EXPERIMENTAL

General
Solvents and reagents were purchased from Aldrich and used as received. Column chromatographies were performed on silica gel (Merck silica gel 60, mesh size 0.2-0.5 mm). NMR spectra were recorded in CDCl₃ on a Bruker Avance 300 with solvent signal as internal standard. Mass spectra were recorded on a Finnigan MAT 95 instrument (FD-MS) and a Bruker Reflex (MALDI-TOF). Elemental Analysis were done in the Microlab of the University of Mainz.

4′-(3,4,5-Trimethoxybenzoyloxy)benzoic acid 4a, 4′-[4''-(3,4,5-Trimethoxybenzoyloxy)benzoyl-oxy]benzoic acid 4b were synthesized by modifying the procedure of reference [1], using N,N-dimethyl-4-aminopyridinium 4-toluenesulfonate (DPTS) instead of N,N-dimethyl-4-aminopyridin (DMAP).

The thermal behaviour of all the materials synthesized was investigated by POM (Olympus Provis microscope equipped with a Mettler FP 82 heating stage and a Jena microscope equipped with a Mettler FP52 hot stage) and DSC (Mettler Toledo DSC 821) with heating and cooling scans performed at 10 °C/min. X-ray diffraction experiments were performed on the X33 camera of the European Molecular Biology Laboratory at the storage ring DORIS III of the Deutsches Elektronen Synchrotron (DESY), Hamburg. Diffraction patterns were collected in transmission in series of frames of 6s each with two position sensitive delay line readout detectors connected in series.² The sample temperature was controlled with a Mettler FP-82 HT heating stage. The scattering vector (s = 2sinθ/λ, where 2θ is the Bragg angle and λ the wavelength (1.5 Å)) was calibrated with tripalmitin and/or rat tail collagen in the small s-region and benzoic acid in the high s-region. Room temperature measurement of the mesophase of 1a were performed on a Siemens D 500 Kristalloflex diffractometer with a graphite-monochromized CuKα X-ray beam emitted from a Rotating Rigaku RV-300 anode.
4'-[4''-[4'''- (3,4,5- Tridodecyloxybenzoyloxy)benzoyloxy]benzoyloxy] benzoic acid 4c: 1.60 g (1.34 mmol) 4b, 0.31 g (1.34 mmol) 4-hydroxybenzoic acid benzylester 2, 0.29 g (1.41 mmol) 1,3-dicyclohexylcarbodiimide (DCC) and 0.09 g (0.31 mmol) DPTS were dissolved in 30 ml dry CH₂Cl₂ and stirred at ambient temperature over night. The solvent was then removed and the product was purified by column chromatography (silica 60/hexane/ethylacetate). The benzylester (1.38 g) was dissolved in 50 ml diethylether, Pd/C (10%) was added and a balloon of H₂ was attached. After stirring the mixture for 2h at 35 °C, the product was filtered over celite and eluted with additional 100 ml CH₂Cl₂. The solvent was evaporated and the product was recrystallized from acetone to give 1.20 g (87 %) of a colorless solid, T<sub>Cl</sub> = 197 °C; <sup>1</sup>H NMR (300 MHz, CDCl₃) δ = 0.88 (m, 9H, CH₃), 1.26-1.87 (m, 60H, CH₂), 4.06, 4.08 (2t, 6H, OCH₂), 7.42 (s, 2H, ArH), 7.37, 7.39, 7.42, 8.23, 8.32, 12H, ArH). <sup>13</sup>C NMR (75 MHz, CDCl₃) δ =14.0 (CH₃), 22.7-31.9 (CH₂), 69.3, 73.6 (OCH₂), 108.7, 121.8, 122.1, 122.3 (aromat. CH), 123.2, 126.4, 126.9 (aromat. C¼), 131.9 (aromat. CH), 143.4, 153.0, 155.6 (aromat C¼), 163.7, 164.4, 170.1 (C=O). FD MS: m/z (%): 1035 (100, M<sup>++</sup>). EA (C₇₈H₉₀O₁₁) calculated %C 74.24, %H 8.76, found %C 74.15, %H 8.65.

4'-[4''-[4'''- (3,4,5- Tridodecyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy) benzoic acid 4d: Starting from molecule 4c, compound 4d was synthesised analogous to 4c. Yield 244 mg (73 %) of a colorless solid, T<sub>Cl</sub> = 262 °C; <sup>1</sup>H NMR (300 MHz, CDCl₃) δ = 0.88 (m, 9H, CH₃), 1.26-1.87 (m, 60H, CH₂), 4.06, 4.08 (2t, 6H, OCH₂), 7.42 (s, 2H, ArH), 7.37, 7.39, 7.43, 8.23, 8.31, 8.32 (AA'BB', 12H, ArH). <sup>13</sup>C NMR (75 MHz, CDCl₃) δ =14.0 (CH₃), 22.7-33.6 (CH₂), 69.3, 73.6 (OCH₂), 108.7, 121.7, 122.1, 122.3 (aromat. CH), 123.1, 126.4, 126.6, 126.7, 126.9, 127.4 (aromat. C¼), 131.9, 132.0 (aromat. CH), 143.4, 153.0, 154.9, 155.2, 155.3, 155.6, 157.7 (aromat C¼), 163.7, 164.4, 170.2 (C=O). MALDI TOF: m/z (%): 658 (100, [C₁₄H₂₇O₄]<sup>++</sup>), 1178 (8, [M+Na]<sup>+</sup>). EA (C₇₁H₇₉O₁₃) calculated %C 73.80, %H 8.20, found %C 73.61, %H 8.36.
1,3,5-Tris[4′-(3,4,5-Tridodecyloxybenzoyloxy)benzoyloxy] benzene 1a: 250 mg (0.31 mmol) 4a, 17 mg (0.10 mmol) phloroglucinol dihydrate, 230 mg (1.11 mmol) DCC and 62 mg (0.22 mmol) DPTS were dissolved in 20 ml dry CH₂Cl₂ and stirred at ambient temperature over night. The solvent was then removed and the product was purified by column chromatography (silica 60/hexane/ethylacetate) followed by recrystallization from acetone; 200 mg of a colorless waxy solid were obtained (yield 79 %), T_C (at rt annealed phase Col) = 55 °C; ¹H, ¹³C NMR and elemental analysis see reference [3]; FD MS: m/z (%): 2458 (69, [M+H]+), 2338 (61, [C₁₄₀H₂₄₂O₁₉+H]+), 2218 (93, [C₁₄₀H₂₃₈O₁₇+H]+), 2098 (100, [C₁₃₅H₂₃₁O₁₅+H]+).

1,3,5-Tris[4′-(3,4,5-Tridodecyloxybenzoyloxy)benzoyloxy][benzoyloxy] benzene 1b: 600 mg (0.66 mmol) 4b, 35 mg (0.22 mmol) phloroglucinol dihydrate, 278 mg (1.35 mmol) DCC and 75 mg (0.27 mmol) DPTS were dissolved in 20 ml dry CH₂Cl₂ and stirred at ambient temperature over night. The solvent was then removed and the product was purified by column chromatography (silica 60/hexane/ethylacetate) followed by recrystallization from acetone; 531 mg of a colorless waxy solid were obtained (yield 86 %), T_C = 98 °C; ¹H NMR (300 MHz, CDCl₃): δ = 0.88 (t, 27H, CH₃), 1.26-1.86 (m, 180H, CH₂), 4.06, 4.08 (2t, 18H, OCH₂), 7.21 (s, 3H, H₂, H₄, H₆), 7.39, 7.42, 8.31 (AABB', 24H, aromat. CH), 7.42 (s, 6H, aromat. CH); ¹³C NMR (75 MHz, CDCl₃): δ = 14.1 (CH₃), 22.7-31.9 (CH₂), 69.3, 73.6 (OCH₂), 108.7, 113.3, 122.1, 122.2 (aromat. CH), 123.2, 126.5, 126.6 (aromat. C_q), 131.9 (aromat. CH), 143.4, 151.5, 153.0, 155.3, 155.6 (aromat C_q), 163.6, 163.7, 164.4 (CO); MALDI TOF: m/z (%): 658 (100, [C₃₃H₇₇O₄]⁺²⁺), 2840 (5, [M-H+Na]⁺); elemental analysis: calcd. for C₁₇₇H₂₅₈O₂₇: C 75.44, H 9.23; found C 75.42, H 9.25.

1,3,5-Tris[4″-[4′′-(3,4,5-Tridodecyloxybenzoyloxy)benzoyloxy]benzoyloxy]benzoyloxy) benzene 1c: The procedure described for 1b, using the arm 4c yielded 397 mg (66 %) of a colorless, waxy solid, T_C = 172 °C; ¹H NMR (300 MHz, CDCl₃): δ = 0.88 (t, 27H, CH₃), 1.26-1.87 (m, 180H,
CH$_2$), 4.06, 4.08 (2t, 18H, OCH$_2$), 7.22 (s, 3H, H2, H4, H6), 7.39, 7.427, 7.433, 8.32, 8.33 (AA'BB', 36H, aromat. CH), 7.427 (s, 6H, aromat. CH); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.1 (CH$_3$), 22.7-31.9 (CH$_2$), 69.3, 73.6 (OCH$_2$), 108.7, 113.3, 122.1, 122.2, 122.3 (aromat. CH), 123.2, 126.4, 126.6 (aromat. C$_q$), 131.9, 132.0 (aromat. CH), 143.4, 151.5, 153.0, 155.27, 155.34, 155.6 (aromat C$_q$), 163.6, 163.7, 163.8, 164.4 (CO); MALDI TOF: m/z (%): 658 (100, [C$_{43}$H$_{77}$O$_4$]$^+$), 872 (13, [C$_{50}$H$_{87}$O$_7$]$^+$), 3199 (5, [M-H+Na]$^+$); elemental analysis: calcd. for C$_{198}$H$_{270}$O$_{33}$: C 74.82, H 8.56; found C 74.78, H 8.55.

1,3,5-Tris[4''-(4''''-3,4,5-Tridecyloxybenzoyloxy)benzoyloxy][benzoyloxy]benzoyloxy] benzene 1d: The procedure described for 1b, using the arm 4d yielded 105 mg (57 %) of a colorless, waxy solid, T$_{CI}$ = 249 °C; $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.89 (t, 27H, CH$_3$), 1.26-1.87 (m, 180H, CH$_2$), 4.06, 4.08 (2t, 18H, OCH$_2$), 7.23 (s, 3H, H2, H4, H6), 7.42 (m, 30H, aromat. CH), 8.32 (m, 24H, aromat. CH); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.1 (CH$_3$), 22.7-31.9 (CH$_2$), 69.3, 73.6 (OCH$_2$), 108.7, 113.2, 122.2, 122.3 (aromat. CH), 123.2, 126.4, 126.7 (aromat. C$_q$), 132.0 (aromat. CH), 143.4, 151.5, 153.26, 153.32, 155.6 (aromat C$_q$), 163.6, 163.7, 163.8, 164.4 (CO); MALDI TOF: m/z (%): 658 (100, [C$_{43}$H$_{77}$O$_4$]$^+$), 3562 (4, [M+H+Na]$^+$); elemental analysis: calcd. for C$_{219}$H$_{282}$O$_{39}$: C 74.33, H 8.03; found C 74.25, H 8.13.

REFERENCES
Figure 1. Pseudo-focal-conic texture of 1b upon cooling from the isotropic phase between crossed polarizers at 86 °C.
Figure 2. DSC traces of 1a at a rate of 10 °/min; top: first cooling (a) and second heating (b); bottom: first heating curve of a sample after being in the isotropic phase and annealing for 18 h at -10 °C (c) or rt (d), respectively.
Figure 3. X-ray diffraction pattern of 1a at rt, performed with an Siemens D 500 diffractometer using CuKα radiation. The sample was annealed at rt prior to the measurement. The inset, gives experimental and the calculated $d$ spacings for a centered rectangular unit cell with $a = 76.1$ Å and $b = 35.2$ Å.