Bent-core liquid crystals based on 6-substituted 3-hydroxybenzoic acid: the role of substitution and linkage group orientation on mesomorphic properties

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Contents

1. Experimental procedures 2
   1.1 Characterization 2
   1.2 Synthesis of central cores 2
   1.3 Synthesis of intermediates 4
   1.4 Synthesis of the target compounds 11

2. Mesomorphic properties 22

3. Ab initio calculations 25
   3.1 Optimization of lengthening arms 25
   3.2 Optimization of hydroxy ester intermediates 29
   3.3 Optimization of the target materials 32

4. References 32
1. Experimental procedures

1.1. Characterization

The structures of intermediates and products were confirmed by $^1$H NMR and $^1$H-$^1$H correlation spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform and acetone-$d_6$ were used as solvents and the signals of the solvent served as internal standard, $J$ values are given in Hz. The spectra of protected as well as deprotected intermediates of a homologue with the shortest aliphatic chain are presented. The spectra of other homologues within the same series differ only in integral intensities of the signals of (CH$_2$)$_n$ groups of the terminal aliphatic chains. Elemental analyses were carried out on Perkin-Elmer 2400 instrument. The purity of all final compounds was confirmed by HPLC analysis (Luna Silica 150 × 4.6 mm ID, 5 µm column) and found >99.7%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 µm). The experimental part summarizes procedures for the synthesis of the representative intermediates and the compounds of the series I–III.

1.2. Synthesis of central cores

6-Fluoro-3-methoxybenzoic acid (7). Potassium permanganate (79.0 g, 500.0 mmol) was added portion wise to a vigorously stirred suspension of 4-fluoro-3-methylanisole (4) (20.0 g, 143.0 mmol) in water (150 ml) and pyridine (55 ml) at 60ºC. The suspension was stirred for 8 h at 60ºC and at room temperature for 3 days. Precipitated manganese dioxide was filtered off, then repeatedly suspended in hot water (500 ml) and filtered. The combined aqueous filtrate was stirred with 10% aq. sodium sulphite till clarification, filtered, and extracted with diethyl ether (100 ml) to remove the unreacted anisole. The aq. solution was acidified with aq. H$_2$SO$_4$ (1/1) to pH = 1, the precipitated product was filtered and dried under reduced pressure. After crystallisation from toluene, 5.40 g (22%) of acid 1 were obtained, m. p. 141–143ºC (ref. [28] 142–143ºC). $^1$H NMR (acetone-$d_6$): 3.84 (s, 3 H, OCH$_3$), 7.17-7.20 (m, 2 H, 2 × CH, H-4, H-5), 7.44 (m, 1 H, CH, H-2).

6-Fluoro-3-hydroxybenzoic acid (9). BBr$_3$ (7.6 ml, 79.3 mmol) was slowly added to a mixture of acid 1 (5.40 g, 31.7 mmol) in dry dichloromethane (180 ml) at 0ºC. The temperature was allowed to rise to room temperature and the reaction mixture was stirred for 24 h. After cooling to 0ºC, the mixture was decomposed with water (120 ml), the crude product was filtered off and washed with water (100 ml). The filtrate was extracted with
dichloromethane (3 × 50 ml), the combined organic solution was washed with water (50 ml) and the aqueous layer was evaporated to yield the second crop of the product. The collected solids were suspended in boiling dichloromethane (100 ml) and cooled to room temperature, the product was filtered, washed with ice-cold water, and dried under reduced pressure to yield 4.60 g (93%) of hydroxy acid 9, m. p. 197–199°C (ref. [29] 198.5–200°C). \(^1\)H NMR (acetone-\(d_6\)): 7.06-7.10 (m, 2 H, 2 × CH, H-4, H-5), 7.38 (m, 1 H, CH, H-2), 8.65 (br s, 1 H, OH).

**3-Benzylxy-6-fluorobenzoic acid (I).** Benzyl bromide (9.4 ml, 79.3 mmol) was added drop wise to acid 9 (4.60 g, 29.5 mmol) and \(K_2\)CO\(_3\) (8.2 g, 47.6 mmol) in acetone (150 ml). The mixture was stirred and heated to boiling for 48 h. After cooling, it was diluted with water (120 ml) and extracted with chloroform (3 × 70 ml). The combined organic solution was dried with anhydrous magnesium sulphate and the solvent was evaporated. The residue was dissolved in a mixture of ethanol (50 ml) and dioxane (40 ml), 25% aq. sodium hydroxide (15 ml) was added and the solution was heated to boiling for 1 h. After cooling to room temperature, water (100 ml) was added, the mixture was acidified with 25% aq. sulfuric acid to pH = 1, cooled to 0°C, and stirred for 0.5 h. The precipitated solid was filtered, washed with hexane and crystallised from toluene to yield 3.91 g (54%) of the protected acid 1, m.p. 144.0–144.5°C. \(^1\)H NMR (CDCl\(_3\)): 5.08 (s, 2 H, PhCH\(_2\)), 7.09 (dd, 1 H, \(^3\)J = 8.8, \(^4\)J = 9.7, CH, H-5), 7.18 (ddd, 1 H, \(^3\)J = 8.8, \(^4\)J = 2.9, \(^4\)J = 4.1, H-4), 7.31-7.46 (m, 5 H, 5 x CH), 7.59 (dd, 1H, \(^4\)J = 2.9, \(^4\)J = 5.6, CH, H-2).

**6-Chloro-3-methoxybenzoic acid (8)** has been obtained by oxidation of anisole 5 (21.3 g, 136.0 mmol) with potassium permanganate (75.0 g, 474.6 mmol) in the same manner as for acid 7. Yield 9.20 g (36%), m.p. 173–175°C (ref. [30] 174–175°C). \(^1\)H NMR (acetone-\(d_6\)): 3.86 (s, 3 H, OCH\(_3\)), 7.12 (dd, 1 H, \(^3\)J = 8.8, \(^4\)J = 2.9, CH, H-4), 7.40 (d, 1 H, \(^4\)J = 2.9, CH, H-2), 7.44 (d, 1 H, \(^3\)J = 8.8, CH, H-5).

**6-Chloro-3-hydroxybenzoic acid (10)** has been prepared by deprotection of acid 8 (6.40 g, 34.3 mmol) by the means of BBr\(_3\) (6.5 ml, 67.7 mmol) as for acid 9. Yield 5.0 g (85%), m.p. 176–178°C (ref. [S1] 169–170°C). \(^1\)H NMR (acetone-\(d_6\)): 7.00 (dd, 1 H, \(^3\)J = 8.8, \(^4\)J = 2.9, CH, H-4), 7.33 (d, 1 H, \(^3\)J = 8.8, CH, H-5), 7.34 (d, 1 H, \(^4\)J = 2.9, CH, H-2), 9.27 (s, 1 H, OH).
3-tert-Butyl(dimethyl)silyloxy-6-chlorobenzoic acid (2). A solution of tert-butyl(dimethyl)silyl chloride (10.9 g, 72.3 mmol) in dry N,N′-dimethylformamide (DMF) (30 ml) was added drop wise to a solution of acid 9 (5.0 g, 29.0 mmol) and imidazole (5.0 g, 73.4 mmol) in dry DMF (60 ml). The solution was stirred at room temperature for 8 h and then decomposed by the addition of 4% aq. hydrochloric acid (100 ml). The product was extracted with ethyl acetate (3 × 60 ml), the combined organic solution was washed with 4% aq. hydrochloric acid (3 × 40 ml), evaporated and the crude product was purified by column chromatography (toluene/tert-butyl methyl ether, 8/1) and crystallisation from toluene to yield 6.0 g (72%) of the protected acid 2, m.p. 91–92°C. 1H NMR (CDCl₃): 0.22 (s, 6 H, 2 × CH₃), 0.98 (s, 9 H, C(CH₃)₃), 6.95 (dd, 1 H, 3J = 8.8, 4J = 2.9, CH, H-4), 7.33 (d, 1 H, 3J = 8.8, CH, H-5), 7.34 (d, 1 H, 4J = 2.9, CH, H-2).

3-Benzylxylo-6-methylbenzoic acid (3)

Benzylation was performed in the same way as for acid 1 starting from acid 6 (4.95 g, 32.5 mmol) and benzyl bromide (11.5 ml, 96.8 mmol). The product was crystallised from hexane, yield 6.03 g (76%), m.p. 139–141.5°C. 1H NMR (acetone-d₆): 2.41 (s, 3 H, CH₃), 5.10 (s, 2 H, PhCH₂), 7.08 (dd, 1 H, 3J = 8.8, 4J = 2.9, CH, H-4), 7.19 (d, 1 H, 3J = 8.8, CH, H-5), 7.27-7.45 (m, 6 H, 6 x CH, C₆H₅, H-2).

1.3. Synthesis of intermediates

4-[(3-Benzylxylo-6-fluorobenzoyl)oxy]phenyl 4-octyloxybenzoate (15a)

A catalytic amount of DMAP (10 mg) was added to a solution of acid 1 (300 mg; 1.22 mmol), phenol 11a (400 mg; 1.17 mmol), and DCC (252 mg; 1.22 mmol) in dry dichloromethane (20 ml). The reaction mixture was stirred at room temperature for 4 h. The precipitated N,N′-dicyclohexylurea was filtered off and washed with dichloromethane (2 × 5 ml). The filtrate was evaporated and the product was purified by crystallisation from ethanol to yield 500 mg (76%) of 15a, m.p. 118–119.5°C. 1H NMR (CDCl₃): 0.90 (t, 3 H, J = 6.7, CH₃), 1.25-1.58 (m, 10 H, (CH₂)₅), 1.82 (m, 2 H, CH₂), 4.05 (t, 2 H, J = 6.7, OCH₂), 5.11 (s, 2 H, PhCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 7.13 (dd, 1 H, 3J = 8.8, 4J = 9.7, CH), 7.18 (ddd, 1 H, 3J = 8.8 Hz, 4J = 3.2, 4J = 4.1, CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.32-7.47 (m, 5 H, 5 × CH), 7.65 (dd, 1 H, 4J = 3.2, 4J = 5.6, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₅H₃₅FO₆ (570.66): calculated C 73.67, H 6.18, F 3.33; found C 73.44, H 6.07, F 3.45%.
Intermediates 15b (R = C\textsubscript{10}H\textsubscript{21}, yield 73%, m.p. 89–90°C), 15c (R = C\textsubscript{12}H\textsubscript{25}, yield 74%, m.p. 99.5–105.5°C) and 15d (R = C\textsubscript{14}H\textsubscript{29}, yield 74%, m.p. 99–100°C) were prepared by the same procedure.

4-[[6-Chloro-3-tert-butyl(dimethyl)silyloxybenzoyl]oxy]phenyl 4-octyloxybenzoate (16a) was obtained by the same method as for 15a by the reaction of acid 2 with phenol 11a. Purification was achieved by column chromatography (toluene/tert-butyl methyl ether, 12/1) yielding 450 mg (63%) of 16a, white solid, m. p. 44–46°C. \(^1\)H NMR (CDCl\textsubscript{3}): 0.24 (s, 6 H, 2 × CH\textsubscript{3}), 0.89 (t, 3 H, \(J = 6.7\), CH\textsubscript{3}), 1.00 (s, 9 H, C(CH\textsubscript{3})\textsubscript{3}), 1.26–1.56 (m, 10 H, (CH\textsubscript{2})\textsubscript{5}), 1.82 (m, 2 H, CH\textsubscript{2}), 4.05 (t, 2 H, \(J = 6.7\), OCH\textsubscript{2}), 6.95-6.99 (m, 3 H, 3 × CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.36 (d, 1 H, \(^3\)J = 8.8, CH), 7.48 (d, 1 H, \(^4\)J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C\textsubscript{34}H\textsubscript{43}ClO\textsubscript{6}Si (611.26): calculated C 66.81, H 7.09, Cl 5.80; found C 66.75, H 7.13, Cl 5.83%.

Intermediates 16b (R = C\textsubscript{10}H\textsubscript{21}, yield 87%, m.p. 39.5–42°C), 16c (R = C\textsubscript{12}H\textsubscript{25}, yield 83%, m.p. 44–47°C) and 16d (R = C\textsubscript{14}H\textsubscript{29}, yield 65%, m.p. 46.5–49.5°C) were prepared in the same way.

4-[(3-Benzyloxy-6-methylbenzoyl)oxy]phenyl 4-octyloxybenzoate (17a) was prepared by the acylation of phenol 11a with acid 3 as above. Yield 92%, m.p. 117–119°C. \(^1\)H NMR (CDCl\textsubscript{3}): 0.88 (t, 3 H, \(J = 6.7\), CH\textsubscript{3}), 1.23-1.55 (m, 10 H, (CH\textsubscript{2})\textsubscript{5}), 1.83 (m, 2 H, CH\textsubscript{2}), 2.60 (s, 3 H, CH\textsubscript{3}), 4.05 (t, 2 H, \(J = 6.7\), OCH\textsubscript{2}), 5.12 (s, 2 H, PhCH\textsubscript{2}), 6.98 (d, 2 H, J = 8.8, 2 × CH), 7.11 (dd, 1 H, \(^3\)J = 8.8, \(^4\)J = 2.9, CH), 7.22 (d, 1 H, \(^3\)J = 8.8, CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.33-7.48 (m, 5 H, 5 × CH), 7.78 (d, 1 H, \(^4\)J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C\textsubscript{36}H\textsubscript{38}O\textsubscript{6} (566.70): calculated C 76.30, H 6.76; found C 76.15, H 6.85%.

Intermediates 17b (R = C\textsubscript{10}H\textsubscript{21}, yield 87%, m.p. 110–113°C), 17c (R = C\textsubscript{12}H\textsubscript{25}, yield 87%, m.p. 98–99.5°C) and 17d (R = C\textsubscript{14}H\textsubscript{29}, yield 95%, m.p. 99.5–101°C) were prepared analogously.

4-Octyloxyphenyl 4-[(3-benzyloxy-6-fluorobenzoyl)oxy]benzoate (21a) was prepared as above by the acylation of phenol 12a with acid 1. Subsequent purification via crystallisation from ethanol afforded 21a, yield 77%, m.p. 79–81°C. \(^1\)H NMR (CDCl\textsubscript{3}): 0.89 (t, 3 H, \(J = 6.7\), CH\textsubscript{3}), 1.25-1.54 (m, 10 H, (CH\textsubscript{2})\textsubscript{5}), 1.79 (m, 2 H, CH\textsubscript{2}), 3.96 (t, 2 H, \(J = 6.7\), OCH\textsubscript{2}), 5.11 (s, 2
H, PhCH₂), 6.93 (d, 2 H, J = 8.8, 2 × CH), 7.10-7.15 (m, 3 H, 3 × CH), 7.19 (ddd, 1 H, ³J = 8.8, ⁴J = 3.2, ⁴J = 4.1, CH), 7.34-7.47 (m, 7 H, 7 × CH), 7.65 (dd, 1 H, ⁴J = 3.2, ⁴J = 5.6, CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₈H₃₅FO₆ (570.66): calculated C 73.67, H 6.18, F 3.33; found C 73.84, H 6.09, F 3.40%.

Compounds 21b (R = C₁₀H₂₁, yield 69%, m.p. 78–80°C), 21c (R = C₁₂H₂₅, yield 50%, m.p. 81.5–83°C) and 21d (R = C₁₄H₂₉, yield 66%, m.p. 82–85°C) were prepared in the same way.

4-Octyloxyphenyl 4-[(6-chloro-3-tert-butyl(dimethyl)stiloxoybenzoyl)oxy]benzoate (22a)

was prepared as for 15a by the reaction of phenol 12a with acid 2. The product was purified by column chromatography (toluene/tert-butyl methyl ether, 12/1), yield 88%, m.p. 43.5–45°C. ¹H NMR (CDCl₃): 0.24 (s, 6 H, 2 × CH₃), 0.89 (t, 3 H, J = 6.7, CH₃), 1.00 (s, 9 H, C(CH₃)₃), 1.27-1.55 (m, 10 H, (CH₂)₅), 1.79 (m, 2 H, CH₂), 2.61 (s, 3 H, CH₃), 3.96 (t, 2 H, J = 6.7, OCH₂), 5.13 (s, 2 H, PhCH₂), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (dd, 1 H, ³J = 8.8, ⁴J = 2.9, CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.38 (d, 1 H, ³J = 8.8, CH), 7.40 (d, 2 H, J = 8.8, 2 × CH), 7.50 (d, 1 H, ⁴J = 2.9, CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₄H₄₃ClO₆Si (611.26): calculated C 66.81, H 7.09, Cl 5.80; found C 66.64, H 7.17, Cl 5.85%.

Intermediates 22b (R = C₁₀H₂₁, yield 82%, m.p. 47–49°C), 22c (R = C₁₂H₂₅, yield 90%, m.p. 53–55°C) and 22d (R = C₁₄H₂₉, yield 89%, m.p. 58.5–60.5°C) were prepared by the same method.

4-Octyloxyphenyl 4-[(3-benzylxy-6-methylbenzoyl)oxy]benzoate (23a)

was obtained by the acylation of phenol 12a with acid 3 and purified by crystallisation from ethanol. Yield 75%, m.p. 82–84°C. ¹H NMR (CDCl₃): 0.88 (t, 3 H, J = 6.7, CH₃), 1.22-1.51 (m, 10 H, (CH₂)₅), 1.79 (m, 2 H, CH₂), 2.61 (s, 3 H, CH₃), 3.96 (t, 2 H, J = 6.7, OCH₂), 5.13 (s, 2 H, PhCH₂), 6.93 (d, 2 H, J = 8.8, 2 × CH), 7.09-7.15 (m, 3 H, 3 × CH), 7.24 (d, 1 H, ³J = 8.8, CH), 7.33-7.48 (m, 7 H, 7 × CH), 7.79 (d, 1 H, ⁴J = 2.9, CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₆H₅₈O₆ (566.70): calculated C 76.30, H 6.76; found C 76.17, H 6.82%.

Intermediates 23b (R = C₁₀H₂₁, yield 75%, m.p. 62–65°C), 23c (R = C₁₂H₂₅, yield 64%, m.p. 87–88°C) and 23d (R = C₁₄H₂₉, yield 81%, m.p. 75–77°C) were prepared in the same way.

Octyl 4-[(4-[(3-benzylxy-6-fluorobenzoyl)oxy]benzoyl)oxy]benzoate (24a)

was synthesised by the reaction of phenol 13a with acid 1 and purified by crystallisation from ethanol. Yield 66%, m.p. 86–87.5°C. ¹H NMR (CDCl₃): 0.89 (t, 3 H, J = 6.7, CH₃), 1.25-1.54 (m, 10 H,
(CH₂)₅, 1.78 (m, 2 H, CH₂), 4.33 (t, 2 H, J = 6.7, OCH₂), 5.11 (s, 2 H, PhCH₂), 7.15 (d, 1 H, 3J = 8.8, 3J = 9.7, CH), 7.21 (ddd, 1 H, 3J = 8.8, 4J = 3.2, 4J = 4.1, CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.35-7.47 (m, 7 H, 7 × CH), 7.66 (dd, 1 H, 4J = 3.2, 4J = 5.6, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₆H₃₅FO₇ (598.67): calculated C 72.23, H 5.89, F 3.17; found C 72.49, H 5.88, F 3.24%.

Intermediates 24b (R = C₁₀H₂₁, yield 78%, m.p. 87.5–88.5°C), 24c (R = C₁₂H₂₅, yield 69%, m.p. 87–87.5°C) and 24d (R = C₁₄H₂₉, yield 75%, m.p. 88.5–90°C) were prepared analogously.

Octyl 4-[[4-[6-chloro-3-tert-butyl(dimethyl)silyloxybenzoyl]oxy]benzoyl]oxy]benzoate (25a). Acylation of phenol 13a with acid 2 was performed by the same method as for 15a. The product was purified by column chromatography (toluene/tert-butyl methyl ether, 12/1), yield 83%, viscous oil. ¹H NMR (CDCl₃): 0.24 (s, 6 H, 2 × CH₃), 0.89 (t, 3 H, J = 6.7, CH₃), 1.00 (s, 9 H, C(CH₃)₃), 1.24-1.52 (m, 10 H, (CH₂)₅), 1.78 (m, 2 H, CH₂), 2.61 (s, 3 H, CH₃), 4.33 (t, 2 H, J = 6.7, OCH₂), 5.13 (s, 2 H, PhCH₂), 7.00 (dd, 1 H, 3J = 8.8, 4J = 2.9, CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.39 (d, 1 H, 3J = 8.8, CH), 7.42 (d, 2 H, J = 8.8, 2 × CH), 7.50 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₅H₄₃ClO₇Si (639.27): calculated C 65.76, H 6.78, Cl 5.55; found C 65.57, H 6.64, Cl 5.50%.

Intermediates 25b (R = C₁₀H₂₁, yield 75%, m.p. 36–38.5°C), 25c (R = C₁₂H₂₅, yield 85%, m.p. 44–46°C) and 25d (R = C₁₄H₂₉, yield 89%, m.p. 52–54.5°C) were prepared by the same procedure.

Octyl 4-[[4-[3-benzylxy-6-methylbenzoyl]oxy]benzoyl]oxy]benzoate (26a) was prepared by the reaction of phenol 13a with acid 3 and purified by crystallisation from ethanol. Yield 85%, m.p. 78.5–80.5°C. ¹H NMR (CDCl₃): 0.88 (t, 3 H, J = 6.7, CH₃), 1.23-1.50 (m, 10 H, (CH₂)₅), 1.78 (m, 2 H, CH₂), 2.61 (s, 3 H, CH₃), 4.33 (t, 2 H, J = 6.7, OCH₂), 5.13 (s, 2 H, PhCH₂), 7.14 (dd, 1 H, 3J = 8.8, 4J = 2.9, CH), 7.25 (d, 1 H, 3J = 8.8, CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.34-7.48 (m, 7 H, 7 × CH), 7.80 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₃₇H₃₈O₇ (594.71): calculated C 74.73, H 6.44; found C 74.90, H 6.46%.

Compounds 26b (R = C₁₀H₂₁, yield 76%, m.p. 72–74°C), 26c (R = C₁₂H₂₅, yield 80%, m.p. 75.5–78.5°C) and 26d (R = C₁₄H₂₉, yield 91%, m.p. 79–80°C) were prepared by the same procedure.
4-[(6-Fluoro-3-hydroxybenzoyl)oxy]phenyl 4-octyloxybenzoate (18a)

Ammonium formate (221 mg; 3.51 mmol) was added to a suspension of benzyl derivative 15a (500 mg, 0.88 mmol) and 10% Pd/C (50 mg). The reaction mixture was stirred and heated to boiling for 3 h in an argon atmosphere, filtered while hot; the catalyst was washed with acetone (15 ml) and the filtrate was evaporated. The product was purified by column chromatography (toluene/tert-butyl methyl ether, 8/1) and crystallisation from toluene. Yield 74%, m.p. 140–140.5°C. 

$^1$H NMR (CDCl$_3$): 0.89 (t, 3 H, $J = 6.7$), 1.25-1.53 (m, 10 H, $(\text{CH}_2)_5$), 1.83 (m, 2 H, CH$_2$), 4.05 (t, 2 H, $J = 6.7$, OCH$_2$), 5.03 (s, 1 H, OH), 6.97 (d, 2 H, $J = 8.8$, 2 × CH), 7.06-7.14 (m, 2 H, 2 × CH), 7.25-7.29 (m, 4 H, 4 × CH), 7.51 (dd, 1 H, $^4$J = 3.2, $^3$J = 5.6, CH), 8.14 (d, 2 H, $J = 8.8$, 2 × CH). 

Elemental analysis: for C$_{28}$H$_{29}$FO$_6$ (480.54): calculated C 69.99, H 6.08, F 3.95; found C 69.78, H 5.97, F 4.02%. 

Intermediates 18b (R = C$_{10}$H$_{21}$, yield 79%, m.p. 141–142°C), 18c (R = C$_{12}$H$_{25}$, yield 82%, m.p. 137–138°C) and 18d (R = C$_{14}$H$_{29}$, yield 76%, m.p. 137.5–138°C) were prepared by the same method.

4-[(3-Hydroxy-6-methylbenzoyl)oxy]phenyl 4-octyloxybenzoate (20a) was prepared by debenzylation of 17a by the method as for 18a. Purification was achieved by column chromatography (toluene/acetone, 14/1) and crystallisation from toluene, yield 77%, m.p. 99.5–101°C. 

$^1$H NMR (CDCl$_3$): 0.88 (t, 3 H, $J = 6.7$, CH$_3$), 1.23-1.53 (m, 10 H, (CH$_2$)$_5$), 1.83 (m, 2 H, CH$_2$), 2.59 (s, 3 H, CH$_3$), 4.05 (t, 2 H, $J = 6.7$, OCH$_2$), 4.87 (s, 1 H, OH), 6.95-7.01 (m, 3 H, 3 × CH), 7.18 (d, 1 H, $^3$J = 8.8, CH), 7.25-7.30 (m, 4 H, 4 × CH), 7.62 (d, 1 H, $^4$J = 2.9, CH), 8.14 (d, 2 H, $J = 8.8$, 2 × CH). 

Elemental analysis: for C$_{29}$H$_{32}$O$_6$ (476.57): calculated C 73.09, H 6.77; found C 73.01, H 6.69%. 

Homologues 20b (R = C$_{10}$H$_{21}$, yield 79%, m.p. 99.5–101°C), 20c (R = C$_{12}$H$_{25}$, yield 82%, m.p. 104–104.5°C) and 20d (R = C$_{14}$H$_{29}$, yield 76%, m.p. 101.5–103°C) were prepared by the same procedure.

4-Octyloxyphenyl 4-[(6-fluoro-3-hydroxybenzoyl)oxy]benzoate (27a) was synthesised by debenzylation of 21a. The product was purified by column chromatography (toluene/tert-butyl methyl ether, 8/1) and crystallisation from toluene. Yield 45%, m.p. 134–136.5°C. 

$^1$H NMR (CDCl$_3$): 0.89 (t, 3 H, $J = 6.7$, CH$_3$), 1.23-1.52 (m, 10 H, (CH$_2$)$_5$), 1.79 (m, 2 H, CH$_2$), 3.96 (t, 2 H, $J = 6.7$, OCH$_2$), 5.05 (s, 1 H, OH), 6.93 (d, 2 H, $J = 8.8$, 2 × CH), 7.08-7.13 (m, 4
H, 4 × CH), 7.37 (d, 2 H, J = 8.8, 2 × CH), 7.53 (dd, 1 H, \(^4J = 3.2, \(^4J = 5.6, \) CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C_{28}H_{29}FO_6 (480.54): calculated C 69.99, H 6.08, F 3.95; found C 69.87, H 5.92, F 3.91%.

Compounds 27b (R = C_{10}H_{21}, yield 48%, m.p. 134–137°C), 27c (R = C_{12}H_{25}, yield 61%, m.p. 130–132°C) and 27d (R = C_{14}H_{29}, yield 71%, m.p. 128.5–131.5°C) were prepared by the same procedure.

4-Octyloxyphenyl 4-[(3-hydroxy-6-methylbenzoyl)oxy]benzoate (29a). Debenzylation of 23a was followed by column chromatography (toluene/acetone, 14/1) and crystallisation from toluene, yield 70%, m.p. 116–118°C. \(^1H \) NMR (CDCl\(_3\)): 0.88 (t, 3 H, \(J = 6.7, \) CH), 1.20-1.51 (m, 10 H, (CH\(_2\))\(_5\)), 1.79 (m, 2 H, CH\(_2\)), 2.59 (s, 3 H, CH\(_3\)), 3.95 (t, 2 H, \(J = 6.7, \) OCH\(_2\)), 5.19 (s, 1 H, OH), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.98 (dd, 1 H, \(^3J = 8.8, \(^4J = 2.9, \) CH), 7.11 (d, 2 H, J = 8.8, 2 × CH), 7.19 (d, 1 H, \(^3J = 8.8, \) CH), 7.33 (d, 2 H, J = 8.8, 2 × CH), 7.64 (d, 1 H, \(^4J = 2.9, \) CH), 8.27 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C_{29}H_{32}O_6 (476.57): calculated C 73.09, H 6.77; found C 73.13, H 6.72%.

Intermediates 29b (R = C_{10}H_{21}, yield 67%, m.p. 100–103°C), 29c (R = C_{12}H_{25}, yield 80%, m.p. 98–99°C) and 29d (R = C_{14}H_{29}, yield 72%, m.p. 102–103.5°C) were prepared by the same procedure.

Octyl 4-[(4-[(6-fluoro-3-hydroxybenzoyl)oxy]benzoyl)oxy]benzoate (30a). Deprotection of 24a was achieved as for 18a and the product was purified by column chromatography (toluene/tert-butyl methyl ether 8/1) and crystallisation from toluene, yield 57%, m.p. 113–114°C. \(^1H \) NMR (CDCl\(_3\)): 0.89 (t, 3 H, \(J = 6.7, \) CH\(_3\)), 1.23-1.51 (m, 10 H, (CH\(_2\))\(_5\)), 1.78 (m, 2 H, CH\(_2\)), 4.33 (t, 2 H, J = 6.7, OCH\(_2\)), 5.19 (s, 1 H, OH), 7.09-7.13 (m, 2 H, 2 × CH), 7.30 (d, 2 H, J = 8.8, 2 × CH), 7.40 (d, 2 H, J = 8.8, 2 × CH), 7.54 (dd, 1 H, \(^4J = 3.2, \(^4J = 5.6, \) CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C_{20}H_{29}FO_7 (508.55), calculated C 68.49, H 5.75, F 3.74; found C 68.66, H 5.76, F 3.68%.

Intermediates 30b (R = C_{10}H_{21}, yield 49%, m.p. 111–113°C), 30c (R = C_{12}H_{25}, yield 56%, m.p. 108–110°C) and 30d (R = C_{14}H_{29}, yield 52%, m.p. 113–118°C) were prepared by the same procedure.

Octyl 4-[(4-[(3-hydroxy-6-methylbenzoyl)oxy]benzoyl)oxy]benzoate (32a) was obtained by deprotection of 26a. The product was purified by column chromatography (toluene/acetone,
14/1) and crystallisation from toluene. Yield 80%, m.p. 115–118°C. $^1$H NMR (CDCl$_3$): 0.88 (t, 3 H, $J$ = 6.7, CH$_3$), 1.21-1.50 (m, 10 H, (CH$_2$)$_5$), 1.78 (m, 2 H, CH$_2$), 2.60 (s, 3 H, CH$_3$), 4.33 (t, 2 H, $J$ = 6.7, OCH$_2$), 4.85 (s, 1 H, OH), 7.01 (dd, 1 H, $^3$J = 8.8, $^4$J = 2.9, CH), 7.21 (d, 1 H, $^3$J = 8.8, CH), 7.30 (d, 2 H, $J$ = 8.8, 2 × CH), 7.37 (d, 2 H, $J$ = 8.8, 2 × CH), 7.66 (d, 1 H, $^4$J = 2.9, CH), 8.14 (d, 2 H, $J$ = 8.8, 2 × CH), 8.29 (d, 2 H, $J$ = 8.8, 2 × CH). Elemental analysis: for C$_{30}$H$_{32}$O$_7$ (504.59): calculated C 71.41, H 6.39; found C 71.24, H 6.45%.

Intermediates 32b (R = C$_{10}$H$_{21}$, yield 78%, m.p. 106–109°C), 32c (R = C$_{12}$H$_{25}$, yield 86%, m.p. 115–118°C) and 32d (R = C$_{14}$H$_{29}$, yield 78%, m.p. 110.5–114°C) were prepared by the same procedure.

4-[(6-Chloro-3-hydroxybenzoyl)oxy]phenyl 4-octyloxybenzoate (19a)
TBAF·3H$_2$O (60 mg; 0.190 mmol) was added to a solution of tert-butyl(dimethyl)silyl-protected ester 16a (450 mg; 0.736 mmol) in a mixture of tetrahydrofuran (50 ml) and water (12 ml). The mixture was stirred at room temperature for 5 h, diluted with water (100 ml) and extracted with ethyl acetate (3 × 80 ml). The combined organic solution was washed with water (100 ml) and brine (100 ml), dried with anhydrous magnesium sulphate and evaporated. The crude product was purified by column chromatography (hexane/ethyl acetate, 3/1) and crystallisation from toluene. Yield 71%, m.p. 105–110°C. $^1$H NMR (CDCl$_3$): 0.89 (t, 3 H, $J$ = 6.7, CH$_3$), 1.25-1.56 (m, 10 H, (CH$_2$)$_5$), 1.83 (m, 2 H, CH$_2$), 4.05 (t, 2 H, $J$ = 6.7, OCH$_2$), 5.36 (s, 1 H, OH), 6.96-7.00 (m, 3 H, 3 × CH), 7.25-7.28 (m, 4 H, 4 × CH), 7.38 (d, 1 H, $^3$J = 8.8, CH), 7.50 (d, 1 H, $^4$J = 2.9, CH), 8.14 (d, 2 H, $J$ = 8.8, 2 × CH). Elemental analysis for: C$_{28}$H$_{29}$ClO$_6$ (496.99): calculated C 67.67, H 5.88, Cl 7.13; found C 67.59, H 5.96, Cl 7.08%.

Homologous derivatives 19b (R = C$_{10}$H$_{21}$, yield 65%, m.p. 104–107°C), 19c (R = C$_{12}$H$_{25}$, yield 82%, m.p. 103–106°C), and 19d (R = C$_{14}$H$_{29}$, yield 84%, m.p. 104-105°C) were prepared by the same procedure.

4-Octyloxyphenyl 4-[(6-chloro-3-hydroxybenzoyl)oxy]benzoate (28a) was prepared using the method described above by deprotection of 22a. Yield 44%, m.p. 106–107.5°C. $^1$H NMR (CDCl$_3$): 0.82 (t, 3 H, $J$ = 6.7, CH$_3$), 1.19-1.46 (m, 10 H, (CH$_2$)$_5$), 1.72 (m, 2 H, CH$_2$), 3.89 (t, 2 H, $J$ = 6.7, OCH$_2$), 5.42 (s, 1 H, OH), 6.86 (d, 2 H, $J$ = 8.8, 2 × CH), 6.94 (dd, 1 H, $^3$J = 8.8, $^4$J = 2.9, CH), 7.05 (d, 2 H, $J$ = 8.8, 2 × CH), 7.31 (d, 2 H, $J$ = 8.8, 2 × CH), 7.32 (d, 1 H, $^3$J = 8.8, CH), 7.47 (d, 1 H, $^4$J = 2.9, CH), 8.21 (d, 2 H, $J$ = 8.8, 2 × CH). Elemental analysis: for C$_{28}$H$_{29}$ClO$_6$ (496.99): calculated C 67.67, H 5.88, Cl 7.13; found C 67.77, H 6.23, Cl 7.02%.
Intermediates 28b (R = C_{10}H_{21}, yield 69%, m.p. 99–102.5°C), 28c (R = C_{12}H_{25}, yield 73%, m.p. 108–111°C), and 28d (R = C_{14}H_{29}, yield 70%, m.p. 113–115°C) were prepared by the same procedure.

Octyl 4-[[4-[(6-chloro-3-hydroxybenzoyl)oxy]benzoyl]oxy]benzoate (31a). Deprotection of 25a was performed as for 19a, yield 57%, m.p. 118.5–121.5°C. \textit{^1}H NMR (CDCl$_3$): 0.89 (t, 3 H, \(J = 6.7\), CH$_3$), 1.21-1.52 (m, 10 H, (CH$_2$)$_5$), 1.78 (m, 2 H, CH$_2$), 4.34 (t, 2 H, \(J = 6.7\), OCH$_2$), 5.79 (s, 1 H, OH), 7.02 (dd, 1 H, \(^3\)J = 8.8, \(^4\)J = 2.9, CH), 7.27 (d, 2 H, \(J = 8.8, 2 \times CH\)), 7.39 (m, 3 H, 3 × CH), 7.58 (d, 1 H, \(^4\)J = 2.9, CH), 8.14 (d, 2 H, \(J = 8.8, 2 \times CH\)), 8.29 (d, 2 H, \(J = 8.8, 2 \times CH\)). Elemental analysis: for C$_{29}$H$_{29}$ClO$_7$ (525.00): calculated C 66.35, H 5.57, Cl 6.75; found C 66.59, H 5.48, Cl 6.67%.

Intermediates 31b (R = C$_{10}$H$_{21}$, yield 44%, m.p. 115–118°C), 31c (R = C$_{12}$H$_{25}$, yield 52%, m.p. 107–119°C) and 31d (R = C$_{14}$H$_{29}$, yield 61%, m.p. 114–117.5°C) were prepared by the same procedure.

1.4. Synthesis of the target compounds

4-[[6-Fluoro-3-[(4-octyloxybenzoyloxy)benzoyloxy]benzoyloxy]phenyl 4-octyloxybenzoate (Ia/F)

DMAP (76 mg, 0.625 mmol) was added to a solution of hydroxy ester 18a (150 mg, 0.312 mmol), in toluene (12 ml) at 100 °C in an argon atmosphere. Then a solution of acid chloride 14a (243 mg, 0.625 mmol) in toluene (5 ml) was added via a syringe. The reaction mixture was stirred for 5 minutes, then cooled down to room temperature and decomposed with cold water (30 ml). Layers were separated and the aqueous layer was extracted with chloroform (3 × 30 ml). The combined organic solution was washed with water (50 ml) and dried with anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the product was purified by column chromatography (toluene/tert-butyl methyl ether, 18/1) and by crystallisation from an ethyl acetate/ethanol mixture. Yield 180 mg (69%). \textit{^1}H NMR (CDCl$_3$): 0.89 (m, 6 H, 2 × CH$_3$), 1.24-1.53 (m, 20 H, 2 × (CH$_2$)$_5$), 1.82 (m, 4 H, 2 × CH$_2$), 4.05 (m, 4 H, 2 × OCH$_2$), 6.97 (d, 2 H, \(J = 8.8, 2 \times CH\)), 6.99 (d, 2 H, \(J = 8.8, 2 \times CH\)), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, \(J = 8.8, 2 \times CH\)), 7.49 (ddd, 1 H, \(^3\)J = 8.8, \(^4\)J = 3.2, \(^4\)J = 4.1, CH), 7.97 (dd, 1 H, \(^4\)J = 3.2, \(^4\)J = 5.8, CH), 8.14 (d, 2 H, \(J = 8.8, 2 \times CH\)), 8.15 (d, 2 H, \(J = 8.8, 2 \times CH\)), 8.28 (d, 2 H, \(J = 8.8, 2 \times CH\)). Elemental analysis: for C$_{50}$H$_{53}$FO$_{10}$ (832.97): calculated C 72.10, H 6.41, F 2.28; found C 71.91, H 6.32, F 2.34%.
By the same way, all compounds of the series Ib-d/X, IIa-d/X, and IIIa-d/X have been synthesised.

4-[3-(4-(4-Decyloxybenzoyloxy)benzoyloxy)-6-fluorobenzoyloxy]phenyl 4-octyloxybenzoate (Ib/F). Yield 59%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.23-1.53 (m, 28 H, 2 × (CH2)7), 1.82 (m, 4 H, 2 × CH2), 4.05 (m, 4 H, 2 × OCH2), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, J = 8.8, 2 × CH), 7.49 (ddd, 1 H, 3J = 8.8, 4J = 3.2, 4J = 4.1, CH), 7.97 (dd, 1 H, 4J = 3.2, 4J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C54H61FO10 (889.08): calculated C 72.95, H 6.92, F 2.13; found C 72.84, H 6.86, F 2.15%.

4-[3-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-6-fluorobenzoyloxy]phenyl 4-octyloxybenzoate (Ic/F). Yield 71%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.22-1.54 (m, 36 H, 2 × (CH2)9), 1.82 (m, 4 H, 2 × CH2), 4.05 (m, 4 H, 2 × OCH2), 6.97 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, J = 8.8, 2 × CH), 7.49 (ddd, 1 H, 3J = 8.8, 4J = 3.2, 4J = 4.1, CH), 7.97 (dd, 1 H, 4J = 3.2, 4J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C58H69FO10 (945.19): calculated C 73.70, H 7.36, F 2.01; found C 73.76, H 7.37, F 1.99%.

4-[6-Fluoro-3-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy]benzoyloxy]phenyl 4-octyloxybenzoate (Id/F). Yield 82%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.22-1.54 (m, 44 H, 2 × (CH2)11), 1.82 (m, 4 H, 2 × CH2), 4.05 (m, 4 H, 2 × OCH2), 6.97 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.33 (m, 5 H, 5 × CH), 7.39 (d, 2 H, J = 8.8, 2 × CH), 7.49 (ddd, 1 H, 3J = 8.8, 4J = 3.2, 4J = 4.1, CH), 7.97 (dd, 1 H, 4J = 3.2, 4J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C62H77FO10 (1001.30): calculated C 74.37, H 7.36, F 1.90; found C 74.28, H 7.72, F 1.84%.

4-[6-Chloro-3-(4-(4-octyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ia/Cl) was prepared as above by acylation of 19a with acid chloride 14a. Yield 71%. 1H NMR (CDCl3): 0.90 (m, 6 H, 2 × CH3), 1.24-1.55 (m, 20 H, 2 × (CH2)8), 1.83 (m, 4 H, 2 ×
CH₂), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, 3J = 8.8, CH), 7.96 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₅₀H₅₃ClO₁₀ (849.43): calculated C 70.70, H 6.29, Cl 4.17; found C 70.52 H 6.30, Cl 4.17%.

4-[6-Chloro-3-(4-(4-decyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ib/Cl). Yield 58%. ¹H NMR (CDCl₃): 0.90 (m, 6 H, 2 × CH₃), 1.24-1.54 (m, 28 H, 2 × (CH₂)₇), 1.83 (m, 4 H, 2 × CH₂), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, 3J = 8.8, CH), 7.96 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₅₄H₆₁ClO₁₀ (905.54): calculated C 71.63, H 6.79, Cl 3.92; found C 71.48, H 6.67, Cl 3.99%.

4-[6-Chloro-3-(4-(4-dodecyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ic/Cl). Yield 68%. ¹H NMR (CDCl₃): 0.90 (m, 6 H, 2 × CH₃), 1.23-1.54 (m, 36 H, 2 × (CH₂)₉), 1.83 (m, 4 H, 2 × CH₂), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, 3J = 8.8, CH), 7.96 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₅₈H₆₉ClO₁₀ (961.64): calculated C 72.44, H 7.23, Cl 3.69; found C 72.31, H 7.19, Cl 3.74%.

4-[6-Chloro-3-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Id/Cl). Yield 89%. ¹H NMR (CDCl₃): 0.90 (m, 6 H, 2 × CH₃), 1.23-1.55 (m, 44 H, 2 × (CH₂)₁₁), 1.83 (m, 4 H, 2 × CH₂), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.26-7.30 (m, 4 H, 4 × CH), 7.38-7.44 (m, 3 H, 3 × CH), 7.60 (d, 1 H, 3J = 8.8, CH), 7.96 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C₆₂H₇₇ClO₁₀ (1017.75): calculated C 73.17, H 7.63, Cl 3.48; found C 73.01, H 7.69, Cl 3.46%.

4-[6-Methyl-3-(4-(4-octyloxybenzoyloxy)benzoyloxy)benzoyloxy]phenyl 4-octyloxybenzoate (Ia/CH₃) was synthesised by acylation of 20a with acid chloride 14a, yield 69%. ¹H NMR (CDCl₃): 0.89 (m, 6 H, 2 × CH₃), 1.22-1.55 (m, 20 H, 2 × (CH₂)₅), 1.82 (m, 4 H, 2 × CH₂),
2.70 (s, 3 H, CH₃), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH).

Elemental analysis: for C₅₁H₅₆O₁₀ (829.01): calculated C 73.89, H 6.81; found C 73.82, H 6.74.

4-[3-(4-(4-Decyloxybenzoyloxy)benzoyloxy)-6-methylbenzoyloxy]phenyl 4-octyloxybenzoate (Ib/CH₃). Yield 78%. ¹H NMR (CDCl₃): 0.89 (m, 6 H, 2 × CH₃), 1.22-1.54 (m, 28 H, 2 × (CH₂)₇), 1.82 (m, 4 H, 2 × CH₂), 2.70 (s, 3 H, CH₃), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis for C₅₅H₆₄O₁₀ (885.12): calculated 74.64% C, 7.29% H; found 74.61% C, 7.40% H.

4-[3-(4-(4-Dodecyloxybenzoyloxy)benzoyloxy)-6-methylbenzoyloxy]phenyl 4-octyloxybenzoate (Ic/CH₃). Yield 56%. ¹H NMR (CDCl₃): 0.89 (m, 6 H, 2 × CH₃), 1.23-1.55 (m, 36 H, 2 × (CH₂)₉), 1.82 (m, 4 H, 2 × CH₂), 2.70 (s, 3 H, CH₃), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis for C₆₃H₈₀O₁₀ (997.33): calculated 75.87% C, 8.09% H; found 75.69% C, 7.98% H.

4-[6-Methyl-3-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy]benzoate (Id/CH₃). Yield 74%. ¹H NMR (CDCl₃): 0.89 (m, 6 H, 2 × CH₃), 1.22-1.55 (m, 44 H, 2 × (CH₂)₁₁), 1.82 (m, 4 H, 2 × CH₂), 2.70 (s, 3 H, CH₃), 4.05 (m, 4 H, 2 × OCH₂), 6.97 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.24-7.29 (m, 4 H, 4 × CH), 7.36-7.42 (m, 4 H, 4 × CH), 8.04 (d, 1 H, 4J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, 2 × CH). Elemental analysis for C₆₃H₈₀O₁₀ (997.33): calculated 75.87% C, 8.09% H; found 75.75% C, 8.06% H.

4-Octyloxyphenyl 4-[6-fluoro-3-[4-(4-octyloxybenzoyloxy)]benzoyloxy]benzoyloxy]benzoate (IIa/F). Reaction of 27a with acid chloride 14a yielded the compound IIa/F, yield 65%. ¹H NMR (CDCl₃): 0.90 (m, 6 H, 2 × CH₃), 1.24-1.54 (m, 20 H, 2 × (CH₂)₅), 1.81 (m, 4 H, 2 × CH₂), 3.96 (t, 2 H, J = 6.7, OCH₂), 4.05 (t, 2 H, J = 6.7, OCH₂), 6.93 (d, 2 H, J = 8.8, 2 ×
CH), 6.99 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.12 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.31 (dd, 1 H, \( ^3J = 8.8, ^3J = 9.7, CH \)), 7.37-7.41 (m, 4 H, \( 4 \times CH \)), 7.51 (ddd, 1 H, \( ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH \)), 7.99 (dd, 1 H, \( ^4J = 3.2, ^4J = 5.8, CH \)), 8.15 (d, 2 H, \( J = 8.8, 2 \times CH \)), 8.28 (m, 4 H, \( 4 \times CH \)).

Elemental analysis: for \( C_{50}H_{53}FO_{10} \) (832.97): calculated C 72.10, H 6.41, F 2.28; found C 71.98, H 6.37, F 2.30%.

4-Decyloxyphenyl 4-{3-[4-(4-decyloxybenzoyloxy)benzoyloxy]-6-fluorobenzoyloxy]benzoate (IIb/F). Yield 72%. \(^1H\) NMR (CDCl\(_3\)): 0.90 (m, 6 H, \( 2 \times CH_3 \)), 1.24-1.53 (m, 28 H, \( 2 \times (CH_2)_2 \)), 1.81 (m, 4 H, \( 2 \times CH_2 \)), 3.96 (t, 2 H, \( J = 6.7, OCH_2 \)), 4.05 (t, 2 H, \( J = 6.7, OCH_2 \)), 6.93 (d, 2 H, \( J = 8.8, 2 \times CH \)), 6.99 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.12 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.31 (dd, 1 H, \( ^3J = 8.8, ^3J = 9.7, CH \)), 7.37-7.41 (m, 4 H, \( 4 \times CH \)), 7.51 (ddd, 1 H, \( ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH \)), 7.99 (dd, 1 H, \( ^4J = 3.2, ^4J = 5.8, CH \)), 8.15 (d, 2 H, \( J = 8.8, 2 \times CH \)), 8.28 (m, 4 H, \( 4 \times CH \)).

Elemental analysis: for \( C_{54}H_{61}FO_{10} \) (889.08): calculated C 72.95, H 6.92, F 2.13; found C 72.78, H 6.87, F 2.18%.

4-Dodecyloxyphenyl 4-{3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-6-fluorobenzoyloxy]benzoate (IIc/F). Yield 74%. \(^1H\) NMR (CDCl\(_3\)): 0.90 (m, 6 H, \( 2 \times CH_3 \)), 1.24-1.54 (m, 36 H, \( 2 \times (CH_2)_9 \)), 1.81 (m, 4 H, \( 2 \times CH_2 \)), 3.96 (t, 2 H, \( J = 6.7, OCH_2 \)), 4.05 (t, 2 H, \( J = 6.7, OCH_2 \)), 6.93 (d, 2 H, \( J = 8.8, 2 \times CH \)), 6.99 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.12 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.31 (dd, 1 H, \( ^3J = 8.8, ^3J = 9.7, CH \)), 7.37-7.41 (m, 4 H, \( 4 \times CH \)), 7.51 (ddd, 1 H, \( ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH \)), 7.99 (dd, 1 H, \( ^4J = 3.2, ^4J = 5.8, CH \)), 8.15 (d, 2 H, \( J = 8.8, 2 \times CH \)), 8.28 (m, 4 H, \( 4 \times CH \)).

Elemental analysis: for \( C_{58}H_{69}FO_{10} \) (945.19): calculated C 73.70, H 7.36, F 2.01; found C 73.63, H 7.32, F 1.95%.

4-Tetradecyloxyphenyl 4-{6-fluoro-3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoate (IId/F). Yield 51%. \(^1H\) NMR (CDCl\(_3\)): 0.90 (m, 6 H, \( 2 \times CH_3 \)), 1.23-1.54 (m, 44 H, \( 2 \times (CH_2)_{11} \)), 1.81 (m, 4 H, \( 2 \times CH_2 \)), 3.96 (t, 2 H, \( J = 6.7, OCH_2 \)), 4.05 (t, 2 H, \( J = 6.7, OCH_2 \)), 6.93 (d, 2 H, \( J = 8.8, 2 \times CH \)), 6.99 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.12 (d, 2 H, \( J = 8.8, 2 \times CH \)), 7.31 (dd, 1 H, \( ^3J = 8.8, ^3J = 9.7, CH \)), 7.37-7.41 (m, 4 H, \( 4 \times CH \)), 7.51 (ddd, 1 H, \( ^3J = 8.8, ^4J = 3.2, ^4J = 4.1, CH \)), 7.99 (dd, 1 H, \( ^4J = 3.2, ^4J = 5.8, CH \)), 8.15 (d, 2 H, \( J = 8.8, 2 \times CH \)), 8.28 (m, 4 H, \( 4 \times CH \)).

Elemental analysis: for \( C_{62}H_{77}FO_{10} \) (1001.30): calculated C 74.37, H 7.75, F 1.90; found C 74.25, H 7.90, F 1.81%.
4-Octyloxyphenyl 4-[6-chloro-3-[4-(4-octyloxybenzoyloxy)]benzoyloxy]benzoyloxy]benzoate (IIa/Cl) has been prepared from intermediate 28a and acid chloride 14a, yield 82%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.23-1.53 (m, 20 H, 2 × (CH2)8), 1.81 (m, 4 H, 2 × CH2), 3.96 (t, 2 H, J = 6.7. OCH2), 4.06 (t, 2 H, J = 6.7, OCH2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, 3J = 8.8, CH), 8.00 (d, 1 H, 4J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for C50H53ClO10 (849.43): calculated C 70.70, H 6.29, Cl 4.17; found C 70.60, H 6.26, Cl 4.18%.

4-Decyloxyphenyl 4-[6-chloro-3-[4-(4-decyloxybenzoyloxy)]benzoyloxy]benzoyloxy]benzoate (IIb/Cl). Yield 75%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.23-1.53 (m, 28 H, 2 × (CH2)7), 1.81 (m, 4 H, 2 × CH2), 3.96 (t, 2 H, J = 6.7. OCH2), 4.06 (t, 2 H, J = 6.7, OCH2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, 3J = 8.8, CH), 8.00 (d, 1 H, 4J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for C54H61ClO10 (905.54): calculated C 71.63, H 6.79, Cl 3.92; found C 71.44, H 6.77, Cl 4.00%.

4-Dodecyloxyphenyl 4-[6-chloro-3-[4-(4-dodecyloxybenzoyloxy)]benzoyloxy]benzoyloxy]benzoate (IIc/Cl). Yield 75%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.23-1.54 (m, 36 H, 2 × (CH2)9), 1.81 (m, 4 H, 2 × CH2), 3.96 (t, 2 H, J = 6.7. OCH2), 4.06 (t, 2 H, J = 6.7, OCH2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, 3J = 8.8, CH), 8.00 (d, 1 H, 4J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for C58H69ClO10 (961.64): calculated C 72.44, H 7.23, Cl 3.69; found C 72.28, H 7.18, Cl 3.60%.

4-Tetradecyloxyphenyl 4-[6-chloro-3-[4-(4-tetradecyloxybenzoyloxy)]benzoyloxy]benzoyloxy]benzoate (IId/Cl). Yield 83%. 1H NMR (CDCl3): 0.89 (m, 6 H, 2 × CH3), 1.22-1.54 (m, 44 H, 2 × (CH2)11), 1.81 (m, 4 H, 2 × CH2), 3.96 (t, 2 H, J = 6.7. OCH2), 4.06 (t, 2 H, J = 6.7, OCH2), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.46 (m, 5 H, 5 × CH), 7.62 (d, 1 H, 3J = 8.8, CH), 8.00 (d, 1 H, 4J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH).
Elemental analysis: for C\textsubscript{62}H\textsubscript{77}ClO\textsubscript{10} (1017.75): calculated C 73.17, H 7.63, Cl 3.48; found C 73.09, H 7.59, Cl 3.39%.

4-Octyloxyphenyl 4-[6-methyl-3-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoate (IIa/CH\textsubscript{3}). Compound 29a (120 mg; 0.252 mmol) was acylated with acid chloride 14a. Yield 73%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 0.88 (m, 6 H, 2 × CH\textsubscript{3}); 1.20-1.52 (m, 20 H, 2 × (CH\textsubscript{2})\textsubscript{5}), 1.80 (m, 4 H, 2 × CH\textsubscript{2}), 2.71 (s, 3 H, CH\textsubscript{3}), 3.96 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 4.05 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C\textsubscript{51}H\textsubscript{56}O\textsubscript{10} (829.01): calculated C 73.89, H 6.81; found C 73.79, H 6.72%.

4-Decyloxyphenyl 4-[3-[4-(4-decyloxybenzoyloxy)benzoyloxy]-6-methylbenzoyloxy]benzoate (IIb/CH\textsubscript{3}). Yield 65%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 0.88 (m, 6 H, 2 × CH\textsubscript{3}); 1.21-1.52 (m, 28 H, 2 × (CH\textsubscript{2})\textsubscript{7}), 1.80 (m, 4 H, 2 × CH\textsubscript{2}), 2.71 (s, 3 H, CH\textsubscript{3}), 3.96 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 4.05 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C\textsubscript{55}H\textsubscript{64}O\textsubscript{10} (885.12): calculated C 74.64, H 7.29; found C 74.68, H 7.42%.

4-Dodecyloxyphenyl 4-[3-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-6-methylbenzoyloxy]benzoate (IIc/CH\textsubscript{3}). Yield 74%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 0.88 (m, 6 H, 2 × CH\textsubscript{3}); 1.20-1.51 (m, 36 H, 2 × (CH\textsubscript{2})\textsubscript{9}), 1.80 (m, 4 H, 2 × CH\textsubscript{2}), 2.71 (s, 3 H, CH\textsubscript{3}), 3.96 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 4.05 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C\textsubscript{59}H\textsubscript{72}O\textsubscript{10} (941.23): calculated C 75.29, H 7.71; found C 75.11, H 7.69%.

4-Tetradecyloxyphenyl 4-[6-methyl-3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy]benzoate (IIId/CH\textsubscript{3}). Yield 60%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 0.88 (m, 6 H, 2 × CH\textsubscript{3}); 1.20-1.52 (m, 44 H, 2 × (CH\textsubscript{2})\textsubscript{11}), 1.80 (m, 4 H, 2 × CH\textsubscript{2}), 2.71 (s, 3 H, CH\textsubscript{3}), 3.96 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 4.05 (t, 2 H, J = 6.7, OCH\textsubscript{2}), 6.93 (d, 2 H, J = 8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, J = 2.9, CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C\textsubscript{61}H\textsubscript{77}ClO\textsubscript{10} (1088.88): calculated C 75.98, H 7.63; found C 75.90, H 7.59%.
8.8, 2 × CH), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.12 (d, 2 H, J = 8.8, 2 × CH), 7.32-7.43 (m, 6 H, 6 × CH), 8.07 (d, 1 H, \(^{1}J = 2.9, \text{CH}\)), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for: C\(_{63}\)H\(_{80}\)O\(_{10}\) (997.33): calculated C 75.87, H 8.09; found C 75.74, H 8.00%.

**Octyl**

4-[4-{6-fluoro-3-[4-(4-

octyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy}benzoate (IIIa/F) was obtained by the reaction of 30a with acid chloride 14a, yield 31%. \(^{1}\)H NMR (CDCl\(_{3}\)): 0.89 (m, 6 H, 2 × CH\(_{3}\)), 1.25-1.54 (m, 20 H, 2 × (CH\(_{2}\))\(_{5}\)), 1.80 (m, 4 H, 2 × CH\(_{2}\)), 4.06 (t, 2 H, J = 6.7, OCH\(_{2}\)), 4.33 (t, 2 H, J = 6.7, OCH\(_{2}\)), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.32 (dd, 1 H, \(^{3}\)J = 8.8, \(^{3}\)J = 9.7, CH), 7.40 (d, 2 H, J = 8.8, 2 × CH), 7.42 (d, 2 H, J = 8.8, 2 × CH), 7.52 (ddd, 1 H, \(^{3}\)J = 8.8, \(^{4}\)J = 3.2, \(^{4}\)J = 4.1, CH), 7.99 (dd, 1 H, \(^{4}\)J = 3.2, \(^{4}\)J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for C\(_{51}\)H\(_{53}\)FO\(_{11}\) (860.98): calculated C 71.15, H 6.20, F 2.21; found C 71.01, H 6.14, F 2.17%.

**Decyl**

4-[4-{3-[4-(4-decylbenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy]benzoate (IIIa/F). Yield 56%. \(^{1}\)H NMR (CDCl\(_{3}\)): 0.89 (m, 6 H, 2 × CH\(_{3}\)), 1.25-1.54 (m, 28 H, 2 × (CH\(_{2}\))\(_{7}\)), 1.80 (m, 4 H, 2 × CH\(_{2}\)), 4.06 (t, 2 H, J = 6.7, OCH\(_{2}\)), 4.33 (t, 2 H, J = 6.7, OCH\(_{2}\)), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.32 (dd, 1 H, \(^{3}\)J = 8.8, \(^{3}\)J = 9.7, CH), 7.40 (d, 2 H, J = 8.8, 2 × CH), 7.42 (d, 2 H, J = 8.8, 2 × CH), 7.52 (ddd, 1 H, \(^{3}\)J = 8.8, \(^{4}\)J = 3.2, \(^{4}\)J = 4.1, CH), 7.99 (dd, 1 H, \(^{4}\)J = 3.2, \(^{4}\)J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for C\(_{55}\)H\(_{61}\)FO\(_{11}\) (917.09): calculated C 72.03, H 6.70, F 2.02%; found C 71.85, H 6.76, F 2.02%.

**Dodecyl**

4-[4-{3-[4-(4-dodecylbenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy]benzoate (IIIc/F). Yield 67%. \(^{1}\)H NMR (CDCl\(_{3}\)): 0.89 (m, 6 H, 2 × CH\(_{3}\)), 1.25-1.53 (m, 36 H, 2 × (CH\(_{2}\))\(_{9}\)), 1.80 (m, 4 H, 2 × CH\(_{2}\)), 4.06 (t, 2 H, J = 6.7, OCH\(_{2}\)), 4.33 (t, 2 H, J = 6.7, OCH\(_{2}\)), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.32 (dd, 1 H, \(^{3}\)J = 8.8, \(^{3}\)J = 9.7, CH), 7.40 (d, 2 H, J = 8.8, 2 × CH), 7.42 (d, 2 H, J = 8.8, 2 × CH), 7.52 (ddd, 1 H, \(^{3}\)J = 8.8, \(^{4}\)J = 3.2, \(^{4}\)J = 4.1, CH), 7.99 (dd, 1 H, \(^{4}\)J = 3.2, \(^{4}\)J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.28 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for C\(_{55}\)H\(_{61}\)FO\(_{11}\) (917.09): calculated C 72.03, H 6.70, F 2.02%; found C 71.85, H 6.76, F 2.02%. 

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18
CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for C$_{59}$H$_{69}$F$_{11}$ (973.20): calculated C 72.82, H 7.15, F 1.95; found C 72.67, H 7.21, F 1.93%.

**Tetradecyl**

4-[(4-{4-[6-fluoro-3-[4-{4-

(tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy]benzoyloxy}benzoate (IIId/F). Yield 83%.

$^1$H NMR (CDCl$_3$): 0.89 (m, 6 H, 2 × CH$_3$), 1.24-1.54 (m, 44 H, 2 × (CH$_2$)$_1$), 1.80 (m, 4 H, 2 × CH$_2$), 4.06 (t, 2 H, J = 6.7, OCH$_2$), 4.33 (t, 2 H, J = 6.7, OCH$_2$), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.32 (dd, 1 H, $^3$J = 8.8, $^3$J = 9.7, CH), 7.40 (d, 2 H, J = 8.8, 2 × CH), 7.42 (d, 2 H, J = 8.8, 2 × CH), 7.52 (dd, 1 H, $^3$J = 8.8, $^4$J = 3.2, $^4$J = 4.1, CH), 7.99 (dd, 1 H, $^4$J = 3.2, $^4$J = 5.8, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis for C$_{63}$H$_{77}$F$_{11}$ (1029.31): calculated C 73.52, H 7.54, F 1.85; found C 73.43, H 7.50, F 1.90%.

**Octyl**

4-[(4-{4-[6-chloro-3-[4-{4-

(octyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy]benzoyloxy}benzoate (IIIa/Cl) has been prepared by acylation of 31a with acid chloride 14a, yield 74%. $^1$H NMR (CDCl$_3$): 0.89 (m, 6 H, 2 × CH$_3$), 1.23-1.55 (m, 20 H, 2 × (CH$_2$)$_5$), 1.80 (m, 4 H, 2 × CH$_2$), 4.06 (t, 2 H, J = 6.7, OCH$_2$), 4.33 (t, 2 H, J = 6.7, OCH$_2$), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, $^3$J = 8.8, CH), 8.00 (d, 1 H, $^4$J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C$_{51}$H$_{53}$ClO$_{11}$ (877.44): calculated C 69.81, H 6.09, Cl 4.04; found C 69.57, H 6.13, Cl 4.01%.

**Decyl**

4-[(4-{4-[6-chloro-3-[4-{4-

(decyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoyloxy}benzoate (IIIb/Cl). Yield 70%. $^1$H NMR (CDCl$_3$): 0.89 (m, 6 H, 2 × CH$_3$), 1.23-1.55 (m, 28 H, 2 × (CH$_2$)$_7$), 1.80 (m, 4 H, 2 × CH$_2$), 4.06 (t, 2 H, J = 6.7, OCH$_2$), 4.33 (t, 2 H, J = 6.7, OCH$_2$), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, $^3$J = 8.8, CH), 8.00 (d, 1 H, $^4$J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH). Elemental analysis: for C$_{55}$H$_{61}$ClO$_{11}$ (933.55): calculated C 69.81, H 6.09, Cl 4.04; found C 69.57, H 6.13, Cl 4.01%.

**Dodecyl**

4-[(4-{4-[6-chloro-3-[4-{4-

dodecyloxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy}benzoyloxy}benzoate (IIIc/Cl). Yield 81%.
\[ \text{\textsuperscript{1}H NMR (CDCl}_3\text{): 0.89 (m, 6 H, 2 × CH}_3\text{), 1.24-1.55 (m, 36 H, 2 × (CH}_2\text{)_9), 1.80 (m, 4 H, 2 × CH}_2\text{), 4.06 (t, 2 H, J = 6.7, OCH}_2\text{), 4.33 (t, 2 H, J = 6.7, OCH}_2\text{), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, \textsuperscript{3}J = 8.8, CH), 8.00 (d, 1 H, \textsuperscript{3}J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH).} \]

Elemental analysis: for C\textsubscript{59}H\textsubscript{69}ClO\textsubscript{11} (989.65): calculated C 71.61, H 7.03, Cl 3.58; found C 71.51, H 7.09, Cl 3.62%.

Tetradecyl

\[ 4\text{-}[4\text{-}(4\text{-chloro-3-[4-(4-}
\text{tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy}benzoyloxy}benzoyloxy}benzoate (III\textsubscript{d}/Cl). \text{Yield 80\%.}\]

\[ \text{\textsuperscript{1}H NMR (CDCl}_3\text{): 0.89 (m, 6 H, 2 × CH}_3\text{), 1.24-1.56 (m, 44 H, 2 × (CH}_2\text{)_11), 1.80 (m, 4 H, 2 × CH}_2\text{), 4.06 (t, 2 H, J = 6.7, OCH}_2\text{), 4.33 (t, 2 H, J = 6.7, OCH}_2\text{), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.38-7.47 (m, 5 H, 5 × CH), 7.63 (d, 1 H, \textsuperscript{3}J = 8.8, CH), 8.00 (d, 1 H, \textsuperscript{3}J = 2.9, CH), 8.14 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (d, 2 H, J = 8.8, 2 × CH), 8.30 (d, 2 H, J = 8.8, 2 × CH).} \]

Elemental analysis: for C\textsubscript{63}H\textsubscript{77}ClO\textsubscript{11} (1045.76): calculated C 72.36, H 7.42, Cl 3.39; found C 72.22, H 7.37, Cl 3.43%.

Octyl

\[ 4\text{-}[4\text{-}(4\text{-methyl-3-[4-(4-}
\text{octyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy}benzoyloxy}benzoyloxy}benzoyloxy}benzoyloxy}benzoyloxy}benzoate (III\textsubscript{a}/CH\textsubscript{3}). \text{Acylation of 32a with acid chloride 14a provided the target product III\textsubscript{a}/CH\textsubscript{3} in 71% yield.}\]

\[ \text{\textsuperscript{1}H NMR (CDCl}_3\text{): 0.88 (m, 6 H, 2 × CH}_3\text{), 1.18-1.53 (m, 20 H, 2 × (CH}_2\text{)_5), 1.80 (m, 4 H, 2 × CH}_2\text{), 2.71 (s, 3 H, CH}_3\text{), 4.05 (t, 2 H, J = 6.7, OCH}_2\text{), 4.32 (t, 2 H, J = 6.7, OCH}_2\text{), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, \textsuperscript{4}J = 2.9, CH), 8.13 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH).} \]

Elemental analysis: for C\textsubscript{52}H\textsubscript{56}O\textsubscript{11} (857.02): calculated C 72.88, H 6.59; found C 72.71, H 6.64%.

Decyl

\[ 4\text{-}[3\text{-}[4-(4-decyloxybenzoyloxy)benzoyloxy]-6-methylbenzoyloxy]benzoyloxy}benzoyloxy}benzoyloxy}benzoyloxy}benzoyloxy}benzoyloxy}benzoate (III\textsubscript{b}/CH\textsubscript{3}). \text{Yield 65\%.}\]

\[ \text{\textsuperscript{1}H NMR (CDCl}_3\text{): 0.88 (m, 6 H, 2 × CH}_3\text{), 1.20-1.53 (m, 28 H, 2 × (CH}_2\text{)_7), 1.80 (m, 4 H, 2 × CH}_2\text{), 2.71 (s, 3 H, CH}_3\text{), 4.05 (t, 2 H, J = 6.7, OCH}_2\text{), 4.32 (t, 2 H, J = 6.7, OCH}_2\text{), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, \textsuperscript{4}J = 2.9, CH), 8.13 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH).} \]

Elemental analysis: for C\textsubscript{56}H\textsubscript{64}O\textsubscript{11} (913.13): calculated C 73.66, H 7.06; found C 73.45, H 7.21%.
Dodecyl 4-{4-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-6-methylbenzoyloxy}benzoyloxy]benzoate (IIIc/CH₃). Yield 69%. ¹H NMR (CDCl₃): 0.88 (m, 6 H, 2 × CH₃), 1.21-1.54 (m, 36 H, 2 × (CH₂)₉), 1.80 (m, 4 H, 2 × CH₂), 2.71 (s, 3 H, CH₃), 4.05 (t, 2 H, J = 6.7, OCH₂), 4.32 (t, 2 H, J = 6.7, OCH₂), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ₄J = 2.9, CH), 8.13 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for C₆₀H₇₂O₁₁ (969.24): calculated C 74.35, H 7.49; found C 74.28, H 7.39%.

Tetradecyl 4-{4-[6-methyl-3-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy}benzoyloxy]benzoate (IIId/CH₃). Yield 80%. ¹H NMR (CDCl₃): 0.88 (m, 6 H, 2 × CH₃), 1.19-1.53 (m, 44 H, 2 × (CH₂)₁₁), 1.80 (m, 4 H, 2 × CH₂), 2.71 (s, 3 H, CH₃), 4.05 (t, 2 H, J = 6.7, OCH₂), 4.32 (t, 2 H, J = 6.7, OCH₂), 6.99 (d, 2 H, J = 8.8, 2 × CH), 7.31 (d, 2 H, J = 8.8, 2 × CH), 7.35-7.44 (m, 6 H, 6 × CH), 8.07 (d, 1 H, ₄J = 2.9, CH), 8.13 (d, 2 H, J = 8.8, 2 × CH), 8.15 (d, 2 H, J = 8.8, 2 × CH), 8.29 (m, 4 H, 4 × CH). Elemental analysis: for C₆₄H₈₀O₁₁ (1025.34): calculated C 74.79, H 7.86; found C 74.60, H 7.74%.
2. Mesomorphic properties

Figure S1
Planar texture of \textbf{Id/F} at T=110°C a) after the field application, b) at intermediate field of about 10 V/µm and c) at field of about 20 V/µm.

Figure S2
Planar texture for \textbf{IIIId/F} on cooling from the isotropic phase (Iso), a) at the Iso- B_{1Rev} phase transition and b) in B_{1Rev} phase at T=125°C.
Figure S3
Temperature dependences of the layer spacing, $d$, in the SmCP$_A$ phase for compound Id/F.

Figure S4
Temperature dependences of the cell parameters for a) IIb/F and b) IIIId/F.
Figure S5
Schematic picture of the molecular arrangements in the columnar a) B₁ and b) B₁Rev phase.
3. *Ab-initio calculations*

In this section, the optimization of side arms of the target materials is described in detail. All calculations were performed in Gaussian 03W®, initial geometries were designed and results visualized in GaussView 3.0®.

3.1 *Optimization of lengthening arms*

Prior to the optimization of the target materials, a thorough conformational analysis of lengthening arms (Figure S6) was performed. We assumed that the energy barrier of the rotation of one dihedral angle is almost independent on the conformation of the others. This assumption allowed us to perform the relaxed scan optimization of the selected molecules with a 15 degrees step. It has already been described [S2] that the carbonyl group connected to an aromatic ring lies within the layer of this unit, whereas the second aromatic ring connected to the oxygen atom of the ester linkage is rotated with respect to this layer. Since the free rotation of terminal functional groups (alkoxy chain, carboxylic group and hydroxy group) has negligible contribution to the total free energy of the molecule, only torsion angle $\delta$ (see Figure S6) remains the key free energy-determining parameter.

![Figure S6](image-url)

**Figure S6** Structures of the studied lengthening arms. The torsion angle $\delta$ of the connecting ester linkage is marked in red colour. (Colour version available online)
The computations were performed on HF/6-31g(d) level to save calculation time. Since the calculation error given by HF method could be considered the same in each case, it was subtracted in the process of determining differences in energies ($\Delta E$) of given conformers (Figures S7-10). The conformers with minimum energy found with HF/6-31g(d) method were further optimized with released coordinates of torsion angle $\delta$ on DFT level (B3LYP/6-31g(d)) to possible global energetic minimum (Figures S11-14).

**Figure S7**: Conformational analysis of 11c: values of $\Delta E$ versus torsion angle $\delta$, figure denotes only angles between 0°-180° for clarity, the profile between 180°-360° is symmetrical.
**Figure S8**: Conformational analysis of 12c: values of $\Delta E$ versus torsion angle $\delta$. Figure denotes only angles between $0^\circ-180^\circ$ for clarity, the profile between $180^\circ-360^\circ$ is symmetrical.

**Figure S9**: Conformational analysis of 13c: values of $\Delta E$ versus torsion angle $\delta$. Figure denotes only angles between $0^\circ-180^\circ$ for clarity, the profile between $180^\circ-360^\circ$ is symmetrical.

**Figure S10**: Conformational analysis of 14c: values of $\Delta E$ versus torsion angle $\delta$. Figure denotes only angles between $0^\circ-180^\circ$ for clarity, the profile between $180^\circ-360^\circ$ is symmetrical.
Figure S11: Conformational analysis of 11c: geometry of found global minimum of energy.

Figure S12: Conformational analysis of 12c: geometry of found global minimum of energy.
3.2 Optimization of hydroxy ester intermediates

Central cores (laterally substituted 3-hydroxybenzoic acids) were connected to the optimized lengthening arms 11c, 12c, or 13c. Based on previously reported calculations [S1], only the angle of 180° between the core itself and its carboxylic function connecting the lengthening
arm to the core, was considered as the starting geometry in each calculation (Figure S15). Resulting structures were optimized on DFT level (B3LYP/6-31g(d)) to minimum.

![Chemical structures and geometries](image)

**Figure S15**: Model of the starting geometries for the optimization of hydroxy ester intermediates.

The most pronounced influence of the molecular structure on the observed mesomorphic behaviour was found for materials of series III (compare Tables 1-3 in the main document). Thus, in the following we focused on the hydroxy esters 30c-32c from this series. The resulting conformers with minimum energy have already documented the influence of lateral substituent. The respective visualizations (Figure S16-S18) depict the steric influence imposed by chlorine and methyl and the resulting tilting of the first aromatic core of the elongating side arm, which is not present for fluoro substituted compound.
**Figure S16** Conformer with minimum energy of compound 30c. Due to the size of the molecule, the main part of the aliphatic chain was omitted in the figure.

**Figure S17** Conformer with minimum energy of compound 31c. Due to the size of the molecule, the main part of the aliphatic chain was omitted in the figure.
Figure S18 Conformer with minimum energy of compound 32c. Due to the size of the molecule, the main part of the aliphatic chain was omitted in the figure.

3.3. **Optimization of the target materials**

Similarly to the hydroxy ester intermediates discussed in the previous section, the second elongating arm 14c was connected under the angle of 180°, and both starting conformations were optimized to minimum on DFT level (B3LYP/6-31g(d)). The obtained conformers with minimum energy of series III serve as the basis for discussion provided in the main document.

Conformers with minimum energy for series I and II (Figure S19 and Figure S20) show features similar to materials of series III. As can be seen, the reorientation of the ester linkage in series I (marked with an arrow) supports the co-planar alignment of the outer phenyl ring with the central core. We assume, that this change could support the self-assembly of the materials that, in consequence, led to the formation of monotropic mesophases.

The change of the dipole moment and overall electrostatic potential distribution will be discussed in our follow up quantum chemical calculation study.
Figure S19 Conformers with minimum energy of materials IIc/F, IIc/Cl and IIc/CH₃.
Figure S20 Conformers with minimum energy of materials Ic/F, Ic/Cl and Ic/CH$_3$. The arrow marks the inversed ester linkage.

4. References
S1. Gunosewoyo H, Guo JL, Bennett MR, Coster MJ, Kassiou M. Cubyl amides: novel P2X$_7$ receptor antagonists. Bioorg Med Chem Lett. 2008;18:3720–3723.
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