

Electronic supporting information

Bent-core dimers with top-to-bottom linkage between central units

Martin Horčič, Jiří Svoboda*^a, Vladimíra Novotná^b, Damian Pocięcha^c, and Ewa Gorecka^c

^a *Department of Organic Chemistry, University of Chemistry and Technology, CZ-166 28 Prague 6, Czech Republic. E-mail: Jiri.Svoboda@vscht.cz; Fax: +420220444182; Tel: +420220444288*

^b *Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, CZ-182 21 Prague 9, Czech Republic. E-mail: novotna@fzu.cz; Fax: +420286890527; Tel: +420266053111*

^c *Laboratory of Dielectrics and Magnetics, Chemistry Department, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland. E-mail: pociu@chem.uw.edu.pl; Fax: +48228221075; Tel: +48228221075*

Contents

1 Synthesis

- 1.1 Synthesis of the central cores
- 1.2 Synthesis of the series of dimers
- 1.3 Experimental
- 2 Mesomorphic properties
- 3 References

1 Synthesis

1.1 Synthesis of the central cores

The synthesis of the target compounds **Dm-n** utilized the corresponding both symmetrical cores **1/m** and **2/m** and non-symmetrical core **3/3**, respectively (Figure S1). Furthermore, the central cores were substituted with a series of versatile lengthening arms **4/n-10** (Figure S1), to obtain broad series of target dimeric materials **Dm-n** with a different molecular structure for detailed physical investigations.

Synthesis of the bent-core units **1/m and **2/m****

In the preliminary contribution^{S1}, the synthetic access to the cores **1/3** and **2/3** has been described. The cores **1/m** and **2/m**, which differ in the length of the alkylene spacer between

the two aromatic units only, have been obtained analogously (see Scheme S1). In the first step, the hydroxyl group of the dibenzyl protected phloroglucinol **11**^{S1} was alkylated with ω -tetrahydropyranyloxy-substituted alkyl iodide^{S2} in *N,N*-dimethylformamide (DMF) in the presence of potassium carbonate to yield compounds **12/m** (86%) (Scheme S1). Standard acid catalysed deprotection of the THP-protecting group released the terminal hydroxyl group and provided alcohols **13/m**. To join the second aromatic unit, the hydroxyl group of **13/m** was subsequently transformed to the corresponding alkyl bromides **14/m** by the reaction with $\text{CBr}_4/\text{Ph}_3\text{P}$ ^{S3}. The second central core – methoxymethyl (MOM) protected pyrogallol **15**^{S4} – was then alkylated with the bromides **14/m** as above to yield the intermediates **16/m**. The MOM protecting groups were removed by an acid catalysed hydrolysis to yield the dibenzyl protected central core **1/m**. The tetraphenol based cores **2/m** were obtained by catalytic hydrogenolysis of **1/m**.

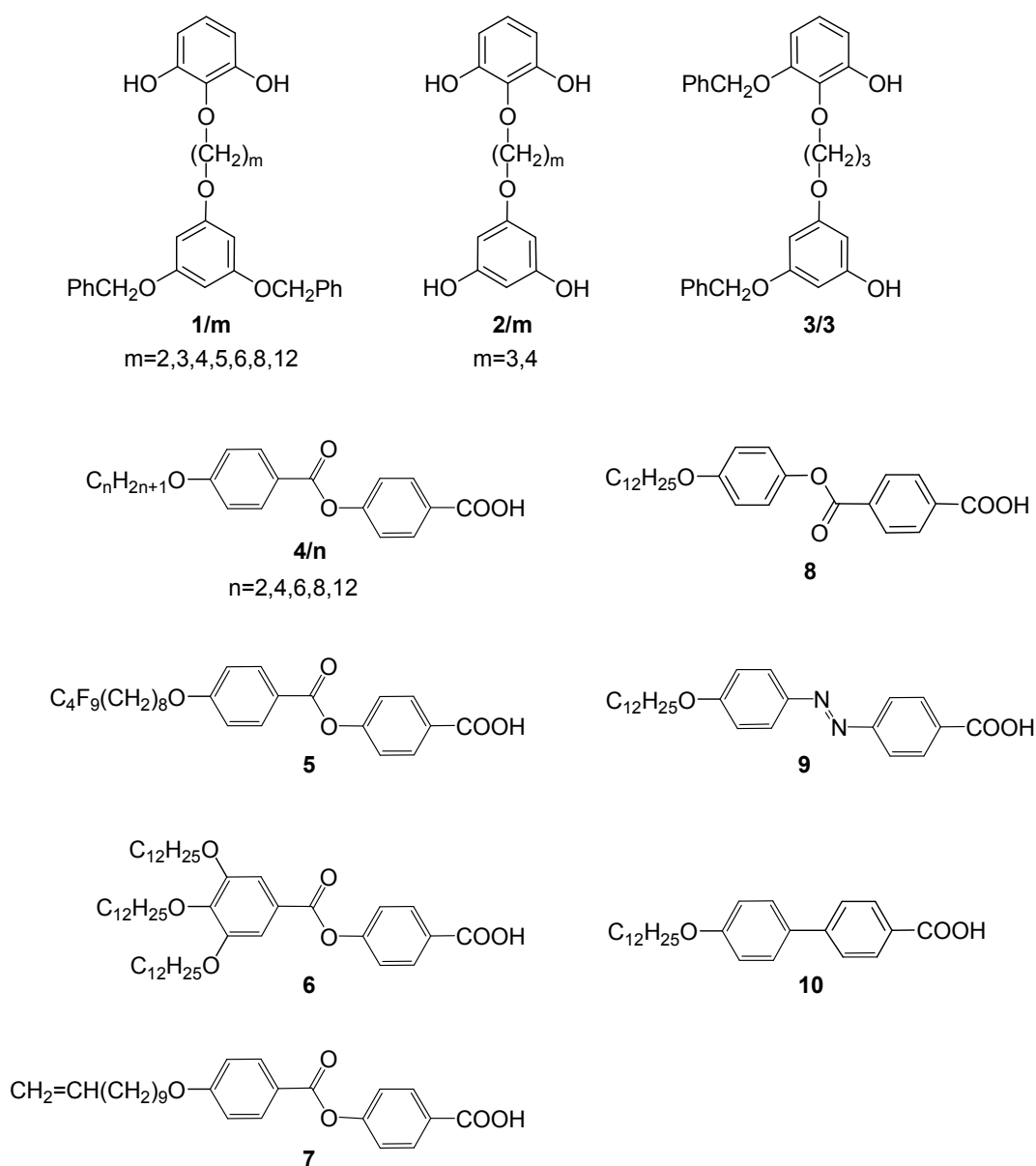
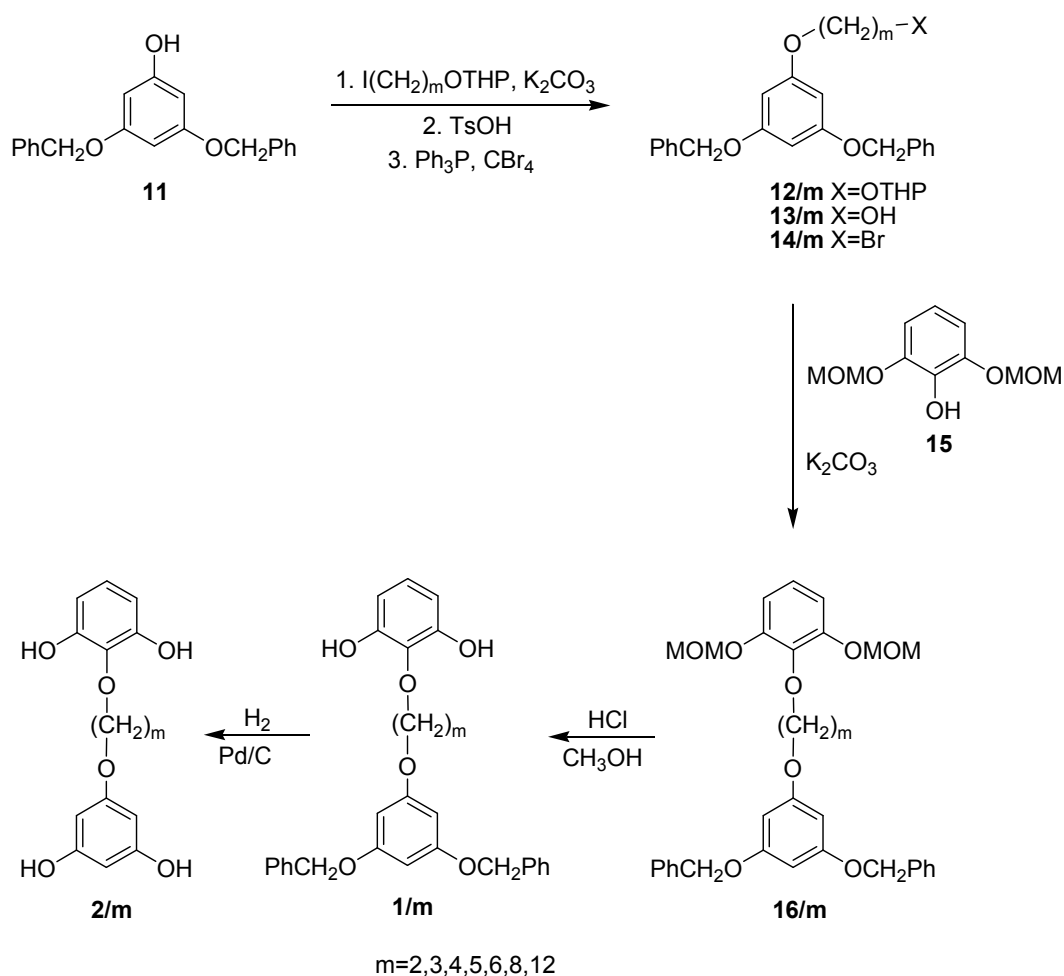


Figure S1 Structure of the bent-core units and utilized lengthening arms.

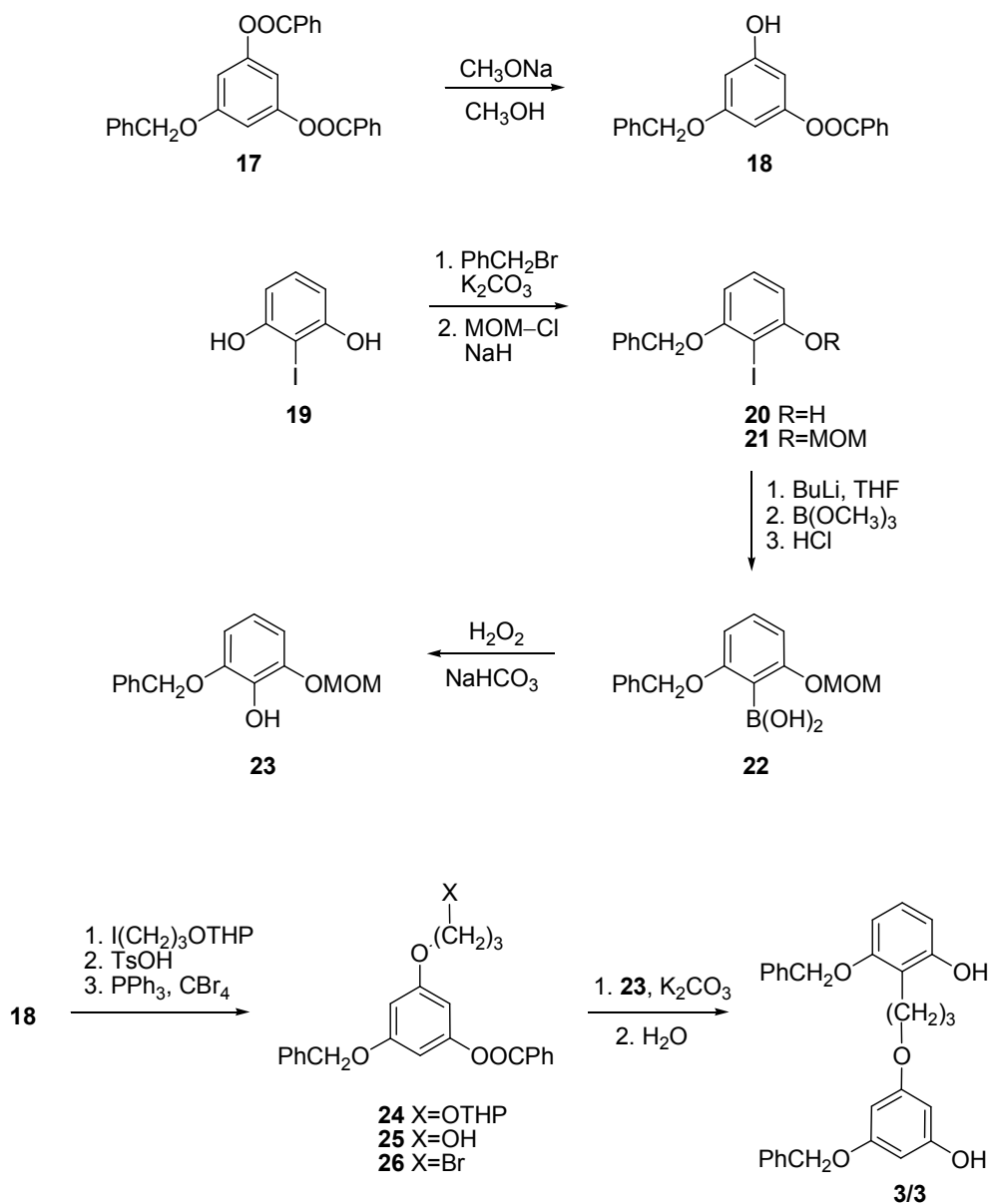


Scheme S1 Synthesis of the bent-core unit **1/m** and **2/m**.

Synthesis of the bent-core unit **3/3**

Synthesis of bent-core unit **3/3** required two intermediates derived from substituted phloroglucinol and pyrogallol (Scheme S2). Synthesis of the former started from the benzyl bisbenzoate **17**^{S5} which was subjected to a partial deprotection of a benzoate group by a base-catalysed reesterification with methanol to yield **18**. To obtain the second core **23** we utilized transformations of the known 2-iodoresorcinol (**19**)^{S6}. A successive monoprotection of one of its hydroxylic group by benzylation with benzyl bromide yielded compound **20**, which was further protected with methoxymethyl (MOM) group using methoxymethyl chloride in basic medium. Lithiation of the protected derivative **21** with butyllithium and trapping the formed lithium salt with trimethyl borate yielded after hydrolysis the corresponding boronic acid **22**. Hydrogen peroxide oxidation of **22** left the target intermediate **23**.

The bis-protected phloroglucinol **18** was then alkylated with THP-protected 3-iodopropanol (Scheme S2), the formed compound **24** was then subjected to deprotection of the hydroxy group and the released hydroxy group of compound **25** was subsequently transformed to the bromo compound **26**. Finally the protected pyrogallol **23** was alkylated with the alkyl bromide **26** which yielded after an aqueous workup the target bent-core unit **3/3**.



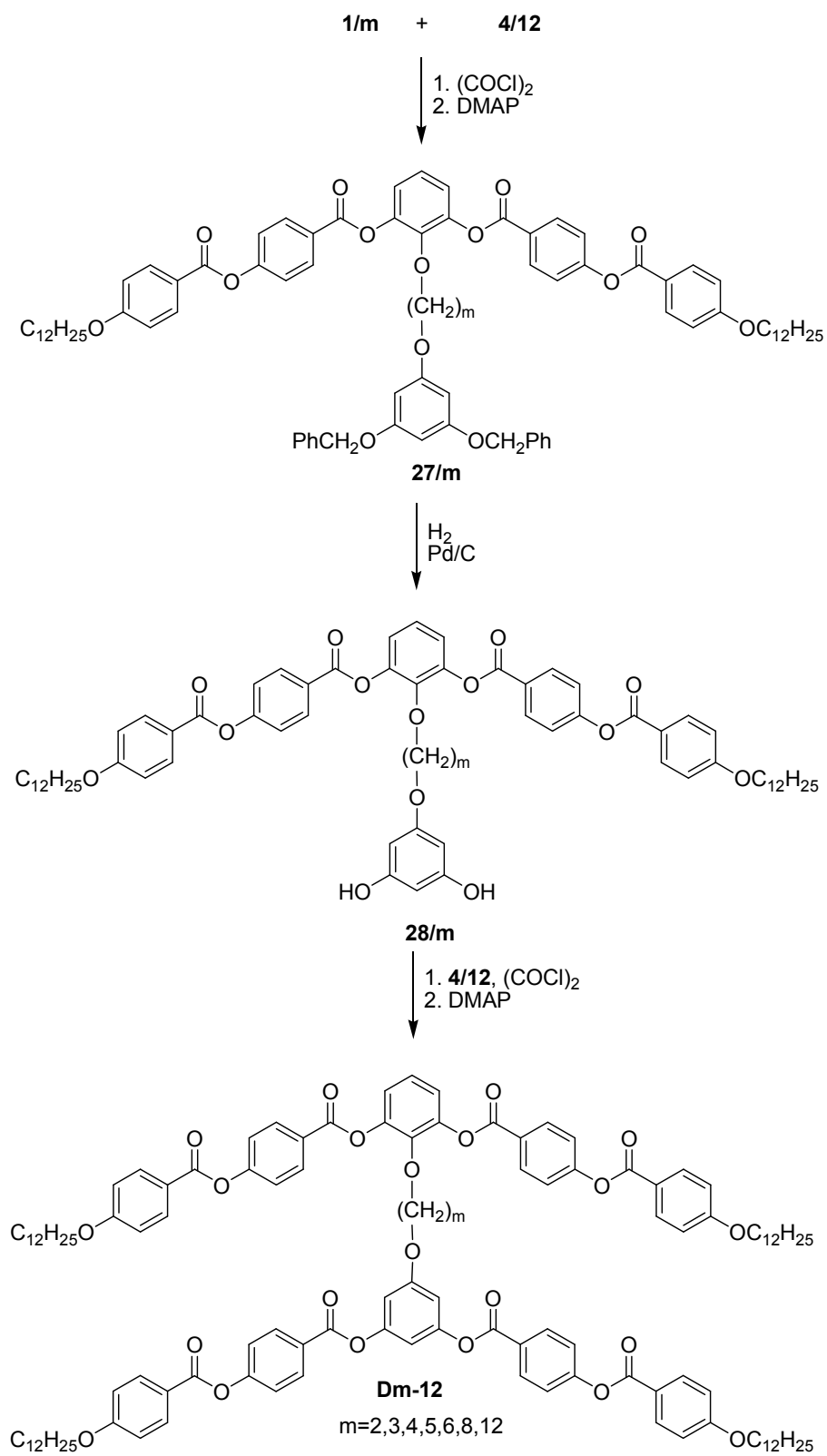
Scheme S2 Synthesis of the bent-core unit **3/3**.

1.2 Synthesis of the series of dimers

Synthesis of dimers differing in the length of alkylene spacer

The first studied series of dimers was prepared by sequential acylation of the core **1/m** with acid chloride of acid **4/12** in the presence of 4-dimethylaminopyridine (DMAP) (Scheme S3). After the first acylation, the benzyl groups in intermediates **27/m** were removed by catalytic hydrogenation and the released hydroxylic groups of compounds **28/m** were acylated

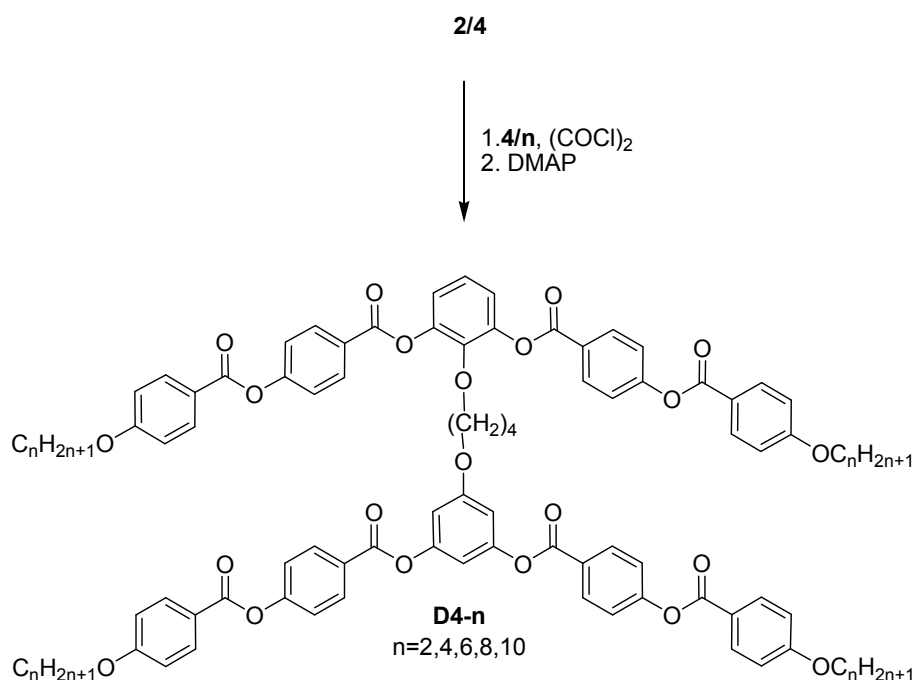
with the acid chloride of **4/12** to yield symmetric dimers **D2-12**, **D3-12**, **D4-12**, **D5-12**, **D6-12**, **D8-12**, and **D12-12**).



Scheme S3 Synthesis of dimers **Dm-12**.

Synthesis of dimers differing in the length of the terminal chain

In the preliminary paper,^{S1} we have investigated the role of the terminal chain length in materials with a three-carbon alkylene spacer. In the continuation analogous series of dimers (**D4-n**) has been synthesised. For this purpose, we utilized the bent core **2/4** which was acylated with an excess of acid chlorides of acids **4/n** under the same conditions as for dimers **Dm-12** (Scheme S4).

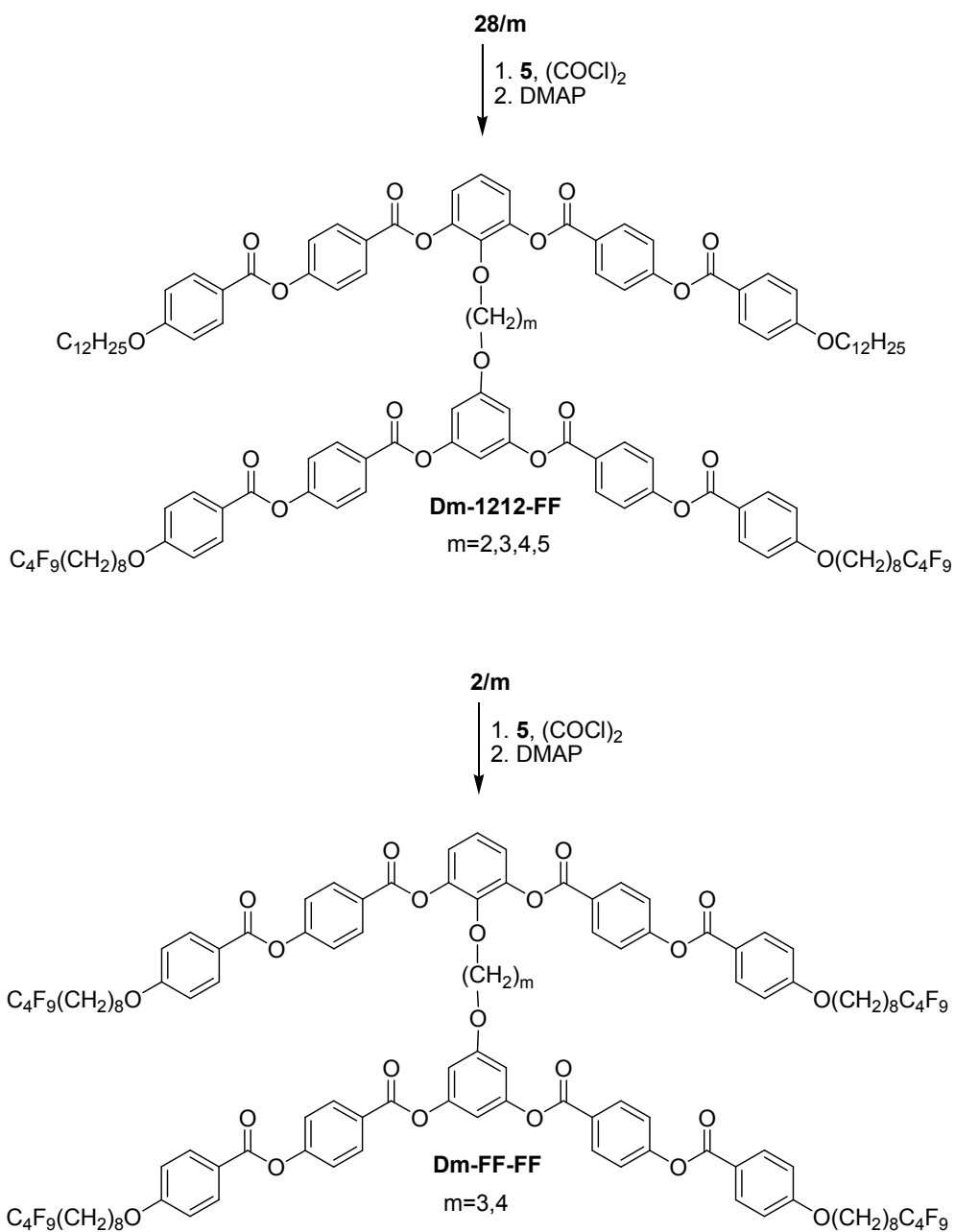


Scheme S4 Synthesis of series of dimers **D4-n**.

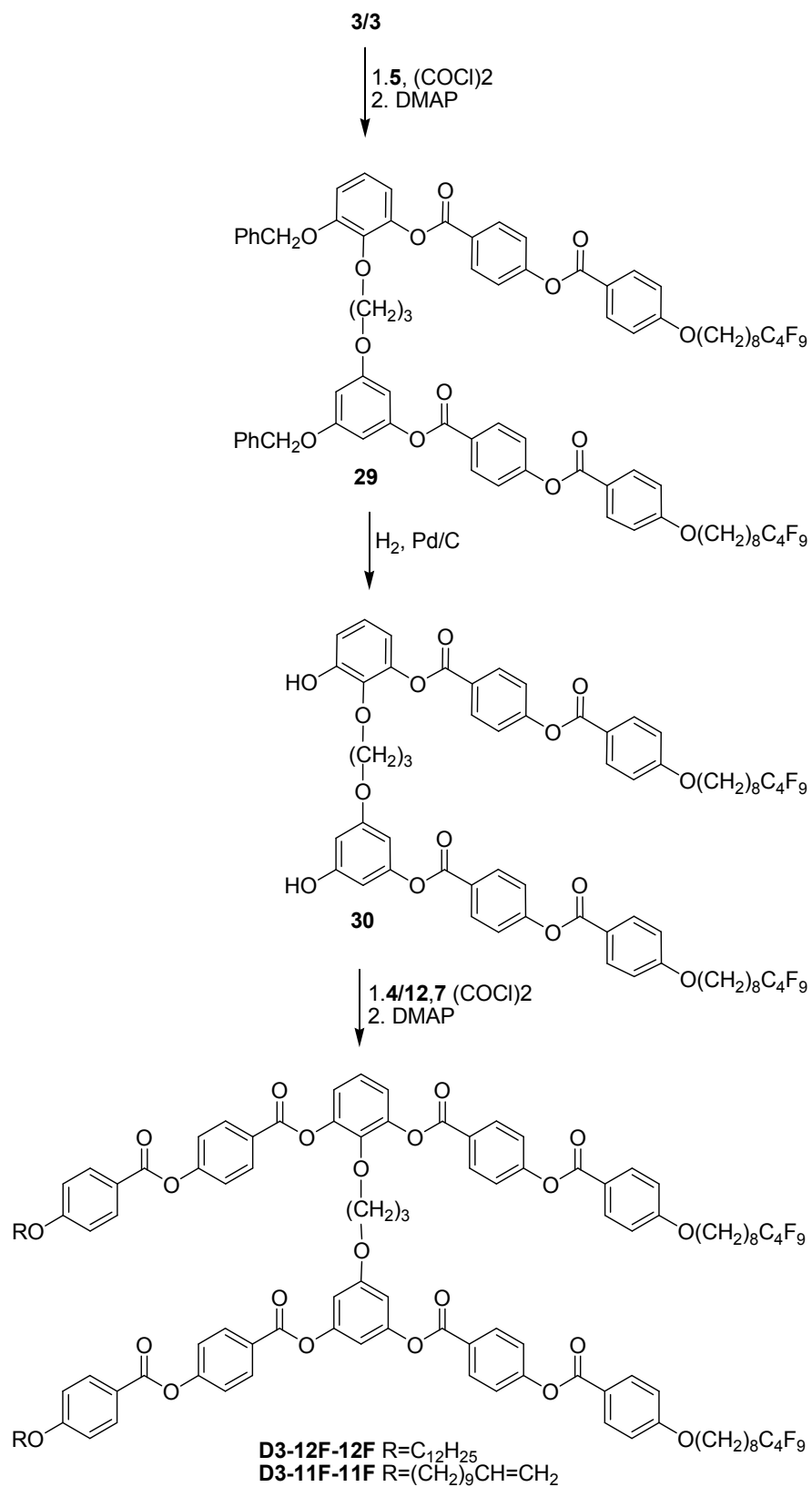
Synthesis of dimers with different lengthening arms in the bent-core units

In the design of non-symmetric bent-core dimers, we intended to change the dodecyl alkyl chain for a polyfluoroalkyl terminal unit. In the first aspect we kept the dodecyl alkyl chains in the upper bent-unit and changed the terminal chains in the bottom unit. Their synthesis was based on utilization of the intermediates **28/m** (m=2,3,4,5) (Scheme S5) which were acylated with acid chloride of acid **5** to yield the dimers **Dm12-12FF**. Furthermore, all the dodecyl units were replaced for the fluorinated ones (dimers **Dm-FF-FF**). The synthesis was achieved by a quadruple acylation of the bent-core unit **2/m** (m=3,4) (Scheme S5). The non-symmetrical dimers along the vertical axis **D3-12F-12F** and **D3-11F-11F** were obtained by a step wise acylation of the bent-core unit **3/3** analogously as for materials of series **Dm-12**. In the first step, by acylation with acid **5** (Scheme S6), the polyfluorinated side arms were introduced, then the protecting benzyl groups were removed from the intermediate **29** by catalytic hydrogenation, and the released hydroxyl groups of **30** were acylated with acid chloride of acid **4/12** and **7**, respectively. The dimer **D3-SiF-SiF** possessing siloxane units in

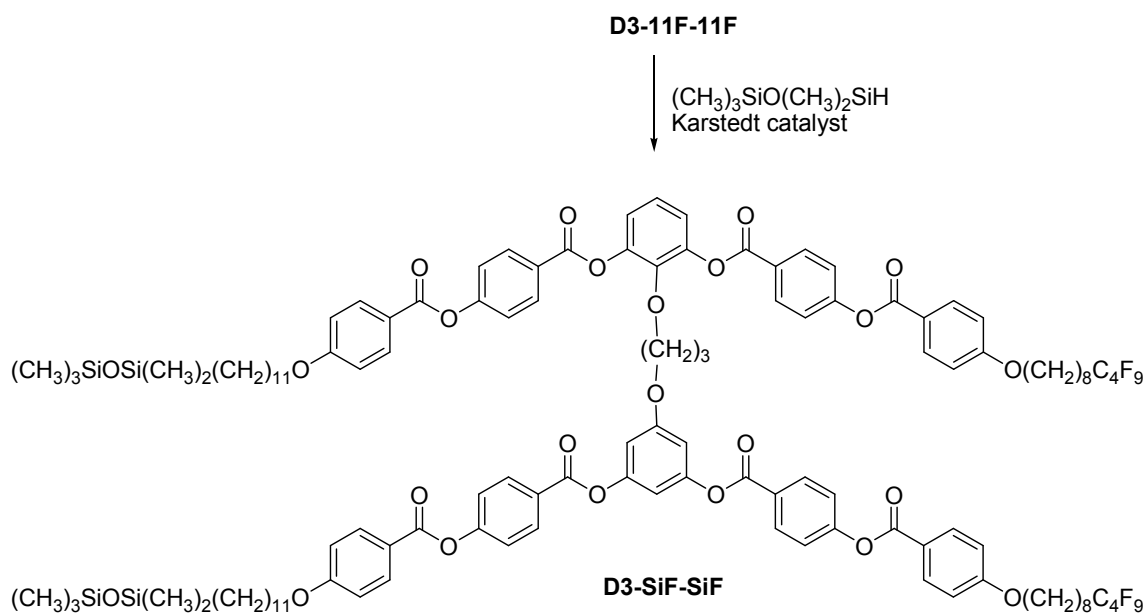
left arms and polyfluoroalkyl chains in the right arms of the dimer was prepared by a radical silylation of the undecenyl chain terminated dimer **D3-11F-11F** (Scheme S7).



Scheme S5 Synthesis of polyfluoroalkyl-terminated dimers **Dm-1212-FF** and **Dm-FF-FF**.



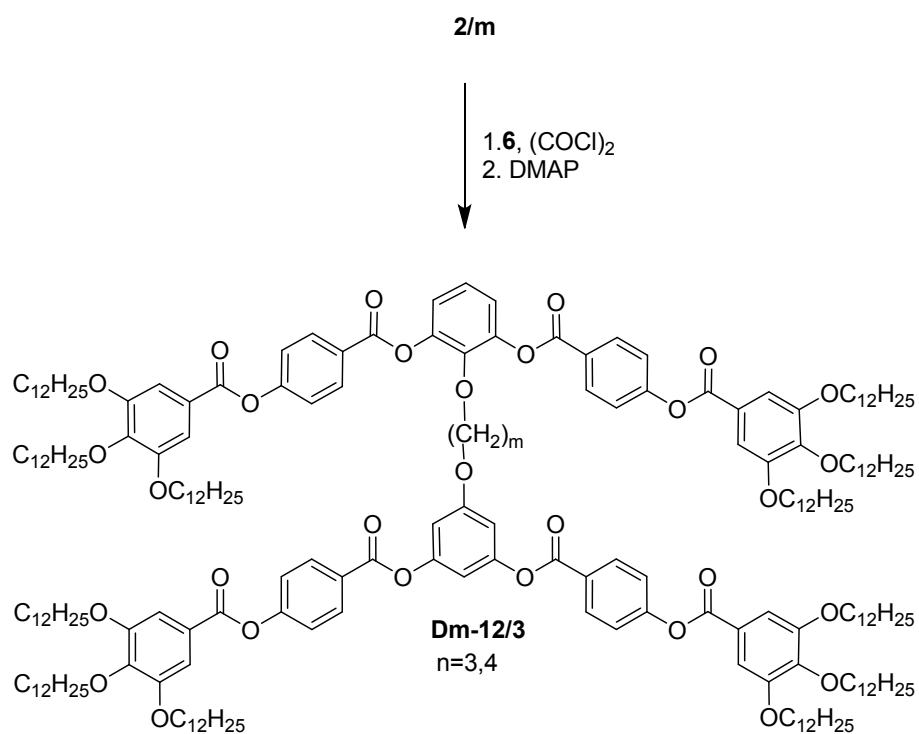
Scheme S6 Synthesis of dimers **D3-12F-12F** and **D3-11F-11F**.



Scheme S7 Synthesis of dimer **D3-SiF-SiF**.

Synthesis of dimers differing in the number of terminal chains

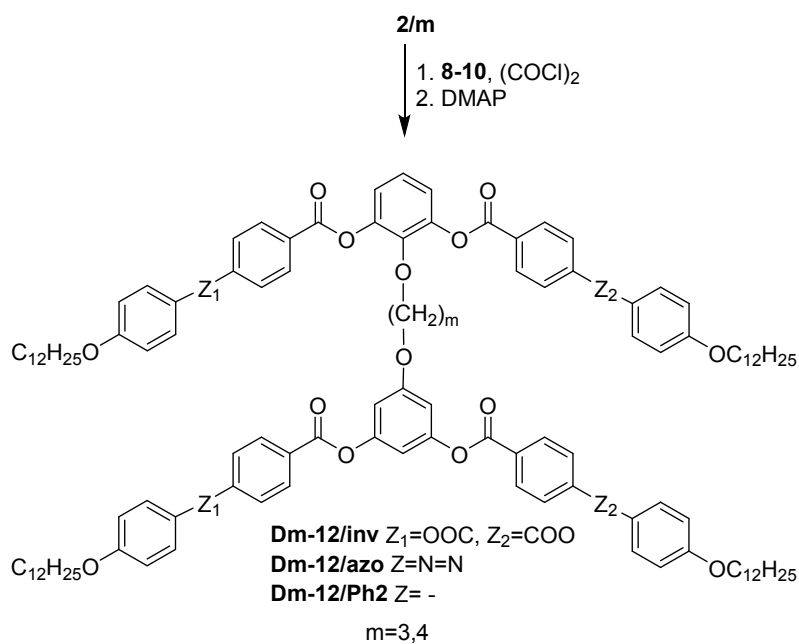
Synthesis was achieved by acylation of the bent cores **2/m** ($m=3,4$) with acid **6** to yield the polycatenar dimers **Dm-12/3** ($m=3,4$) (Scheme S8).



Scheme S8 Synthesis of polycatenar dimer **D3-12/3**.

Synthesis of dimers with modified linking groups in the lengthening arms

The series of dimers, in which the linking groups in the outer position of the lengthening arms were modified, was synthesised by a quadruple acylation of the bent-core unit **2/m** ($m=3,4$) with acid chlorides of acids **8-10** yielding dimers **Dm-12/inv**, **Dm-12/azo**, and **Dm-12/Ph2**, where *inv* denotes the inverted orientation of the carboxylic group ($Z=\text{OOC}$), *azo* stands for an azo linking group ($Z=\text{N}=\text{N}$), and *Ph2* means the presence a biphenyl unit due to absence of any linking group ($Z=-$) (Scheme S9).



Scheme S9 Synthesis of dimers with modified linking groups.

1.3 Experimental

Characterisation

The structures of all intermediates and products were confirmed by proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform (CDCl_3) and methanol- d_4 , resp., were used as solvents and signals of the solvents served as internal standards, J values are given in Hz. ^{19}F NMR spectra are referenced to CFCl_3 . 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%. The HR-MS of dimers has been performed on spectrometer LTQ Orbitrap Velos, hybrid ion-trap-orbitrap (Thermo Scientific), positive electrospray. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm) in indicated solvents.

General methods of synthesis

Method 1 Alkylation of phenols

Alkyl bromide (10 mmol) was added to a mixture of phenol (11 mmol) and freshly fused potassium carbonate (11 mmol) in dry DMF (50 ml). The mixture was stirred and heated to 70°C for 18 h in an argon atmosphere. After cooling to room temperature, it was diluted with water (200 ml) and extracted with toluene and ethyl acetate, respectively (3×50 ml). The combined organic solution was washed with brine (30 ml) and dried with anhydrous magnesium sulphate. The solvent was removed and the crude product was purified by column chromatography or crystallisation.

Method 2 Deprotection of the THP group

A catalytic amount of TsOH was added into a solution of protected alcohol (1.0 g) in a mixture of methanol (20 ml) and dichloromethane (45 ml). After stirring at room temperature for 24 h, the mixture was evaporated and the product was isolated by column chromatography (usually toluene/*tert*-butyl methyl ether (8/1)) and crystallisation, respectively.

Method 3 Synthesis of alkyl bromides by the means of $\text{Ph}_3\text{P/CBr}_4$

Tetrabromomethane (0.5 g; 1.5 mmol) and triphenylphosphine (420 mg; 1.6 mmol) were added to a solution of alcohol (1 mmol) in dry dichloromethane (50 ml) at 0°C . The mixture was stirred for 30 min at 0°C , 30 min at room temperature, and then evaporated. The crude product was purified by column chromatography (usually hexane/ethyl acetate (10/1)).

Method 4 Deprotection of the MOM groups

To a solution of the MOM ether (1 mmol) in methanol (25 ml), 35% aq. hydrochloric acid (0.4 ml; 4 mmol) and water (0.4 ml) were added. The mixture was stirred under heating to 60°C for 1.5 h. After cooling to room temperature it was diluted with water (50 ml), and extracted with ethyl acetate (3×25 ml). The combined extracts were washed with saturated aqueous solution of sodium hydrogen carbonate (10 ml), brine (10 ml), and dried with

anhydrous magnesium sulphate. After removing the solvent, the product was obtained by column chromatography (toluene/*tert*-butyl methyl ether 12/1).

Method 5 Deprotection of the benzyl group

To a slurry of benzyl derivative (0.5 g) in ethyl acetate (50 ml), 10% Pd/C (0.05 g) was added and the mixture was hydrogenated in a Parr apparatus at room temperature for 20 h. The catalyst was filtered off and washed with ethyl acetate (2 × 15 ml), the filtrate was evaporated and the product purified by column chromatography.

Method 6 General method of preparation of acid chlorides

To a slurry of carboxylic acid (1 mmol) in dry dichloromethane (20 ml), oxalyl chloride (0.42 ml; 5 mmol) and a drop of DMF were added. The mixture was stirred at room temperature for 24 h and evaporated. To the residue was added toluene (10 ml) and the mixture was evaporated. The acid chloride was used immediately in the acylation reaction.

Method 7 Acylation of phenols with acid chlorides

To a solution of phenol (1 mmol) and 4-dimethylaminopyridine (DMAP) (171 mg; 1.4 mmol) in dichloromethane (30 ml), a solution of freshly prepared acid chloride (1.4 mmol) (in case of diols and tetraols 6–8 equivalents of acid chloride) in dichloromethane (20 ml) was added. The mixture was heated to boiling under stirring for 3–8 h. After cooling to room temperature, water (1 ml) was added and stirred overnight. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 15 ml). The combined organic solution was dried with anhydrous magnesium sulphate, filtered and the filtrate was evaporated. The crude product was purified by column chromatography and crystallisation.

Method 8 Introduction of the MEM protecting group

To a slurry of sodium hydride (60% in oil) (0.52 g; 13 mmol) (washed in advance with hexane (3 × 10 ml)) in dry DMF (8 ml) cooled to 0°C, a solution of phenol (10 mmol) in dry DMF (5 ml) was added within 0.5 h. The mixture was stirred for 0.5 h at room temperature, cooled back to 0°C, and chloromethyl methyl ether (0.9 ml; 11.5 mmol) was added. The mixture was stirred at room temperature for 1.5 h and poured on a cold saturated solution of ammonium chloride (20 ml). The product was extracted with *tert*-butyl methyl ether (3 × 15 ml), the combined extracts were washed with water (10 ml), brine (10 ml), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the residue was purified by column chromatography.

Synthesis of the bent-core units 1/m and 2/m (Scheme S1)

Synthesis of compounds 12/m

Compounds **12/m** have been obtained by the reaction of phenol **11** with a series of THP-protected ω-bromoalcohols using the general method 1 (see Scheme S1).

2-{2-[3,5-Bis(benzyloxy)phenoxy]ethoxy}tetrahydro-2H-pyran (12/2). Yield 88%, viscous oil. ¹H NMR spectrum (CDCl₃): 1.53-1.87 (m, 6 H, 3 × CH₂); 3.53 (m, 1 H, CH₂O); 3.81 (m, 1 H, CH₂O); 3.91 (m, 1 H, CH₂O); 4.04 (m, 1 H, CH₂O); 4.11 (t, 2 H, ³J=6.4, CH₂O); 4.71 (dd, 1 H, ³J=3.3, OCHO); 5.01 (s, 4 H, 2 × PhCH₂O); 6.23 (d, 2 H, ⁴J=2.1); 6.27 (dd, 1 H, ⁴J=2.1); 7.32-7.44 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.0 (C); 160.8 (2 × C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 99.2 (CH); 95.0 (3 × CH); 70.3 (2 × CH₂); 67.7 (CH₂); 66.0 (CH₂); 62.4 (CH₂); 30.8 (CH₂); 25.7 (CH₂); 19.6 (CH₂).

2-{4-[3,5-Bis(benzyloxy)phenoxy]butoxy}tetrahydro-2H-pyran (12/4). Yield 85%, yellowish oil. ¹H NMR spectrum (CDCl₃): 1.53-1.64 (m, 4 H, 2 × CH₂); 1.73-1.91 (m, 6 H, 3 × CH₂); 3.47 (m, 1 H, CH₂O); 3.53 (m, 1 H, CH₂O); 3.83 (m, 1 H, CH₂O); 3.89 (m, 1 H, CH₂O); 3.96 (t, 2 H, ³J=6.3, CH₂O); 4.62 (dd, 1 H, ³J=4.1, ³J=2.6, OCHO); 5.02 (s, 4 H, 2 × PhCH₂O); 6.21 (d, 2 H, ⁴J=2.3); 6.27 (dd, 1 H, ⁴J=2.1); 7.34-7.46 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 137.1 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 99.1 (CH); 94.8 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.0 (CH₂); 67.3 (CH₂); 62.6 (CH₂); 31.0 (CH₂); 26.6 (CH₂); 26.4 (CH₂); 25.7 (CH₂); 19.9 (CH₂).

2-{5-[3,5-Bis(benzyloxy)phenoxy]pentyloxy}tetrahydro-2H-pyran (12/5). Yield 91%, oil. ¹H NMR spectrum (CDCl₃): 1.51-1.74 (m, 8 H, 4 × CH₂); 1.81 (m, 4 H, 2 × CH₂); 3.43 (m, 1 H, CH₂O); 3.52 (m, 1 H, CH₂O); 3.79 (m, 1 H, CH₂O); 3.87 (m, 1 H, CH₂O); 3.93 (t, 2 H, ³J=6.4, CH₂O); 4.60 (dd, 1 H, ³J=4.0, ³J=2.5, OCHO); 5.01 (s, 4 H, 2 × PhCH₂O); 6.20 (d, 2 H, ⁴J=2.1); 6.26 (dd, 1 H, ⁴J=2.2); 7.33-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 99.1 (CH); 94.7 (2 × CH); 94.6 (CH); 70.3 (2 × CH₂); 68.1 (CH₂); 67.6 (CH₂); 62.6 (CH₂); 31.0 (CH₂); 29.7 (CH₂); 29.3 (CH₂); 25.7 (CH₂); 23.1 (CH₂); 19.9 (CH₂).

2-{6-[3,5-Bis(benzyloxy)phenoxy]hexyloxy}tetrahydro-2H-pyran (12/6). Yield 88% of viscous oil. ¹H NMR spectrum (CDCl₃): 1.45-1.83 (m, 14 H, 7 × CH₂); 3.42 (m, 1 H, CH₂O); 3.52 (m, 1 H, CH₂O); 3.78 (m, 1 H, CH₂O); 3.90 (m, 3 H, CH₂O); 4.60 (dd, 1 H, ³J=2.6, ³J=4.4, OCHO); 5.02 (s, 4 H, 2 × PhCH₂O); 6.21 (d, 2 H, ⁴J=2.1); 6.26 (dd, 1 H, ⁴J=2.1); 7.33-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 99.1 (CH); 94.78 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.2 (CH₂); 67.8 (CH₂); 62.6 (CH₂); 31.0 (CH₂); 30.0 (CH₂); 29.4 (CH₂); 26.3 (CH₂); 26.2 (CH₂); 25.8 (CH₂); 20.0 (CH₂).

2-{8-[3,5-Bis(benzyloxy)phenoxy]octyloxy}tetrahydro-2H-pyran (12/8). Yield 95%, oil. ¹H NMR spectrum (CDCl₃): 1.38-1.86 (m, 18 H, 9 × CH₂); 3.42 (m, 1 H, CH₂O); 3.53 (m, 1 H, CH₂O); 3.77 (m, 1 H, CH₂O); 3.90 (m, 3 H, CH₂O); 4.61 (dd, 1 H, ³J=2.9, ³J=4.4, OCHO); 5.02 (s, 4 H, 2 × PhCH₂O); 6.21 (d, 2 H, ⁴J=2.1); 6.27 (dd, 1 H, ⁴J=2.2); 7.34-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 160.9 (2 × C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 99.1 (CH); 94.8 (2 × CH); 94.6 (CH); 70.3 (2 × CH₂); 68.3 (CH₂); 67.9 (CH₂); 62.6 (CH₂); 31.1 (CH₂); 30.0 (CH₂); 29.7 (CH₂); 29.6 (CH₂); 29.4 (CH₂); 26.5 (CH₂); 26.3 (CH₂); 25.8 (CH₂); 20.0 (CH₂).

2-{12-[3,5-Bis(benzyloxy)phenoxy]dodecyloxy}tetrahydro-2H-pyran (12/12). Yield 95%, oil. ¹H NMR spectrum (CDCl₃): 1.34-1.47 (m, 14 H, 7 × CH₂); 1.53-1.67 (m, 8 H, 4 × CH₂); 1.78 (m, 4 H, 2 × CH₂); 3.43 (m, 1 H, CH₂O); 3.54 (m, 1 H, CH₂O); 3.79 (m, 1 H, CH₂O); 3.91 (m, 3 H, CH₂O); 4.62 (dd, 1 H, ³J=4.4, ³J=3.7, OCHO); 5.03 (s, 4 H, 2 × PhCH₂O); 6.23 (d, 2 H, ⁴J=2.1); 6.29 (dd, 1 H, ⁴J=2.2); 7.34-7.47 (m, 10 H). ¹³C NMR spectrum (CDCl₃):

161.3 (C); 160.9 (2 × C); 137.2 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 99.1 (CH); 94.8 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.3 (CH₂); 67.9 (CH₂); 62.5 (CH₂); 31.1 (CH₂); 30.1 (CH₂); 29.9 (4 × CH₂); 29.8 (CH₂); 29.7 (CH₂); 29.5 (CH₂); 26.6 (CH₂); 26.3 (CH₂); 25.8 (CH₂); 20.0 (CH₂).

Synthesis of compounds 13/m

By the general method 2, deprotection of compounds **12/m** provided the series of alcohols **13/m**.

2-[3,5-Bis(benzyloxy)phenoxy]ethanol (13/2). Yield 81%, yellowish oil. ¹H NMR spectrum (CDCl₃): 3.93 (t, 2 H, ³J=4.2, CH₂O); 4.03 (t, 2 H, ³J=4.8, CH₂O); 5.02 (s, 4 H, 2 × PhCH₂O); 6.24 (d, 2 H, ⁴J=2.1); 6.31 (dd, 1 H, ⁴J=2.1); 7.35-7.46 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 160.9 (2 × C); 160.7 (C); 137.0 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 95.2 (CH); 94.9 (2 × CH); 70.4 (2 × CH₂); 69.5 (CH₂); 61.6 (CH₂).

4-[3,5-Bis(benzyloxy)phenoxy]butanol (13/4). Yield 72%, yellowish oil. ¹H NMR spectrum (CDCl₃): 1.77 (m, 2 H, CH₂); 1.88 (m, 2 H, CH₂); 3.71 (t, 2 H, ³J=6.3, CH₂O); 3.98 (t, 2 H, ³J=6.2, CH₂O); 5.03 (s, 4 H, 2 × PhCH₂O); 6.24 (d, 2 H, ⁴J=2.1); 6.31 (dd, 1 H, ⁴J=1.8, ⁴J=2.3); 7.36-7.48 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.1 (C); 160.9 (2 × C); 137.1 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 94.8 (3 × CH); 70.4 (2 × CH₂); 68.1 (CH₂); 62.7 (CH₂); 29.7 (CH₂); 26.0 (CH₂).

5-[3,5-Bis(benzyloxy)phenoxy]pentanol (13/5). Yield 83%, m.p. 45-46°C. ¹H NMR spectrum (CDCl₃): 1.56 (m, 2 H, CH₂); 1.63 (m, 2 H, CH₂); 1.81 (tt, 2 H, ³J=7.2, CH₂); 3.67 (t, 2 H, ³J=6.3, CH₂O); 3.93 (t, 2 H, ³J=6.4, CH₂O); 5.02 (s, 4 H, 2 × PhCH₂O); 6.21 (d, 2 H, ⁴J=2.1); 6.27 (dd, 1 H, ⁴J=2.2); 7.34-7.46 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 137.1 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 94.8 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.1 (CH₂); 63.0 (CH₂); 32.7 (CH₂); 29.2 (CH₂); 22.6 (CH₂).

6-[3,5-Bis(benzyloxy)phenoxy]hexanol (13/6). Yield 97%, oil. ¹H NMR spectrum (CDCl₃): 1.48 (m, 4 H, 2 × CH₂); 1.62 (tt, 2 H, ³J=7.0, CH₂CH₂O); 1.80 (tt, 2 H, ³J=6.7, ³J=7.6, CH₂CH₂O); 3.66 (t, 2 H, ³J=6.6, CH₂OH); 3.94 (t, 2 H, ³J=6.4, CH₂O); 5.03 (s, 4 H, 2 × PhCH₂O); 6.23 (d, 2 H, ⁴J=2.1); 6.29 (dd, 1 H, ⁴J=2.1); 7.35-7.47 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 137.1 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 94.8 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.2 (CH₂); 63.1 (CH₂); 32.9 (CH₂); 29.4 (CH₂); 26.2 (CH₂); 25.8 (CH₂).

8-[3,5-Bis(benzyloxy)phenoxy]octanol (13/8). Yield 93%, oil. ¹H NMR spectrum (CDCl₃): 1.37-1.45 (m, 8 H, 4 × CH₂); 1.58 (tt, 2 H, ³J=6.7, CH₂CH₂O); 1.77 (tt, 2 H, ³J=6.8, ³J=7.6, CH₂CH₂O); 3.64 (t, 2 H, ³J=6.5, CH₂OH); 3.91 (t, 2 H, ³J=6.5, CH₂O); 5.01 (s, 4 H, 2 × PhCH₂O); 6.20 (d, 2 H, ⁴J=2.1); 6.26 (dd, 1 H, ⁴J=2.2); 7.33-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 94.8 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.3 (CH₂); 63.3 (CH₂); 33.0 (CH₂); 29.6 (2 × CH₂); 29.4 (CH₂); 26.2 (CH₂); 25.9 (CH₂).

12-[3,5-Bis(benzyloxy)phenoxy]dodecanol (13/12). Yield 64%, oil. ¹H NMR spectrum (CDCl₃): 1.33-1.46 (m, 16 H, 8 × CH₂); 1.59 (m, 2 H, CH₂CH₂O); 1.78 (tt, 4 H, ³J=8.0, CH₂CH₂O); 3.64 (t, 2 H, ³J=6.4, CH₂O); 3.93 (t, 2 H, ³J=6.6, CH₂O); 5.03 (s, 4 H, 2 ×

PhCH₂O); 6.23 (d, 2 H, ⁴J=2.4); 6.28 (dd, 1 H, ⁴J=1.9, ⁴J=2.4); 7.34-7.46 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 160.9 (2 × C); 137.2 (2 × C); 128.8 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 94.8 (2 × CH); 94.7 (CH); 70.3 (2 × CH₂); 68.4 (CH₂); 63.3 (CH₂); 33.1 (CH₂); 29.9 (CH₂); 29.8 (3 × CH₂); 29.7 (CH₂); 29.6 (CH₂); 29.5 (CH₂); 26.3 (CH₂); 26.0 (CH₂).

Synthesis of alkyl bromides 14/m

Compounds of series 14/m were prepared from alcohols 13/m by the general method 3.

1,3-Bis(benzyloxy)-5-(2-bromoethoxy)benzene (14/2). Yield 91%, m.p. 74.5-76°C. ¹H NMR spectrum was in agreement with ref.[171]. ¹³C NMR spectrum (CDCl₃): 161.0 (2 × C); 160.1 (C); 137.0 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 95.4 (CH); 95.0 (2 × CH); 70.4 (2 × CH₂); 68.1 (CH₂); 29.3 (CH₂).

1,3-Bis(benzyloxy)-5-(4-bromobutoxy)benzene (14/4). Yield 93%, oil. ¹H NMR spectrum (CDCl₃): 1.95 (m, 2 H, CH₂); 2.08 (m, 2 H, CH₂); 3.51 (t, 2 H, ³J=6.5, CH₂Br); 3.97 (t, 2 H, ³J=6.1, CH₂O); 5.05 (s, 4 H, 2 × PhCH₂O); 6.24 (d, 2 H, ⁴J=2.1); 6.32 (dd, 1 H, ⁴J=2.1); 7.37-7.49 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.0 (3 × C); 137.1 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 94.9 (CH); 94.8 (2 × CH); 70.4 (2 × CH₂); 67.2 (CH₂); 33.8 (CH₂); 29.8 (CH₂); 28.1 (CH₂).

1,3-Bis(benzyloxy)-5-(5-bromopentyloxy)benzene (14/5). Yield 98%, oil. The spectral data corresponded with those of ref.^{S9}.

1,3-Bis(benzyloxy)-5-(6-bromohexyloxy)benzene (14/6). Yield 96%, m.p. 74-75°C. ¹H NMR spectrum (CDCl₃): 1.53 (m, 4 H, 2 × CH₂); 1.81 (tt, 2 H, ³J=6.5, CH₂CH₂Br); 1.93 (tt, 2 H, ³J=6.7, CH₂CH₂O); 3.46 (t, 2 H, ³J=6.7, CH₂Br); 3.95 (t, 2 H, ³J=6.5, CH₂O); 5.05 (s, 4 H, 2 × PhCH₂O); 6.25 (d, 2 H, ⁴J=1.8); 6.31 (dd, 1 H, ⁴J=1.8); 7.37-7.49 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 161.0 (2 × C); 137.2 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 94.8 (3 × CH); 70.3 (2 × CH₂); 68.1 (CH₂); 34.1 (CH₂); 33.0 (CH₂); 29.3 (CH₂); 28.2 (CH₂); 25.6 (CH₂).

1,3-Bis(benzyloxy)-5-(8-bromooctyloxy)benzene (14/8). Yield 95%, m.p. 62.5-63.5°C. ¹H NMR spectrum (CDCl₃): 1.42-1.50 (m, 8 H, 4 × CH₂); 1.81 (tt, 2 H, ³J=7.6, ³J=6.7, CH₂CH₂O); 1.91 (tt, 2 H, ³J=7.6, ³J=7.0, CH₂CH₂O); 3.45 (t, 2 H, ³J=6.7, CH₂Br); 3.95 (t, 2 H, ³J=6.6, CH₂O); 5.05 (s, 4 H, 2 × PhCH₂O); 6.26 (d, 2 H, ⁴J=2.1); 6.32 (dd, 1 H, ⁴J=2.1); 7.37-7.49 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 161.0 (2 × C); 137.2 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 94.9 (2 × CH); 94.8 (CH); 70.3 (2 × CH₂); 68.3 (CH₂); 34.3 (CH₂); 33.1 (CH₂); 29.5 (2 × CH₂); 29.0 (CH₂); 28.4 (CH₂); 26.3 (CH₂).

1,3-Bis(benzyloxy)-5-(12-bromododecyloxy)benzene (14/12). Yield 97%, m.p. 83-86°C. ¹H NMR spectrum (CDCl₃): 1.31-1.44 (m, 16 H, 8 × CH₂); 1.77 (tt, 2 H, ³J=7.6, ³J=6.7, CH₂CH₂Br); 1.87 (tt, 2 H, ³J=7.6, ³J=7.0, CH₂CH₂O); 3.42 (t, 2 H, ³J=6.8, CH₂Br); 3.92 (t, 2 H, ³J=6.5, CH₂O); 5.02 (s, 4 H, 2 × PhCH₂O); 6.21 (d, 2 H, ⁴J=2.4); 6.27 (dd, 1 H, ⁴J=2.1); 7.34-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 160.9 (2 × C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 94.8 (2 × CH); 94.6 (CH); 70.3 (2 × CH₂); 68.3 (CH₂); 34.3 (CH₂); 33.1 (CH₂); 29.8 (3 × CH₂); 29.7 (CH₂); 29.6 (CH₂); 29.5 (CH₂); 29.0 (CH₂); 28.4 (CH₂); 26.3 (CH₂).

Synthesis of intermediates 16/m

Compounds **16/m** were prepared by the general method 1 by reaction of bromides **14/m** with the protected pyrogallol **15**.

2-{2-[3,5-Bis(benzyloxy)phenoxy]ethoxy}-1,3-bis(methoxymethoxy)benzene (16/2). The product was purified by column chromatography (toluene/*tert*-butyl methyl ether 12/1). Yield 74 % of a viscous oil. ¹H NMR spectrum (CDCl₃): 3.46 (s, 6 H, 2 × CH₃O); 4.22 (t, 2 H, ³J=5.9, CH₂O); 4.37 (t, 2 H, ³J=5.8, CH₂O); 5.00 (s, 4 H, 2 × PhCH₂O); 5.15 (s, 4 H, 2 × OCH₂O); 6.20 (d, 2 H, ⁴J=2.1); 6.26 (dd, 1 H, ⁴J=2.1); 6.83 (d, 2 H, ³J=7.9); 6.95 (dd, 1 H, ³J=7.3); 7.32-7.41 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 160.9 (3 × C); 151.6 (2 × C); 139.3 (C); 137.1 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 124.3 (CH); 111.2 (2 × CH); 95.8 (2 × CH₂); 95.0 (3 × CH); 71.6 (CH₂); 70.3 (2 × CH₂); 67.5 (CH₂); 56.5 (2 × CH₃).

2-{4-[3,5-Bis(benzyloxy)phenoxy]butoxy}-1,3-bis(methoxymethoxy)benzene (16/4). Yield 88% of an oil. ¹H NMR spectrum (CDCl₃): 2.04 (m, 4 H, 2 × CH₂); 3.54 (s, 6 H, 2 × CH₃O); 4.07 (t, 2 H, ³J=6.2, CH₂O); 4.15 (t, 2 H, ³J=6.0, CH₂O); 5.05 (s, 4 H, 2 × PhCH₂O); 5.24 (s, 4 H, 2 × OCH₂O); 6.27 (d, 2 H, ⁴J=2.1); 6.32 (dd, 1 H, ⁴J=2.2); 6.90 (d, 2 H, ³J=7.9); 7.00 (dd, 1 H, ³J=7.0); 7.37-7.49 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 161.0 (2 × C); 151.7 (2 × C); 139.7 (C); 137.2 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 123.9 (CH); 111.0 (2 × CH); 95.7 (2 × CH₂); 94.9 (2 × CH); 94.7 (CH); 73.4 (CH₂); 70.3 (2 × CH₂); 68.0 (CH₂); 56.5 (2 × CH₃); 27.1 (CH₂); 26.2 (CH₂).

2-{5-[3,5-Bis(benzyloxy)phenoxy]pentyloxy}-1,3-bis(methoxymethoxy)benzene (16/5). Yield 58%, oil. ¹H NMR spectrum (CDCl₃): 1.65 (m, 2 H, CH₂); 1.84 (m, 4 H, 2 × CH₂CH₂O); 3.53 (s, 6 H, 2 × CH₃O); 3.93 (t, 2 H, ³J=6.4, CH₂O); 4.03 (t, 2 H, ³J=6.4, CH₂O); 5.00 (s, 4 H, 2 × PhCH₂O); 5.18 (s, 4 H, 2 × OCH₂O); 6.18 (d, 2 H, ⁴J=2.3); 6.24 (dd, 1 H, ³J=2.1); 6.82 (d, 2 H, ³J=7.9); 6.93 (dd, 1 H, ³J=7.3); 7.32-7.44 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 161.0 (2 × C); 151.7 (2 × C); 139.8 (C); 137.2 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 123.8 (CH); 111.3 (2 × CH); 95.8 (2 × CH₂); 94.9 (3 × CH); 73.7 (CH₂); 70.4 (2 × CH₂); 68.1 (CH₂); 56.5 (2 × CH₃); 30.2 (CH₂); 29.3 (CH₂); 22.9 (CH₂).

2-{6-[3,5-Bis(benzyloxy)phenoxy]hexyloxy}-1,3-bis(methoxymethoxy)benzene (16/6). Yield 89%, oil. ¹H NMR spectrum (CDCl₃): 1.56 (m, 4 H, 2 × CH₂); 1.81 (m, 4 H, 2 × CH₂CH₂O); 3.52 (s, 6 H, 2 × CH₃O); 3.93 (t, 2 H, ³J=6.4, CH₂O); 4.04 (t, 2 H, ³J=6.5, CH₂O); 5.02 (s, 4 H, 2 × PhCH₂O); 5.21 (s, 4 H, 2 × OCH₂O); 6.21 (d, 2 H, ⁴J=2.1); 6.27 (dd, 1 H, ⁴J=1.8, ⁴J=2.1); 6.85 (d, 2 H, ³J=8.2); 6.95 (dd, 1 H, ³J=7.2); 7.33-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 151.7 (2 × C); 139.9 (C); 137.1 (2 × C); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 123.8 (CH); 111.2 (2 × CH); 95.7 (2 × CH₂); 94.8 (2 × CH); 94.7 (CH); 73.8 (CH₂); 70.3 (2 × CH₂); 68.2 (CH₂); 56.5 (2 × CH₃); 30.4 (CH₂); 29.5 (CH₂); 26.1 (CH₂); 26.0 (CH₂).

2-{8-[3,5-Bis(benzyloxy)phenoxy]octyloxy}-1,3-bis(methoxymethoxy)benzene (16/8). Yield 94%, oil. ¹H NMR spectrum (CDCl₃): 1.40-1.49 (m, 8 H, 4 × CH₂); 1.77 (tt, 4 H, ³J=7.1, 2 × CH₂CH₂O); 3.52 (s, 6 H, 2 × CH₃O); 3.91 (t, 2 H, ³J=6.4, CH₂O); 4.02 (t, 2 H, ³J=6.7, CH₂O); 5.01 (s, 4 H, 2 × PhCH₂O); 5.20 (s, 4 H, 2 × OCH₂O); 6.20 (d, 2 H, ⁴J=1.5); 6.26 (dd, 1 H, ⁴J=1.8); 6.84 (d, 2 H, ³J=6.9); 6.94 (dd, 1 H, ³J=7.0); 7.33-7.44 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 151.6 (2 × C); 139.9 (C); 137.1 (2 × C);

128.8 (4 × CH); 128.2 (2 × CH); 127.8 (4 × CH); 123.7 (CH); 111.2 (2 × CH); 95.7 (2 × CH₂); 94.8 (2 × CH); 94.7 (CH); 73.9 (CH₂); 70.3 (2 × CH₂); 68.3 (CH₂); 56.5 (2 × CH₃); 30.4 (CH₂); 29.6 (CH₂); 29.4 (CH₂); 27.1 (CH₂); 26.3 (CH₂); 26.1 (CH₂).

2-{12-[3,5-Bis(benzyloxy)phenoxy]dodecyloxy}-1,3-bis(methoxymethoxy)benzene

(16/12). Yield 74%, oil. ¹H NMR spectrum (CDCl₃): 1.37-1.54 (m, 16 H, 8 × CH₂); 1.83 (m, 4 H, 2 × CH₂CH₂O); 3.56 (s, 6 H, 2 × CH₃O); 3.95 (t, 2 H, ³J=6.4, CH₂O); 4.08 (t, 2 H, ³J=6.7, CH₂O); 5.04 (s, 4 H, 2 × PhCH₂O); 5.24 (s, 4 H, 2 × OCH₂O); 6.26 (d, 2 H, ⁴J=2.1); 6.31 (dd, 1 H, ⁴J=2.2); 6.89 (d, 2 H, ³J=7.6); 6.98 (dd, 1 H, ³J=7.0); 7.34-7.48 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 160.9 (2 × C); 151.7 (2 × C); 140.0 (C); 137.2 (2 × C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 123.8 (CH); 111.3 (2 × CH); 95.8 (2 × CH₂); 94.8 (2 × CH); 94.7 (CH); 74.0 (CH₂); 70.3 (2 × CH₂); 68.3 (CH₂); 56.5 (2 × CH₃); 30.5 (CH₂); 30.0 (2 × CH₂); 29.9 (2 × CH₂); 29.8 (CH₂); 29.7 (CH₂); 29.5 (CH₂); 26.4 (CH₂); 26.3 (CH₂).

Synthesis of the bent-cores units 1/m

By the general method 4, the MOM protecting group was removed from the series of compounds **16/m**.

2-{2-[3,5-Bis(benzyloxy)phenoxy]ethoxy}benzene-1,3-diol (1/2). Yield 99%, m.p. 83-86°C. ¹H NMR spectrum (CDCl₃): 4.14 (m, 2 H, CH₂O); 4.30 (m, 2 H, CH₂O); 5.05 (s, 4 H, 2 × PhCH₂O); 6.34 (d, 2 H, ⁴J=2.1); 6.41 (dd, 1 H, ⁴J=2.1); 6.62 (d, 2 H, ³J=8.2); 6.70 (bs, 2 H, 2 × OH); 6.97 (dd, 1 H, ³J=8.2); 7.40-7.51 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.1 (2 × C); 159.8 (C); 150.0 (2 × C); 136.9 (2 × C); 134.2 (C); 129.0 (4 × CH); 128.5 (2 × CH); 128.1 (4 × CH); 125.7 (CH); 108.5 (2 × CH); 96.0 (CH); 95.0 (2 × CH); 73.0 (CH₂); 70.5 (2 × CH₂); 67.3 (CH₂).

2-{4-[3,5-Bis(benzyloxy)phenoxy]butoxy}benzene-1,3-diol (1/4). Yield 93%, m.p. 104.5-108.5°C. ¹H NMR spectrum (CDCl₃): 1.98 (m, 4 H, 2 × CH₂); 4.02 (t, 2 H, ³J=6.2, CH₂O); 4.08 (t, 2 H, ³J=6.0, CH₂O); 5.01 (s, 4 H, 2 × PhCH₂O); 5.55 (s, 4 H, 2 × OH); 6.24 (d, 2 H, ⁴J=2.1); 6.28 (dd, 1 H, ⁴J=2.2); 6.51 (d, 2 H, ³J=8.2); 6.87 (dd, 1 H, ³J=7.9); 7.33-7.44 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 160.9 (2 × C); 160.8 (C); 149.4 (2 × C); 137.0 (2 × C); 134.0 (C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 124.9 (CH); 108.4 (2 × CH); 95.1 (CH); 95.0 (2 × CH); 73.6 (CH₂); 70.4 (2 × CH₂); 68.3 (CH₂); 27.7 (CH₂); 25.8 (CH₂).

2-{5-[3,5-Bis(benzyloxy)phenoxy]pentyloxy}benzene-1,3-diol (1/5). Yield 96%, oil. ¹H NMR spectrum (CDCl₃): 1.64 (tt, 2 H, ³J=6.7, CH₂); 1.85 (tt, 4 H, ³J=6.3, ³J=7.9, 2 × CH₂CH₂O); 3.96 (t, 2 H, ³J=6.1, CH₂O); 4.05 (t, 2 H, ³J=6.5, CH₂O); 5.04 (s, 4 H, 2 × PhCH₂O); 5.58 (s, 4 H, 2 × OH); 6.25 (d, 2 H, ⁴J=2.1); 6.31 (dd, 1 H, ⁴J=2.1); 6.52 (d, 2 H, ³J=8.2); 6.87 (dd, 1 H, ³J=8.2); 7.35-7.47 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.1 (C); 160.9 (2 × C); 149.5 (2 × C); 137.1 (2 × C); 134.0 (C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 124.8 (CH); 108.5 (2 × CH); 95.0 (3 × CH); 73.9 (CH₂); 70.4 (2 × CH₂); 68.0 (CH₂); 30.0 (CH₂); 29.0 (CH₂); 22.7 (CH₂).

2-{6-[3,5-Bis(benzyloxy)phenoxy]hexyloxy}benzene-1,3-diol (1/6). Yield 95%, oil. ¹H NMR spectrum (CDCl₃): 1.54 (m, 4 H, 2 × CH₂); 1.82 (m, 4 H, 2 × CH₂CH₂O); 3.94 (t, 2 H, ³J=6.4, CH₂O); 4.03 (t, 2 H, ³J=6.3, CH₂O); 5.03 (s, 4 H, 2 × PhCH₂O); 5.45 (bs, 2 H, 2 × OH); 6.23 (d, 2 H, ⁴J=2.3); 6.29 (dd, 1 H, ⁴J=2.2); 6.52 (d, 2 H, ³J=8.2); 6.88 (dd, 1 H, ³J=7.9); 7.35-7.46 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.1 (C); 160.9 (2 × C); 149.4 (2

× C); 137.1 (2 × C); 134.0 (C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 124.8 (CH); 108.4 (2 × CH); 94.9 (2 × CH); 94.8 (CH); 74.2 (CH₂); 70.4 (2 × CH₂); 68.1 (CH₂); 30.3 (CH₂); 29.3 (CH₂); 26.1 (CH₂); 25.9 (CH₂).

2-{8-[3,5-Bis(benzyloxy)phenoxy]octyloxy}benzene-1,3-diol (1/8). Yield 62%, oil. ¹H NMR spectrum (CDCl₃): 1.40-1.47 (m, 8 H, 4 × CH₂); 1.78 (m, 4 H, 2 × CH₂CH₂O); 3.92 (t, 2 H, ³J=6.4, CH₂O); 4.00 (t, 2 H, ³J=6.8, CH₂O); 5.01 (s, 4 H, 2 × PhCH₂O); 5.39 (bs, 2 H, 2 × OH); 6.21 (d, 2 H, ⁴J=2.3); 6.26 (dd, 1 H, ⁴J=2.2); 6.51 (d, 2 H, ³J=8.2); 6.87 (dd, 1 H, ³J=7.9); 7.33-7.45 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.2 (C); 160.9 (2 × C); 149.4 (2 × C); 137.1 (2 × C); 134.0 (C); 128.8 (4 × CH); 128.3 (2 × CH); 127.8 (4 × CH); 124.8 (CH); 108.3 (2 × CH); 94.8 (2 × CH); 94.7 (CH); 74.4 (CH₂); 70.3 (2 × CH₂); 68.2 (CH₂); 30.4 (CH₂); 29.5 (CH₂); 29.4 (2 × CH₂); 26.2 (CH₂); 26.1 (CH₂).

2-{12-[3,5-Bis(benzyloxy)phenoxy]dodecyloxy}benzene-1,3-diol (1/12). Yield 98%, m.p. 42-45°C. ¹H NMR spectrum (CDCl₃): 1.38-1.51 (m, 16 H, 8 × CH₂); 1.84 (tt, 4 H, ³J=6.6, 2 × CH₂CH₂O); 3.98 (t, 2 H, ³J=6.6, CH₂O); 4.06 (t, 2 H, ³J=7.0, CH₂O); 5.07 (s, 4 H, 2 × PhCH₂O); 5.83 (bs, 2 H, 2 × OH); 6.31 (d, 2 H, ⁴J=2.3); 6.35 (dd, 1 H, ⁴J=2.2); 6.57 (d, 2 H, ³J=8.2); 6.91 (dd, 1 H, ³J=7.9, ³J=8.5); 7.39-7.50 (m, 10 H). ¹³C NMR spectrum (CDCl₃): 161.3 (C); 160.9 (2 × C); 149.6 (2 × C); 137.2 (2 × C); 134.2 (C); 128.9 (4 × CH); 128.3 (2 × CH); 127.9 (4 × CH); 124.8 (CH); 108.5 (2 × CH); 95.0 (2 × CH); 94.8 (CH); 74.4 (CH₂); 70.4 (2 × CH₂); 68.5 (CH₂); 30.5 (CH₂); 29.9 (5 × CH₂); 29.7 (CH₂); 29.5 (CH₂); 26.4 (CH₂); 26.2 (CH₂).

2,5'-[Butane-1,3-diyloxy]bis(benzen-1,3-diol) (2/4)

The core **2/4** was obtained by the deprotection of compound **1/4** by the general method 5. Purification by column chromatography (chloroform/methanol 9/1), yield 97%, m.p. 82-84°C. ¹H NMR spectrum (methanol-*d*₄): 1.90 (m, 4 H, 2 × CH₂CH₂O); 3.94 (t, 2 H, ³J=5.7, CH₂O); 4.03 (t, 2 H, ³J=6.2, CH₂O); 5.86 (dd, 1 H, ⁴J=1.8); 5.88 (d, 2 H, ⁴J=2.1); 6.33 (d, 2 H, ³J=8.2); 6.70 (dd, 1 H, ³J=7.9, ³J=8.2). ¹³C NMR spectrum (methanol-*d*₄): 161.3 (C); 158.9 (2 × C); 150.9 (2 × C); 134.6 (C); 123.4 (CH); 107.5 (2 × CH); 95.2 (CH); 93.5 (2 × CH); 72.3 (CH₂); 67.5 (CH₂); 26.5 (CH₂); 25.8 (CH₂).

Synthesis of the bent-core unit 3/3 (Scheme S2)

(3-Benzyloxy-5-hydroxyphenyl) benzoate (18)

To a solution of bisbenzoate **17** [S5] (1.40 g; 3.3 mmol) in dry dichloromethane (40 ml) cooled to 0°C, a solution of sodium methoxide in methanol (1 ml of a 0.6 M solution). The mixture was stirred at 0°C for 0.5 h and decomposed by addition of acetic acid (1 ml). The mixture was evaporated and the crude product was purified by column chromatography (chloroform/methanol 97/3). Yield 830 mg (78%), m.p. 148-150°C. ¹H NMR spectrum (acetone-*d*₆): 5.10 (s, 2 H, PhCH₂O); 6.43 (dd, 1 H, ⁴J=2.1); 6.47 (dd, 1 H, ⁴J=2.2); 6.51 (dd, 1 H, ⁴J=2.2); 7.33-7.42 (m, 3 H); 7.48 (d, 2 H, ³J=6.5); 7.58 (dd, 2 H, ³J=7.3, ³J=7.9); 7.71 (dd, 1 H, ³J=7.3, ³J=7.6); 8.16 (d, 2 H, ³J=8.2); 8.74 (s, 1 H, OH). ¹³C NMR spectrum (acetone-*d*₆): 168.0 (C); 164.2 (C); 162.6 (C); 156.4 (C); 140.8 (C); 137.3 (CH); 133.5 (2 ×

CH); 133.3 (C); 132.4 (2 × CH); 132.0 (2 × CH); 131.4 (CH); 131.2 (2 × CH); 105.8 (CH); 103.8 (CH); 103.5 (CH); 73.4 (CH₂).

3-Benzyloxy-2-iodophenol (20)

Phenol **20** was obtained by the general method 1 starting from 2-iodoresorcinol (**19**) [S6] (3.0 g; 12.7 mmol) and benzyl bromide (725 mg; 4.2 mmol). Purification by column chromatography (chloroform/methanol 99/1), yield 810 mg (59%) of oily compound **20**. Spectral data were in agreement with ref.^{S7}

1-Benzyloxy-2-iodo-3-methoxymethoxybenzene (21)

Compound **26** was prepared according to general procedure 8 from phenol **20** (1.30 g; 3.9 mmol). Purification by column chromatography (toluene), yield 1.39 g (96%), oil. The spectral characteristics are identical with ref.^{S8}

2-Benzyloxy-6-methoxymethoxyphenylboronic acid (22)

A solution of **21** (1.39 g; 3.8 mmol), in dry THF (15 ml) was cooled to -78°C in an argon atmosphere and treated with a solution of (1.7 ml of 2.5 M solution in hexanes, 4.2 mmol) and the mixture was stirred for 15 min. Trimethyl borate was added (5 mmol) and the mixture was stirred at room temperature for 20 h. The reaction was quenched by addition of 10% aq. hydrochloric acid (10 ml) and diluted with water. The product was extracted with ethyl acetate (3 × 15 ml), the combined organic solution was washed with brine (10 ml) and dried with anhydrous magnesium sulphate. After evaporation the product was washed with hexane, yield 820 mg (76%), m.p. 90-94°C. ¹H NMR spectrum (CDCl₃): 3.51 (s, 3 H, CH₃O); 5.15 (s, 2 H, PhCH₂O); 5.29 (s, 2 H, OCH₂O); 6.73 (d, 1 H, ³J=8.3); 6.85 (d, 1 H, ³J=8.2); 7.22 (s, 2 H, 2 × OH); 7.35 (dd, 1 H, ³J=8.4); 7.38-7.42 (m, 5 H). ¹³C NMR spectrum (CDCl₃): 164.8 (C); 163.5 (C); 135.8 (C); 133.2 (CH); 129.2 (2 × CH); 128.9 (CH); 128.0 (2 × CH); 108.0 (CH); 106.7 (CH); 95.1 (CH₂); 71.5 (CH₂); 56.9 (CH₃).

2-Benzyloxy-6-methoxymethoxyphenol (23)

A mixture of boronic acid **22** (820 mg; 2.8 mmol), sodium hydrogen carbonate (235 mg; 2.8 mmol) and 30% aq. hydrogen peroxide (1.2 ml; 11.2 mmol) in acetonitrile (25 ml) was stirred at room temperature for 4 h. The mixture was diluted with water (40 ml) and acidified with hydrochloric acid to pH = 2. The product was extracted with ethyl acetate (3 × 20 ml), washed with an aqueous sodium hydrogen carbonate solution (10 ml), brine (10 ml), and dried with anhydrous magnesium sulphate. The unstable crude product was used immediately in the next step.

3-Benzyloxy-5-[3-(tetrahydro-2H-pyran-2-yloxy)propoxy]phenyl benzoate (24)

Compound **24** was synthesised by alkylation of phenol **18** (700 mg; 2.2 mmol) by the general method 1. The crude product was purified by column chromatography (hexane/ethyl acetate 6/1), yield 770 mg (75%) of a yellowish oil. ¹H NMR spectrum (CDCl₃): 1.51-1.61 (m, 4 H, 2 × CH₂); 1.70-1.82 (m, 2 H, CH₂); 2.07 (tt, 2 H, ³J=6.1, CH₂); 3.51 (m, 1 H, CH₂O); 3.57 (m, 1 H, CH₂O); 3.84 (m, 1 H, CH₂O); 3.93 (m, 1 H, CH₂O); 4.07 (t, 2 H, ³J=6.1, CH₂O); 4.61 (dd, 1 H, ³J=2.7, OCHO); 5.04 (s, 2 H, PhCH₂O);

6.44 (dd, 1 H, $^4J=2.1$); 6.49 (d, 2 H, $^4J=2.1$); 7.33-7.45 (m, 5 H); 7.51 (dd, 2 H, $^3J=7.3$, $^3J=7.9$); 7.64 (dd, 1 H, $^3J=7.3$); 8.20 (d, 2 H, $^3J=8.5$). ^{13}C NMR spectrum (CDCl_3): 165.2 (C); 160.9 (C); 160.6 (C); 152.7 (C); 136.8 (C); 133.9 (CH); 130.4 (2 \times CH); 129.8 (C); 128.9 (2 \times CH); 128.8 (2 \times CH); 128.3 (CH); 127.8 (2 \times CH); 101.5 (CH); 101.3 (CH); 99.9 (CH); 99.2 (CH); 70.5 (CH_2); 65.4 (CH_2); 64.1 (CH_2); 62.5 (CH_2); 30.9 (CH_2); 29.8 (CH_2); 25.7 (CH_2); 19.8 (CH_2).

3-Benzyloxy-5-(3-hydroxypropoxy)phenyl benzoate (25)

By the general method 2, deprotection of **24** (770 mg; 1.7 mmol) yielded 545 mg (87%) of **25**, m.p. 87-90°C. ^1H NMR spectrum (CDCl_3): 2.01 (tt, 2 H, $^3J=6.2$, CH_2); 2.25 (s, 1 H, OH); 3.81 (t, 2 H, $^3J=5.8$, CH_2OH); 4.08 (t, 2 H, $^3J=6.0$, CH_2O); 5.03 (s, 2 H, PhCH_2O); 6.46 (dd, 1 H, $^4J=2.1$); 6.51 (m, 2 H); 7.34-7.45 (m, 5 H); 7.51 (dd, 2 H, $^3J=7.3$, $^3J=7.9$); 7.64 (dd, 1 H, $^3J=7.3$); 8.20 (d, 2 H, $^3J=8.5$). ^{13}C NMR spectrum (CDCl_3): 165.3 (C); 160.7 (C); 160.6 (C); 152.7 (C); 136.8 (C); 133.9 (CH); 130.4 (2 \times CH); 129.7 (C); 128.9 (4 \times CH); 128.4 (CH); 127.8 (2 \times CH); 101.5 (2 \times CH); 99.9 (CH); 70.5 (CH_2); 65.9 (CH_2); 60.2 (CH_2); 32.2 (CH_2).

3-Benzyloxy-5-(3-bromopropoxy)phenyl benzoate (26)

Alkyl bromide **26** was obtained from the alcohol **25** (545 mg; 1.44 mmol) by the general method 3. Purification by column chromatography (hexane/ethyl acetate 10/1), yield 620 mg (98%), m.p. 91-92°C. ^1H NMR spectrum (CDCl_3): 2.31 (tt, 2 H, $^3J=6.2$, CH_2); 3.60 (t, 2 H, $^3J=6.4$, CH_2Br); 4.10 (t, 2 H, $^3J=5.9$, CH_2O); 5.06 (s, 2 H, PhCH_2O); 6.47 (dd, 1 H, $^4J=2.1$); 6.52 (dd, 1 H, $^4J=2.2$); 6.55 (dd, 1 H, $^4J=2.1$); 7.36-7.47 (m, 5 H); 7.53 (dd, 2 H, $^3J=7.0$, $^3J=7.9$); 7.66 (dd, 1 H, $^3J=7.3$, $^3J=7.6$); 8.22 (d, 2 H, $^3J=8.5$). ^{13}C NMR spectrum (CDCl_3): 165.3 (C); 160.7 (C); 160.5 (C); 152.8 (C); 136.8 (C); 133.9 (CH); 130.5 (2 \times CH); 129.7 (C); 128.9 (4 \times CH); 128.4 (CH); 127.9 (2 \times CH); 101.6 (2 \times CH); 99.9 (CH); 70.5 (CH_2); 65.9 (CH_2); 32.5 (CH_2); 30.2 (CH_2).

3-Benzyloxy-2-[3-(3-benzyloxy-5-hydroxyphenoxy)propoxy]phenol (3/3)

The compound **3/3** was prepared by the general method 1 by alkylation of phenol **23** (450 mg; 1.7 mmol) with alkyl bromide **26** (956 mg; 2.2 mmol). Purification by column chromatography (toluene/*tert*-butyl methyl ether 12/1), yield 230 mg (28%), yellowish oil. ^1H NMR spectrum (CDCl_3): 2.13 (dd, 2 H, $^3J=5.7$, $\text{CH}_2\text{CH}_2\text{O}$); 4.11 (t, 2 H, $^3J=5.7$, CH_2O); 4.28 (t, 2 H, $^3J=5.7$, CH_2O); 4.94 (s, 2 H, PhCH_2O); 5.09 (s, 2 H, PhCH_2O); 5.84 (s, 1 H, OH); 6.06 (dd, 1 H, $^4J=2.1$); 6.13 (dd, 1 H, $^4J=2.1$); 6.21 (dd, 1 H, $^4J=2.1$); 6.54 (dd, 1 H, $^3J=8.2$, $^4J=1.1$); 6.66 (dd, 1 H, $^3J=8.2$, $^4J=1.2$); 6.77 (s, 1 H, OH); 6.92 (dd, 1 H, $^3J=8.2$); 7.33-7.46 (m, 10 H). ^{13}C NMR spectrum (CDCl_3): 161.1 (C); 160.6 (C); 157.8 (C); 152.2 (C); 150.4 (C); 137.2 (C); 137.1 (C); 135.3 (C); 128.9 (2 \times CH); 128.8 (2 \times CH); 128.3 (2 \times CH); 127.9 (2 \times CH); 127.6 (2 \times CH); 124.5 (CH); 109.0 (CH); 106.0 (CH); 95.8 (CH); 95.6 (CH); 94.9 (CH); 71.3 (CH_2); 71.0 (CH_2); 70.3 (CH_2); 66.3 (CH_2); 29.7 (CH_2).

Synthesis of dimers **Dm-12** differing in the length of the alkylene spacer (Scheme S3)

The compounds were prepared by a successive acylation of the bent-core unit **1/m** with acid chloride of acid **4/12** by the method 6 and 7 to yield intermediates **27/m**, debenzoylation of whose according the method 5 yielded the diphenols **28/m**. Final acylation with acid chloride of acid **4/12** provided the series of target dimers **Dm-12**.

2-{2-[3,5-Bis(benzyloxy)phenoxy]ethoxy}benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (27/2). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from an ethyl acetate/hexane mixture. Yield 87%, m.p. 94°C. ¹H NMR spectrum (CDCl₃): 0.93 (t, 6 H, ³J=6.5, 2 × CH₃); 1.32-1.52 (m, 36 H, 2 × (CH₂)₉); 1.86 (tt, 4 H, ³J=6.8, ³J=7.6, 2 × CH₂CH₂O); 4.07 (m, 6 H, 3 × CH₂O); 4.40 (m, 2 H, CH₂O); 4.91 (s, 4 H, 2 × PhCH₂O); 5.93 (d, 2 H, ⁴J=2.1); 6.21 (dd, 1 H, ⁴J=1.8); 6.98 (d, 4 H, ³J=9.1); 7.23 (m, 3 H); 7.32-7.36 (m, 10 H); 7.41 (d, 4 H, ³J=7.6); 8.11 (d, 4 H, ³J=8.8); 8.28 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.4 (2 × C); 164.1 (2 × C); 164.0 (2 × C); 160.7 (2 × C); 160.6 (C); 155.7 (2 × C); 145.1 (2 × C); 143.7 (C); 137.2 (2 × C); 132.7 (4 × CH); 132.2 (4 × CH); 128.8 (4 × CH); 128.1 (2 × CH); 127.8 (4 × CH); 126.6 (2 × C); 124.1 (CH); 122.4 (4 × CH); 121.5 (2 × CH); 121.2 (2 × C); 114.7 (4 × CH); 95.3 (CH); 94.6 (2 × CH); 72.5 (CH₂); 70.2 (2 × CH₂); 68.6 (2 × CH₂); 67.3 (CH₂); 32.2 (2 × CH₂); 30.0 (4 × CH₂); 29.9 (4 × CH₂); 29.8 (2 × CH₂); 29.6 (2 × CH₂); 29.4 (2 × CH₂); 26.3 (2 × CH₂); 23.0 (2 × CH₂); 14.4 (2 × CH₃).

2-{4-[3,5-Bis(benzyloxy)phenoxy]butoxy}benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (27/4). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from ethyl acetate/hexane. Yield 90%, m.p. 72°C. ¹H NMR spectrum (CDCl₃): 0.94 (t, 6 H, ³J=6.7, 2 × CH₃); 1.32-1.52 (m, 36 H, 2 × (CH₂)₉); 1.71 (m, 4 H, 2 × CH₂CH₂O); 1.86 (tt, 4 H, ³J=6.7, ³J=7.9, 2 × CH₂CH₂O); 3.71 (t, 2 H, ³J=6.0, CH₂O); 4.05 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.12 (t, 2 H, ³J=6.0, CH₂O); 4.99 (s, 4 H, 2 × PhCH₂O); 6.12 (d, 2 H, ⁴J=2.1); 6.23 (dd, 1 H, ⁴J=2.2); 6.97 (d, 4 H, ³J=9.1); 7.21 (m, 3 H); 7.30-7.42 (m, 14 H); 8.16 (d, 4 H, ³J=9.1); 8.32 (d, 4 H, ³J=9.1). ¹³C NMR spectrum (CDCl₃): 164.5 (2 × C); 164.1 (2 × C); 164.0 (2 × C); 161.1 (C); 160.8 (2 × C); 155.8 (2 × C); 145.1 (2 × C); 144.0 (C); 137.2 (2 × C); 132.7 (4 × CH); 132.1 (4 × CH); 128.8 (4 × CH); 128.1 (2 × CH); 127.8 (4 × CH); 126.6 (2 × C); 123.6 (CH); 122.5 (4 × CH); 121.5 (2 × CH); 121.2 (2 × C); 114.7 (4 × CH); 94.9 (CH); 94.8 (2 × CH); 74.0 (CH₂); 70.3 (2 × CH₂); 68.6 (2 × CH₂); 67.6 (CH₂); 32.2 (2 × CH₂); 29.9 (8 × CH₂); 29.8 (2 × CH₂); 29.6 (2 × CH₂); 29.4 (2 × CH₂); 27.1 (CH₂); 26.3 (2 × CH₂); 26.0 (CH₂); 23.0 (2 × CH₂); 14.4 (2 × CH₃).

2-{5-[3,5-Bis(benzyloxy)phenoxy]pentyloxy}benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (27/5). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from ethyl acetate/hexane. Yield 88%, m.p. 93°C. ¹H NMR spectrum (CDCl₃): 0.90 (t, 6 H, ³J=6.6, 2 × CH₃); 1.29-1.58 (m, 42 H, 2 × (CH₂)₉ a 3 × CH₂); 1.83 (tt, 4 H, ³J=6.7, ³J=7.9, 2 × CH₂CH₂O); 3.61 (t, 2 H, ³J=6.3, CH₂O); 4.04 (m, 6 H, 3 × CH₂O); 4.95 (s, 4 H, 2 × PhCH₂O); 6.11 (d, 2 H, ⁴J=2.1); 6.18 (dd, 1 H, ⁴J=2.1); 6.95 (d, 4 H, ³J=8.8); 7.18 (m, 3 H); 7.29-7.37 (m, 14 H); 8.12 (d, 4 H, ³J=9.1); 8.30 (d, 4 H, ³J=9.1).

^{13}C NMR spectrum (CDCl_3): 164.5 ($2 \times \text{C}$); 164.1 ($2 \times \text{C}$); 164.0 ($2 \times \text{C}$); 161.2 (C); 160.8 ($2 \times \text{C}$); 155.8 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 144.1 (C); 137.2 ($2 \times \text{C}$); 132.7 ($4 \times \text{CH}$); 132.1 ($4 \times \text{CH}$); 128.8 ($4 \times \text{CH}$); 128.1 ($2 \times \text{CH}$); 127.7 ($4 \times \text{CH}$); 126.6 ($2 \times \text{C}$); 123.6 (CH); 122.5 ($4 \times \text{CH}$); 121.5 ($2 \times \text{CH}$); 121.1 ($2 \times \text{C}$); 114.6 ($4 \times \text{CH}$); 94.8 (CH); 94.7 ($2 \times \text{CH}$); 74.3 (CH_2); 70.2 ($2 \times \text{CH}_2$); 68.6 ($2 \times \text{CH}_2$); 67.8 (CH_2); 32.2 ($2 \times \text{CH}_2$); 30.2 (CH_2); 29.9 ($6 \times \text{CH}_2$); 29.8 ($4 \times \text{CH}_2$); 29.6 ($2 \times \text{CH}_2$); 29.3 ($2 \times \text{CH}_2$); 29.1 (CH_2); 26.2 ($2 \times \text{CH}_2$); 22.9 ($2 \times \text{CH}_2$); 22.8 (CH_2); 14.4 ($2 \times \text{CH}_3$).

2-{6-[3,5-Bis(benzyloxy)phenoxy]hexyloxy}benzene-1,3-diyl bis[4-(4-dodecyloxybenzyloxy)benzoate] (27/6). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from ethyl acetate/hexane. Yield 91%, viscous oil. ^1H NMR spectrum (CDCl_3): 0.95 (t, 6 H, $^3J=6.6$, $2 \times \text{CH}_3$); 1.34-1.58 (m, 44 H, $2 \times (\text{CH}_2)_9$ a $4 \times \text{CH}_2$); 1.85 (tt, 4 H, $^3J=6.5$, $^3J=7.6$, $2 \times \text{CH}_2\text{CH}_2\text{O}$); 3.76 (t, 2 H, $^3J=6.3$, CH_2O); 4.02 (t, 4 H, $^3J=6.6$, $2 \times \text{CH}_2\text{O}$); 4.07 (t, 2 H, $^3J=5.8$, CH_2O); 4.98 (s, 4 H, $2 \times \text{PhCH}_2\text{O}$); 6.20 (d, 2 H, $^4J=2.1$); 6.25 (dd, 1 H, $^4J=2.1$); 6.98 (d, 4 H, $^3J=8.8$); 7.21 (m, 3 H); 7.33-7.42 (m, 14 H); 8.16 (d, 4 H, $^3J=8.8$); 8.34 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 ($2 \times \text{C}$); 164.1 ($4 \times \text{C}$); 161.2 (C); 160.9 ($2 \times \text{C}$); 155.8 ($2 \times \text{C}$); 145.2 ($2 \times \text{C}$); 144.2 (C); 137.2 ($2 \times \text{C}$); 132.7 ($4 \times \text{CH}$); 132.2 ($4 \times \text{CH}$); 128.8 ($4 \times \text{CH}$); 128.2 ($2 \times \text{CH}$); 127.8 ($4 \times \text{CH}$); 126.7 ($2 \times \text{C}$); 123.6 (CH); 122.5 ($4 \times \text{CH}$); 121.5 ($2 \times \text{CH}$); 121.2 ($2 \times \text{C}$); 114.7 ($4 \times \text{CH}$); 94.7 ($3 \times \text{CH}$); 74.5 (CH_2); 70.2 ($2 \times \text{CH}_2$); 68.6 ($2 \times \text{CH}_2$); 68.1 (CH_2); 32.2 ($2 \times \text{CH}_2$); 30.5 (CH_2); 30.0 ($6 \times \text{CH}_2$); 29.9 ($4 \times \text{CH}_2$); 29.7 ($2 \times \text{CH}_2$); 29.4 ($2 \times \text{CH}_2$); 29.2 (CH_2); 26.3 ($2 \times \text{CH}_2$); 26.1 (CH_2); 26.0 (CH_2); 23.0 ($2 \times \text{CH}_2$); 14.5 ($2 \times \text{CH}_3$).

2-{8-[3,5-Bis(benzyloxy)phenoxy]octyloxy}benzene-1,3-diyl bis[4-(4-dodecyloxybenzyloxy)benzoate] (27/8). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from ethyl acetate/hexane. Yield 85%, m.p. 46-48°C. ^1H NMR spectrum (CDCl_3): 0.91 (t, 6 H, $^3J=6.6$, $2 \times \text{CH}_3$); 1.30-1.52 (m, 46 H, $2 \times (\text{CH}_2)_9$ a $5 \times \text{CH}_2$); 1.66 (m, 2 H, $\text{CH}_2\text{CH}_2\text{O}$); 1.82 (tt, 4 H, $^3J=6.4$, $^3J=8.2$, $2 \times \text{CH}_2\text{CH}_2\text{O}$); 3.84 (t, 2 H, $^3J=6.5$, CH_2O); 4.02 (t, 6 H, $^3J=6.5$, $3 \times \text{CH}_2\text{O}$); 4.98 (s, 4 H, $2 \times \text{PhCH}_2\text{O}$); 6.17 (d, 2 H, $^4J=2.3$); 6.23 (dd, 1 H, $^4J=2.1$); 6.97 (d, 4 H, $^3J=9.1$); 7.18 (m, 3 H); 7.32-7.43 (m, 14 H); 8.15 (d, 4 H, $^3J=9.1$); 8.32 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 ($2 \times \text{C}$); 164.1 ($4 \times \text{C}$); 161.3 (C); 160.9 ($2 \times \text{C}$); 155.8 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 144.2 (C); 137.1 ($2 \times \text{C}$); 132.7 ($4 \times \text{CH}$); 132.2 ($4 \times \text{CH}$); 128.8 ($4 \times \text{CH}$); 128.2 ($2 \times \text{CH}$); 127.8 ($4 \times \text{CH}$); 126.7 ($2 \times \text{C}$); 123.5 (CH); 122.4 ($4 \times \text{CH}$); 121.5 ($2 \times \text{CH}$); 121.1 ($2 \times \text{C}$); 114.7 ($4 \times \text{CH}$); 94.7 ($3 \times \text{CH}$); 74.6 (CH_2); 70.3 ($2 \times \text{CH}_2$); 68.6 ($2 \times \text{CH}_2$); 68.3 (CH_2); 32.2 ($2 \times \text{CH}_2$); 30.5 (CH_2); 29.9 ($6 \times \text{CH}_2$); 29.8 ($4 \times \text{CH}_2$); 29.6 ($2 \times \text{CH}_2$); 29.4 ($3 \times \text{CH}_2$); 29.3 ($2 \times \text{CH}_2$); 26.2 ($3 \times \text{CH}_2$); 26.1 (CH_2); 23.0 ($2 \times \text{CH}_2$); 14.4 ($2 \times \text{CH}_3$).

2-{12-[3,5-Bis(benzyloxy)phenoxy]dodecyloxy}benzene-1,3-diyl bis[4-(4-dodecyloxybenzyloxy)benzoate] (27/12). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from ethyl acetate/hexane. Yield 90%, m.p. 55°C. ^1H NMR spectrum (CDCl_3): 0.92 (t, 6 H, $^3J=6.5$, $2 \times \text{CH}_3$); 1.31-1.52 (m, 54 H, $3 \times (\text{CH}_2)_9$); 1.73 (tt, 2 H, $^3J=6.7$, $^3J=7.6$, $\text{CH}_2\text{CH}_2\text{O}$); 1.84 (tt, 4 H, $^3J=6.7$, $^3J=7.6$, $2 \times \text{CH}_2\text{CH}_2\text{O}$); 3.88 (t, 2 H, $^3J=6.6$, CH_2O); 4.05 (m, 6 H, $3 \times \text{CH}_2\text{O}$); 5.01 (s, 4 H, $2 \times \text{PhCH}_2\text{O}$); 6.20 (d, 2 H, $^4J=2.1$); 6.27 (dd, 1 H, $^4J=1.8$); 7.00 (d, 4 H, $^3J=8.8$); 7.19 (m, 3 H); 7.33-7.45 (m, 14 H); 8.18 (d, 4 H,

$^3J=8.8$); 8.33 (d, 4 H, $^3J=8.5$). ^{13}C NMR spectrum (CDCl_3): 164.5 (2 \times C); 164.1 (4 \times C); 161.3 (C); 160.9 (2 \times C); 155.8 (2 \times C); 145.1 (2 \times C); 144.2 (C); 137.2 (2 \times C); 132.7 (4 \times CH); 132.2 (4 \times CH); 128.8 (4 \times CH); 128.2 (2 \times CH); 127.8 (4 \times CH); 126.8 (2 \times C); 123.5 (CH); 122.4 (4 \times CH); 121.4 (2 \times CH); 121.2 (2 \times C); 114.7 (4 \times CH); 94.9 (2 \times CH); 94.7 (CH); 74.0 (CH_2); 70.3 (2 \times CH_2); 68.6 (2 \times CH_2); 68.3 (CH_2); 32.2 (2 \times CH_2); 30.5 (CH_2); 29.9 (8 \times CH_2); 29.8 (4 \times CH_2); 29.7 (2 \times CH_2); 29.6 (4 \times CH_2); 29.5 (CH_2); 29.4 (2 \times CH_2); 26.3 (4 \times CH_2); 23.0 (2 \times CH_2); 14.4 (2 \times CH_3).

2-[2-(3,5-Dihydroxyphenoxy)ethoxy]benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)-benzoate] (28/2). Yield 86%, m.p. 112°C. ^1H NMR spectrum (CDCl_3): 0.89 (t, 6 H, $^3J=6.6$, 2 \times CH_3); 1.28-1.48 (m, 36 H, 2 \times (CH_2)₉); 1.83 (tt, 4 H, $^3J=6.7$, $^3J=7.9$, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 3.76 (m, 2 H, CH_2O); 4.05 (t, 4 H, $^3J=6.5$, 2 \times CH_2O); 4.23 (m, 2 H, CH_2O); 5.41 (d, 2 H, $^4J=2.1$); 5.88 (dd, 1 H, $^4J=2.1$); 6.30 (s, 2 H, 2 \times OH); 6.98 (d, 4 H, $^3J=9.1$); 7.21 (m, 3 H); 7.35 (d, 4 H, $^3J=8.8$); 8.15 (d, 4 H, $^3J=9.1$); 8.30 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 165.8 (2 \times C); 164.4 (2 \times C); 164.3 (2 \times C); 160.4 (C); 158.1 (2 \times C); 155.5 (2 \times C); 145.8 (2 \times C); 143.0 (C); 132.9 (4 \times CH); 132.4 (4 \times CH); 127.0 (2 \times C); 124.5 (CH); 122.6 (4 \times CH); 121.5 (2 \times CH); 120.6 (2 \times C); 114.8 (4 \times CH); 96.1 (CH); 94.2 (2 \times CH); 72.4 (CH_2); 68.7 (2 \times CH_2); 66.8 (CH_2); 32.2 (2 \times CH_2); 29.9 (6 \times CH_2); 29.8 (4 \times CH_2); 29.6 (2 \times CH_2); 29.3 (2 \times CH_2); 26.2 (2 \times CH_2); 22.9 (2 \times CH_2); 14.4 (2 \times CH_3).

2-[4-(3,5-Dihydroxyphenoxy)butoxy]benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)-benzoate] (28/4). Yield 93%, m.p. 65°C. ^1H NMR spectrum (CDCl_3): 0.89 (t, 6 H, $^3J=6.7$, 2 \times CH_3); 1.28-1.48 (m, 36 H, 2 \times (CH_2)₉); 1.65 (m, 4 H, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 1.83 (tt, 4 H, $^3J=6.7$, $^3J=7.9$, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 3.53 (t, 2 H, $^3J=6.0$, CH_2O); 4.04 (m, 6 H, 3 \times CH_2O); 5.79 (d, 2 H, $^4J=2.1$); 5.91 (dd, 1 H, $^4J=1.8$); 6.26 (bs, 2 H, 2 \times OH); 6.99 (d, 4 H, $^3J=8.8$); 7.17 (m, 3 H); 7.37 (d, 4 H, $^3J=8.8$); 8.15 (d, 4 H, $^3J=9.1$); 8.29 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 165.4 (2 \times C); 164.3 (2 \times C); 164.2 (2 \times C); 160.9 (C); 158.1 (2 \times C); 155.6 (2 \times C); 145.0 (2 \times C); 144.0 (C); 132.8 (4 \times CH); 132.2 (4 \times CH); 126.7 (2 \times C); 123.7 (CH); 122.5 (4 \times CH); 121.5 (2 \times CH); 120.7 (2 \times C); 114.8 (4 \times CH); 95.8 (CH); 94.6 (2 \times CH); 74.1 (CH_2); 68.7 (2 \times CH_2); 67.1 (CH_2); 32.2 (2 \times CH_2); 29.9 (6 \times CH_2); 29.8 (4 \times CH_2); 29.6 (2 \times CH_2); 29.3 (2 \times CH_2); 27.2 (CH_2); 26.2 (2 \times CH_2); 25.7 (CH_2); 22.9 (2 \times CH_2); 14.4 (2 \times CH_3).

2-[5-(3,5-Dihydroxyphenoxy)pentyl]benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (28/5). Yield 90%, m.p. 116°C. ^1H NMR spectrum (CDCl_3): 0.89 (t, 6 H, $^3J=6.7$, 2 \times CH_3); 1.28-1.55 (m, 42 H, 2 \times (CH_2)₉ a 3 \times CH_2); 1.82 (tt, 4 H, $^3J=6.7$, $^3J=7.9$, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 3.45 (t, 2 H, $^3J=6.3$, CH_2O); 4.04 (m, 6 H, 3 \times CH_2O); 5.86 (d, 2 H, $^4J=2.1$); 5.90 (dd, 1 H, $^3J=2.1$); 6.21 (s, 2 H, 2 \times OH); 6.98 (d, 4 H, $^3J=9.1$); 7.15 (m, 3 H); 7.37 (d, 4 H, $^3J=8.8$); 8.14 (d, 4 H, $^3J=8.8$); 8.28 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 165.2 (2 \times C); 164.3 (4 \times C); 161.1 (C); 158.1 (2 \times C); 155.7 (2 \times C); 145.1 (2 \times C); 143.9 (C); 132.8 (4 \times CH); 132.2 (4 \times CH); 126.7 (2 \times C); 123.7 (CH); 122.4 (4 \times CH); 121.5 (2 \times CH); 120.8 (2 \times C); 114.8 (4 \times CH); 95.8 (CH); 94.6 (2 \times CH); 74.1 (CH_2); 68.7 (2 \times CH_2); 67.6 (CH_2); 32.2 (2 \times CH_2); 30.0 (CH_2); 29.9 (6 \times CH_2); 29.8 (4 \times CH_2); 29.6 (2 \times CH_2); 29.3 (2 \times CH_2); 29.0 (CH_2); 26.2 (2 \times CH_2); 22.9 (2 \times CH_2); 22.8 (CH_2); 14.4 (2 \times CH_3).

2-[6-(3,5-Dihydroxyphenoxy)hexyloxy]benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)-benzoate] (28/6). Yield 83%, m.p. 102-103.5°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³J=6.5, 2 × CH₃); 1.28-1.47 (m, 44 H, 2 × (CH₂)₉ a 4 × CH₂); 1.82 (tt, 4 H, ³J=6.7, ³J=7.9, 2 × CH₂CH₂O); 3.61 (t, 2 H, ³J=6.4, CH₂O); 4.00 (t, 2 H, ³J=6.2, CH₂O); 4.03 (t, 4 H, ³J=6.5, 2 × CH₂O); 5.85 (dd, 1 H, ⁴J=2.1); 5.89 (d, 2 H, ⁴J=2.1); 6.07 (s, 2 H, 2 × OH); 6.97 (d, 4 H, ³J=8.8); 7.15 (m, 3 H); 7.37 (d, 4 H, ³J=8.8); 8.14 (d, 4 H, ³J=8.8); 8.28 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.9 (2 × C); 164.5 (2 × C); 164.2 (2 × C); 161.2 (C); 158.0 (2 × C); 155.8 (2 × C); 145.0 (2 × C); 144.0 (C); 132.8 (4 × CH); 132.2 (4 × CH); 126.5 (2 × C); 123.7 (CH); 122.4 (4 × CH); 121.5 (2 × CH); 120.9 (2 × C); 114.7 (4 × CH); 95.8 (CH); 94.8 (2 × CH); 74.5 (CH₂); 68.7 (2 × CH₂); 67.7 (CH₂); 32.2 (2 × CH₂); 30.2 (CH₂); 29.9 (6 × CH₂); 29.8 (4 × CH₂); 29.6 (2 × CH₂); 29.3 (2 × CH₂); 28.9 (CH₂); 26.2 (2 × CH₂); 25.7 (CH₂); 25.6 (CH₂); 22.9 (2 × CH₂); 14.4 (2 × CH₃).

2-[8-(3,5-Dihydroxyphenoxy)octyloxy]benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)-benzoate] (28/8). Yield 87%, m.p. 104.5-105.5°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³J=6.6, 2 × CH₃); 1.28-1.47 (m, 46 H, 2 × (CH₂)₉ a 5 × CH₂); 1.58 (m, 2 H, CH₂CH₂O); 1.82 (tt, 4 H, ³J=6.7, ³J=7.6, 2 × CH₂CH₂O); 3.74 (t, 2 H, ³J=6.3, CH₂O); 4.01 (m, 6 H, 3 × CH₂O); 5.81 (dd, 1 H, ⁴J=1.8); 5.92 (d, 2 H, ⁴J=1.8); 6.17 (bs, 2 H, 2 × OH); 6.97 (d, 4 H, ³J=8.8); 7.16 (m, 3 H); 7.37 (d, 4 H, ³J=8.8); 8.14 (d, 4 H, ³J=8.8); 8.28 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.8 (2 × C); 164.6 (2 × C); 164.1 (2 × C); 161.3 (C); 158.0 (2 × C); 155.8 (2 × C); 145.0 (2 × C); 144.0 (C); 132.7 (4 × CH); 132.3 (4 × CH); 126.5 (2 × C); 123.7 (CH); 122.4 (4 × CH); 121.5 (2 × CH); 121.0 (2 × C); 114.7 (4 × CH); 95.8 (CH); 94.8 (2 × CH); 74.8 (CH₂); 68.7 (2 × CH₂); 68.1 (CH₂); 32.2 (2 × CH₂); 30.3 (CH₂); 29.9 (6 × CH₂); 29.8 (4 × CH₂); 29.6 (3 × CH₂); 29.3 (2 × CH₂); 29.2 (2 × CH₂); 26.2 (2 × CH₂); 26.0 (CH₂); 25.9 (CH₂); 23.0 (2 × CH₂); 14.4 (2 × CH₃).

2-[12-(3,5-Dihydroxyphenoxy)dodecyloxy]benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (28/12). Yield 94%, m.p. 72°C. ¹H NMR spectrum (CDCl₃): 0.90 (t, 6 H, ³J=6.4, 2 × CH₃); 1.29-1.51 (m, 54 H, 3 × (CH₂)₉); 1.66 (tt, 2 H, ³J=6.8, ³J=7.6, CH₂CH₂O); 1.83 (tt, 4 H, ³J=6.8, ³J=7.9, 2 × CH₂CH₂O); 3.79 (t, 2 H, ³J=6.5, CH₂O); 4.03 (m, 6 H, 3 × CH₂O); 5.82 (dd, 1 H, ⁴J=2.1); 5.91 (s, 2 H, 2 × OH); 5.94 (d, 2 H, ⁴J=2.1); 6.99 (d, 4 H, ³J=9.1); 7.17 (m, 3 H); 7.39 (d, 4 H, ³J=8.8); 8.16 (d, 4 H, ³J=9.1); 8.29 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.7 (2 × C); 164.5 (2 × C); 164.1 (2 × C); 161.4 (C); 157.9 (2 × C); 155.8 (2 × C); 145.0 (2 × C); 144.1 (C); 132.7 (4 × CH); 132.2 (4 × CH); 126.5 (2 × C); 123.7 (CH); 122.4 (4 × CH); 121.5 (2 × CH); 121.1 (2 × C); 114.7 (4 × CH); 95.8 (CH); 94.9 (2 × CH); 74.8 (CH₂); 68.7 (2 × CH₂); 68.1 (CH₂); 32.2 (2 × CH₂); 30.5 (CH₂); 29.9 (8 × CH₂); 29.8 (6 × CH₂); 29.6 (4 × CH₂); 29.5 (CH₂); 29.3 (2 × CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 22.9 (2 × CH₂); 14.4 (2 × CH₃).

5-(2-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}ethoxy)benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (D2-12). Purification by column chromatography (toluene/tert-butyl methyl ether 30/1) and crystallisation from a chloroform/hexane mixture, yield 94%, m.p. 103°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 12 H, ³J=6.5, 4 × CH₃); 1.28-1.46 (m, 72 H, 4 × (CH₂)₉); 1.81 (tt, 8 H, ³J=6.7, ³J=7.9, 4 × CH₂CH₂O); 4.00 (t, 4 H, ³J=6.5, 2 × CH₂O); 4.06 (m, 6 H, 3 × CH₂O); 4.40 (m, 2 H, CH₂O); 6.37 (d, 2 H, ⁴J=2.1); 6.75 (dd, 1 H, ⁴J=2.1); 6.95 (d, 4 H, ³J=8.8); 6.99 (d, 4 H, ³J=9.1); 7.21 (m, 3 H); 7.28 (d, 4 H,

$^3J=9.1$); 7.35 (d, 4 H, $^3J=8.8$); 8.08 (d, 4 H, $^3J=8.8$); 8.14 (d, 4 H, $^3J=9.1$); 8.20 (d, 4 H, $^3J=9.1$); 8.27 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.4 (4 \times C); 164.1 (4 \times C); 164.0 (4 \times C); 160.0 (C); 155.8 (2 \times C); 155.6 (2 \times C); 151.9 (2 \times C); 145.1 (2 \times C); 143.5 (C); 132.6 (8 \times CH); 132.2 (4 \times CH); 132.0 (4 \times CH); 126.8 (2 \times C); 126.5 (2 \times C); 124.2 (CH); 122.4 (4 \times CH); 122.2 (4 \times CH); 121.5 (2 \times CH); 121.2 (4 \times C); 114.6 (8 \times CH); 108.5 (CH); 106.2 (2 \times CH); 72.2 (CH_2); 68.6 (4 \times CH_2); 67.8 (CH_2); 32.2 (4 \times CH_2); 29.9 (8 \times CH_2); 29.8 (12 \times CH_2); 29.6 (4 \times CH_2); 29.3 (4 \times CH_2); 26.2 (4 \times CH_2); 22.9 (4 \times CH_2); 14.3 (4 \times CH_3). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{118}\text{H}_{142}\text{O}_{22}\text{Na}$ 1933.9896; found: 1933.9876.

5-(4-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (D4-12). Yield 99%, m.p. 102°C (toluene/ethanol). ^1H NMR spectrum (CDCl_3): 0.90 (t, 12 H, $^3J=6.5$, 4 \times CH_3); 1.29-1.49 (m, 72 H, 4 \times (CH_2)₉); 1.72 (m, 4 H, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 1.81 (m, 8 H, 4 \times $\text{CH}_2\text{CH}_2\text{O}$); 3.74 (m, 2 H, CH_2O); 4.02 (t, 4 H, $^3J=6.4$, 2 \times CH_2O); 4.06 (t, 4 H, $^3J=6.5$, 2 \times CH_2O); 4.11 (m, 2 H, CH_2O); 6.64 (d, 2 H, $^4J=2.1$); 6.76 (dd, 1 H, $^4J=1.8$, $^4J=2.1$); 6.95 (d, 4 H, $^3J=9.1$); 7.00 (d, 4 H, $^3J=9.1$); 7.18 (m, 3 H); 7.32 (d, 4 H, $^3J=8.8$); 7.38 (d, 4 H, $^3J=8.8$); 8.12 (d, 4 H, $^3J=9.1$); 8.16 (d, 4 H, $^3J=9.1$); 8.20 (d, 4 H, $^3J=8.8$); 8.30 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 (2 \times C); 164.4 (2 \times C); 164.2 (4 \times C); 164.1 (2 \times C); 164.0 (2 \times C); 160.5 (C); 155.8 (2 \times C); 155.6 (2 \times C); 152.1 (2 \times C); 145.1 (2 \times C); 143.9 (C); 132.6 (8 \times CH); 132.1 (4 \times CH); 132.0 (4 \times CH); 126.9 (2 \times C); 126.6 (2 \times C); 123.7 (CH); 122.5 (4 \times CH); 122.2 (4 \times CH); 121.5 (2 \times CH); 121.2 (4 \times C); 114.6 (8 \times CH); 108.1 (CH); 106.3 (2 \times CH); 73.9 (CH_2); 68.6 (4 \times CH_2); 68.1 (CH_2); 32.2 (4 \times CH_2); 29.9 (8 \times CH_2); 29.8 (12 \times CH_2); 29.6 (4 \times CH_2); 29.3 (4 \times CH_2); 27.0 (CH_2); 26.2 (4 \times CH_2); 25.9 (CH_2); 22.9 (4 \times CH_2); 14.3 (4 \times CH_3). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{120}\text{H}_{146}\text{O}_{22}\text{Na}$ 1962.0210; found 1962.0232.

5-(5-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}pentyloxy)benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (D5-12). Yield 80%, m.p. 72°C (toluene/ethanol). ^1H NMR spectrum (CDCl_3): 0.89 (t, 12 H, $^3J=6.4$, 4 \times CH_3); 1.27-1.56 (m, 78 H, 36 \times CH_2); 1.81 (m, 8 H, 4 \times $\text{CH}_2\text{CH}_2\text{O}$); 3.66 (t, 2 H, $^3J=6.0$, CH_2O); 4.03 (m, 10 H, 5 \times CH_2O); 6.67 (d, 2 H, $^4J=2.1$); 6.73 (dd, 1 H, $^4J=2.1$); 6.94 (d, 4 H, $^3J=9.1$); 6.99 (d, 4 H, $^3J=8.8$); 7.17 (m, 3 H); 7.32 (d, 4 H, $^3J=8.8$); 7.36 (d, 4 H, $^3J=8.8$); 8.11 (d, 4 H, $^3J=8.8$); 8.15 (d, 4 H, $^3J=8.8$); 8.17 (d, 4 H, $^3J=8.8$); 8.30 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 (4 \times C); 164.2 (4 \times C); 164.0 (4 \times C); 160.6 (C); 155.8 (2 \times C); 155.6 (2 \times C); 152.1 (2 \times C); 145.1 (2 \times C); 144.0 (C); 132.6 (8 \times CH); 132.1 (4 \times CH); 132.0 (4 \times CH); 126.8 (2 \times C); 126.6 (2 \times C); 123.6 (CH); 122.5 (4 \times CH); 122.3 (4 \times CH); 121.5 (2 \times CH); 121.2 (2 \times C); 121.1 (2 \times C); 114.6 (8 \times CH); 108.0 (CH); 106.3 (2 \times CH); 74.2 (CH_2); 68.6 (4 \times CH_2); 68.3 (CH_2); 32.2 (4 \times CH_2); 30.2 (CH_2); 29.9 (12 \times CH_2); 29.8 (8 \times CH_2); 29.6 (4 \times CH_2); 29.3 (4 \times CH_2); 29.0 (CH_2); 26.2 (4 \times CH_2); 22.9 (5 \times CH_2); 14.4 (4 \times CH_3). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{121}\text{H}_{148}\text{O}_{22}\text{Na}$ 1976.0366; found: 1976.0388.

5-(6-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}hexyloxy)benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (D6-12). Yield 93%, m.p. 120°C

(toluene/ethanol). ^1H NMR spectrum (CDCl_3): 0.89 (t, 12 H, $^3J=6.7$, $4 \times \text{CH}_3$); 1.28-1.49 (m, 80 H, $40 \times \text{CH}_2$); 1.82 (tt, 8 H, $^3J=6.7$, $^3J=7.4$, $4 \times \text{CH}_2\text{CH}_2\text{O}$); 3.79 (t, 2 H, $^3J=6.2$, CH_2O); 4.03 (m, 10 H, $5 \times \text{CH}_2\text{O}$); 6.70 (d, 2 H, $^4J=1.8$); 6.76 (dd, 1 H, $^4J=2.0$); 6.95 (d, 4 H, $^3J=9.1$); 6.99 (d, 4 H, $^3J=9.1$); 7.17 (m, 3 H); 7.35 (d, 4 H, $^3J=8.8$); 7.39 (d, 4 H, $^3J=8.5$); 8.12 (d, 4 H, $^3J=8.8$); 8.16 (d, 4 H, $^3J=9.1$); 8.21 (d, 4 H, $^3J=8.8$); 8.31 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 ($4 \times \text{C}$); 164.2 ($2 \times \text{C}$); 164.1 ($4 \times \text{C}$); 164.0 ($2 \times \text{C}$); 160.7 (C); 155.8 ($2 \times \text{C}$); 155.6 ($2 \times \text{C}$); 152.1 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 144.1 (C); 132.6 ($8 \times \text{CH}$); 132.1 ($4 \times \text{CH}$); 132.0 ($4 \times \text{CH}$); 126.9 ($2 \times \text{C}$); 126.7 ($2 \times \text{C}$); 123.6 (CH); 122.5 ($4 \times \text{CH}$); 122.3 ($4 \times \text{CH}$); 121.5 ($2 \times \text{CH}$); 121.2 ($2 \times \text{C}$); 121.1 ($2 \times \text{C}$); 114.6 ($8 \times \text{CH}$); 107.9 (CH); 106.3 ($2 \times \text{CH}$); 74.4 (CH_2); 68.6 ($4 \times \text{CH}_2$); 68.5 (CH_2); 32.2 ($4 \times \text{CH}_2$); 30.4 (CH_2); 29.9 ($12 \times \text{CH}_2$); 29.8 ($8 \times \text{CH}_2$); 29.6 ($4 \times \text{CH}_2$); 29.3 ($4 \times \text{CH}_2$); 29.0 (CH_2); 26.2 ($4 \times \text{CH}_2$); 26.0 (CH_2); 25.8 (CH_2); 22.9 ($4 \times \text{CH}_2$); 14.4 ($4 \times \text{CH}_3$). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{122}\text{H}_{150}\text{O}_{22}\text{Na}$ 1990.0523; found: 1990.0511.

5-(8-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}octyloxy)benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (D8-12). Yield 77%, m.p. 118°C (toluene/ethanol). ^1H NMR spectrum (CDCl_3): 0.89 (t, 12 H, $^3J=6.5$, $4 \times \text{CH}_3$); 1.27-1.49 (m, 82 H, $41 \times \text{CH}_2$); 1.66 (m, 2 H, $\text{CH}_2\text{CH}_2\text{O}$); 1.82 (tt, 8 H, $^3J=6.7$, $^3J=7.6$, $4 \times \text{CH}_2\text{CH}_2\text{O}$); 3.90 (t, 2 H, $^3J=6.5$, CH_2O); 4.03 (m, 10 H, $5 \times \text{CH}_2\text{O}$); 6.71 (d, 2 H, $^4J=1.8$); 6.77 (dd, 1 H, $^4J=1.0$); 6.96 (d, 4 H, $^3J=8.2$); 6.99 (d, 4 H, $^3J=9.1$); 7.17 (m, 3 H); 7.36 (d, 4 H, $^3J=9.1$); 7.39 (d, 4 H, $^3J=9.1$); 8.14 (d, 4 H, $^3J=9.1$); 8.16 (d, 4 H, $^3J=8.8$); 8.24 (d, 4 H, $^3J=8.8$); 8.31 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 ($4 \times \text{C}$); 164.2 ($2 \times \text{C}$); 164.1 ($6 \times \text{C}$); 160.7 (C); 155.8 ($2 \times \text{C}$); 155.7 ($2 \times \text{C}$); 152.1 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 144.2 (C); 132.6 ($8 \times \text{CH}$); 132.1 ($4 \times \text{CH}$); 132.0 ($4 \times \text{CH}$); 126.9 ($2 \times \text{C}$); 126.7 ($2 \times \text{C}$); 123.5 (CH); 122.4 ($4 \times \text{CH}$); 122.3 ($4 \times \text{CH}$); 121.4 ($2 \times \text{CH}$); 121.2 ($2 \times \text{C}$); 121.1 ($2 \times \text{C}$); 114.7 ($8 \times \text{CH}$); 108.0 (CH); 106.3 ($2 \times \text{CH}$); 74.6 (CH_2); 68.6 ($5 \times \text{CH}_2$); 32.2 ($4 \times \text{CH}_2$); 30.4 (CH_2); 29.9 ($12 \times \text{CH}_2$); 29.8 ($8 \times \text{CH}_2$); 29.6 ($6 \times \text{CH}_2$); 29.3 ($5 \times \text{CH}_2$); 26.2 ($5 \times \text{CH}_2$); 26.0 (CH_2); 22.9 ($4 \times \text{CH}_2$); 14.4 ($4 \times \text{CH}_3$). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{124}\text{H}_{154}\text{O}_{22}\text{Na}$ 2018.0836; found: 2018.0824.

5-(12-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}dodecyloxy)benzene-1,3-diyl bis[4-(4-dodecyloxybenzoyloxy)benzoate] (D12-12). Yield 99%, m.p. 108°C (toluene/ethanol). ^1H NMR spectrum (CDCl_3): 0.89 (t, 12 H, $^3J=6.4$, $4 \times \text{CH}_3$); 1.28-1.48 (m, 88 H, $44 \times \text{CH}_2$); 1.81 (m, 12 H, $6 \times \text{CH}_2\text{CH}_2\text{O}$); 3.93 (t, 2 H, $^3J=6.6$, CH_2O); 3.99 (t, 2 H, $^3J=6.1$, CH_2O); 4.05 (m, 8 H, $4 \times \text{CH}_2\text{O}$); 6.72 (d, 2 H, $^4J=2.1$); 6.78 (dd, 1 H, $^4J=2.1$); 6.98 (d, 8 H, $^3J=9.1$); 7.16 (m, 3 H); 7.37 (d, 4 H, $^3J=8.8$); 7.38 (d, 4 H, $^3J=8.8$); 8.15 (d, 8 H, $^3J=8.5$); 8.26 (d, 4 H, $^3J=9.1$); 8.30 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 ($4 \times \text{C}$); 164.2 ($2 \times \text{C}$); 164.1 ($6 \times \text{C}$); 160.7 (C); 155.7 ($4 \times \text{C}$); 152.2 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 144.1 (C); 132.6 ($8 \times \text{CH}$); 132.1 ($4 \times \text{CH}$); 132.0 ($4 \times \text{CH}$); 126.9 ($2 \times \text{C}$); 126.7 ($2 \times \text{C}$); 123.4 (CH); 122.3 ($8 \times \text{CH}$); 121.4 ($2 \times \text{CH}$); 121.2 ($4 \times \text{C}$); 114.7 ($8 \times \text{CH}$); 108.0 (CH); 106.3 ($2 \times \text{CH}$); 74.7 (CH_2); 68.8 (CH_2); 68.6 ($4 \times \text{CH}_2$); 32.2 ($4 \times \text{CH}_2$); 30.4 (CH_2); 29.9 ($16 \times \text{CH}_2$); 29.8 ($12 \times \text{CH}_2$); 29.6 ($5 \times \text{CH}_2$); 29.3 ($4 \times \text{CH}_2$); 26.2 ($4 \times \text{CH}_2$); 22.9 ($4 \times \text{CH}_2$); 14.3 ($4 \times \text{CH}_3$). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{128}\text{H}_{162}\text{O}_{22}\text{Na}$ 2074.1462; found: 2074.1454.

Synthesis of dimers D4-n (Scheme S4)

Compounds of this series were obtained from the bent-core unit **2/4** and acid chlorides of acids **4/n** by the general methods 6 and 7.

5-(4-{2,6-Bis[4-(4-ethoxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis[4-(4-ethoxybenzoyloxy)benzoate] (D4-2). Yield 92%, m.p. 203°C. ¹H NMR spectrum (CDCl₃): 1.46 (m, 12 H, 4 × CH₃); 1.71 (m, 4 H, 2 × CH₂CH₂O); 3.74 (m, 2 H, CH₂O); 4.11 (m, 10 H, 5 × CH₂O); 6.63 (d, 2 H, ⁴J=1.8); 6.75 (dd, 1 H, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 6.99 (d, 4 H, ³J=9.1); 7.18 (m, 3 H); 7.31 (d, 4 H, ³J=8.8); 7.37 (d, 4 H, ³J=8.8); 8.12 (d, 4 H, ³J=8.8); 8.15 (d, 4 H, ³J=9.1); 8.19 (d, 4 H, ³J=8.5); 8.30 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.5 (4 × C); 164.2 (4 × C); 163.9 (2 × C); 163.8 (2 × C); 160.5 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 143.9 (C); 132.7 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.6 (2 × C); 123.7 (CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.5 (2 × CH); 121.2 (4 × C); 114.6 (8 × CH); 108.1 (CH); 106.3 (2 × CH); 73.9 (CH₂); 68.1 (CH₂); 64.1 (4 × CH₂); 27.0 (CH₂); 25.9 (CH₂); 14.9 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₈₀H₆₆O₂₂Na 1401.3946; found: 1401.3938.

5-(4-{2,6-Bis[4-(4-butoxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis[4-(4-butoxybenzoyloxy)benzoate] (D4-4). Yield 86%, m.p. 163°C. ¹H NMR spectrum (CDCl₃): 0.99 (m, 12 H, 4 × CH₃); 1.51 (m, 8 H, 4 × CH₂); 1.69 (m, 4 H, 2 × CH₂CH₂O); 1.79 (m, 8 H, 4 × CH₂CH₂O); 3.72 (m, 2 H, CH₂O); 4.04 (m, 10 H, 5 × CH₂O); 6.61 (d, 2 H, ⁴J=1.8); 6.73 (dd, 1 H, ⁴J=1.8); 6.94 (d, 4 H, ³J=9.1); 6.99 (d, 4 H, ³J=8.8); 7.17 (m, 3 H); 7.30 (d, 4 H, ³J=8.8); 7.36 (d, 4 H, ³J=8.5); 8.11 (d, 4 H, ³J=8.8); 8.14 (d, 4 H, ³J=8.8); 8.18 (d, 4 H, ³J=8.8); 8.29 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.5 (4 × C); 164.2 (4 × C); 164.1 (2 × C); 164.0 (2 × C); 160.5 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 143.9 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.6 (2 × C); 123.7 (CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.5 (2 × CH); 121.2 (4 × C); 114.6 (8 × CH); 108.1 (CH); 106.3 (2 × CH); 73.9 (CH₂); 68.3 (4 × CH₂); 68.1 (CH₂); 31.4 (4 × CH₂); 27.0 (CH₂); 25.8 (CH₂); 19.4 (4 × CH₂); 14.1 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₈₈H₈₂O₂₂Na 1513.5198; found: 1513.5190.

5-(4-{2,6-Bis[4-(4-hexyloxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis[4-(4-hexyloxybenzoyloxy)benzoate] (D4-6). Yield 70%, m.p. 153°C. ¹H NMR spectrum (CDCl₃): 0.91 (m, 12 H, 4 × CH₃); 1.35 (m, 16 H, 8 × CH₂); 1.47 (m, 8 H, 4 × CH₂); 1.69 (m, 4 H, 2 × CH₂CH₂O); 1.81 (m, 8 H, 4 × CH₂CH₂O); 3.72 (m, 2 H, CH₂O); 4.02 (t, 4 H, ³J=6.5, 2 × CH₂O); 4.05 (m, 6 H, 3 × CH₂O); 6.61 (d, 2 H, ⁴J=2.1); 6.73 (dd, 1 H, ⁴J=1.8, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 6.98 (d, 4 H, ³J=9.1); 7.17 (m, 3 H); 7.30 (d, 4 H, ³J=8.5); 7.36 (d, 4 H, ³J=8.8); 8.11 (d, 4 H, ³J=8.8); 8.14 (d, 4 H, ³J=8.8); 8.18 (d, 4 H, ³J=8.8); 8.29 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.5 (4 × C); 164.2 (4 × C); 164.1 (2 × C); 164.0 (2 × C); 160.5 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 143.9 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.6 (2 × C); 123.7 (CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.5 (2 × CH); 121.2 (4 × C); 114.7 (4 × CH); 114.6 (4 × CH); 108.1 (CH); 106.3 (2 × CH); 73.9 (CH₂); 68.6 (4 × CH₂); 68.1 (CH₂); 31.8 (4 × CH₂); 29.3 (4 ×

CH₂); 27.0 (CH₂); 25.9 (5 × CH₂); 22.8 (4 × CH₂); 14.3 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₉₆H₉₈O₂₂Na 1625.6451; found: 1625.6428.

5-(4-{2,6-Bis[4-(4-octyloxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis[4-(4-octyloxybenzoyloxy)benzoate] (D4-8). Yield 89%, m.p. 154°C. ¹H NMR spectrum (CDCl₃): 0.90 (t, 12 H, ³J=6.7, 4 × CH₃); 1.31-1.48 (m, 40 H, 4 × (CH₂)₅); 1.70 (m, 4 H, 2 × CH₂CH₂O); 1.82 (m, 8 H, 4 × CH₂CH₂O); 3.73 (m, 2 H, CH₂O); 4.02 (t, 4 H, ³J=6.6, 2 × CH₂O); 4.05 (t, 4 H, ³J=6.6, 2 × CH₂O); 4.09 (m, 2 H, CH₂O); 6.63 (d, 2 H, ⁴J=2.0); 6.75 (dd, 1 H, ⁴J=2.0); 6.94 (d, 4 H, ³J=9.2); 6.99 (d, 4 H, ³J=9.2); 7.18 (m, 3 H); 7.31 (d, 4 H, ³J=8.9); 7.37 (d, 4 H, ³J=8.9); 8.11 (d, 4 H, ³J=9.2); 8.15 (d, 4 H, ³J=9.2); 8.19 (d, 4 H, ³J=8.9); 8.30 (d, 4 H, ³J=8.9). ¹³C NMR spectrum (CDCl₃): 164.5 (4 × C); 164.2 (4 × C); 164.1 (2 × C); 164.0 (2 × C); 160.5 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 143.9 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.6 (2 × C); 123.7 (CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.5 (2 × CH); 121.2 (4 × C); 114.6 (8 × CH); 108.1 (CH); 106.3 (2 × CH); 73.9 (CH₂); 68.6 (4 × CH₂); 68.1 (CH₂); 32.0 (4 × CH₂); 29.6 (4 × CH₂); 29.5 (4 × CH₂); 29.3 (4 × CH₂); 27.0 (CH₂); 26.2 (4 × CH₂); 25.9 (CH₂); 22.9 (4 × CH₂); 14.4 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₀₄H₁₁₄O₂₂Na 1737.7704; found: 1737.7728.

5-(4-{2,6-Bis[4-(4-decyloxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis[4-(4-decyloxybenzoyloxy)benzoate] (D4-10). Yield 94%, m.p. 122°C. ¹H NMR spectrum (CDCl₃): 0.90 (t, 12 H, ³J=6.3, 4 × CH₃); 1.28-1.48 (m, 56 H, 4 × (CH₂)₇); 1.71 (m, 4 H, 2 × CH₂CH₂O); 1.81 (m, 8 H, 4 × CH₂CH₂O); 3.73 (m, 2 H, CH₂O); 4.02 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.05 (t, 4 H, ³J=6.5, 2 × CH₂O); 4.10 (m, 2 H, CH₂O); 6.63 (d, 2 H, ⁴J=1.8); 6.75 (dd, 1 H, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 6.99 (d, 4 H, ³J=9.1); 7.18 (m, 3 H); 7.31 (d, 4 H, ³J=8.8); 7.37 (d, 4 H, ³J=8.8); 8.11 (d, 4 H, ³J=8.8); 8.15 (d, 4 H, ³J=9.1); 8.19 (d, 4 H, ³J=8.5); 8.30 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.5 (4 × C); 164.2 (6 × C); 164.0 (2 × C); 160.5 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 143.8 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.6 (2 × C); 123.6 (CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.4 (2 × CH); 121.2 (4 × C); 114.6 (8 × CH); 108.0 (CH); 106.2 (2 × CH); 73.9 (CH₂); 68.6 (4 × CH₂); 68.0 (CH₂); 32.1 (4 × CH₂); 29.8 (8 × CH₂); 29.7 (4 × CH₂); 29.6 (4 × CH₂); 29.3 (4 × CH₂); 27.0 (CH₂); 26.2 (4 × CH₂); 25.9 (CH₂); 22.9 (4 × CH₂); 14.4 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₁₂H₁₃₀O₂₂Na 1849.8957; found: 1849.8970.

Synthesis of non-symmetric dimers Dm-1212-FF, Dm-FF-FF, Dm-12F-12F, D3-11F-11F, and D3-SiF-SiF (Scheme S5-S7)

The series of compounds has been prepared according to Scheme 5-7, resp. Dimers **Dm-1212-FF** were obtained by the reaction of intermediates **28/m** with acid chloride of acid **5**. Purification by column chromatography (toluene/*tert*-butyl methyl ether 30/1) and crystallisation.

5-(2-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}ethoxy)benzene-1,3-diyl bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D2-1212-FF). Crystallisation from ethyl acetate. Yield 91%, m.p. 90°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³J=6.6, 2 × CH₃); 1.28-1.63 (m, 56 H, 28 × CH₂); 1.82 (m, 8 H, 4 × CH₂CH₂O); 2.07 (m, 4 H, 2 × CH₂CF₂); 4.01 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.06 (m, 6 H, 3 × CH₂O); 4.41 (m, 2 H, CH₂O); 6.38 (d, 2 H, ⁴J=1.8); 6.77 (dd, 1 H, ⁴J=2.1); 6.95 (d, 4 H, ³J=8.8); 7.00 (d, 4 H, ³J=9.1); 7.22 (m, 3 H); 7.28 (d, 4 H, ³J=8.8); 7.36 (d, 4 H, ³J=8.8); 8.09 (d, 4 H, ³J=9.1); 8.15 (d, 4 H, ³J=9.1); 8.21 (d, 4 H, ³J=8.8); 8.28 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.4 (4 × C); 164.1 (2 × C); 164.0 (6 × C); 160.0 (C); 155.8 (2 × C); 155.6 (2 × C); 152.0 (2 × C); 145.2 (2 × C); 143.5 (C); 132.6 (8 × CH); 132.2 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.5 (2 × C); 124.2 (CH); 122.4 (4 × CH); 122.2 (4 × CH); 121.5 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 108.5 (CH); 106.2 (2 × CH); 72.3 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 67.9 (CH₂); 32.2 (2 × CH₂); 31.0 (t, J=22.5, 2 × CH₂); 29.9 (6 × CH₂); 29.8 (4 × CH₂); 29.6 (4 × CH₂); 29.4 (2 × CH₂); 29.3 (4 × CH₂); 29.2 (2 × CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 22.9 (2 × CH₂); 20.3 (2 × CH₂); 14.3 (2 × CH₃). ¹⁹F NMR spectrum (CDCl₃): -81.5 (m, 6 F, 2 × CF₃); -115.0 (m, 4 F, 2 × CF₂); -124.9 (m, 4 F, 2 CF₂); -126.4 (m, 4 F, 2 × CF₂). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₁₈H₁₂₄F₁₈O₂₂Na 2257.8200; found: 2257.8205.

5-(3-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}propoxy)benzene-1,3-diyl bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D3-1212-FF). Crystallisation from a toluene/ethanol mixture. Yield 61 %, m.p. 114°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³J=6.6, 2 × CH₃); 1.27-1.62 (m, 56 H, 28 × CH₂); 1.82 (tt, 8 H, ³J=6.9, 4 × CH₂CH₂O); 2.05 (m, 6 H, 2 × CH₂CF₂ a CH₂CH₂O); 3.92 (t, 2 H, ³J=5.4, CH₂O); 4.01 (t, 4 H, ³J=6.5, 2 × CH₂O); 4.06 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.24 (t, 2 H, ³J=5.6, CH₂O); 6.50 (d, 2 H, ⁴J=2.1); 6.75 (dd, 1 H, ⁴J=1.8, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 6.99 (d, 4 H, ³J=9.1); 7.18 (m, 3 H); 7.30 (d, 4 H, ³J=8.8); 7.35 (d, 4 H, ³J=8.8); 8.11 (d, 4 H, ³J=8.8); 8.15 (d, 4 H, ³J=8.8); 8.20 (d, 4 H, ³J=8.8); 8.28 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.4 (4 × C); 164.1 (4 × C); 164.0 (4 × C); 160.2 (C); 155.8 (2 × C); 155.6 (2 × C); 152.0 (2 × C); 145.0 (2 × C); 143.8 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.4 (2 × C); 123.8 (CH); 122.5 (4 × CH); 122.3 (4 × CH); 121.5 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 108.2 (CH); 106.2 (2 × CH); 70.5 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 64.7 (CH₂); 32.2 (2 × CH₂); 31.0 (t, J=22.5, 2 × CH₂); 30.2 (CH₂); 29.9 (6 × CH₂); 29.8 (4 × CH₂); 29.6 (4 × CH₂); 29.4 (2 × CH₂); 29.3 (6 × CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 22.9 (2 × CH₂); 20.3 (2 × CH₂); 14.4 (2 × CH₃). ¹⁹F NMR spectrum (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). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₁₉H₁₂₆F₁₈O₂₂Na 2271.8356; found: 2271.8348.

5-(4-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}butoxy)benzene-1,3-diyl bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D4-12-12-FF). Crystallisation from a toluene/ethanol mixture. Yield 90%, m.p. 89°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³J=6.7, 2 × CH₃); 1.28-1.63 (m, 56 H, 28 × CH₂); 1.71 (m, 4 H, 2 × CH₂CH₂O); 1.83 (m, 8 H, 4 × CH₂CH₂O); 2.07 (m, 4 H, 2 × CH₂CF₂); 3.74 (m, 2 H,

CH₂O); 4.02 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.06 (t, 4 H, ³J=6.3, 2 × CH₂O); 4.10 (m, 2 H, CH₂O); 6.64 (d, 2 H, ³J=2.1); 6.76 (dd, 1 H, ⁴J=2.1); 6.95 (d, 4 H, ³J=9.1); 6.99 (d, 4 H, ³J=9.1); 7.18 (m, 3 H); 7.32 (d, 4 H, ³J=8.5); 7.38 (d, 4 H, ³J=8.8); 8.12 (d, 4 H, ³J=8.8); 8.16 (d, 4 H, ³J=8.8); 8.20 (d, 4 H, ³J=8.5); 8.30 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.5 (2 × C); 164.4 (2 × C); 164.2 (4 × C); 164.0 (4 × C); 160.6 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 143.9 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.6 (2 × C); 123.7 (CH); 122.5 (4 × CH); 122.2 (4 × CH); 121.5 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 108.1 (CH); 106.3 (2 × CH); 73.9 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 68.1 (CH₂); 32.2 (2 × CH₂); 31.0 (t, J=22.5, 2 × CH₂); 29.9 (6 × CH₂); 29.8 (4 × CH₂); 29.6 (4 × CH₂); 29.2 (2 × CH₂); 29.3 (4 × CH₂); 27.0 (CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 25.9 (CH₂); 22.9 (2 × CH₂); 20.3 (2 × CH₂); 14.3 (2 × CH₃). ¹⁹F NMR spectrum (CDCl₃): -81.5 (m, 6 F, 2 × CF₃); -115.0 (m, 4 F, 2 × CF₂); -124.9 (m, 4 F, 2 × CF₂); -126.4 (m, 4 F, 2 × CF₂). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₂₀H₁₂₈F₁₈O₂₂Na 2285.8513; found: 2285.8505.

5-(5-{2,6-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]phenoxy}pentyloxy)benzene-1,3-diyl bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D5-12-12-FF). Crystallisation from a toluene/ethanol mixture. Yield 34 %, m.p. 123°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³J=6.6, 2 × CH₃); 1.27-1.60 (m, 60 H, 30 × CH₂); 1.82 (m, 10 H, 5 × CH₂CH₂O); 2.07 (m, 4 H, 2 × CH₂CF₂); 3.67 (t, 2 H, ³J=6.0, CH₂O); 4.04 (m, 10 H, 5 × CH₂O); 6.67 (d, 2 H, ⁴J=2.1); 6.74 (dd, 1 H, ⁴J=2.1); 6.94 (d, 4 H, ³J=9.1); 6.99 (d, 4 H, ³J=9.1); 7.17 (m, 3 H); 7.32 (d, 4 H, ³J=8.8); 7.36 (d, 4 H, ³J=9.1); 8.11 (d, 4 H, ³J=8.8); 8.15 (d, 4 H, ³J=9.1); 8.18 (d, 4 H, ³J=9.1); 8.30 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.5 (2 × C); 164.4 (2 × C); 164.1 (4 × C); 164.0 (4 × C); 160.6 (C); 155.8 (2 × C); 155.6 (2 × C); 152.1 (2 × C); 145.1 (2 × C); 144.0 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.7 (2 × C); 123.6 (CH); 122.5 (4 × CH); 122.2 (4 × CH); 121.4 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 108.0 (CH); 106.3 (2 × CH); 74.2 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 68.4 (CH₂); 32.1 (2 × CH₂); 31.0 (t, J=22.5, 2 × CH₂); 30.0 (CH₂); 29.9 (6 × CH₂); 29.8 (6 × CH₂); 29.6 (2 × CH₂); 29.3 (6 × CH₂); 29.2 (2 × CH₂); 29.0 (CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 22.9 (3 × CH₂); 20.3 (2 × CH₂); 14.3 (2 × CH₃). ¹⁹F NMR spectrum (CDCl₃): -81.5 (m, 6 F, 2 × CF₃); -115.0 (m, 4 F, 2 × CF₂); -124.9 (m, 4 F, 2 × CF₂); -126.4 (m, 4 F, 2 × CF₂). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₂₁H₁₃₀F₁₈O₂₂Na 2299.8669; found: 2299.8662.

Compounds **Dm-FF-FF** have been obtained by acylation of the bent-core units **2/m** with acid chloride of acid **5**. Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture.

5-[3-(2,6-Bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]-benzoyloxy}phenoxy)propoxy]benzene-1,3-diyl bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D3-FF-FF). Yield 85%, m.p. 84°C. ¹H NMR spectrum (CDCl₃): 1.41-1.50 (m, 32 H, 4 × (CH₂)₄); 1.62 (m, 8 H, 4 × CH₂CH₂CF₂); 1.83 (m, 8 H, 4 × CH₂CH₂O); 2.07 (m, 10 H, 4 × CH₂CF₂ a CH₂CH₂O); 3.93 (t, 2 H, ³J=5.6, CH₂O); 4.02 (t, 4 H, ³J=6.7, 2 × CH₂O); 4.06 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.25 (t, 2 H, ³J=5.6, CH₂O); 6.51 (d, 2 H, ⁴J=1.8); 6.76 (dd, 1 H, ⁴J=1.8, ⁴J=2.1); 6.95 (d, 4 H, ³J=8.8); 7.00 (d, 4

H, $^3J=9.1$); 7.18 (m, 3 H); 7.31 (d, 4 H, $^3J=8.8$); 7.35 (d, 4 H, $^3J=8.8$); 8.12 (d, 4 H, $^3J=8.8$); 8.16 (d, 4 H, $^3J=8.8$); 8.21 (d, 4 H, $^3J=8.5$); 8.28 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.4 (4 \times C); 164.1 (4 \times C); 164.0 (4 \times C); 160.3 (C); 155.8 (2 \times C); 155.6 (2 \times C); 152.0 (2 \times C); 145.0 (2 \times C); 143.8 (C); 132.6 (8 \times CH); 132.1 (4 \times CH); 132.0 (4 \times CH); 126.9 (2 \times C); 126.4 (2 \times C); 123.8 (CH); 122.4 (4 \times CH); 122.2 (4 \times CH); 121.5 (2 \times CH); 121.3 (4 \times C); 114.6 (8 \times CH); 108.2 (CH); 106.2 (2 \times CH); 70.5 (CH_2); 68.5 (2 \times CH_2); 68.4 (2 \times CH_2); 64.7 (CH_2); 31.0 (t, $J=22.5$, 4 \times CH_2); 30.2 (CH_2); 29.4 (4 \times CH_2); 29.3 (4 \times CH_2); 29.2 (8 \times CH_2); 26.1 (4 \times CH_2); 20.3 (4 \times CH_2). ^{19}F NMR spectrum (CDCl_3): -81.5 (m, 12 F, 2 \times CF_3); -115.1 (m, 8 F, 2 \times CF_2); -124.9 (m, 8 F, 2 \times CF_2); -126.5 (m, 8 F, 2 \times CF_2). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{119}\text{H}_{108}\text{F}_{36}\text{O}_{22}\text{Na}$ 2595.6659; found: 2595.6650.

5-[4-(2,6-Bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]-benzoyloxy}phenoxy)butoxy]benzene-1,3-diy bis{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D4-FF-FF). Yield 86 %, m.p. 86°C. ^1H NMR spectrum (CDCl_3): 1.40-1.50 (m, 32 H, 4 \times (CH_2)₄); 1.62 (m, 8 H, 4 \times $\text{CH}_2\text{CH}_2\text{CF}_2$); 1.71 (m, 4 H, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 1.83 (m, 8 H, 4 \times $\text{CH}_2\text{CH}_2\text{O}$); 2.07 (m, 8 H, 4 \times CH_2CF_2); 3.74 (m, 2 H, CH_2O); 4.03 (t, 4 H, $^3J=6.4$, 2 \times CH_2O); 4.06 (t, 4 H, $^3J=6.3$, 2 \times CH_2O); 4.10 (m, 2 H, CH_2O); 6.64 (d, 2 H, $^4J=2.1$); 6.76 (dd, 1 H, $^4J=1.8$); 6.95 (d, 4 H, $^3J=9.1$); 6.99 (d, 4 H, $^3J=8.8$); 7.19 (m, 3 H); 7.32 (d, 4 H, $^3J=8.5$); 7.38 (d, 4 H, $^3J=8.5$); 8.12 (d, 4 H, $^3J=8.8$); 8.16 (d, 4 H, $^3J=9.1$); 8.20 (d, 4 H, $^3J=8.8$); 8.30 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.5 (4 \times C); 164.2 (4 \times C); 164.0 (4 \times C); 160.5 (C); 155.8 (2 \times C); 155.6 (2 \times C); 152.1 (2 \times C); 145.1 (2 \times C); 143.9 (C); 132.6 (8 \times CH); 132.1 (4 \times CH); 132.0 (4 \times CH); 126.9 (2 \times C); 126.6 (2 \times C); 123.7 (CH); 122.5 (4 \times CH); 122.2 (4 \times CH); 121.5 (2 \times CH); 121.3 (4 \times C); 114.6 (8 \times CH); 108.1 (CH); 106.3 (2 \times CH); 73.9 (CH_2); 68.5 (4 \times CH_2); 68.1 (CH_2); 31.0 (t, $J=22.5$, 4 \times CH_2); 29.4 (4 \times CH_2); 29.3 (4 \times CH_2); 29.2 (8 \times CH_2); 26.9 (CH_2); 26.1 (4 \times CH_2); 25.9 (CH_2); 20.3 (4 \times CH_2). ^{19}F NMR spectrum (CDCl_3): -81.5 (m, 12 F, 2 \times CF_3); -115.0 (m, 8 F, 2 \times CF_2); -124.9 (m, 8 F, 2 \times CF_2); -126.5 (m, 8 F, 2 \times CF_2). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{120}\text{H}_{110}\text{F}_{36}\text{O}_{22}\text{Na}$ 2609.6816; found: 2609.6806.

Dimers **Dm-12F-12F** were prepared by a multistep procedure involving acylation of the bent-core unit **3/3** with acid chloride of acid **5**, debenzoylation and second acylation of the intermediate with acid chloride of acid **4/12** and **7**, respectively..

3-Benzyloxy-2-[3-(3-benzyloxy-5-{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)-benzoyloxy]benzoyloxy}phenoxy)propoxy]phenyl {4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (29). Purification was achieved by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture. Yield 81%, m.p. 118-120°C. ^1H NMR spectrum (CDCl_3): 1.41-1.51 (m, 16 H, 2 \times (CH_2)₄); 1.63 (m, 4 H, 2 \times $\text{CH}_2\text{CH}_2\text{CF}_2$); 1.85 (m, 4 H, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 2.08 (m, 6 H, 2 \times CH_2CF_2 a $\text{CH}_2\text{CH}_2\text{O}$); 4.03 (m, 6 H, 3 \times CH_2O); 4.28 (t, 2 H, $^3J=5.8$, CH_2O); 4.99 (s, 2 H, PhCH_2O); 5.13 (s, 2 H, PhCH_2O); 6.29 (dd, 1 H, $^4J=2.1$); 6.33 (dd, 1 H, $^4J=2.2$); 6.47 (dd, 1 H, $^4J=1.8$, $^4J=2.1$); 6.85 (dd, 1 H, $^3J=7.9$, $^4J=1.4$); 6.92 (dd, 1 H, $^3J=8.5$, $^4J=1.5$); 6.97 (d, 2 H, $^3J=9.1$); 7.01 (d, 2 H, $^3J=9.1$); 7.06 (dd, 1 H, $^3J=8.2$); 7.30-7.47 (m, 14 H); 8.14 (d, 2 H, $^3J=8.8$); 8.18 (d, 2 H, $^3J=8.8$); 8.25 (d, 2 H, $^3J=8.5$); 8.27 (d, 2 H, $^3J=8.8$). ^{13}C NMR

spectrum (CDCl₃): 164.5 (2 × C); 164.4 (2 × C); 164.0 (2 × C); 160.8 (C); 160.5 (C); 155.6 (2 × C); 153.3 (C); 152.5 (C); 145.0 (C); 141.1 (C); 137.0 (C); 136.9 (C); 132.7 (4 × CH); 132.0 (4 × CH); 128.8 (4 × CH); 128.2 (2 × CH); 127.8 (2 × CH); 127.5 (2 × CH); 127.2 (C); 126.8 (C); 123.7 (CH); 122.3 (4 × CH); 121.3 (2 × C); 115.9 (CH); 114.6 (4 × CH); 112.4 (CH); 101.4 (CH); 101.3 (CH); 99.6 (CH); 71.4 (CH₂); 70.4 (CH₂); 70.1 (CH₂); 68.5 (2 × CH₂); 65.0 (CH₂); 31.0 (t, *J*=22.5, 2 × CH₂); 30.3 (CH₂); 29.4 (4 × CH₂); 29.3 (4 × CH₂); 26.2 (2 × CH₂); 20.3 (2 × CH₂). ¹⁹F NMR spectrum (CDCl₃): -81.5 (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).

3-Hydroxy-2-[3-(3-hydroxy-5-{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)-benzoyloxy]benzoyloxy}phenoxy)propoxy]phenyl {4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (30). By the general method of debenzoylation, compound **29** was hydrogenolysed and purified by column chromatography (toluene/*tert*-butyl methyl ether 8/1). Yield 87%, m.p. 169.5-171°C. ¹H NMR spectrum (CDCl₃): 1.39-1.49 (m, 16 H, 2 × (CH₂)₄); 1.62 (m, 4 H, 2 × CH₂CH₂CF₂); 1.83 (tt, 4 H, ³*J*=6.7, ³*J*=7.6, 2 × CH₂CH₂O); 2.06 (m, 6 H, 2 × CH₂CF₂ a CH₂CH₂O); 4.05 (m, 6 H, 3 × CH₂O); 4.19 (t, 2 H, ³*J*=6.0, CH₂O); 6.02 (dd, 1 H, ⁴*J*=2.1); 6.28 (dd, 1 H, ⁴*J*=2.1); 6.31 (bs, 2 H, OH a Ar-H); 6.53 (s, 1 H, OH); 6.73 (dd, 1 H, ³*J*=8.0, ⁴*J*=1.6); 6.88 (dd, 1 H, ³*J*=8.2, ⁴*J*=1.5); 6.98 (d, 2 H, ³*J*=9.1); 6.99 (d, 2 H, ³*J*=8.8); 7.02 (dd, 1 H, ³*J*=8.2); 7.33 (d, 2 H, ³*J*=9.1); 7.36 (d, 2 H, ³*J*=9.1); 8.14 (d, 2 H, ³*J*=8.8); 8.16 (d, 2 H, ³*J*=8.8); 8.22 (d, 2 H, ³*J*=8.8); 8.28 (d, 2 H, ³*J*=8.8). ¹³C NMR spectrum (CDCl₃): 165.6 (C); 164.6 (2 × C); 164.3 (C); 164.1 (C); 164.0 (C); 160.2 (C); 158.0 (C); 155.6 (C); 155.5 (C); 152.6 (C); 150.5 (C); 143.8 (C); 138.4 (C); 132.9 (2 × CH); 132.7 (2 × CH); 132.2 (2 × CH); 132.0 (2 × CH); 127.1 (C); 126.9 (C); 124.5 (CH); 122.5 (2 × CH); 122.3 (2 × CH); 121.2 (C); 120.8 (C); 114.9 (CH); 114.8 (2 × CH); 114.6 (2 × CH); 113.9 (CH); 102.8 (CH); 100.6 (CH); 99.1 (CH); 71.1 (CH₂); 68.5 (2 × CH₂); 65.0 (CH₂); 31.0 (t, *J*=22.5, 2 × CH₂); 29.9 (CH₂); 29.4 (2 × CH₂); 29.3 (2 × CH₂); 29.2 (4 × CH₂); 26.1 (2 × CH₂); 20.3 (2 × CH₂). ¹⁹F NMR spectrum (CDCl₃): -81.5 (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).

3-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-2-[3-(3-[4-(4-dodecyloxybenzoyloxy)-benzoyloxy]-5-{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoyloxy}phenoxy)propoxy]phenyl {4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D3-12F-12F). Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture. Yield 89%, m.p. 113°C. ¹H NMR spectrum (CDCl₃): 0.89 (t, 6 H, ³*J*=6.3, 2 × CH₃); 1.27-1.48 (m, 52 H, 2 × (CH₂)₄ a 2 × (CH₂)₉); 1.62 (m, 4 H, 2 × CH₂CH₂CF₂); 1.82 (m, 8 H, 4 × CH₂CH₂O); 2.06 (m, 6 H, 2 × CH₂CF₂ a CH₂CH₂O); 3.92 (t, 2 H, ³*J*=5.6, CH₂O); 4.01 (t, 4 H, ³*J*=6.7, 2 × CH₂O); 4.06 (t, 4 H, ³*J*=6.5, 2 × CH₂O); 4.23 (t, 2 H, ³*J*=5.6, CH₂O); 6.50 (d, 2 H, ⁴*J*=1.5); 6.75 (dd, 1 H, ⁴*J*=1.8); 6.94 (d, 4 H, ³*J*=8.8); 6.99 (d, 4 H, ³*J*=8.8); 7.18 (m, 3 H); 7.30 (d, 4 H, ³*J*=8.8); 7.34 (d, 4 H, ³*J*=8.5); 8.11 (d, 4 H, ³*J*=8.8); 8.15 (d, 4 H, ³*J*=8.8); 8.20 (d, 4 H, ³*J*=8.8); 8.28 (d, 4 H, ³*J*=8.5). ¹³C NMR spectrum (CDCl₃): 164.4 (4 × C); 164.1 (4 × C); 164.0 (2 × C); 163.9 (2 × C); 160.2 (C); 155.8 (2 × C); 155.6 (2 × C); 152.0 (2 × C); 145.0 (2 × C); 143.8 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0

(4 × CH); 126.9 (2 × C); 126.4 (2 × C); 123.8 (CH); 122.4 (4 × CH); 122.2 (4 × CH); 121.5 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 108.2 (CH); 106.2 (2 × CH); 70.5 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 64.7 (CH₂); 32.2 (2 × CH₂); 31.0 (t, *J*=22.4, 2 × CH₂); 30.2 (CH₂); 29.9 (4 × CH₂); 29.8 (4 × CH₂); 29.6 (2 × CH₂); 29.4 (4 × CH₂); 29.3 (4 × CH₂); 29.2 (4 × CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 22.9 (2 × CH₂); 20.3 (2 × CH₂); 14.3 (2 × CH₃). ¹⁹F NMR spectrum (CDCl₃): -81.5 (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). HRMS (ESI-LTQ) *m/z*: [M + Na]⁺ calculated: for C₁₁₉H₁₂₆F₁₈O₂₂Na 2271.8356; found: 2271.8346.

3-[4-(4-Undec-10-enyloxybenzoyloxy)benzoyloxy]-2-[3-(3-[4-(4-undec-10-enyloxybenzoyloxy)benzoyloxy]-5-{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoyloxy}phenoxy)propoxy]phenyl {4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} D3-11F-11F. Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture. Yield 84%, m.p. 82°C. ¹H NMR spectrum (CDCl₃): 1.33-1.49 (m, 40 H, 2 × (CH₂)₄ a 2 × (CH₂)₆); 1.62 (m, 4 H, 2 × CH₂CH₂CF₂); 1.82 (m, 8 H, 4 × CH₂CH₂O); 2.07 (m, 10 H, 2 × CH₂CF₂, CH₂CH₂O a 2 × CH₂CH=CH₂); 3.93 (t, 2 H, ³*J*=5.4, CH₂O); 4.02 (t, 4 H, ³*J*=6.6, 2 × CH₂O); 4.06 (t, 4 H, ³*J*=6.4, 2 × CH₂O); 4.25 (t, 2 H, ³*J*=5.5, CH₂O); 4.95 (d, 2 H, ³*J*=10.2, CH₂=CH); 5.01 (d, 2 H, ³*J*=17.9, CH₂=CH); 5.83 (m, 2 H, 2 × CH=CH₂); 6.51 (d, 2 H, ⁴*J*=1.8); 6.77 (dd, 1 H, ⁴*J*=2.1); 6.95 (d, 4 H, ³*J*=8.8); 7.00 (d, 4 H, ³*J*=8.8); 7.19 (m, 3 H); 7.31 (d, 4 H, ³*J*=8.8); 7.36 (d, 4 H, ³*J*=8.5); 8.12 (d, 4 H, ³*J*=9.1); 8.16 (d, 4 H, ³*J*=8.8); 8.21 (d, 4 H, ³*J*=8.5); 8.28 (d, 4 H, ³*J*=8.5). ¹³C NMR spectrum (CDCl₃): 164.4 (4 × C); 164.1 (4 × C); 164.0 (4 × C); 160.3 (C); 155.8 (2 × C); 155.6 (2 × C); 152.0 (2 × C); 145.0 (2 × C); 143.8 (C); 139.4 (2 × CH); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.4 (2 × C); 123.8 (CH); 122.4 (4 × CH); 122.2 (4 × CH); 121.5 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 114.4 (2 × CH₂); 108.2 (CH); 106.2 (2 × CH); 70.5 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 64.8 (CH₂); 34.0 (2 × CH₂); 31.0 (t, *J*=22.5, 2 × CH₂); 30.2 (CH₂); 29.7 (4 × CH₂); 29.6 (2 × CH₂); 29.3 (10 × CH₂); 29.2 (4 × CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 20.3 (2 × CH₂). ¹⁹F NMR spectrum (CDCl₃): -81.5 (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). HRMS (ESI-LTQ) *m/z*: [M + Na]⁺ calculated: for C₁₁₇H₁₁₈F₁₈O₂₂Na 2239.7730; found: 2239.7720.

3-(4-{4-[11-(1,1,3,3,3-Pentamethyldisiloxanyl)undecyloxy]benzoyloxy}benzoyloxy)-2-[3-(3-(4-{4-[11-(1,1,3,3,3-pentamethyldisiloxanyl)undecyloxy]benzoyloxy}benzoyloxy)-5-{4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoyloxy}phenoxy)-propoxy]phenyl {4-[4-(9,9,10,10,11,11,12,12,12-nonafluorododecyloxy)benzoyloxy]benzoate} (D3-SiF-SiF)

To a solution of dimer **D3-11F-11F** (250 mg; 0.11 mmol) and 1,1,1,3,3-pentamethyldisiloxane (40 mg; 0.27 mmol) in dry toluene (12 ml) in an argon atmosphere, a catalytic amount of Karstedt catalyst (2 drops) was added. The mixture was stirred at room temperature for 18 h and evaporated. The crude product was purified by column chromatography (toluene/*tert*-butyl methyl ether 30/1) and crystallised from a toluene/ethanol (1/4) mixture. Yield 260 mg (94%) of dimer **D3-SiF-SiF**, m.p. 62°C. ¹H NMR spectrum (CDCl₃): 0.04 (s, 12 H, 4 × CH₃Si); 0.07 (s, 18 H, 6 × CH₃Si); 0.51 (t, 4 H, ³*J*=7.0, 2 ×

CH₂Si); 1.29-1.48 (m, 48 H, 2 × (CH₂)₄ a 2 × (CH₂)₈); 1.62 (m, 4 H, 2 × CH₂CH₂CF₂); 1.81 (m, 8 H, 4 × CH₂CH₂O); 2.03 (m, 6 H, 2 × CH₂CF₂ a CH₂CH₂O); 3.92 (t, 2 H, ³J=5.7, CH₂O); 4.01 (t, 4 H, ³J=6.5, 2 × CH₂O); 4.06 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.23 (t, 2 H, ³J=5.8, CH₂O); 6.49 (d, 2 H, ⁴J=2.1); 6.74 (dd, 1 H, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 6.99 (d, 4 H, ³J=9.1); 7.18 (m, 3 H); 7.30 (d, 4 H, ³J=8.8); 7.34 (d, 4 H, ³J=8.8); 8.11 (d, 4 H, ³J=8.8); 8.15 (d, 4 H, ³J=9.1); 8.20 (d, 4 H, ³J=8.8); 8.27 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.4 (4 × C); 164.1 (4 × C); 164.0 (2 × C); 163.9 (2 × C); 160.3 (C); 155.8 (2 × C); 155.6 (2 × C); 152.0 (2 × C); 145.0 (2 × C); 143.8 (C); 132.6 (8 × CH); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.4 (2 × C); 123.8 (CH); 122.4 (4 × CH); 122.2 (4 × CH); 121.5 (2 × CH); 121.3 (2 × C); 121.2 (2 × C); 114.6 (8 × CH); 108.2 (CH); 106.2 (2 × CH); 70.5 (CH₂); 68.6 (2 × CH₂); 68.5 (2 × CH₂); 64.8 (CH₂); 33.6 (2 × CH₂); 31.0 (t, J=22.5, 2 × CH₂); 30.2 (CH₂); 29.8 (4 × CH₂); 29.6 (4 × CH₂); 29.3 (12 × CH₂); 26.2 (2 × CH₂); 26.1 (2 × CH₂); 23.5 (2 × CH₂); 20.3 (2 × CH₂); 18.6 (2 × CH₂); 2.2 (6 × CH₃); 0.6 (4 × CH₃). ¹⁹F NMR spectrum (CDCl₃): -81.5 (m, 6 F, 2 × CF₃); -115.0 (m, 4 F, 2 × CF₂); -124.9 (m, 4 F, 2 × CF₂); -126.4 (m, 4 F, 2 × CF₂). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₂₇H₁₅₀F₁₈O₂₄Si₄Na 2536.3554; found: 2536.3599.

Synthesis of polycatenar dimers Dm-12/3 (Scheme S8)

Compound Dm-12/3 were obtained by acylation of 2/m with acid chloride of acid 6.

5-[3-(2,6-Bis{4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoyloxy}phenoxy)propoxy]-benzene-1,3-diyl bis{4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoate} (D3-12/3).

Purification by column chromatography (toluene/*tert*-butyl methyl ether 30/1) and crystallisation from a toluene/ethanol mixture. Yield 84%, m.p. -30°C. ¹H NMR spectrum (CDCl₃): 0.88 (m, 36 H, 12 × CH₃); 1.27-1.47 (m, 216 H, 12 × (CH₂)₉); 1.80 (m, 24 H, 12 × CH₂CH₂O); 2.02 (tt, 2 H, ³J=5.6, ³J=6.7, CH₂CH₂O); 3.92 (t, 2 H, ³J=5.6, CH₂O); 4.05 (m, 24 H, 12 × CH₂O); 4.23 (t, 2 H, ³J=5.4, CH₂O); 6.50 (d, 2 H, ⁴J=2.1); 6.74 (dd, 1 H, ⁴J=1.8, ⁴J=2.1); 7.19 (m, 3 H); 7.29 (d, 4 H, ³J=8.8); 7.34 (d, 4 H, ³J=8.8); 7.40 (s, 8 H); 8.20 (d, 4 H, ³J=8.5); 8.28 (d, 4 H, ³J=8.8). ¹³C NMR spectrum (CDCl₃): 164.6 (4 × C); 164.1 (4 × C); 160.3 (C); 155.7 (2 × C); 155.6 (2 × C); 153.3 (8 × C); 152.0 (2 × C); 145.0 (2 × C); 143.7 (C); 143.6 (2 × C); 143.5 (2 × C); 132.1 (4 × CH); 132.0 (4 × CH); 126.9 (2 × C); 126.5 (2 × C); 123.9 (CH); 123.6 (2 × C); 123.5 (2 × C); 122.5 (4 × CH); 122.3 (4 × CH); 121.5 (2 × CH); 108.9 (8 × CH); 108.2 (CH); 106.2 (2 × CH); 73.8 (4 × CH₂); 70.6 (CH₂); 69.5 (8 × CH₂); 64.8 (CH₂); 32.2 (12 × CH₂); 30.2 (CH₂); 30.0 (24 × CH₂); 29.9 (24 × CH₂); 29.8 (12 × CH₂); 29.7 (12 × CH₂); 29.6 (12 × CH₂); 26.3 (12 × CH₂); 22.9 (12 × CH₂); 14.4 (12 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]²⁺ calculated: for C₂₁₅H₃₃₆O₃₀Na₂ 3444.4577; found: 3444.4500.

5-[4-(2,6-Bis{4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoyloxy}phenoxy)butoxy]benzene-1,3-diyl bis{4-[3,4,5-tris(dodecyloxy)benzoyloxy]benzoate} (D4-12/3).

Purification by column chromatography (toluene/*tert*-butyl methyl ether 30/1) and crystallisation from a toluene/ethanol mixture. Yield 96%, m.p. -30°C. ¹H NMR spectrum (CDCl₃): 0.89 (m, 36 H, 12 × CH₃); 1.27-1.49 (m, 216 H, 12 × (CH₂)₉); 1.74-1.85 (m, 28 H, 14 × CH₂CH₂O); 3.76 (m, 2 H, CH₂O); 4.06 (m, 26 H, 13 × CH₂O); 6.63 (d, 2 H, ⁴J=2.1); 6.74 (dd, 1 H, ⁴J=1.8, ⁴J=2.1);

7.19 (m, 3 H); 7.31 (d, 4 H, $^3J=8.8$); 7.37 (d, 4 H, $^3J=8.8$); 7.41 (s, 4 H); 7.42 (s, 4 H); 8.20 (d, 4 H, $^3J=8.8$); 8.31 (d, 4 H, $^3J=8.8$). ^{13}C NMR spectrum (CDCl_3): 164.6 (4 \times C); 164.2 (2 \times C); 164.1 (2 \times C); 160.5 (C); 155.8 (2 \times C); 155.6 (2 \times C); 153.3 (4 \times C); 153.2 (4 \times C); 152.1 (2 \times C); 145.1 (2 \times C); 143.9 (C); 143.6 (2 \times C); 143.5 (2 \times C); 132.2 (4 \times CH); 132.0 (4 \times CH); 127.0 (2 \times C); 126.7 (2 \times C); 123.9 (CH); 123.5 (4 \times C); 122.5 (4 \times CH); 122.3 (4 \times CH); 121.5 (2 \times CH); 108.9 (8 \times CH); 108.3 (CH); 106.2 (2 \times CH); 73.8 (5 \times CH_2); 69.5 (8 \times CH_2); 68.1 (CH_2); 32.2 (12 \times CH_2); 30.0 (24 \times CH_2); 29.9 (24 \times CH_2); 29.8 (12 \times CH_2); 29.7 (12 \times CH_2); 29.6 (12 \times CH_2); 27.1 (CH_2); 26.3 (12 \times CH_2); 26.0 (CH_2); 22.9 (12 \times CH_2); 14.4 (12 \times CH_3). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^{2+}$ calculated: for $\text{C}_{216}\text{H}_{338}\text{O}_{30}\text{Na}_2$ 3458.4734; found: 3458.4706.

Synthesis of dimers with modified linking groups (Scheme S9)

Dimers of this series were synthesised by a quadruple acylation of the core unit **2/m** with acid chlorides of acids **8-10** by the general methods 6 and 7. Purification by column chromatography (toluene/*tert*-butyl methyl ether) and crystallisation from a toluene/ethanol mixture.

5-(3-{2,6-Bis[4-(4-dodecyloxyphenoxy)carbonyl]benzoyloxy}phenoxy)propoxy)benzene-1,3-diyl bis[4-(4-dodecyloxyphenoxy)benzoate] (D3-12/inv). The dimer was prepared by acylation of the unit **2/3** with acid chloride of acid **8**. Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture. Yield 88%, m.p. 118°C. ^1H NMR spectrum (CDCl_3): 0.89 (t, 12 H, $^3J=6.4$, 4 \times CH_3); 1.28-1.47 (m, 72 H, 4 \times (CH_2)₉); 1.79 (m, 8 H, 4 \times $\text{CH}_2\text{CH}_2\text{O}$); 1.99 (tt, 2 H, $^3J=5.6$, $\text{CH}_2\text{CH}_2\text{O}$); 3.93 (t, 6 H, $^3J=6.6$, 3 \times CH_2O); 3.98 (t, 4 H, $^3J=6.6$, 2 \times CH_2O); 4.23 (t, 2 H, $^3J=5.6$, CH_2O); 6.48 (d, 2 H, $^4J=2.1$); 6.78 (dd, 1 H, $^4J=2.1$); 6.90 (d, 4 H, $^3J=9.1$); 6.95 (d, 4 H, $^3J=9.1$); 7.11 (d, 4 H, $^3J=9.1$); 7.15 (d, 4 H, $^3J=9.1$); 7.23 (m, 3 H); 8.27 (s, 8 H); 8.30 (m, 8 H). ^{13}C NMR spectrum (CDCl_3): 164.8 (2 \times C); 164.7 (2 \times C); 164.0 (2 \times C); 163.9 (2 \times C); 160.2 (C); 157.4 (2 \times C); 157.3 (2 \times C); 151.9 (2 \times C); 145.0 (2 \times C); 144.3 (2 \times C); 144.2 (2 \times C); 143.6 (C); 134.5 (2 \times C); 134.4 (2 \times C); 133.6 (2 \times C); 133.1 (2 \times C); 130.5 (16 \times CH); 124.1 (CH); 122.5 (4 \times CH); 122.4 (4 \times CH); 121.6 (2 \times CH); 115.4 (4 \times CH); 115.3 (4 \times CH); 108.1 (CH); 106.2 (2 \times CH); 70.4 (CH_2); 68.7 (4 \times CH_2); 64.6 (CH_2); 32.2 (4 \times CH_2); 30.2 (CH_2); 29.9 (8 \times CH_2); 29.8 (8 \times CH_2); 29.7 (4 \times CH_2); 29.6 (4 \times CH_2); 29.5 (4 \times CH_2); 26.3 (4 \times CH_2); 22.9 (4 \times CH_2); 14.4 (4 \times CH_3). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{119}\text{H}_{144}\text{O}_{22}\text{Na}$ 1948.0053; found: 1948.0042.

5-(4-{2,6-Bis[4-(4-dodecyloxyphenoxy)carbonyl]benzoyloxy}phenoxy)butoxy)benzene-1,3-diyl bis[4-(4-dodecyloxyphenoxy)benzoate] (D4-12/inv). The dimer was prepared by acylation of the unit **2/4** with acid chloride of acid **8**. Purification by column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture. Yield 86%, m.p. 119°C. ^1H NMR spectrum (CDCl_3): 0.90 (t, 12 H, $^3J=6.5$, 4 \times CH_3); 1.29-1.46 (m, 72 H, 4 \times (CH_2)₉); 1.70 (m, 4 H, 2 \times $\text{CH}_2\text{CH}_2\text{O}$); 1.78 (tt, 8 H, $^3J=6.7$, $^3J=7.9$, 4 \times $\text{CH}_2\text{CH}_2\text{O}$); 3.74 (m, 2 H, CH_2O); 3.94 (t, 4 H, $^3J=6.4$, 2 \times CH_2O); 3.98 (t, 4 H, $^3J=6.4$, 2 \times CH_2O); 4.11 (m, 2 H, CH_2O); 6.62 (d, 2 H, $^4J=2.1$); 6.83 (dd, 1 H, $^4J=1.8$,

$^4J=2.1$); 6.91 (d, 4 H, $^3J=9.1$); 6.96 (d, 4 H, $^3J=9.1$); 7.13 (d, 4 H, $^3J=9.3$); 7.16 (d, 4 H, $^3J=9.1$); 7.23 (m, 3 H); 8.27 (m, 8 H); 8.34 (m, 8 H). ^{13}C NMR spectrum (CDCl_3): 164.8 ($2 \times \text{C}$); 164.7 ($2 \times \text{C}$); 164.1 ($2 \times \text{C}$); 164.0 ($2 \times \text{C}$); 160.4 (C); 157.4 ($2 \times \text{C}$); 157.3 ($2 \times \text{C}$); 152.0 ($2 \times \text{C}$); 145.0 ($2 \times \text{C}$); 144.3 ($2 \times \text{C}$); 144.2 ($2 \times \text{C}$); 143.7 (C); 134.6 ($2 \times \text{C}$); 134.4 ($2 \times \text{C}$); 133.6 ($2 \times \text{C}$); 133.4 ($2 \times \text{C}$); 130.6 ($8 \times \text{CH}$); 130.5 ($8 \times \text{CH}$); 124.1 (CH); 122.5 ($4 \times \text{CH}$); 122.4 ($4 \times \text{CH}$); 121.6 ($2 \times \text{CH}$); 115.4 ($4 \times \text{CH}$); 115.3 ($4 \times \text{CH}$); 108.1 (CH); 106.2 ($2 \times \text{CH}$); 73.7 (CH_2); 68.7 ($4 \times \text{CH}_2$); 68.1 (CH_2); 32.2 ($4 \times \text{CH}_2$); 29.9 ($8 \times \text{CH}_2$); 29.8 ($8 \times \text{CH}_2$); 29.7 ($4 \times \text{CH}_2$); 29.6 ($4 \times \text{CH}_2$); 29.5 ($4 \times \text{CH}_2$); 26.8 (CH_2); 26.3 ($4 \times \text{CH}_2$); 25.9 (CH_2); 22.9 ($4 \times \text{CH}_2$); 14.4 ($4 \times \text{CH}_3$). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{120}\text{H}_{146}\text{O}_{22}\text{Na}$ 1962.0210; found: 1962.0200.

(*E,E*)-5-(3-{2,6-Bis[4-(4-dodecyloxyphenyldiazenyl)benzoyloxy]phenoxy}propoxy)-benzene-1,3-diyl bis[4-(4-dodecyloxyphenyldiazenyl)benzoate] (D3-12/azo). Acylation of the bent-core unit **2/3** with acid chloride of acid **9** provided after column chromatography (toluene/*tert*-butyl methyl ether 40/1) and crystallisation from a toluene/ethanol mixture the dimer **D3-12/azo**, yield 73%, m.p. 140°C. ^1H NMR spectrum (CDCl_3): 0.90 (t, 12 H, $^3J=6.2$, $4 \times \text{CH}_3$); 1.28-1.46 (m, 72 H, $4 \times (\text{CH}_2)_9$); 1.77 (m, 4 H, $2 \times \text{CH}_2\text{CH}_2\text{O}$); 1.84 (m, 4 H, $2 \times \text{CH}_2\text{CH}_2\text{O}$); 2.00 (tt, 2 H, $^3J=5.6$, $\text{CH}_2\text{CH}_2\text{O}$); 3.92 (t, 2 H, $^3J=4.4$, CH_2O); 3.97 (t, 4 H, $^3J=6.5$, $2 \times \text{CH}_2\text{O}$); 4.05 (t, 4 H, $^3J=6.4$, $2 \times \text{CH}_2\text{O}$); 4.27 (t, 2 H, $^3J=5.0$, CH_2O); 6.46 (d, 2 H, $^4J=2.1$); 6.74 (dd, 1 H, $^4J=2.0$); 6.95 (d, 4 H, $^3J=8.2$); 7.03 (d, 4 H, $^3J=8.5$); 7.21 (m, 3 H); 7.90 (d, 4 H, $^3J=9.1$); 7.91 (d, 4 H, $^3J=9.4$); 7.94 (d, 4 H, $^3J=9.4$); 7.98 (d, 4 H, $^3J=8.8$); 8.23 (d, 4 H, $^3J=7.9$); 8.33 (d, 4 H, $^3J=7.9$). ^{13}C NMR spectrum (CDCl_3): 164.4 ($2 \times \text{C}$); 164.3 ($2 \times \text{C}$); 162.7 ($4 \times \text{C}$); 160.2 (C); 156.1 ($2 \times \text{C}$); 155.9 ($2 \times \text{C}$); 151.9 ($2 \times \text{C}$); 147.1 ($2 \times \text{C}$); 147.0 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 143.7 (C); 131.5 ($4 \times \text{CH}$); 131.4 ($4 \times \text{CH}$); 130.4 ($2 \times \text{C}$); 129.9 ($2 \times \text{C}$); 125.6 ($8 \times \text{CH}$); 123.9 (CH); 122.9 ($4 \times \text{CH}$); 122.7 ($4 \times \text{CH}$); 121.5 ($2 \times \text{CH}$); 115.0 ($8 \times \text{CH}$); 108.2 (CH); 106.0 ($2 \times \text{CH}$); 70.3 (CH_2); 68.7 ($2 \times \text{CH}_2$); 68.6 ($2 \times \text{CH}_2$); 64.5 (CH_2); 32.2 ($4 \times \text{CH}_2$); 30.2 (CH_2); 29.9 ($8 \times \text{CH}_2$); 29.8 ($8 \times \text{CH}_2$); 29.7 ($4 \times \text{CH}_2$); 29.6 ($4 \times \text{CH}_2$); 29.4 ($4 \times \text{CH}_2$); 26.2 ($4 \times \text{CH}_2$); 23.0 ($4 \times \text{CH}_2$); 14.4 ($4 \times \text{CH}_3$). HRMS (ESI-LTQ) m/z : $[\text{M} + \text{Na}]^+$ calculated: for $\text{C}_{115}\text{H}_{144}\text{N}_8\text{O}_{14}\text{Na}$ 1884.0706; found: 1884.0700.

(*E,E*)-5-(4-{2,6-Bis[4-(4-dodecyloxyphenyldiazenyl)benzoyloxy]phenoxy}butoxy)-benzene-1,3-diyl bis[4-(4-dodecyloxyphenyldiazenyl)benzoate] (D4-12/azo). Yield 72%, m.p. 137°C. ^1H NMR spectrum (CDCl_3): 0.89 (t, 12 H, $^3J=6.3$, $4 \times \text{CH}_3$); 1.27-1.46 (m, 72 H, $4 \times (\text{CH}_2)_9$); 1.71 (m, 4 H, $2 \times \text{CH}_2\text{CH}_2\text{O}$); 1.81 (m, 8 H, $4 \times \text{CH}_2\text{CH}_2\text{O}$); 3.72 (m, 2 H, CH_2O); 3.99 (t, 4 H, $^3J=6.5$, $2 \times \text{CH}_2\text{O}$); 4.06 (t, 4 H, $^3J=6.4$, $2 \times \text{CH}_2\text{O}$); 4.12 (m, 2 H, CH_2O); 6.57 (d, 2 H, $^4J=2.1$); 6.77 (dd, 1 H, $^4J=1.8$, $^4J=2.1$); 6.95 (d, 4 H, $^3J=9.1$); 7.02 (d, 4 H, $^3J=9.1$); 7.21 (m, 3 H); 7.92 (d, 4 H, $^3J=9.1$); 7.93 (d, 4 H, $^3J=9.4$); 7.96 (d, 4 H, $^3J=8.8$); 7.97 (d, 4 H, $^3J=9.1$); 8.25 (d, 4 H, $^3J=8.5$); 8.35 (d, 4 H, $^3J=8.5$). ^{13}C NMR spectrum (CDCl_3): 164.4 ($4 \times \text{C}$); 162.7 ($4 \times \text{C}$); 160.2 (C); 156.1 ($2 \times \text{C}$); 155.9 ($2 \times \text{C}$); 152.0 ($2 \times \text{C}$); 147.1 ($2 \times \text{C}$); 147.0 ($2 \times \text{C}$); 145.1 ($2 \times \text{C}$); 142.3 (C); 131.6 ($4 \times \text{CH}$); 131.4 ($4 \times \text{CH}$); 130.4 ($2 \times \text{C}$); 129.9 ($2 \times \text{C}$); 125.5 ($8 \times \text{CH}$); 123.9 (CH); 122.9 ($4 \times \text{CH}$); 122.7 ($4 \times \text{CH}$); 121.5 ($2 \times \text{CH}$); 115.0 ($8 \times \text{CH}$); 108.1 (CH); 106.1 ($2 \times \text{CH}$); 73.8 (CH_2); 68.7 ($2 \times \text{CH}_2$); 68.6 ($2 \times \text{CH}_2$); 68.0 (CH_2); 32.2 ($4 \times \text{CH}_2$); 29.9 ($8 \times \text{CH}_2$); 29.8 ($8 \times \text{CH}_2$); 29.7 ($4 \times \text{CH}_2$); 29.6 ($4 \times \text{CH}_2$); 29.4 ($4 \times \text{CH}_2$); 27.0 (CH_2); 26.2 ($4 \times \text{CH}_2$); 25.9 (CH_2); 23.0 ($4 \times \text{CH}_2$); 14.4 ($4 \times$

CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₁₆H₁₄₆N₈O₁₄Na 1898.0862; found: 1898.0851.

5-{3-[2,6-Bis(4'-dodecyloxybiphenyl-4-carbonyloxy)phenoxy]propoxy}benzene-1,3-diyl bis(4'-dodecyloxybiphenyl-4-carboxylate) (D3-12/Ph2). Acylation of the unit 2/3 with acid chloride of acid **10** provided the crude product, which was purified by column chromatography (chloroform) and crystallisation from a toluene/ethanol mixture. Yield 86%, m.p. 150°C. ¹H NMR spectrum (CDCl₃): 0.91 (t, 12 H, ³J=6.3, 4 × CH₃); 1.29-1.48 (m, 72 H, 4 × (CH₂)₉); 1.81 (m, 8 H, 4 × CH₂CH₂O); 2.02 (tt, 2 H, ³J=5.7, CH₂CH₂O); 3.94 (t, 6 H, ³J=6.5, 3 × CH₂O); 4.03 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.28 (t, 2 H, ³J=5.6, CH₂O); 6.47 (d, 2 H, ⁴J=2.1); 6.72 (dd, 1 H, ⁴J=1.8, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 7.02 (d, 4 H, ³J=8.8); 7.19 (m, 3 H); 7.58 (d, 4 H, ³J=8.8); 7.61 (d, 4 H, ³J=8.8); 7.66 (d, 4 H, ³J=8.2); 7.67 (d, 4 H, ³J=8.5); 8.11 (d, 4 H, ³J=8.2); 8.25 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.8 (4 × C); 160.2 (C); 159.9 (2 × C); 159.8 (2 × C); 152.1 (2 × C); 146.3 (2 × C); 146.2 (2 × C); 145.1 (2 × C); 143.8 (C); 132.1 (2 × C); 132.0 (2 × C); 131.0 (8 × CH); 128.6 (8 × CH); 127.5 (2 × C); 127.1 (2 × C); 126.9 (4 × CH); 126.8 (4 × CH); 123.7 (CH); 121.5 (2 × CH); 115.2 (4 × CH); 115.1 (4 × CH); 108.2 (CH); 106.0 (2 × CH); 70.4 (CH₂); 68.4 (2 × CH₂); 68.3 (2 × CH₂); 64.7 (CH₂); 32.2 (4 × CH₂); 30.2 (CH₂); 29.9 (16 × CH₂); 29.7 (4 × CH₂); 29.6 (4 × CH₂); 29.5 (4 × CH₂); 26.3 (4 × CH₂); 23.0 (4 × CH₂); 14.4 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₁₅H₁₄₄O₁₄Na 1772.0460; found: 1772.0448.

5-{4-[2,6-Bis(4'-dodecyloxybiphenyl-4-carbonyloxy)phenoxy]butoxy}benzene-1,3-diyl bis(4'-dodecyloxybiphenyl-4-carboxylate) (D4-12/Ph2). Yield 81%, m.p. 134°C. ¹H NMR spectrum (CDCl₃): 0.88 (t, 12 H, ³J=6.8, 4 × CH₃); 1.27-1.46 (m, 72 H, 4 × (CH₂)₉); 1.71 (m, 4 H, 2 × CH₂CH₂O); 1.79 (m, 8 H, 4 × CH₂CH₂O); 3.70 (m, 2 H, CH₂O); 3.94 (t, 4 H, ³J=6.5, 2 × CH₂O); 4.01 (t, 4 H, ³J=6.4, 2 × CH₂O); 4.11 (m, 2 H, CH₂O); 6.54 (d, 2 H, ⁴J=1.8); 6.74 (dd, 1 H, ⁴J=2.1); 6.94 (d, 4 H, ³J=8.8); 7.00 (d, 4 H, ³J=8.8); 7.17 (m, 3 H); 7.56 (d, 4 H, ³J=8.5); 7.59 (d, 4 H, ³J=8.5); 7.67 (d, 4 H, ³J=8.2); 7.68 (d, 4 H, ³J=8.2); 8.16 (d, 4 H, ³J=8.2); 8.25 (d, 4 H, ³J=8.5). ¹³C NMR spectrum (CDCl₃): 164.8 (4 × C); 160.2 (C); 159.9 (2 × C); 159.8 (2 × C); 152.1 (2 × C); 146.3 (2 × C); 146.2 (2 × C); 145.1 (2 × C); 143.8 (C); 132.1 (2 × C); 132.0 (2 × C); 131.0 (8 × CH); 128.6 (8 × CH); 127.5 (2 × C); 127.1 (2 × C); 126.9 (4 × CH); 126.8 (4 × CH); 123.7 (CH); 121.5 (2 × CH); 115.2 (4 × CH); 115.1 (4 × CH); 108.2 (CH); 106.0 (2 × CH); 73.8 (CH₂); 68.4 (2 × CH₂); 68.3 (2 × CH₂); 68.0 (CH₂); 32.2 (4 × CH₂); 29.9 (16 × CH₂); 29.7 (4 × CH₂); 29.6 (4 × CH₂); 29.5 (4 × CH₂); 27.0 (CH₂); 26.3 (4 × CH₂); 25.9 (CH₂); 23.0 (4 × CH₂); 14.4 (4 × CH₃). HRMS (ESI-LTQ) m/z: [M + Na]⁺ calculated: for C₁₁₆H₁₄₆O₁₄Na 1786.0617; found: 1787.0618.

2 Mesomorphic properties

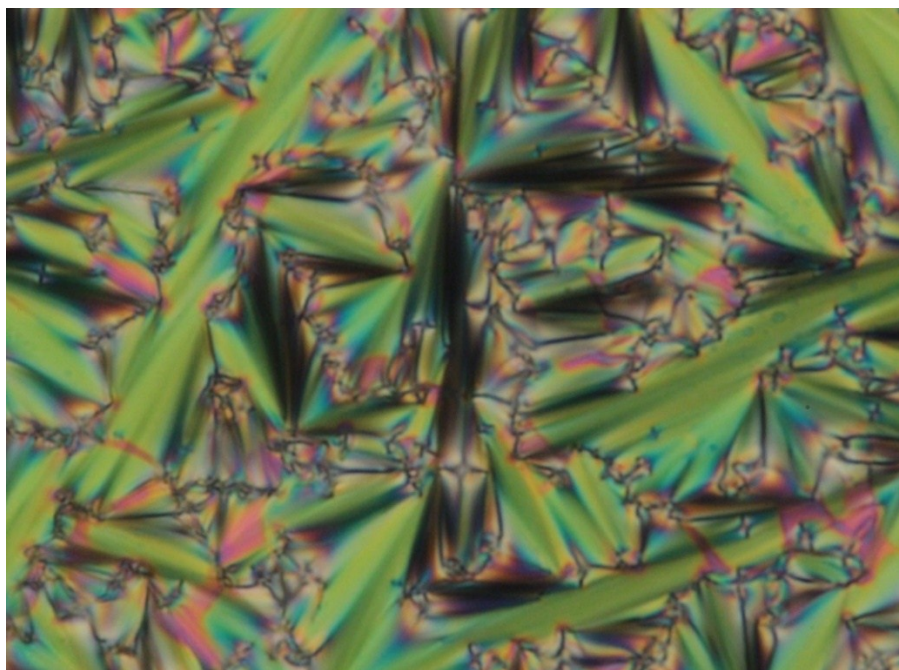


Fig. S1 Planar texture of **D4-2** in the SmA phase at the temperature $T=160^{\circ}\text{C}$.

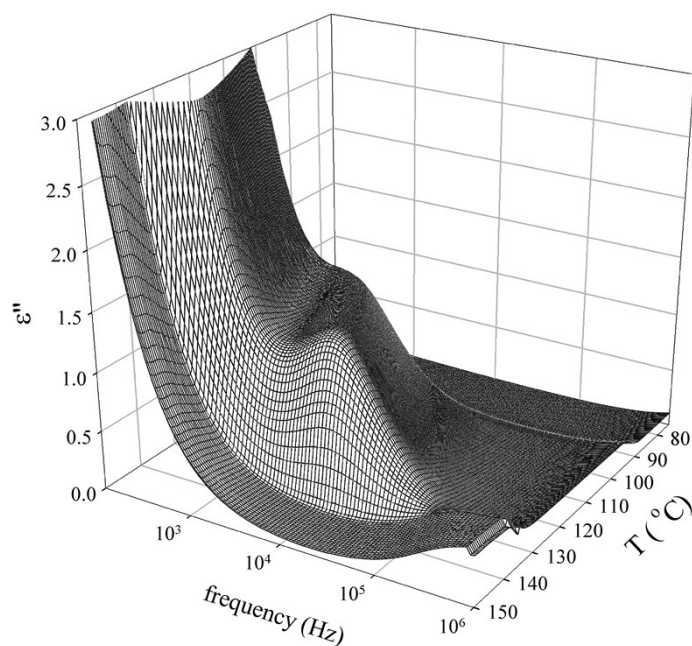


Fig. S2 Three-dimensional plot of the imaginary part of dielectric permittivity, ϵ'' , versus temperature, T , and frequency in the $\text{SmC}_{\text{A}}\text{P}_{\text{A}}$ phase for **D4-10**.

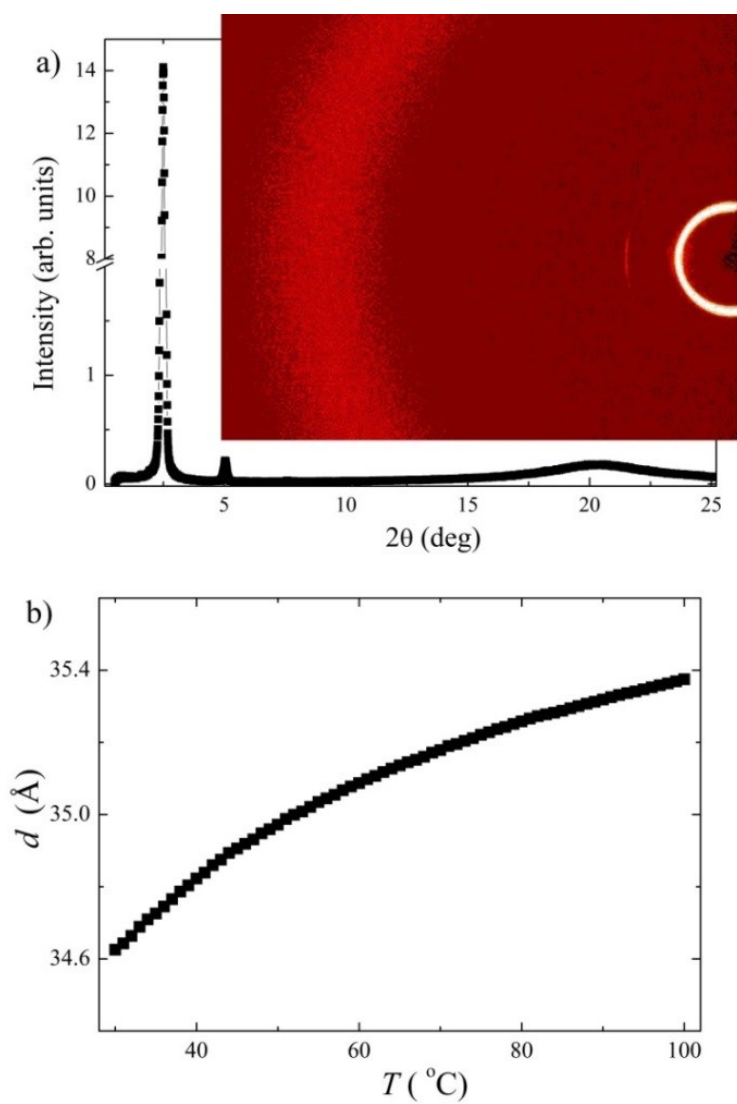


Fig. S3 X-ray measurements for compound **D5-12**: (a) the intensity versus the scattering angle at $T=35^\circ\text{C}$ the SmC_AP_A phase. In the inset in right upper corner 2D x-ray pattern is shown at the same temperature; (b) Temperature dependence of the layer spacing, d , taken on cooling.

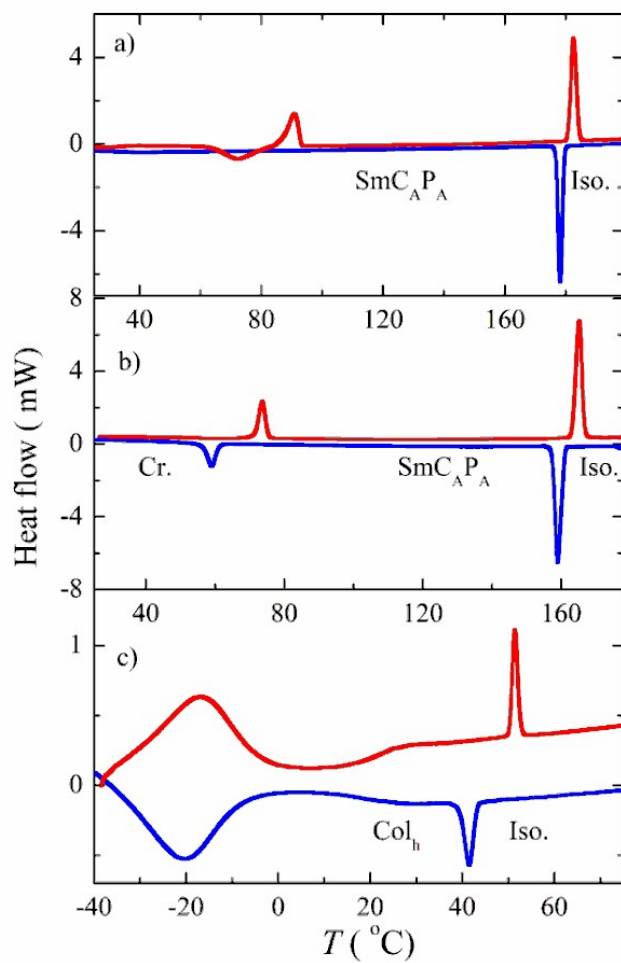


Fig. S4 DSC plots taken at the second heating (red) and the subsequent second cooling run (blue colour) for selected compounds: a) **D3-FF-FF**, b) **D3-SiF-SiF** and c) **D4-12/3**. Phases are designated in the corresponding temperature interval.

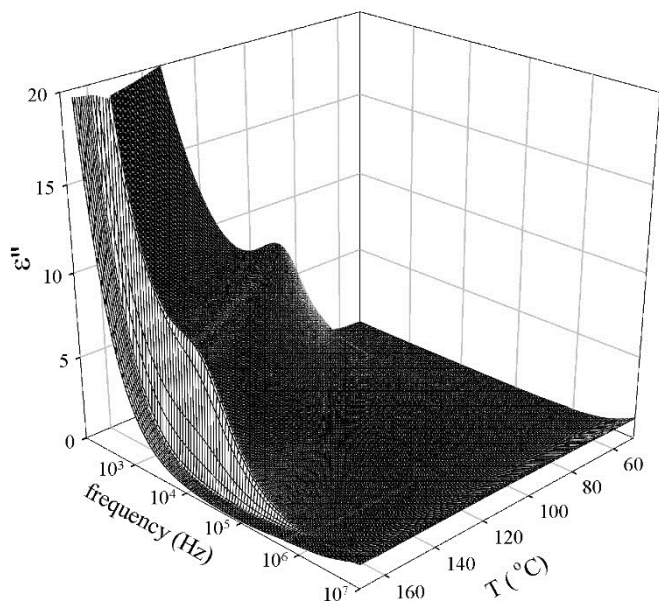


Fig. S5 Three-dimensional plot of the imaginary part of dielectric permittivity, ϵ'' , versus temperature, T , and frequency in the SmC_AP_A phase for **D3-SiF-SiF**.

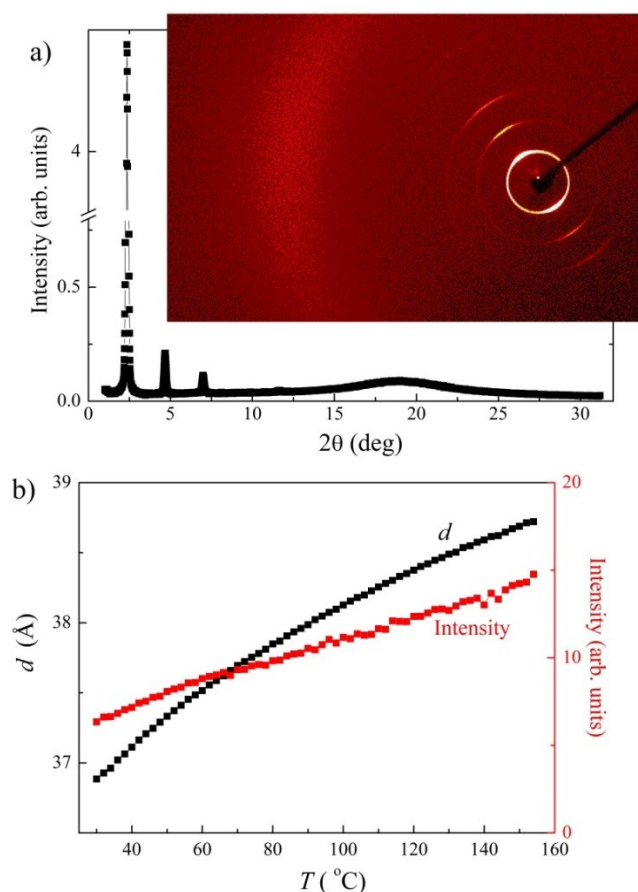


Fig. S6 X-ray measurements for compound **D4-1212-FF**: (a) the intensity versus the scattering angle at $T=120^\circ\text{C}$ in the SmC_AP_A phase. In the inset in right upper corner 2D x-ray pattern is shown at the same temperature; (b) Temperature dependence of the layer spacing, d , and intensity of the first harmonic x-ray signal taken on cooling from the isotropic phase.

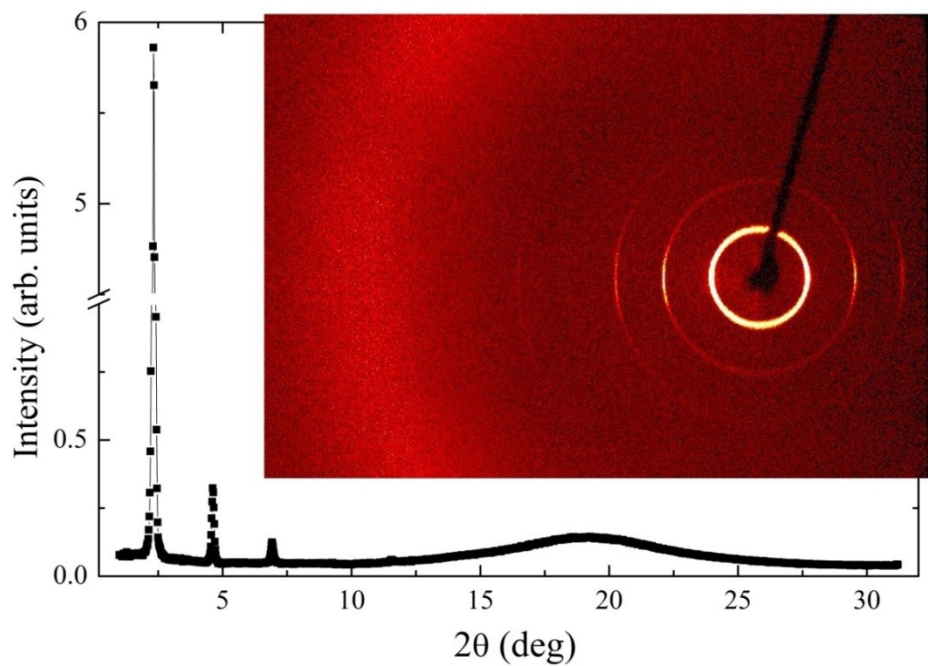


Fig. S7 The X-ray intensity versus the scattering angle at $T=100^{\circ}\text{C}$ in the SmC_AP_A phase for compound **D3-11F-11F**. In the inset in right upper corner 2D x-ray pattern is shown at the same temperature. The layer spacing, d , was established as 38.7 \AA .

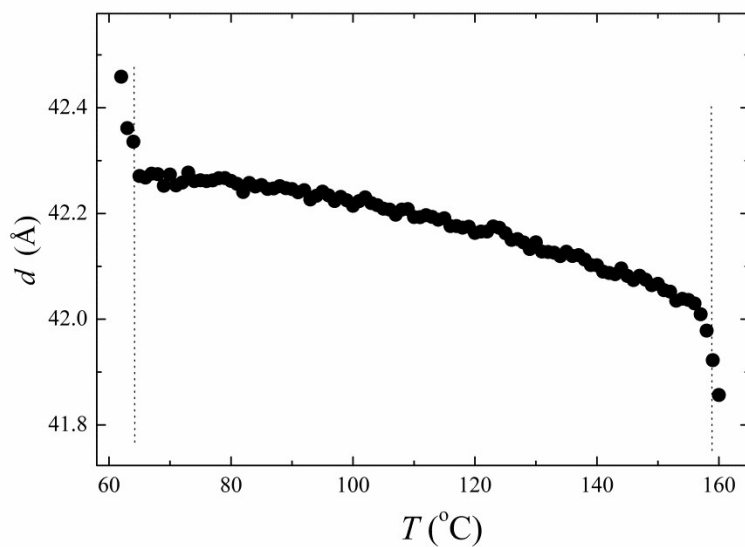


Fig. S8 Temperature dependence of the layer spacing, d , taken on cooling from the isotropic phase for **D3-SiF-SiF**.

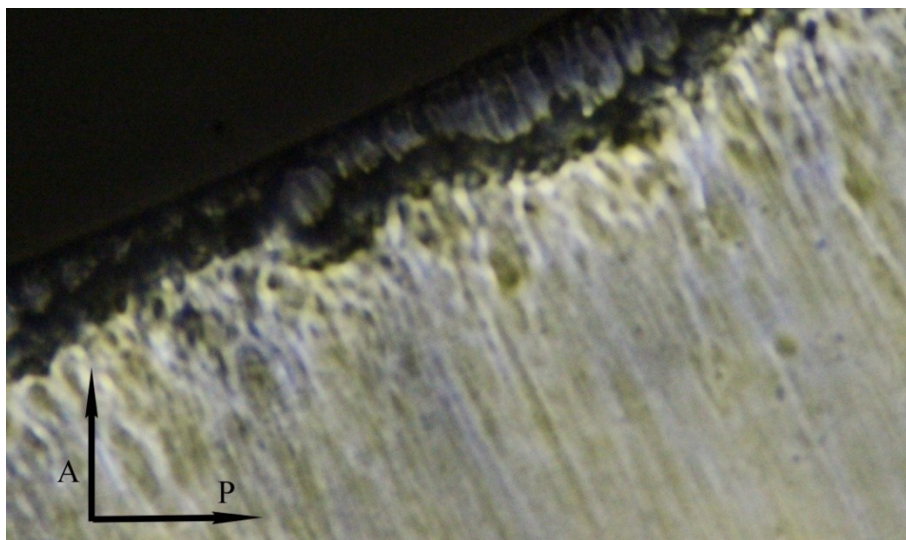


Fig. S9 Texture of **D3-12/3** at room temperature after a shearing process. Polarizers (A,P) are in crossed position and upper part shows the edge of the sample for contrast.

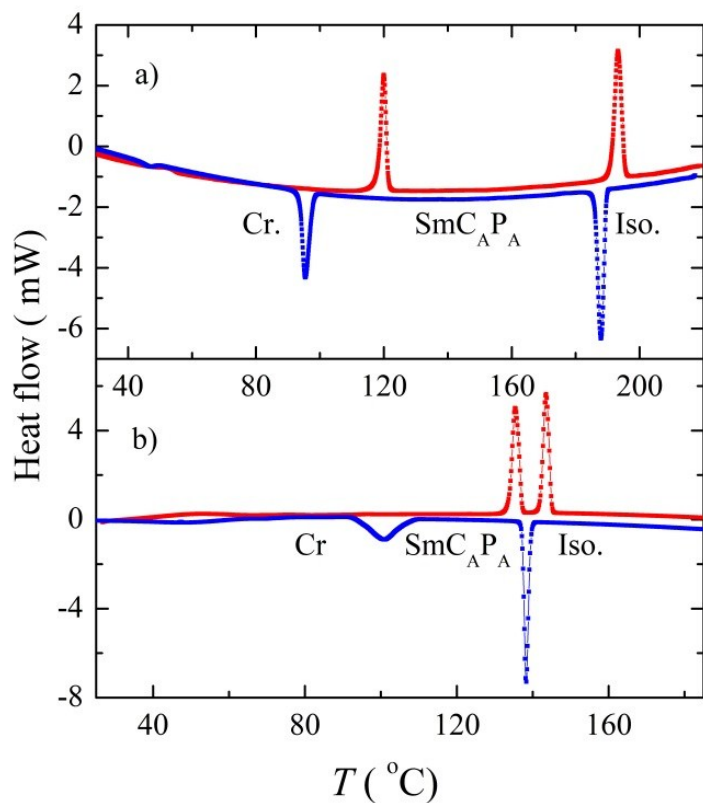


Fig. S10 DSC plots taken at the second heating (red) and the subsequent second cooling run (blue colour) for selected compounds: a) **D4-12/inv** and b) **D4-12/Ph2**. Phases are designated in corresponding temperature interval.

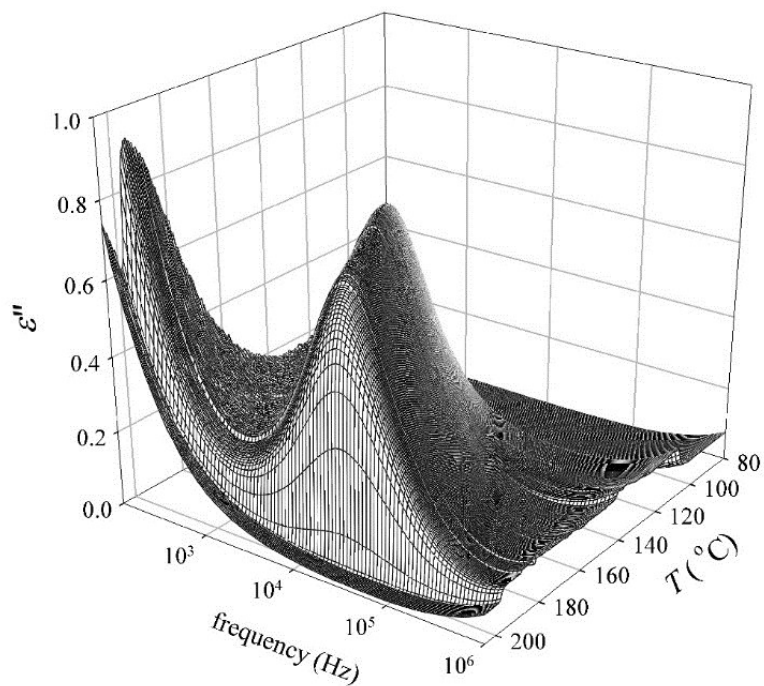


Fig. S11 3D plot of the imaginary part of dielectric permittivity, ϵ'' , versus temperature, T , and frequency in the SmC_AP_A phase for **D4-12/inv**.

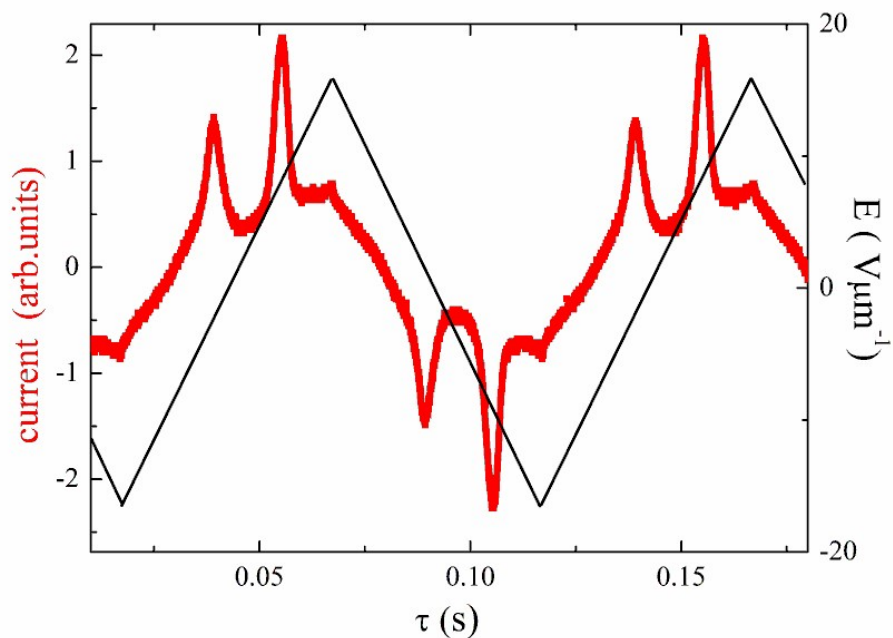


Fig. S12 For **D4-12/Ph2**, the switching current versus time, τ , for applied triangular voltage with intensity, E , at a frequency of 10 Hz, taken in the SmC_AP_A at $T=120^\circ\text{C}$.

Table S1

Cell parameters in the B₁ phase of compound **D4-8** at temperature *T*.

<i>T</i> / °C	<i>a</i> / Å	<i>c</i> / Å
130	33.1	40.2
120	32.9	40.3

Table S2

Cell parameters in the Col_h phase of compounds **Dm-12/3** at temperature *T*.

<i>T</i> / °C	<i>a</i> / Å
D3-12/3	
40	43.5
25	44.4
D4-12/3	
40	43.2
25	44.2

3 References

- S1. M. Horčic, J. Svoboda, V. Novotná, D. Pocięcha and E. Gorecka, *Chem. Commun.*, 2017, **53**, 2721.
- S2. Y. Uetake, T. Niwa and M. Nakada, *Tetrahedron Lett.*, 2014, **55**, 6847.
- S3. T. W. Baughman, J.C. Sworen and K. B. Wagener, *Tetrahedron*, 2004, **60**, 10943.
- S4. A. Carrieri, A. Piergentili, F. Del Bello, M. Giannella, M. Pignini, A. Leonardi, F. Fanelli and W. Quaglia, *Bioorg. Med. Chem.*, 2010, **18**, 7065.
- S5. D. S. Nagvekar and H. W. Gibson, *Org. Prep. Proced. Int.*, 1997, **29**, 240.
- S6. F. L. Weitzl, *J. Org. Chem.*, 1976, **41**, 2044.
- S7. C. W. Holzapfel, D. Williams, G. Bradley, *Tetrahedron* 1995, **51**, 8555.
- S8. T. Hosoya, E. Takashiro, T. Matsumoto and K. Suzuki, *J. Am. Chem. Soc.* 1994, **116**, 1004.
- S9. J. Nithyanandhan and N. Jayaraman, *J. Org. Chem.*, 2002, **67**, 6282.