.02, N 2.56%. HRMS (ESI-LTQ) m/z: $[M + H]^+$ calcd for $C_{130}H_{147}N_4O_{20}$ 2085.0642; found 2085.0637.

Bis{12-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yloxycarbonyl}-phenoxycarbonyl)phenoxy]dodecyl} isophthalate (D-3)

Dimer **D-3** was prepared by the general procedure **4.7**, yield 33%, m.p. 133 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 6 H, *J* = 6.6, 2 × CH_3); 1.27-1.48 (m, 68 H, $(CH_2)_{34}$); 1.82 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 4.05 (t, 8 H, *J* = 6.6, 4 × CH_2O); 4.35 (t, 4 H, *J* = 6.7, 2 × CH_2O); 6.99 (d, 8 H, *J* = 9.1); 7.36-7.41 (m, 12 H); 7.53 (dd, 1 H, *J* = 7.9); 7.70 (d, 4 H, *J* = 2.1); 7.94 (d, 4 H, *J* = 9.1); 8.16 (d, 8 H, *J* = 8.8); 8.23 (dd, 2 H, ^3J = 7.9, ^4J = 1.8); 8.33 (d, 8 H, *J* = 9.1); 8.69 (dd, 1 H, *J* = 1.8). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (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); 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); 118.8 (4 × CH); 114.7 (8 × CH); 68.6 (4 × CH_2); 65.7 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (4 × CH_2); 29.8 (12 × CH_2); 29.6 (4 × CH_2); 29.5 (2 × CH_2); 29.3 (4 × CH_2); 28.9 (2 × CH_2); 27.4 (2 × CH_2); 27.3 (2 × CH_2); 26.2 (4 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3). Elemental analysis: $C_{132}H_{146}O_{24}$ (2116.62) calcd C 74.91, H 6.95; found C 74.83, H 6.88%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{132}H_{146}O_{24}Na$ 2139. 0135; found 2139.0130.

4.10.2 Dimers with 7-hydroxynaphthalene-2-carboxylic acid central unit

Bis{12-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-ylcarbonyloxy}-phenoxycarbonyl)phenoxy]dodecyl} isophthalate (D-4)

Dimer **D-4** was prepared by the general procedure **4.7**, yield 47%, white solid, m.p. 156 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 6 H, *J* = 6.6, 2 × CH_3); 1.27-1.48 (m, 68 H, $(CH_2)_{34}$); 1.83 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 4.05 (m, 8 H, 4 × CH_2O); 4.36 (t, 4 H, *J* = 6.7, 2 × CH_2O); 6.98 (d, 4 H, *J* = 9.1); 6.99 (d, 4 H, *J* = 8.8); 7.31 (m, 8 H); 7.41 (d, 4 H, *J* = 8.5); 7.53 (m, 3 H); 7.87 (d, 2 H, *J* = 2.1); 8.00 (d, 4 H, *J* = 8.8); 8.15 (d, 4 H, *J* = 8.8); 8.16 (d, 4 H, *J* = 9.1); 8.22 (m, 4 H); 8.34 (d, 4 H, *J* = 8.5); 8.69 (dd, 1 H, *J* = 1.5); 8.79 (s, 2 H). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (2 × C); 165.3 (2 × C); 165.1 (2 × C); 164.7 (2 × C); 164.6 (2 × C); 164.1 (2 × C); 163.8 (2 × C); 155.8 (2 × C); 149.5 (2 × C); 148.9 (2 × C); 148.5 (2 × C); 134.1 (2 × C); 133.9 (2 × CH); 133.2 (2 × C); 132.7 (4 × CH); 132.6 (4 × CH); 132.2 (4 × CH); 131.8 (2 × CH); 131.2 (2 × C); 130.9 (CH); 129.7 (2 × CH); 128.8 (CH); 128.6 (2 × CH); 127.7 (2 × C); 126.8 (2 × C); 125.7 (2 × CH); 124.4 (2 × CH); 123.0 (4 × CH); 122.8 (4 × CH); 122.5 (4 ×

CH); 121.6 (2 × C); 121.1 (2 × C); 120.5 (2 × CH); 114.7 (4 × CH); 114.6 (4 × CH); 68.6 (4 × CH_2); 65.7 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (8 × CH_2); 29.8 (12 × CH_2); 29.6 (4 × CH_2); 29.5 (2 × CH_2); 29.3 (4 × CH_2); 28.9 (2 × CH_2); 26.2 (4 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3).). Elemental analysis: $C_{132}H_{146}O_{24}$ (2116.62) calcd C 74.91, H 6.95; found C 74.80, H 6.90%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{132}H_{146}O_{24}Na$ 2139. 0135; found 2139.0130.

Dimers **D-5** to **D-7** were obtained analogously.

Bis{12-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-ylcarbonyloxy}-benzoyloxy)phenoxy]dodecyl} isophthalate (D-5). Yield 25%, white solid, m.p. 146 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.89 (t, 6 H, *J* = 6.7, 2 × CH_3); 1.27-1.48 (m, 68 H, $(CH_2)_{34}$); 1.80 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 3.96 (t, 4 H, *J* = 6.6, 2 × CH_2O); 4.06 (t, 4 H, *J* = 6.4, 2 × CH_2O); 4.35 (t, 4 H, *J* = 6.7, 2 × CH_2O); 6.93 (d, 4 H, *J* = 8.8); 6.99 (d, 4 H, *J* = 9.1); 7.13 (d, 4 H, *J* = 8.8); 7.43 (m, 8 H); 7.53 (m, 3 H); 7.88 (d, 2 H, *J* = 1.8); 8.01 (d, 4 H, *J* = 8.6); 8.16 (d, 4 H, *J* = 9.1); 8.22 (m, 4 H); 8.33 (m, 8 H); 8.69 (dd, 1 H, *J* = 1.8); 8.80 (s, 2 H). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (2 × C); 165.0 (2 × C); 164.8 (2 × C); 164.7 (2 × C); 164.6 (2 × C); 164.1 (2 × C); 157.2 (2 × C); 155.8 (2 × C); 155.3 (2 × C); 149.6 (2 × C); 144.4 (2 × C); 134.2 (2 × C); 133.9 (2 × CH); 133.2 (2 × C); 132.7 (4 × CH); 132.2 (4 × CH); 132.1 (6 × CH); 131.2 (2 × C); 130.9 (CH); 129.7 (2 × CH); 128.8 (3 × CH); 127.6 (2 × C); 127.3 (2 × C); 126.8 (2 × C); 125.6 (2 × CH); 124.6 (2 × CH); 122.6 (4 × CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.1 (2 × C); 120.5 (2 × CH); 115.4 (4 × CH); 114.7 (4 × CH); 68.6 (4 × CH_2); 65.8 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (8 × CH_2); 29.8 (12 × CH_2); 29.6 (4 × CH_2); 29.5 (4 × CH_2); 29.3 (2 × CH_2); 28.9 (2 × CH_2); 26.3 (2 × CH_2); 26.2 (2 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3).). Elemental analysis: $C_{132}H_{146}O_{24}$ (2116.62) calcd C 74.91, H 6.95; found C 74.84, H 6.81%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{132}H_{146}O_{24}Na$ 2139. 0135; found 2139.0130.

Bis{12-[4-(4-{7-[4-(4-dodecyloxybenzoyloxy)phenoxycarbonyl]naphthalen-2-yloxy-carbonyl}phenoxycarbonyl)phenoxy]dodecyl} isophthalate (D-6). Yield 35%, white solid, m.p. 159 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 6 H, *J* = 6.7, 2 × CH_3); 1.27-1.48 (m, 68 H, $(CH_2)_{34}$); 1.81 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 4.05 (t, 8 H, *J* = 6.4, 4 × CH_2O); 4.35 (t, 4 H, *J* = 6.7, 2 × CH_2O); 6.98 (d, 4 H, *J* = 8.8); 6.99 (d, 4 H, *J* = 9.1); 7.32 (m, 8 H); 7.40 (d, 4 H, *J* = 8.8); 7.53 (m, 3 H); 7.87 (d, 2 H, *J* = 2.3); 8.00 (d, 4 H, *J* = 9.1); 8.15 (d, 4 H, *J* = 8.8); 8.16 (d, 4 H, *J* = 8.8); 8.22 (m, 4 H); 8.33 (d, 4 H, *J* = 8.8); 8.69 (s, 1 H); 8.79 (s, 2 H). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (2 × C); 165.3 (2 × C); 165.0 (2 × C); 164.7 (2 × C); 164.5 (2 × C); 164.1 (2 × C); 163.9 (2 × C); 155.8 (2 × C); 149.5 (2 × C); 148.9 (2 × C); 148.5 (2 × C); 134.1 (2 × C); 133.9 (2 × CH); 133.2 (2 × C); 132.7 (4 × CH); 132.5 (4 × CH); 132.1 (4 × CH); 131.8 (2 × CH); 131.2 (2 × C); 130.9 (CH); 129.7 (2 × CH); 128.8 (CH); 128.6 (2 × CH); 127.7 (2 × C); 126.8 (2 × C); 125.7 (2 × CH); 124.4 (2 × CH); 123.0 (4 × CH); 122.8 (4 × CH); 122.4 (4 × CH); 121.6 (2 × C); 121.2 (2 × C); 120.5 (2 × CH); 114.7 (4 × CH); 114.6 (4 × CH); 68.6 (4 × CH_2); 65.7 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (8 × CH_2); 29.8 (12 × CH_2); 29.6 (4 × CH_2); 29.5 (2 × CH_2); 29.3 (4 × CH_2); 28.9 (2 × CH_2); 26.2 (4 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3). Elemental analysis: $C_{132}H_{146}O_{24}$ (2116.62) calcd C 74.91, H 6.95; found C

74.87, H 6.82%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{132}H_{146}O_{24}Na$ 2139. 0135; found 2139.0130.

Bis{12-[4-(4-{7-[4-(4-dodecyloxyphenoxycarbonyl)phenoxycarbonyl]naphthalen-2-yloxy-carbonyl}phenoxycarbonyl)phenoxy]dodecyl} isophthalate (D-7). Yield 43%, white solid, m.p. 110 °C. ^{1}H NMR spectrum ($CDCl_3$): 0.88 (t, 6 H, J = 6.6, 2 × CH_3); 1.27-1.46 (m, 68 H, $(CH_2)_{34}$); 1.79 (m, 12 H, 6 × $\underline{CH_2}CH_2O$); 3.96 (t, 4 H, J = 6.6, 2 × CH_2O); 4.05 (t, 4 H, J = 6.3, 2 × CH_2O); 4.35 (t, 4 H, J = 6.7, 2 × CH_2O); 6.94 (d, 4 H, J = 9.1); 6.99 (d, 4 H, J = 9.1); 7.13 (d, 4 H, J = 9.1); 7.42 (m, 8 H); 7.53 (m, 3 H); 7.88 (d, 2 H, J = 2.1); 8.01 (d, 4 H, J = 8.8); 8.16 (d, 4 H, J = 8.8); 8.22 (m, 4 H); 8.32 (m, 8 H); 8.69 (s, 1 H); 8.80 (d, 2 H, J = 1.6). ^{13}C NMR spectrum ($CDCl_3$): 166.1 (2 × C); 165.0 (2 × C); 164.8 (2 × C); 164.7 (2 × C); 164.5 (2 × C); 164.1 (2 × C); 157.2 (2 × C); 155.8 (2 × C); 155.3 (2 × C); 149.6 (2 × C); 144.4 (2 × C); 134.2 (2 × C); 133.9 (2 × CH); 133.2 (2 × C); 132.7 (4 × CH); 132.2 (4 × CH); 132.1 (6 × CH); 131.2 (2 × C); 130.9 (CH); 129.7 (2 × CH); 128.7 (3 × CH); 127.6 (2 × C); 127.3 (2 × C); 126.8 (2 × C); 125.6 (2 × CH); 124.6 (2 × CH); 122.6 (4 × CH); 122.5 (4 × CH); 122.2 (4 × CH); 121.1 (2 × C); 120.5 (2 × CH); 115.4 (4 × CH); 114.7 (4 × CH); 68.7 (4 × CH_2); 65.7 (2 × CH_2); 32.2 (2 × CH_2); 29.9 (12 × CH_2); 29.8 (8 × CH_2); 29.6 (4 × CH_2); 29.5 (4 × CH_2); 29.3 (2 × CH_2); 28.9 (2 × CH_2); 26.3 (2 × CH_2); 26.2 (2 × CH_2); 22.9 (2 × CH_2); 14.4 (2 × CH_3). Elemental analysis: $C_{132}H_{146}O_{24}$ (2116.62) calcd C 74.91, H 6.95; found C 74.85, H 6.92%. HRMS (ESI-LTQ) m/z: $[M + Na]^+$ calcd for $C_{132}H_{146}O_{24}Na$ 2139. 0135; found 2139.0130.

5. Set-ups and measurement methods

We studied presented compounds using differential scanning calorimetry (DSC), namely a calorimeter Perkin–Elmer Pyris Diamond has been utilized. The materials of 2-5 mg were hermetically closed in the aluminium pans and placed into a working space filled with the gaseous nitrogen. The calorimeter data were calibrated on extrapolated onset temperatures and enthalpy changes of water, indium and zinc. The measurements were performed on cooling/heating runs at a rate of 5 K min^{-1}.

For electro-optical experiments and texture observations the cells were prepared from glass plates with transparent indium tin-oxide (ITO) electrodes having an area of 5×5 mm^2. The thickness was defined by a polymer sheet 6 μm. The cells were filled with a studied compound in the isotropic phase by capillary action. Other samples were prepared in the isotropic phase by spreading the droplet on the glass surface (one-free-surface sample) or by spreading the melted material over a hole in the metal plate (free-standing film). The polarizing microscope Nikon Eclipse was used for the texture observations. The cells were placed into the hot stage Linkam LTSE350 and the temperature was stabilized with accuracy ±0.1 K.

Bruker Nanostar (CuKα radiation, cross-coupled Goebel mirrors, three-pinhole collimation system, Vantec 2000 area detector, MRI TCPU H heating stage) and Bruker GADDS (CuKα radiation, Goebel mirror, two-pinhole collimator, Vantec 2000 area detector, modified Linkam heating stage) systems were utilized for x-ray diffraction studies. In both

systems the temperature stability was 0.1 K. Samples were prepared in thin-walled glass capillaries (1.5 mm diameter) or as droplets on a heated surface, in the latter case samples showed partial alignment.

6. Results

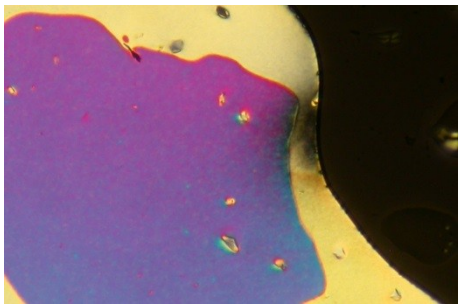


Fig. S1 Planar texture of **M-1** in the nematic phase at T=120°C.

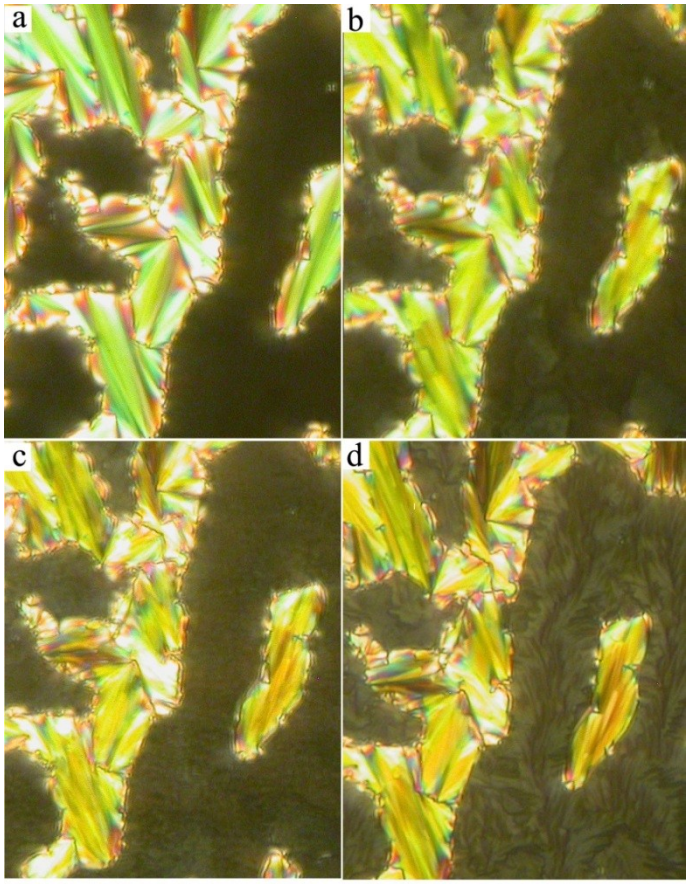


Fig. S2 One-free-surface sample of **D-5** in (a) the SmA phase at T=190°C, (b) the SmC phase at T=180°C, (c) the columnar B_{1Rev} phase at T=170°C and (d) the CrX phase at T=140°C phase.

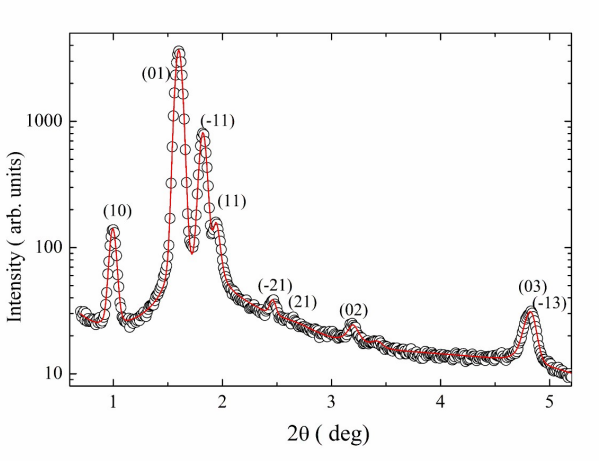


Fig. S3 X-ray intensity versus the scattering angle for compound **D-5** at T=140°C in the B_{1Rev} phase. Red line shows the fit assuming 2D oblique structure with a = 88.9 Å, b = 55.4 Å, and γ = 94.3 deg.

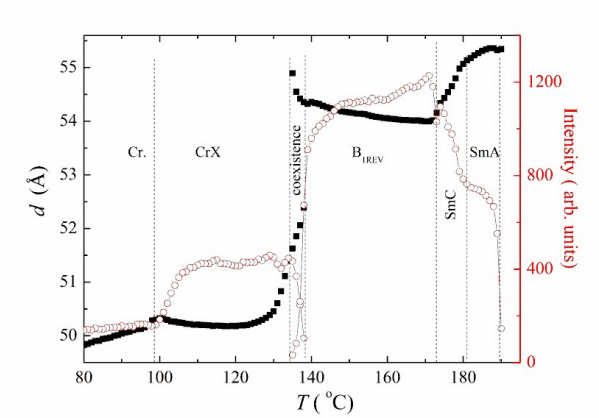


Fig. S4 Temperature dependence of the layer spacing, *d*, for **D-5**. In the B_{1Rev} phase, *d* value corresponds to the most intensive peak in the X-ray pattern.

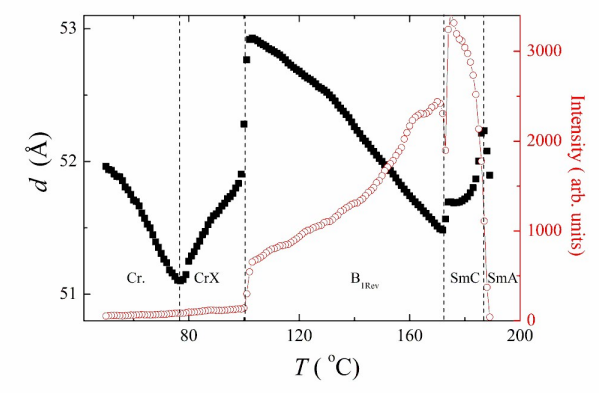


Fig. S5 Temperature dependence of the layer spacing, *d*, for **D-7**. In the B_{1Rev} phase, *d* value corresponds to the most intensive peak in the X-ray pattern.

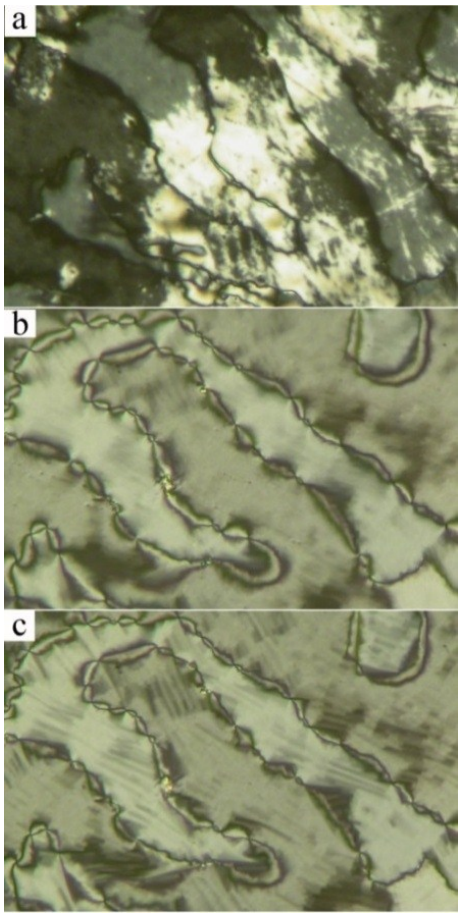


Fig. S6 Texture taken at the sample with one-free surface for **D-6** in (a) the N phase at T=165°C, (b) the SmC phase at T=150°C and (c) the columnar B_{1Rev} phase at T=140°C.

7. References

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