Star-shaped oligobenzoates with a naphthalene chromophore as potential semiconducting liquid crystal materials?[†]

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A series of star-shaped non- C_3 -symmetrical mesogens containing one naphthalene chromophore at a defined position have been synthesised to study the influence of phase symmetry and nano-segregation on the order of the chromophores and their interactions in potential semiconducting materials. Structural investigations reveal a rich mesomorphism from columnar hexagonal, columnar rectangular, lamellar to cubic phases depending on the type of oligobenzoate arms attached to the core. Although the decoration of the naphthalene containing arm with peripheral semi-perfluorinated chains results in a confinement of the chromophores to the interface between cores and perfluorinated units, the naphthalenes do not strongly interact among themselves as evidenced by the photophysical studies. The latter is attributed to the *E*-shaped conformer and the increased intra-columnar separation owing to the fluorinated chains.

Introduction

Non-conventional mesogens are currently of enormous interest owing to their amazing self-assembly into complex soft materials.1 Among these molecules are for example dendrimers2 and dendrons,^{3,4} which do not possess any shape anisotropy, but nevertheless organise by nano-segregation of the chemically and/ or physically different building blocks.^{1,5} Incorporation of chromophores into such scaffolds introduces functions and thus may transform these compounds into organic semiconductors⁴ or light harvesting molecules.⁶ One fascinating type of material, which was designed following nature's example in the tobacco mosaic virus, are dendrons, possessing a chromophore on the focal point and peripheral semi-perfluorinated flexible chains.⁴ The chains are known to be incompatible with the other molecular units and, thus, the molecules self-organise in helical columns by nano-segregation of the chromophores in the centre of the column. Owing to the good charge carrier mobility and the simple design, these materials are of interest for plastic electronics. Note that the latter molecules assemble the chromophores only in the last step by supramolecular interactions. A different concept can be pursued if chromophores are preorganised in a single molecule and the superstructure is built in the second step, as observed for peptides and DNA.

Our interest focussed on three-armed star-shaped compounds which can be in principle tailor-made by attaching up to three different arms. Many molecules are known with C_3 -symmetry, owing to the great number of C_3 -symmetric cores. They form liquid crystal (LC) structures if the peripheral chains are adequately selected.7-15 Thereby, a great variation in thermotropic phases can be found from nematic, to lamellar, to columnar structures, which depends on the fine-tuning of the core scaffold and the number, preorganisation and type of peripheral flexible chains. Recently, we have shown that symmetrical oligobenzoate star-shaped mesogens, with a phloroglucinol core and peripheral dodecyloxy chains form various columnar mesophases.^{15,16} In the low-temperature columnar phases, the individual columns are correlated with each other in 3D assemblies, owing to undulation which is attributed to a helical packing of folded, E-shaped conformers. Naphthalene was chosen as a chromophore for two reasons: first, it is sufficiently small, thus it is expected not to alter the self-organisation process; and second, because naphthalene derivatives are known for their excellent charge carrier mobilities in crystals, liquid crystals and polymers.¹⁷⁻²⁰ Indeed, incorporation of a naphthalene in each individual oligobenzoate arm does not in principle change the self-assembly compared with the parent oligobenzoates.¹⁶ Moreover, preliminary measurements of the charge carrier mobility by the electrode-less PR-TRMC technique revealed a very high value of up to 0.09 cm² V⁻¹ s⁻¹, which is similar to that of hexahexylsulfanyltriphenylene, one of the most efficient triphenylene derivatives.²¹ In the present investigation, we aim to study the structural requirements for semiconducting materials, *i.e.* the influence of the mesophase structure and nanosegregation on the order of chromophores. Therefore, we synthesised non- C_3 -symmetric mesogens with one naphthalene chromophore attached to the phloroglucinol core, by a previously reported strategy.²² The oligobenzoate arms are different in length and one of the molecules possesses semi-perfluorinated chains on the arm where the chromophore is incorporated. Desymmetrisation was proposed to alter the shape of the mesogens and consequently the mesophase structure. The

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semi-perfluorinated lateral chains are strongly segregating, thus, we expect that chromophores attached to these building blocks are confined to the interface of perfluorinated chains and the benzoate core which might result in defined chromophore stacks. Here, we report the synthesis, LC characterisation and photophysical properties of non- C_3 -symmetrical star-shaped mesogens 1 containing one naphthalene chromophore (Fig. 1).

Synthesis

The synthesis of the C_2 -symmetric star molecule 1a starts with a twofold benzyl protected phloroglucinol as shown in Scheme 1 (Route A). Esterification with acid 3c, cleavage of the protecting group and final esterification of the two newly formed phenolic OH groups with arm 3b yielded molecule 1a. Compound 1b was prepared by a different process (Route B) to avoid the more difficult work-up, when semi-perfluorinated alkyl chains are present in the molecule. A mono-protected phloroglucinol was first coupled to the oligobenzoate arms 3b by a twofold esterification. Cleavage of the benzyl ether and subsequent coupling of the arm 3d, bearing the naphthalene chromophore and lateral perfluorinated chains, provided mesogen 1b in good yield and high purity. Mesogens with three different arms have been synthesised as reported previously, by using a newly designed ABC building block.²² The five step synthesis affords the products 1c and 1d after a series of coupling and deprotection steps (Scheme 1, Route C).

Thermotropic properties

The thermotropic properties were studied by polarised optical microscopy (POM) and differential scanning calorimetry (DSC) and the results are summarised in Table 1. All materials show liquid crystal phases from room temperature to their clearing point. The latter is a function of the number of benzoate repeating units, as was already observed for the C_3 -symmetric mesogens. For example compounds **1a** and **1d** with the same



(i) DCC, DPTS, CH₂Cl₂, R¹⁻³COOH (**3a-e**); (ii) Pd/C, H₂; (iii) (*n*-C₄H₉)₄NF, AcOH
 Bn benzyl; DCC dicyclohexylcarbodiimide, DPTS dimethylpyridinium toluylsulfonate
 Scheme 1 Synthesis of star-shaped mesogens 1.

 $\begin{array}{c} c_{12} H_{25} \bigcirc (C_{12} H_{25} \\ c_{12} H_{25} \frown (C_{12} H_{25} \\ c_{12} H_{25} \hline c_{12} H_$

Route A

Table 1 Mesomorphic properties of 1a–c: DSC results from the secondheating and the first cooling cycles (heating rate $10 \ ^{\circ}C \ min^{-1}$)

Compound	Onset [°C]/ ΔH [kJ mol ⁻¹] ^{<i>a</i>}				
1a	Col _{hd} 65.1/4.4 I				
	I 60.7/-4.4 Col _{hd}				
1b	Col _{rd} 151.9/1.6 SmA 190.9/2.2 1				
	I 190.0/-1.9 L 151.1/-1.5 Col _{re}				
1c	Col _{hd} 43.2/4.8 I				
	I 34.5/-4.8 Col _{bd}				
1d	Cub 60.6/2.3 I				
	I 46.1/–2.3 Cub				

^{*a*} Col_{hd} columnar hexagonal LC phase, Col_{rd} columnar rectangular LC phase (*p*2*mg*, see X-ray section), SmA smectic A (lamellar) phase, Cub cubic LC phase, I isotropic phase.

number of repeating units show clearing temperatures in the same temperature range (61-65 °C), whereas 1c with one benzoate group less clears at a 20 °C lower temperature. An exception is compound 1b, because the strong interactions between the semi-perfluorinated chains increase the transition temperature to the isotropic phase by more than 135 °C. POM observations reveal typical pseudo-focal conic textures for 1a, 1b and 1c indicating a columnar nature of the mesophases (Fig. 2). Compound 1d presents only an optical isotropic texture pointing to a cubic phase. The low viscous, high-temperature mesophase of 1b exhibit also an optical isotropic phase when sandwiched between glass plates, but a sample prepared without a cover sheet becomes birefringent. These observations indicate a lamellar phase. The dark texture of the sample between two glass slides is observed even upon rotation of the sample and shows the homeotropic alignment of a uniaxial LC phase. Fig. 2B reveals that planar aligned columns can be uniformly grown upon slow cooling from the lamellar phase. These features are evidence against an L_{Col} (lamellar columnar) phase and point rather to a SmA type lamellar phase.



Fig. 2 Textures of the liquid crystal phases of **1a–c**. A: Pseudo-focalconic texture of **1a** at 63.8 °C. B: Pseudo-focal-conic texture (bottom right) and planar alignment (top left) of **1b** at 158 °C. C, D: Pseudo-focalconic texture (C) and mosaic texture (D) of **1c** at 39.5 °C.



Fig. 3 A,B: X-Ray diffraction patterns of extruded fibres. Compound **1a** in its Col_n phase at 40 °C (A) and compound **1b** in its Col_{rd} phase (*p2mg*) at 70 °C (B). The framed diffuse reflections on the meridian correspond to the average separation of the mesogens along the column. C, D: Diffraction pattern of **1d** in the Cub phase at 40 °C (C) and the magnification of the small angle region (D).

X-Ray diffraction studies and structure of the mesophases

X-Ray diffraction on aligned samples reveals the columnar structure of the mesophases of 1a-c. Fig. 3 exhibits typical wide angle patterns with fibres of 1a and 1b aligned parallel with the meridian. The reflections on the equator can be attributed to a two-dimensional order of columns, whereas the intense but diffuse meridional signals at the halo indicate the intra-columnar average separation of the mesogens. The data are collected in Table 2. The reciprocal *d*-spacings of the equatorial reflections of **1a** and **1c** are in the ratio $1 : \sqrt{3} : 2$, thus clearly showing the hexagonal packing of columns. In contrast, the diffraction pattern of 1b exhibits a large number of equatorial reflections, which could be resolved in the small angle X-ray studies (Fig. 4). The least-squares fit of the signals reveals a rectangular phase with a = 44.7 Å and b = 81.0 Å. The indexation of the reflections can be performed according to the plane group p2mg with the reflection conditions *hk*: no conditions; h0: h = 2n (Table 2). The broad meridional peaks on the halo disclose the intra-columnar spacing of the mesogens. Whereas there is an average intracolumnar separation of 4.5 Å for the mesogens exclusively decorated with alkyl chains (1a, 1c), the separation increases for 1b owing to the larger semi-perfluorinated chains. For the hightemperature phase of 1b, the alignment was lost at the phase transition because of the low viscosity and the subsequent deformation of the fibre sample. The two reflections at small angles support a SmA phase with a lamella thickness of 75.5 Å, which compares well with the b parameter of the rectangular phase. However, the shrinkage is incompatible with the increase

Table 2 Structural data of the columnar mesophases

Compound	<i>T</i> /°C	Phase	hk; $d_{exp}/\text{\AA}$; $d_{calc}/\text{\AA}$	$V_{\rm M}{}^a/{\rm \AA}^3$	a/Å	b/Å	halo (meridian)/Å	$V_{\text{cell}}/\text{\AA}^3$	Ζ	Density/g cm ⁻³
1a	60	Col_h	10; 36.8; 36.8 11; 21.2; 21.2	4236	42.5	_	4.5	6945	1.6	0.98
1b	165	SmA	$\begin{array}{c} 20; 18.5; 18.4\\ 02; 35.7; 37.5^{b}\\ 03; 26.6; 25.2 \end{array}$		_	75.5 ^b	5.3			
1b	70	Col _{rd}	01; 80.7; 81.0 02; 40.9; 40.5 11; 39.1; 39.2 12; 30.1; 30.0 03; 27 3; 27 0	4615	44.7	81.0	5.2	18841	4.1	1.23
1c	40	Col_h	10; 34.6; 34.6 11; 19.3; 20.0 20; 17.3; 17.3	4033	40.0	_	4.4	6082	1.5	0.98

^{*a*} The molecular volume was calculated following reference 23. The obtained value was corrected by a factor using the experimental dilatometry data.¹⁶ ^{*b*} Broad reflections in the small angle region of the WAXS pattern. The value *b* was therefore calculated with $b = (2d_{02} + 3d_{03})/2$.



Fig. 4 SAXS of **1b** in the Col_{rd} phase at 70 °C; integration of the equatorial reflections. The reflections can be indexed according to a rectangular phase in the plane group p2mg (a = 44.7 Å, b = 81.0 Å), which is indicated by the missing 10 reflection ($2\theta = 1.98^{\circ}$).

of temperature by 100 °C. Thus, the expansion must consist of increasing distances within the layers, which allows fast molecular motions of single molecules or aggregates and consequently the formation of a uniaxial SmA phase. Fig. 3C and D present the WAXS diffraction pattern of 1d and its expansion of the small angle region. No alignment was observed by fibre extrusion. The relatively intense discrete reflections are obtained only upon slow cooling from the isotropic phase without shearing the sample. This behaviour is typical for cubic phases. A mono domain could not be grown, which prevented more detailed characterisation.

Model of the columnar phases

E-Shaped conformers have been reported for the parent molecules forming the hexagonal columns owing to the small columnar diameter compared with the diameter of the all-*s*-*trans* conformation of the mesogens.¹⁶ Such conformers are the result of frustration and the energy minimisation by optimising nanosegregation and space-filling. The structure of mesogen **1a** differs only slightly from the molecular structure of the parent oligobenzoate. In 1a one benzene unit of the parent star is substituted by naphthalene. The unit cell parameters of both Col_b phases are almost identical (Table 2).15,16 This indicates a very similar supramolecular organisation. Table 2 also shows the calculated molecular volume, the number of molecules per columnar unit and the density. All these values are nearly matching the previously reported data of the parent oligobenzoate, and thus indicate a closely related structure. Therefore, we propose that E-shaped mesogens 1a self organise in columnar stacks by nanosegregation of their nonpolar aliphatic chains and the polar oligobenzoate cores. The characteristic parameters for the hexagonal mesophase of 1c (Table 2) and the similar molecular structure compared with 1a indicate an analogous model for the mesophase of the small star molecule. Interestingly, although all symmetric star-shaped oligobenzoates have been shown to transform to ordered columnar phases at low temperatures with a helical supramolecular aggregation of mesogens,¹⁶ such a transition is missing for the desymmetrised stars 1a and 1c. This suggests that desymmetrised mesogens prevent the formation of a highly ordered mesophase, and consequently a statistical orientational distribution of the naphthalene chromophores around the columnar axis remains at room temperature.

A different model has to be considered for the phases of compound 1b. The rectangular phase can be assigned to a plane group with p2mg symmetry owing to the missing 10 reflection (Fig. 4). The relatively small unit cell parameters point again to a compact LC building block, such as an E-shaped mesogen. Fig. 5 shows a model of the phase. A pair of antiparallel aligned E-shaped mesogens constitutes the building block of the columnar phase. This unit exposes the semi-perfluorinated chains only to one side of the assembly. Consequently, the semi-perfluorinated chains of different columns can nano-segregate along the *a* direction of the unit cell. Thereby, the columns interdigitate similarly to the teeth of two gear wheels. This row of columns comprises only half of the depicted unit cells. The same columnar aggregates occupy the space of the second half by nano-segregation of the alkyl chains in the central part of the cell. Thereby, they form the C_2 -symmetric structure of the plane group. The unit cell contains a total of two columns. In a unit cell slice with



Fig. 5 Model of the rectangular columnar phase and its transformation to the lamellar uniaxial phase at high temperature. The distance between the perfluorinated lamellae decreases with increasing temperature, however, the distance of mesogens in the column increases. At the phase transition Col_{rd} to the lamellar phase the positions of the columns and most probably also of the mesogens within the columns are no longer well defined, indicating a SmA phase.

a height of 5.2 Å, which is the intracolumnar separation of mesogens, there are 4 mesogens filling the space, which results in a reasonable density for molecules containing perfluorinated alkyl chains of 1.23 g cm⁻³. In this model, the chromophores are indeed confined to the interface between semi-perfluorinated chains and oligobenzoate building blocks. The model also explains the transition to the lamellar phase. The columns are already preorganised in lamellae in the p2mg phase, however, they are locked in defined positions. At the temperature of the phase transition to the SmA phase, the identical molecules without semi-perfluorinated chains are already in the isotropic phase. This indicates that the interactions of the oligobenzoate cores and the aliphatic chains are weak at this temperature and the lamellar structure is maintained mainly by the fluorophilic interactions of the perfluorinated building blocks. Consequently, the lamellae are not formed by columns, but by single molecules or small columnar aggregates, which leads to homeotropic aligned samples between two glass plates.

Such a transition from a SmA phase to a columnar phase may be of interest for the facile, uniform planar alignment of columns for applications, for example in organic field effect transistors. If slowly cooled, columns grow preferentially along the homeotropically oriented layers. Similar thermotropic behaviour for fluorinated molecules has also been found in the series of nonconventional polycatenar²⁴ and swallow-tailed²⁵ mesogens.

Absorption and fluorescence studies in solution and thin films

The performance of LC materials in plastic electronic devices depends strongly on the order of chromophores.^{1*a*,26} For the hopping transport of charges, theory predicts high charge carrier mobility in co-planar stacks of hopping sites, consisting of the condensed aromatic building blocks.²⁷ Investigation of the absorption and the fluorescence of these materials can provide information about the chromophore order in organised media, based on the exciton theory.²⁸ The absorption spectra of **1** in CH₂Cl₂ and thin spin coated films are shown in Fig. 6. All



Fig. 6 UV/Vis absorption spectra of star mesogens in solution (solid lines) and as thin spin coated films (dotted lines). The inset is an expansion of the long-wavelength absorption edge at 345 nm for the solution spectra.

solution spectra exhibit large absorption bands at short wavelengths with a maximum at 282 nm. These signals consist of overlapping absorptions from different aromatic building blocks, *i.e.* naphthalene, benzene and gallic acid ester units. The long-wavelength absorptions at about 338 nm possesses a very low intensity, which might be attributed to the forbidden α -band of naphthalene derivatives.²⁹ If aggregates are present in the organised material considerable changes should be observed in the absorption spectra. The exciton model predicts bathochromic shifts of absorption maxima in J-type and hypsochromic shifts in H-type aggregates.²⁸ Comparison of the absorption spectra of all star-shaped mesogens with one naphthalene in solution and thin solid films clearly excludes a bathochromic shift, which is evidence that J-type aggregates are not formed. Owing to the aggregation of E-shaped mesogens in columnar phases, H-type aggregates are most probable. Although a small hypsochromic

shift of the maxima at 338 nm is observed, the overall shape of the absorption spectra in solution and solid state remains similar. The hypsochromic shift does not necessarily account for H-type aggregates and might have its origin in the different environment of the absorbing species without the solvent matrix. The overlap of absorption bands from different building blocks prevents a more detailed analysis.

Fluorescence spectroscopy can give further information about the order of the naphthalene derivatives in the solid state. Recently, naphthalene has been studied in amorphous solids,³⁰ in LC polymers,³¹ as guests in cyclodextrins³² and confined in micelles of block copolymers.33 In less ordered, amorphous materials, naphthalene exhibits a typical broad emission with a maximum between 380 to 410 nm and a band width of about 2800–5000 cm⁻¹, which is attributed to excimer formation.³⁰ In the single crystal only monomer-like emission at short wavelengths can be observed. In contrast, a confined space of micelles leads to the formation of aggregates, which results in different structured emission bands with emission maxima even above 500 nm.³³ Similar structured fluorescence spectra were recently found for symmetric star-shaped mesogens with three naphthalenes directly attached to the phloroglucinol core in its high ordered columnar phase, which showed an excellent charge carrier mobility.²¹ Fig. 7 presents the fluorescence spectra of two arm derivatives 3a and 3b as well as the spectra of the stars 1a and 1b. The arms containing only benzoate and gallic acid ester units show a slight hypsochromic shift by approximately 5 nm of the emission maxima in the solid state. Star-shaped mesogens with only one naphthalene chromophore exhibit significantly different behaviour. The solid state spectra show bathochromically shifted emission maxima by 31 nm, however, they are very broad and centred around 390 nm with a shoulder at 410 nm, which are features frequently attributed to naphthalene excimer emission or the fluorescence of the statistical LC copolymer Vectra A910[®]. It should be noted that, in contrast to block copolymers,33 the variation of the excitation wavelength did not result



Fig. 7 Comparison of fluorescence spectra of 1a,b and 3a,b in $CHCl_3$ solution and thin spin coated films. The maxima of all spectra are normalised.

in different fluorescence spectra in liquid and solid states, thus indicating the homogeneity of the phases and the fact that all chromophores possess on average a similar environment. Although there is a large difference in structure of the columnar phases of 1a and 1b, no difference can be discovered in the photophysical studies. Consequently, the confinement of naphthalene to the interface of semi-perfluorinated chains and oligobenzoate scaffold does not lead to a stronger interaction of these functional building blocks. This might be attributed first to the proposed E-shaped conformers, which are suggested to selforganise in these types of columnar phases. In order to form these conformers, the chromophores which are close to the core of the mesogens have to incline, thus, the formation of strong interacting aggregates along the column is less probable. Second, the semi-perfluorinated alkyl chains result in an increased separation of chromophores owing to the larger volume of the perfluorinated methylene segments compared with conventional alkyl chains.

Summary and conclusions

Desymmetrised star-shaped mesogens with only one naphthalene chromophore in the scaffold were synthesised efficiently. In contrast to previously reported C_3 -symmetric derivatives, no highly ordered helical columnar mesophase is observed at low temperature. Instead, attachment of arms of different lengths around the phloroglucinol core results in stable columnar hexagonal phases if the lengths of the oligobenzoate arms are not too different, otherwise, a cubic phase is formed. If only one arm is decorated with semi-perfluorinated chains, molecules arrange in a more complex rectangular phase with p2mg symmetry and inherently preorganised lamellar structure. The latter transforms to a SmA type lamellar phase at higher temperature above 159 °C, where the interaction of the semi-perfluorinated chains holds the molecules in a layered structure. Such transitions might be useful for the uniform planar alignment of columnar phases. Compared to the non-fluorinated derivatives in the series, the latter was expected to segregate the chromophores at the interface between semi-perfluorinated chains and oligobenzoate scaffold. The chromophores are, however, not strongly interacting, which is indicated by results from UV-Vis absorption and emission studies. Fluorescence spectra show characteristic features of excimer emission, thus pointing to chromophores in close proximity without forming defined ground-state aggregates. This is attributed to the E-shaped conformers and the large intra-columnar separation because of the semi-perfluorinated chains.

Experimental

General methods

Chemicals were obtained from Acros and Sigma-Aldrich and used as received. The syntheses of compounds **3a,b,c,e**, **9–13** were described previously.^{15,21,22} Column chromatography was carried out on silica 60 (Merck, mesh 70–230). PFT ¹H and ¹³C NMR spectra were recorded in CDCl₃ with a Varian Oxford 400 MHz spectrometer with the residual solvent signal at 7.26 ppm as a reference. Mass spectra were obtained on a Finnigan MAT95 (FD MS). Elemental analysis was carried out in the

microanalytical laboratory at the University of Mainz. POM observations were made with a Zeiss Axioscop 40 equipped with a Linkam THMS600 hot stage. DSC was performed using a Perkin Elmer Pyris 1. X-Ray diffraction measurements were carried out on both powder and aligned samples in glass capillaries of 2 mm diameter. The aligned fibres were obtained by extrusion from the LC phase.

The WAXS measurements were performed by using a standard copper anode (2.2 kW) source with pinhole collimation equipped with a X-ray mirror (Osmic typ CMF15-sCu6) and a Bruker detector (High-star) with 1024 \times 1024 pixels. The SAXS measurements were completed by using a rotating anode (mikromax 007, copper, Rigaku) source with pinhole collimation equipped with a X-ray mirror (Osmic type 140-0040 12) and a Bruker detector (High-star) with 1024 \times 1024 pixels. The diffraction data were calibrated by using silver behenate as a calibration standard.³⁴ The X-ray patterns were evaluated using the datasqueeze software (http://www.datasqueezesoftware.com/).

Thin films were prepared by spin coating from CHCl_3 solution.

6'-(3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyloxybenzoyloxy)naphthoic acid (3d). 1.10 g (0.69 mmol) 3,4,5-Tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyloxy)benzoic acid was coupled with 0.21 g (0.75 mmol) 4-hydroxybenzoic acid benzyl ester using 0.31 g (1.49 mmol) N,N'-dicyclohexylcarbodiimide (DCC) and 0.11 g (0.37 mmol) 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) as coupling reagents. All materials were dissolved in 40 mL dry methylene chloride and stirred under nitrogen atmosphere overnight. The solvent was removed under vacuum and the crude product was extracted with hexane. DPTS and a part of DCC were removed by filtration. Further purification by column chromatography (hexaneethyl acetate-chloroform = 9 : 1 : 1) and recrystallisation from acetone yielded 0.65 g, 51% of a colourless solid. 0.6 g (0.32 mmol) of the benzyl ester was then dissolved in 50 mL diethyl ether and one spatula of Pd/C (10%) was added. The mixture was stirred under hydrogen atmosphere overnight. Filtration over Celite 512 and evaporation of the solvent under vacuum yielded the crude product. Crystallization from acetone afforded the carboxylic acid 3d as a colourless solid (0.45 g, 79%). ¹H NMR (400 MHz, CDCl₃, 5% CF₂Cl-CFCl₂): $\delta = 1.84-2.25$ (m, 18 H, CH_2 ; 4.08 (t, 2 H, OCH₂); 4.13 (t, 4 H, OCH₂); 7.43 (dd, ${}^{3}J = 8.9$, ${}^{4}J = 2.2, 1$ H, CH); 7.48 (s, 2 H, CH); 7.74 (dd, ${}^{4}J = 2.2, {}^{5}J = 0.8,$ 1 H, CH); 7.91 (dd, ${}^{3}J = 8.8$, ${}^{5}J = 0.8$, 1 H, CH); 8.06 (dd, ${}^{3}J =$ $8.9, {}^{5}J = 0.8, 1 \text{ H}, \text{CH}$; $8.14 \text{ (dd, } {}^{3}J = 8.8, {}^{4}J = 1.6, 1 \text{ H}, \text{CH}$); 8.72 $(dd, {}^{4}J, = 1.6, {}^{5}J = 0.8, 1 H, CH); {}^{13}C NMR (100 MHz, CDCl_3;$ 5% CF₂Cl-CFCl₂): $\delta = 17.51$ (d, CH₂, ${}^{3}J_{C-F} = 14$ Hz); 29.0, 30.0 (CH₂); 30.9 (t, CF₂CH₂, ${}^{2}J_{C-F} = 22.7$ Hz); 68.9, 72.9 (OCH₂); 109.2, 119.0 (C_t); 122.5 (C_t), 124.6 (C_q); 126.5 (C_t); 126.8 (C_q), 128.2 (C_t); 130.8 (C_a); 131.3, 132.1 (C_t); 136.9; 143.3; 151.1; 153.1 (C_q); 164.7, 171.1 (C_q, C=O); MS (FD): m/z (%): M⁺ = 1762.1 (100, M⁺); EA: Calc. for C₅₄H₃₃F₅₁O₇: C, 36.79; H, 1.89, Found: C, 36.67; H, 1.98%.

3,5-Bis[4'-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxy]-1-phenol (8). 0.19 g (0.88 mmol) 1-Benzyloxy-3,5-dihydroxybenzene, 1.54 g **3b** (1.93 mmol), 0.80 g (3.87 mmol) DCC and 0.23 g (0.77 mmol) DPTS were dissolved in 50 mL dry methylene chloride and converted and worked up as described for the first step of compound 3d. After purification by column chromatography (hexane–ethyl acetate = 6:1) and crystallisation from acetone, the product was obtained as a colourless solid (1.23 g, 79%). 1.22 g (0.69 mmol) of the benzyl ester was then deprotected and purified analogously to compound 3d. Crystallisation from acetone afforded phenol 8 as a colourless solid (0.85 g, 73%). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.876$, 0.88 (2 t, 18 H, CH₃); 1.24– 1.38 (m, 96 H, CH₂); 1.45–1.52 (m, 12 H, CH₂); 1.73–1.87 (m, 12 H, CH₂); 4.05 (t, 8 H, OCH₂); 4.07 (t, 4 H, OCH₂); 5.81 (br s, 1 H, OH); 6.67 (m, 2 H, aromat. CH); 6.77 (m, 1 H, aromat. CH); 7.35 (AA'BB', 2 H, CH); 7.41 (s, 4 H, CH); 8.26 (AA'BB', 4 H, CH); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.1$ (CH₃); 22.69, 22.7, 26.0, 26.1, 29.26, 29.36, 29.39, 29.40, 29.57, 29.66, 29.7, 29.73, 29.74, 29.76, 30.3, 31.92, 31.94 (CH₂); 69.3, 73.6 (OCH₂); 107.2, 107.9, 108.6, 122.2 (Ct); 123.2 (Cq); 126.7 (Cq); 131.9 (Ct); 143.2, 151.9, 153.0, 155.4, 157.1 (C_q); 164.0; 164.5 (C_q, C=O)

1"-[6'-(3,4,5-Tridodecyloxybenzoyloxy)-2-naphthoyloxy]-3,5dihvdroxybenzene (5). 0.40 g (0.47 mmol) 3c, 0.14 g (0.45 mmol) 3,5-dibenzyloxyphenol, 0.20 g (0.95 mmol) DCC and 0.06 g (0.19 mmol) DPTS were converted and isolated analogously to the esterification procedure of 3d. Purification by column chromatography (hexane-ethyl acetate = 10:1) and crystallisation from acetone yielded compound 5 as colourless solid (0.20 g, 40%). The cleavage of the benzyl protecting group was performed analogously to compound 3d. 0.20 g (0.18 mmol) dibenzyl ether was converted and after purification by column chromatography, the product was obtained as a colourless solid (0.16 g, 95%). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (2 t, 9 H, CH₃); 1.26–1.55 (m, 54 H, CH₂); 1.74–1.88 (m, 6 H, CH₂); 4.07 (2 t, 18 H, OCH₂); 5.38 (bs, 2 H, OH); 6.27 (t, 1 H, CH); 6.36 (d, 2 H, CH); 7.44 (dd, ${}^{3}J = 8.9$, ${}^{4}J = 2.5$, 1 H, CH); 7.45 (s, 2 H, CH); 7.75 (dd, ${}^{4}J = 2.5$, ${}^{5}J = 0.9$, 1 H, CH); 7.93 (dd, ${}^{3}J = 8.7$, ${}^{5}J = 0.7$, 1 H, CH); 8.06 (dd, ${}^{3}J = 8.9$, ${}^{5}J = 0.9$, 1 H, CH); 8.19 (dd, ${}^{3}J =$ $8.7, {}^{4}J = 1.7, 1$ H, CH); 8.78 (dd, ${}^{4}J = 1.7, {}^{5}J = 0.7, 1$ H, CH); ${}^{13}C$ NMR (100 MHz, CDCl₃): $\delta = 14.1$ (CH₃); 22.69, 22.71, 26.06, 26.08, 29.3, 29.37, 29.4, 29.57, 29.64, 29.66, 29.7, 29.73, 30.3, 31.9, 31.95 (CH₂); 69.3, 73.6 (OCH₂); 101.0, 102.1, 108.6, 118.9, 122.6 (C_t); 123.5 (C_q); 126.2 (C_t); 126.4 (C_q); 128.2 (C_t); 130.5 (C_q); 131.1; 131.9 (C_t); 136.5, 143.2, 151.0, 152.4, 153.0, 157.3 (C_q); 165.0, 165.2 (C=O)

3,5-Bis[4'-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxy]-1-[6'-(3,4,5-tridodecyloxybenzoyloxy)-2-naphthoyloxylbenzene (1a). The esterification procedure was performed analogously to the synthesis of compound 3d by conversion of 0.16 g (0.17 mmol) diphenol 5, 0.30 g (0.38 mmol) 4-(3,4,5-tridodecyloxybenzoyloxy)benzoic acid, 0.16 g (0.75 mmol) DCC and 0.05 g (0.15 mmol) DPTS in 40 mL dry methylene chloride. Purification by column chromatography (hexane-ethyl acetate = 10:1) and crystallisation from acetone yielded a colourless solid (0.38 g, 90%). ¹H NMR (400 MHz; CDCl₃): $\delta = 0.88$ (2 t, 27 H, CH₃); 1.26–1.52 (m, 162 H, CH₂); 1.73–1.88 (m, 12 H, CH₂); 4.07 (2 t 18 H, OCH₂); 7.22 (t, 1 H, CH); 7.255 (d, 2 H, CH, partially superimposed with solvent signal); 7.37 (AA'BB', 4 H, aromat. CH); 7.41 (s, 4 H, CH); 7.46 (s, 2 H, CH); 7.47 (dd, ${}^{3}J =$ 8.1, ${}^{4}J = 2.1$, 1 H, CH, partially superimposed); 7.77 (dd, ${}^{4}J =$ 2.1, ${}^{5}J = 0.7, 1$ H, CH), 7.95 (dd, ${}^{3}J = 8.6, {}^{5}J = 0.7, 1$ H, CH);

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8.09 (dd, ${}^{3}J = 8.1$, ${}^{5}J = 0.7$, 1 H, CH); 8.22 (dd, ${}^{3}J = 8.6$, ${}^{4}J = 1.7$, 1 H, CH); 8.30 (AA'BB', 4 H, CH); 8.82 (dd, ${}^{4}J = 1.7$, ${}^{5}J = 0.7$, 1 H, CH); 13 C NMR (100 MHz; CDCl₃): $\delta = 14.1$ (CH₃); 22.7, 26.05, 26.08, 29.3, 29.37, 29.4, 29.57, 29.63, 29.66, 29.7, 29.74, 30.3, 31.9, 31.95 (CH₂); 69.3, 73.6 (OCH₂); 108.6, 113.32, 113.42, 118.9, 122.3, 122.7 (C₁); 123.2, 123.5 (C_q); 126.2 (C₁); 126.5 (C_q); 128.3 (C₁); 130.5 (C_q); 131.2, 131.94, 132.0 (C₁); 136.6, 143.16, 143.24, 151.0, 151.5, 151.6, 153.0, 155.5 (C_q); 163.7; 164.4, 165.0 (C=O); MS (FD) *m*/*z* (%): 2606.8 (100, [M + 1]⁺); EA: Calc. for C₁₆₀H₂₄₈O₂₁: C, 76.63; H, 9.97; Found: C, 76.56; H, 9.97%.

5-(3,4,5-Tridodecyloxybenzoyloxy)-3-[4'-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxy]-1-[4'-(3,4,5-tridodecyloxybenzoyloxy)naphthoyloxy]benzene (1c). The esterification procedure was performed as described for compound 3d, by conversion of 0.20 g (0.13 mmol) 13, 0.12 g (0.14 mmol) 3c, 0.06 g (0.28 mmol) DCC and 0.02 g (0.06 mmol) DPTS in 40 mL dry methylene chloride. Further purification by column chromatography (hexane: ethyl acetate = 10: 1) and crystallisation from acetone yielded 0.22 g (72%) of a colourless solid. ¹H NMR (400 MHz, CDCl₃): δ = 0.88 (m, 27 H, CH₃), 1.26–1.37 (m, 144 H, CH₂); 1.46–1.53 (m, 18 H, CH₂); 1.73–1.88 (m, 18 H, CH₂), 4.03–4.10 (m, 18 H OCH₂), 7.18 (m, 1 H, CH); 7.21 (m, 1 H, CH), 7.23 (m, 1 H, CH); 7.37 (2 H, CH, AA'BB'); 7.41 (s, 2 H, CH), 7.413 (s, 2 H, CH), 7.46 (s, 2 H, CH); 7.464 (dd, ${}^{3}J = 8.9$, ${}^{4}J = 2.5$, 1 H, CH partially superimposed); 7.76 (dd, ${}^{4}J = 2.5$, ${}^{5}J = 0.8$, 1 H, CH); 7.95 (dd, ${}^{3}J =$ $8.7, {}^{5}J = 0.8, 1 \text{ H}, \text{CH}$; $8.08 \text{ (dd, } {}^{3}J = 8.9, {}^{5}J = 0.8, 1 \text{ H}, \text{CH}$); 8.22 $(dd, {}^{3}J = 8.7, {}^{4}J = 1.8, 1 H, CH); 8.29 (AA'BB', 2 H, CH); 8.82$ $(dd, {}^{4}J = 1.8, {}^{5}J = 0.8, 1 H, CH); {}^{13}C NMR (100 MHz, CDCl_3):$ $\delta = 14.1$ (CH₃); 22.69, 22.7, 26.05, 26.08, 29.28, 29.37, 29.40, 29.57, 29.64, 29.66, 29.7, 29.74, 29.76, 30.3, 31.92, 31.94 (CH₂); 69.25, 69.28, 73.59, 73.62 (OCH₂); 108.5, 108.6, 113.2, 113.45, 113.54, 118.9, 122.2, 122.7 (Ct), 123.2, 123.3, 123.5, 126.13 (Ca), 126.14 (Ct); 126.5, (Cq); 128.3, 130.5 (Cq); 131.2, 131.9, 132.0 (C_t) ; 136.6, 143.15, 143.2, 143.3, 151.0; 151.5, 151.6, 151.7, 152.96, 153.0, 155.5, (C_q); 163.7, 164.3, 164.43, 164.46, 164.9 (C_q, C=O); MS (FD): *m*/*z* (%): 2387.2 (100, [M + 1]⁺⁺); EA: Calc. for C₁₅₃H₂₄₄O₁₉: C, 76.93; H, 10.30; Found: C, 76.81; H, 10.17%.

5-(3,4,5-Tridodecyloxybenzoyloxy)-3-[4'-(3,4,5-tridodecyl-oxybenzoyloxy)benzoyloxy]-1-{4'-[4"-(3,4,5-tridodecyl-oxybenzoyloxy) benzoyloxy|napthoyloxy|benzene (1d). The esterification procedure was performed as described for compound 3d, by conversion of 0.20 g (0.13 mmol) 13, 0.14 g (0.14 mmol) 3e, 0.06 g (0.28 mmol) DCC and 0.02 g (0.06 mmol) DPTS in 40 mL dry methylene chloride. Further purification by column chromatography (hexane-ethyl acetate = 10:1) and crystallisation from acetone yielded 0.23 g (72%) of a colourless solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (m, 27 H, CH₃); 1.26–1.37 (m, 144 H, CH₂); 1.45-1.53 (m, 18 H, CH₂); 1.73-1.88 (m, 18 H, CH₂); 4.04-4.10 (m, 18 H OCH₂); 7.18 (m, 1 H, CH); 7.22 (m, 1 H, CH); 7.24 (m, 1 H, CH); 7.37 (AA'BB', 2 H, CH); 7.40 (AA'BB', 2 H, CH partially superimposed); 7.41 (s, 2 H, CH); 7.414 (s, 2 H, CH); 7.43 (s, 2 H, CH); 7.50 (dd, ${}^{3}J = 9.0$, ${}^{4}J = 2.3$, 1 H, CH); 7.81 (dd, ${}^{4}J = 2.3, {}^{5}J = 0.7, 1 \text{ H}, \text{CH}$; 7.97 (dd, ${}^{3}J = 8.7, {}^{5}J = 0.7, 1 \text{ H}, \text{CH}$); 8.10 (dd, ${}^{3}J = 9.0$, ${}^{5}J = 0.7$, 1 H, CH); 8.23 (dd, ${}^{3}J = 8.7$, ${}^{4}J = 1.7$, 1 H, CH); 8.29 (2 H, CH, AA'BB'); 8.35 (2 H, CH, AA'BB'); 8.83 $(dd, {}^{4}J = 1.7, {}^{5}J = 0.7, 1 H, CH); {}^{13}C NMR (100 MHz, CDCl_3):$

$$\begin{split} \delta &= 14.1 \ (\mathrm{CH}_3); \ 22.69, \ 22.7, \ 26.05, \ 26.08, \ 29.28, \ 29.37, \ 29.40, \\ 29.57, \ 29.64, \ 29.66, \ 29.7, \ 29.73, \ 29.74, \ 29.76, \ 30.3, \ 31.92, \ 31.94 \\ (\mathrm{CH}_2); \ 69.24, \ 69.28, \ 69.30, \ 73.58, \ 73.61, \ 73.62 \ (\mathrm{OCH}_2); \ 108.52, \\ 108.60, \ 108.62, \ 113.2, \ 113.46, \ 113.53, \ 118.9, \ 122.23, \ 122.27, \ 122.5 \\ (\mathrm{C}_1); \ 123.21, \ 123.22, \ 123.27 \ (\mathrm{C}_q); \ 126.2 \ (\mathrm{C}_1), \ 126.21, \ 126.5, \ 126.7 \\ (\mathrm{C}_q); \ 128.3 \ (\mathrm{C}_1); \ 130.5 \ (\mathrm{C}_q); \ 131.2, \ 131.92, \ 131.95, \ 132.0 \ (\mathrm{C}_1); \\ 136.6, \ 143.1, \ 143.28, \ 143.32, \ 150.8, \ 151.5, \ 151.6, \ 151.7, \ 152.96, \\ 153.0, \ 153.02, \ 155.5, \ 155.51 \ (\mathrm{C}_q); \ 163.7, \ 164.3, \ 164.42, \ 164.44, \\ 164.47 \ (\mathrm{C}_q, \ C=O); \ MS \ (\mathrm{FD}): \ m/z \ (\%): \ 2507.2 \ (100, \ [\mathrm{M} + 1]^+); \\ \mathrm{EA: \ Calc. \ for \ C_{160}\mathrm{H}_{248}\mathrm{O}_{21}: \ \mathrm{C}, \ 76.63; \ \mathrm{H}, \ 9.97; \ \mathrm{Found: \ C}, \ 76.71; \\ \mathrm{H}, \ 10.11\%. \end{split}$$

3,5-Bis[4'-(3,4,5-tridodecyloxybenzoyloxy)benzoyloxy]-1-[6'-(3, 4,5-tris(1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyloxybenzoyloxy)-2-naphthoyloxy]benzene (1b). The esterification procedure was performed as described for compound 3d, by conversion of 0.22 g (0.13 mmol) 8, 0.22 g (0.13 mmol) 3d, 0.06 g (0.26 mmol) DCC and 0.02 g (0.05 mmol) DPTS in 40 mL dry methylene chloride. Further purification by column chromatography (hexane-ethyl acetate = 10:1) and crystallisation from acetone yielded 0.13 g (31%) of a colourless solid. ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 0.876$, 0.88 (2 t, 18 H, CH₃); 1.25–1.40 (m, 96 H, CH₂); 1.45–1.53 (m, 12 H, CH₂); 1.73–2.00 (m, 24 H, CH2); 2.09-2.26 (m, 6 H, CH2); 4.04-4.10 (3 t, 14 H, OCH2); 4.14 (t, 4 H, OCH₂); 7.22 (m, 2 H, aromat. CH); 7.26 (m, 1 H, aromat. CH, partially superimposed with solvent signal); 7.38 (AA'BB', 2 H, CH); 7.41 (s, 4 H, CH); 7.46 (dd, ${}^{3}J = 8.9$, ${}^{4}J = 2.7$, 1 H, CH); 7.49 (s, 2 H, CH); 7.76 (dd, ${}^{4}J = 2.7$, ${}^{5}J = 0.8$, 1 H, CH); 7.95 (dd, ${}^{3}J = 8.8, {}^{5}J = 0.8, 1 \text{ H}, \text{ CH}$; 8.09 (dd, ${}^{3}J = 8.9, {}^{5}J = 0.8, 1 \text{ H}, \text{ CH}$); 8.23 (dd, ³*J* = 8.8, ⁴*J* = 1.9, 1 H, CH); 8.30 (AA'BB', 4 H, CH), 8.83 (dd, ${}^{4}J = 1.9$, ${}^{5}J = 0.8$, 1 H, CH); ${}^{13}C$ NMR (100 MHz, CDCl₃): $\delta = 14.1$ (CH₃); 17.2 (d), 22.69, 22.7, 26.05, 26.08, 28.7, 29.27, 29.37, 29.39, 29.57, 29.63, 29.66, 29.7, 29.73, 29.74, 29.76, 30.3, 30.6 (t), 31.92; 31.94 (CH₂); 68.5, 69.3, 72.8, 73.6 (OCH₂); 108.54, 108.58; 113.36, 113.42; 118.9, 122.3, 122.5 (Ct); 123.2, 124.1; 126.2 (C_q); 126.23 (C_t); 126.5 (C_q); 128.3 (C_t); 130.5 (C_q); 131.3, 131.9, 132.0 (Ct); 136.6, 142.6, 143.2; 150.9, 151.5, 151.6, 152.7, 153.0 (C_q); 155.5 (C_q); 163.7, 164.4, 164.44, 164.7 (C_q, C=O). MS (FD): *m*/*z* (%): 3421.4 (37), 3422.4 (100), 3423.2 (90). EA: Calc. for C₁₆₀H₁₉₇F₅₁O₂₁ C 56.11, H 5.80; Found: C 56.25, H 5.77%.

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