The Importance of Micro Segregation for Mesophase Formation: Thermotropic Columnar Mesophases of Tetrahedral and other Low-Aspect-Ratio Organic Materials

Annegret Pegenau,[a] Torsten Hegmann,[a] Carsten Tschierske,*[a] and Siegmar Diele[b]

Abstract: Several low-aspect-ratio organic molecules [tetrahedral pentaerythritol derivatives, peracylated polyhydroxy compounds and aminoalcohols, a tetraphenylmethane derivative, a tetraphenylstannane, and a tetrahedral zinc bis(1,3-diketonate) all carrying long aliphatic chains] have been synthesized. These compounds were investigated by polarizing optical microscopy and differential scanning calorimetry, and some of them by X-ray diffraction. Most compounds show columnar liquid-crystalline mesophases. Their mesogenic properties are neither caused by a specific anisometric shape of these molecules nor by a strong amphiphilicity as known from conventional liquid crystals. Instead their mesogenity is mainly driven by micro segregation of the incompatible molecular parts (polar central regions and lipophilic alkyl chains) into well-organized different microdomains. It is shown that, in analogy to block copolymers, the mesophase stability rises on enlarging the number of repeat units connected with each other and on increasing the degree of incompatibility between the incompatible segments. During the process of self-organization the average conformation of the molecules is changed in such a way that it allows a most efficient packing of the molecules. Consequently, rigid molecules with a fixed tetrahedral geometry are not mesogenic. The molecules described herein can be regarded as the most simple star-shaped low-aspect-ratio block molecules that form liquid-crystalline phases. They bridge the gap between classical amphiphilic mesogens, several nonconventional dendritic and oligomeric liquid crystals, and mesomorphic block copolymers.

Keywords: block molecules · liquid crystals · micro segregation · noncovalent interactions · supramolecular chemistry

Introduction

The combination of order and mobility on a molecular level is a typical feature of the liquid-crystalline (LC) state. It leads to many applications, such as electro-optical displays and temperature sensors, and it is an important prerequisite for the existence of life (e.g. cell membranes). Therefore novel LC materials are of great interest. Additionally, liquid-crystalline mesophases are of general scientific interest because they represent typical examples of artificial self-organizing systems on a supramolecular level.[1]

According to the molecular order nematic, smectic, columnar, and cubic mesophases can be distinguished. These mesophases can be found in different classes of compounds. Most common are anisometric rod-shaped or disc-shaped molecules, which consist of an anisometric central unit grafted with flexible chains. Usually these chains are alkyl chains and provide the mobility, whereas the order is provided by the packing arrangement of the anisometric groups. Liquid-crystalline phases are also formed by amphiphilic molecules either in the pure state (thermotropic mesophases) or in their aqueous solutions (lyotropic systems). Here supermolecular aggregates are built up by the attractive forces between the strongly polar groups of the amphiphiles, which can organize in ordered structures. Most liquid-crystalline materials synthesized up to now belong to one of these two rough structural guidelines.

However, in the recent years mesomorphic properties have been reported for some nonconventional molecules; these have neither an anisometric shape nor belong to classical amphiphiles. Their mesomorphic properties could not be explained on the basis of these classical concepts. For example, some linear and branched oligoamides and polyamides,[2, 3] and some dendritic molecules[4, 5] display thermotropic liquid-crystalline behavior. Columnar mesomorphism

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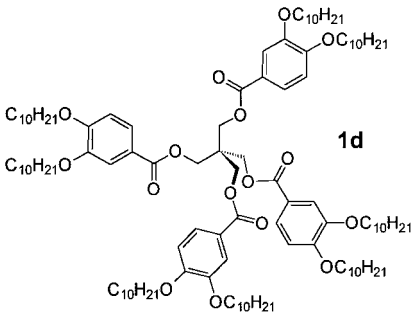
was found for a few octahedral metal complexes[6] and for the so called diabolo compounds.[7] We have synthesized pentaerythritol tetrabenzoates, such as compound **1d**, which can form columnar mesophases.[8] These molecules can be regarded as consisting of a tetrahedral central core to which a varying number of alkyl chains is grafted through aromatic linking units. In a preliminary communication we have pointed out the importance of micro segregation for their mesomorphic properties and proposed a cylinder model for the organization of the molecules in the columnar mesophases of these compounds.[8] In the meanwhile the same model was used to explain the mesomorphism of polyamides and some dendrimers.[3d, 4, 5]

Though micro segregation was realized to be a main reason for the transition from the nematic phase to the smectic phases and it is well known as driving force for the formation of lyotropic and thermotropic mesophases of strongly amphiphilic molecules.[9] The directed design of mesogenic materials without anisometric rigid units and without a strong amphiphilicity is a new approach in liquid crystal chemistry.

Herein we report on systematic structural variations at these novel low-aspect-ratio materials. For this purpose we have synthesized molecules related to **1d**. We have changed

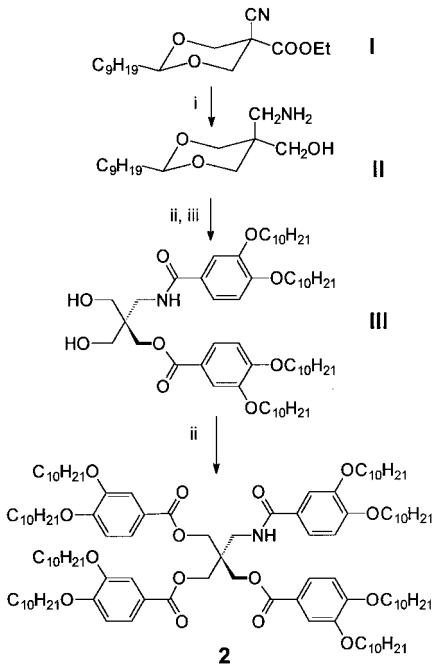


the number and length of the alkyl chains. The ester groups in the polar centers of these molecules were replaced by more-polar amide groups or by less-polar ether units. Furthermore, we have changed the number of repeat units and the topology of their connection and we have synthesized some rigid tetrahedral molecules. These investigations were carried out to evaluate the importance of micro segregation for mesophase formation of low-molecular-weight organic molecules.

Results and Discussion

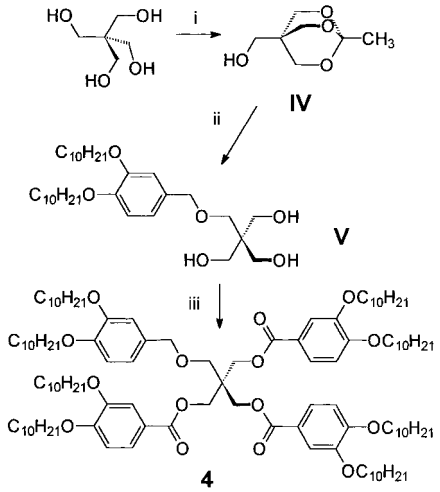
Synthesis: Most compounds (**1, 3, 12 – 14**, and **17 – 26**) were obtained in a straight forward manner by acylation of commercially available polyhydroxy compounds and polyhydroxyamines with an excess of substituted benzoic acid by the use of a water-soluble carbodiimide [*N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide methyl-*p*-toluenesulfonate, CMC] in the presence of 4-(dimethylamino)pyridine (DMAP).[10]

The amide **2** was synthesized according to Scheme 1. Ethyl-5-cyano-2-nonyl-1,3-dioxan-5-carboxylate[11] (**I**) was reduced to 5-aminomethyl-5-hydroxymethyl-2-nonyl-1,3-dioxan **II**. After acylation of the amino group and the hydroxy group, the protecting acetal group was cleaved and the diol **III** was benzoylated to give the amide **2**.



Scheme 1. Synthesis of the amide **2**. Reagents and conditions: i) $LiAlH_4$, Et_2O, 20 °C, 4 h, then H_2O; ii) 3,4-$(C_{10}H_{21}O)_2$PhCOOH, CMC, DMAP, CH_2Cl_2, 20 °C, 72 h; iii) EtOH, H_2O, PPTS, reflux, 5 h.

The pentaerythritol derivative **4**, which combines three acyloxy groups with one ether unit, was prepared according to Scheme 2. At first, selective protection of three of the hydroxy



Scheme 2. Synthesis of compound **4**. Reagents and conditions: i) $CH_3C(OEt)_3$, TosOH, PhMe, reflux, 5 h; ii) 1. NaH, 3,4-$(C_{10}H_{21}O)_2$PhCH$_2$Br, DMF, 5 h, 50 °C, then 20 °C, 12 h; 2. HCl, H_2O, EtOH, 20 °C, 1 h; iii) 3,4-$(C_{10}H_{21}O)_2$PhCOOH, CMC, DMAP, CH_2Cl_2, 20 °C, 72 h.

groups of pentaerythritol was achieved by formation of the bicyclic orthoacetate **IV**.[12] Etherification with 3,4-didecyloxybenzyl bromide[13] (obtained from ethyl 3,4-didecyloxybenzoate by reduction with $LiAlH_4$[14] and subsequent treatment with PBr_3[15]) followed by acidolytic cleavage of the protecting group afforded the triol **V**, which after acylation gave the triester **4**.

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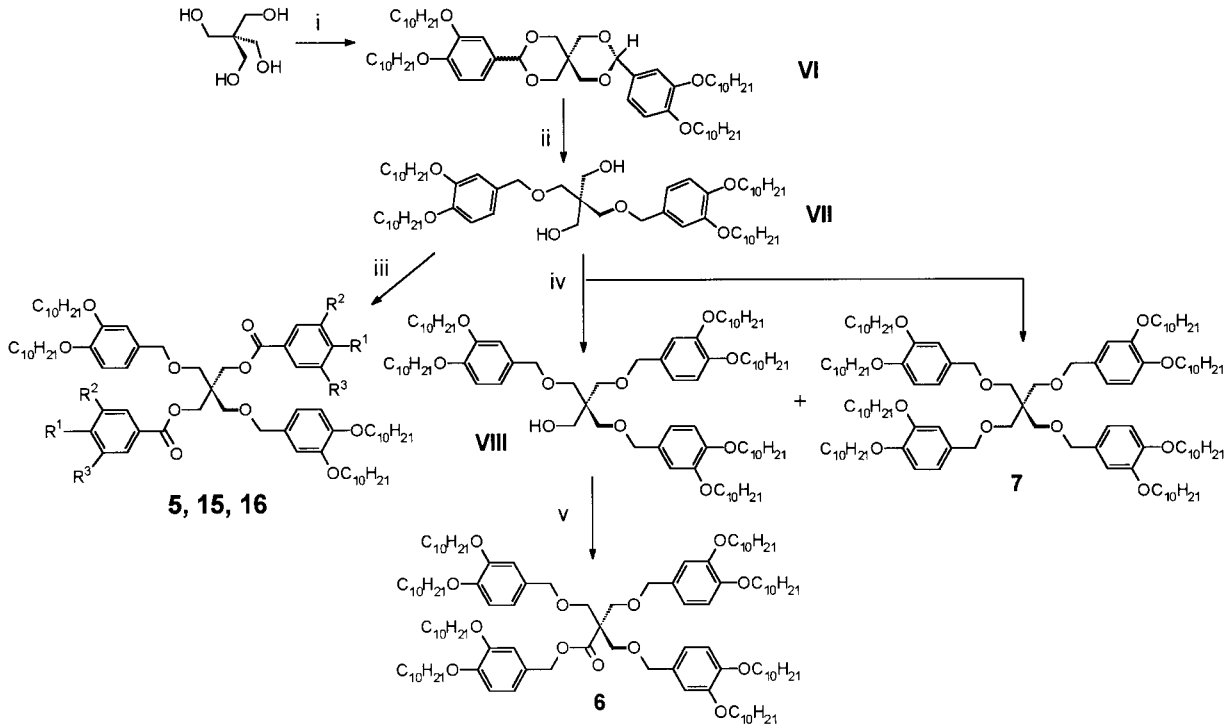
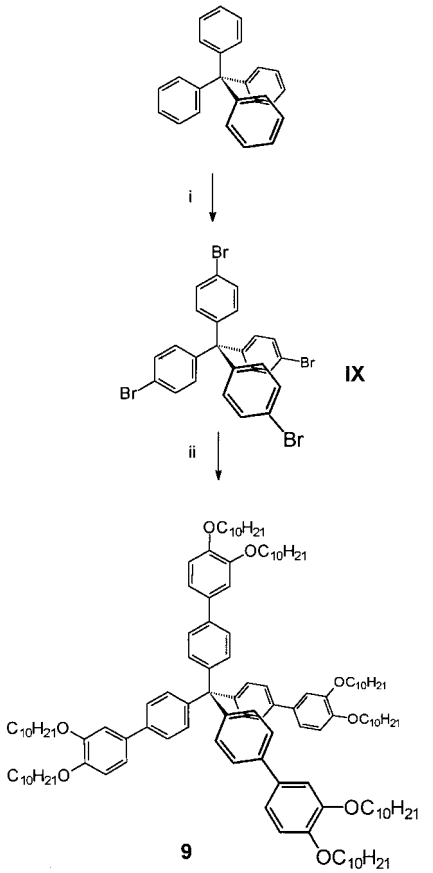


Scheme 3. Synthesis of the pentaerythritol derivatives **5**–**7**, **15** and **16**. Reagents and conditions i) 3,4-$(C_{10}H_{21}O)_2$PhCHO, PPTS, benzene, reflux, 20 h; ii) 1. $NaBH_4$, CF_3COOH, THF, 0 °C, then 20 °C, 4 h; 2. KOH, H_2O, 20 °C, 5 min; iii) 4-R^1-3-R^2-5-R^3PhCOOH, CMC, DMAP, CH_2Cl_2, 20 °C, 72h; iv) NaH, 3,4-$(C_{10}H_{21}O)_2$PhCH$_2$Br, DMF, 50 °C, 5 h, then 20 °C, 12 h; v) 3,4-$(C_{10}H_{21}O)_2$PhCOOH, CMC, DMAP, CH_2Cl_2, 20 °C, 72 h.

The compounds **5**–**7**, **15**, and **16** were prepared as outlined in Scheme 3. At first the spiroacetal **VI** was synthesized,[16] which was subsequently cleaved to give the dibenzyl ether **VII** by reduction with $NaBH_4$ in the presence of trifluoro acetic acid.[17] The diol **VII** was acylated with appropriately substituted benzoic acids to give the compounds **5, 15**, and **16**. Etherification of **VII** with three equivalents of 3,4-didecyloxybenzyl bromide yields a mixture of the triether **VIII** (from which compound **6** was obtained) and the tetraether **7**, which could be separated by preparative centrifugal thin-layer chromatography with a Chromatotron (Harrison Research).

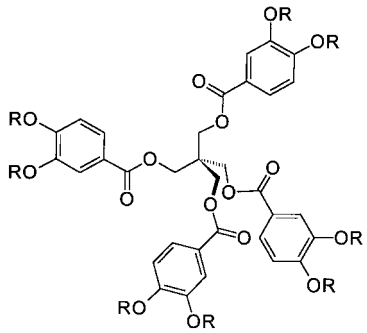
The tetraphenylmethane derivative **9** was obtained by Pd^0-catalyzed cross-coupling[18] of tetrakis(4-bromophenyl)-methane[19] with 3,4-didecyloxyphenylboronic acid[20] as shown in Scheme 4. To synthesize the tetraphenylstannane **10**, 3,4-didecyloxyphenyl bromide was subjected to a metal halogen exchange that afforded the corresponding lithiated species, which afterwards was treated with $SnCl_4$ to yield **10**.[21] For the preparation of **11**, the sodium salt of 1,3-bis(3,4-didecyloxyphenyl)-1,3-propanedione[22] was treated with $ZnCl_2 \cdot Et_2O$ in refluxing glyme.

Pentaerythritol tetrakis(3,4-dialkoxybenzoates): The phase transition temperatures and associated enthalpy values of the pentaerythritol 3,4-dialkoxybenzoates **1** are given in Table 1. Most of the compounds **1** show liquid-crystalline properties. On cooling of these compounds from the isotropic liquid state a spherulithic texture can be observed between crossed polarizers, which on slight shearing turns into a nonspecific birefringent texture. These are typical features of columnar mesophases.



Scheme 4. Synthesis of the tetraphenylmethane derivative **9**. Reagents and conditions: i) Br_2, cat. Fe, CCl_4, 30–35 °C, 8 h, then 20 h, reflux; ii) 3,4-$(C_{10}H_{21}O)_2$PhB$(OH)_2$, $Pd(PPh_3)_4$, $NaHCO_3$, DME, reflux, 8 h.

Table 1. Phase transition temperatures (T [°C]) and transition enthalpies ΔH [kJ mol^{-1}] (italics) of the pentaerythritol tetrakis(3,4-dialkoxybenzoates) **1**.



	R	K		Col		I
1a	OC_6H_{13}	·	45	–	–	·
			35.3			
1b	OC_8H_{17}	·	55	(·	31)	·
			88.9		*3.9*	
1c	OC_9H_{19}	·	55	(·	42)	·
			68.6		*4.2*	
1d	$OC_{10}H_{21}$	·	54	(·	47)	·
			102.3		*5.4*	
1e	$OC_{11}H_{23}$	·	14	·	53	·
			22.0		*6.0*	
1f	$OC_{12}H_{25}$	·	24	·	53	·
			40.4		*6.1*	
1g	$OC_{16}H_{33}$	·	58	–	–	·
			241.9			

The appearance of mesomorphic properties, however, strongly depends on the length of the alkyl chains. The hexyl derivative **1a** was obtained as an oily liquid that can be supercooled to −30 °C without a phase transition. Crystallization sets in after storage for several months at room temperature (m.p. 45 °C). The mesophase stability continuously rises with elongation of the chains and then decreases again. The melting temperatures increase at first (maximum at compounds **1b** and **1c**), then they decrease (minimum at compound **1e**) and finally strongly rise again. This leads to enantiotropic mesophases for compounds **1e** and **1f**. Remarkably, the long-chain compounds **1e**–**1g** crystallize much more rapidly than the short-chain compounds **1a**–**1d**. While the liquid-crystalline samples of compounds **1a**–**1d** can be stored for several days at room temperature without crystallization, the crystalline state of the hexadecylderivative **1g** can only be supercooled to 46 °C by rapid cooling. Above this temperature no mesophase was detected. Therefore, we conclude that a maximum of mesophase stability (53 °C) is reached for compounds **1e** and **1f**, and that the clearing temperatures decrease on further elongation of the alkyl chains.

The didecyloxybenzoate **1d** was investigated in more detail. The DSC (differential scanning calorimetry) heating and cooling traces of this compound are shown in Figure 1. Though its liquid-crystalline phase is monotropic (metastable), the crystalline state can easily be supercooled down to −30 °C without crystallization (see cooling curve). Slow crystallization occurs only after prolonged storage at room temperature.

The X-ray diffraction pattern of its mesophase is characterized by a diffuse scattering in the wide-angle region corresponding to 0.45 nm and three sharp scatterings in the small-angle region with a ratio of their positions 1:3$^{0.5}$:2 which confirms a hexagonal columnar organization in this mesophase (Col_h). The lattice parameter a_{hex} is nearly independent on the temperature and has been determined to be a_{hex} = 3.3 nm at 25 °C.

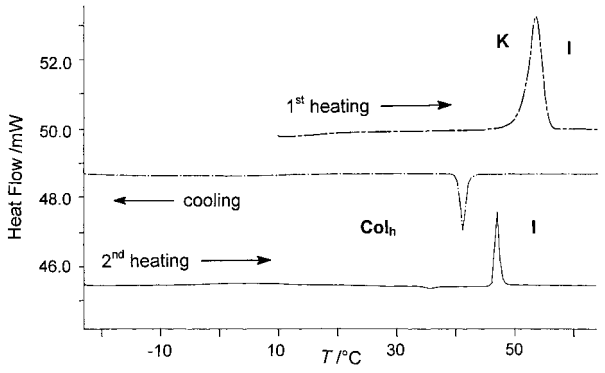


Figure 1. DSC heating and cooling traces of compound **1d** (10 K min^{-1}).

The question arises, how these molecules with a tetrahedral central core could organize into columns. Typically, thermotropic hexagonal columnar phases are formed by anisometric disclike molecules[23] or by amphiphilic or polymeric taper-shaped molecules.[24–26] However, no flat disclike molecular shape or taper shape is provided by the tetrahedral central core of the pentaerythritol tetrabenzoates. Rather, these molecules can adapt different conformations with the alkyl chains more or less randomly distributed around the central tetrahedral linking unit. The CPK models of two selected conformations of the pentaerythritol tetrabenzoate **1d** are shown in Figure 2. A conformer with a tetrahedral shape is shown in Figure 2a. A rather flat arrangement of the 3,4-dialkoxybenzoyl units is also possible as shown in Figure 2b, but it is impossible to arrange all four 3,4-dialkoxybenzoyl units in such a way that they form a really over-all flat disc. Furthermore, energy is necessary to force the molecules into the flat conformation and, additionally, any restriction of the number of conformations would be entropically disfavored. This situation is different from molecules with a flat and rigid core in which the disclike shape is inherently given.

More detailed inspection of the molecular models reveals that in the center of the molecules the polar building blocks (−COO−, phenyl, −O−) are concentrated, thus creating distinct polar regions. In these polar regions a large part of the cohesive energy is provided by polar forces, whereas the cohesive forces in the periphery result exclusively from the dispersion forces between the alkyl chains. Therefore, the polar regions of neighboring molecules should preferably interact with each other, rather than be distributed between the aliphatic chains. This leads to the aggregation of the polar groups with formation of segregated regions. During the process of self-organization the average conformation of the individual molecules is influenced. Conformers with a rather flat shape, similar to that one shown in Figure 2b should be favored in respect to other conformers, because they enable the most efficient interaction of their polar regions with those of neighboring molecules (induced fit). Thus, the central polar units can aggregate with formation of extended cylinders.

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Figure 2. CPK models of possible conformations of compound **1d**: a) conformer with a tetrahedral preorganization of the 3,4-didecyloxyphenyl groups; b) conformer with most flat, disclike arrangement of the 3,4-didecyloxyphenyl units.

Furthermore, in these conformers the alkyl chains are radially preorganized around the central cores; this additionally favors their organization in cylinders. As shown in Figure 3

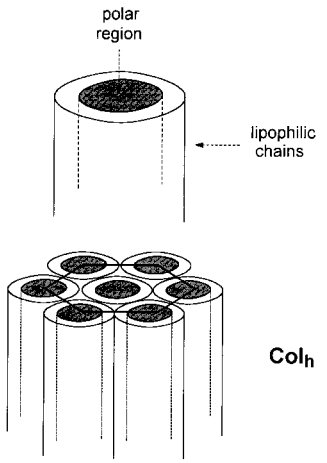


Figure 3. Core-shell model of the organization of the compounds **1** in their hexagonal columnar mesophases.[8]

these cylinders are surrounded by the liquidlike aliphatic chains and organize into a hexagonal 2D-lattice, which allows the most efficient space filling.

The diameter of the molecule **1d** in the disclike conformation as shown in Figure 2b with all-*trans*-conformations of the alkyl chains amounts to $D = 4.2$ nm. Taking into account the molten disordered state of the alkyl chains and the possibility of interdigitation of the alkyl chains of neighboring molecules in the liquid-crystalline state, the hexagonal lattice parameter ($a_{hex} = 3.3$ nm) corresponds very well ($a_{hex}/D = 0.79$) with the proposed arrangement of the molecules.

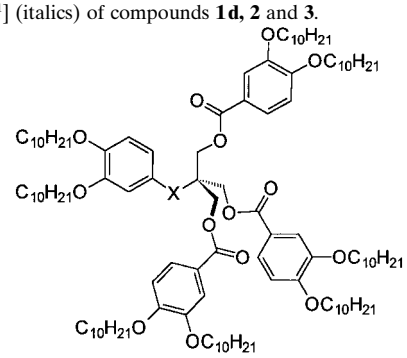
Thus, the thermotropic liquid-crystalline properties of these molecules are not caused by a well-defined anisometric molecular shape, instead their mesogenity is mainly driven by micro segregation of distinct incompatible molecular parts.[27] In this respect the molecules described here can be regarded as (starlike) block molecules, that is, as low-molecular-weight analogues of block-copolymers.[28]

As in block copolymers, the incompatibility of different molecular parts gives rise to the segregation of chemically slightly different segments into well-organized different microdomains. In AB-diblock copolymers, consisting of two different polymer chains A and B, the micro segregation is determined by the size of the blocks (number of statistical segments in the blocks $N = N_A + N_B$) and the degree of chemical and structural difference between the blocks. The latter is described by the segment interaction parameter χ_{AB},[29, 30] which is related to the difference of cohesive energy in the different blocks and can be estimated according to $\chi_{AB} = V_R(\delta_A - \delta_B)^2/RT$ from the solubility parameter δ_A and δ_B. The morphology of the micro-segregated regions is influenced by the volume fractions of the blocks (f) and the difference in conformational properties of the two blocks (ε). Since χ depends on temperature, micro segregation is temperature dependent and occurs below a certain order–disorder transition temperature.

In analogy to block-copolymers the stability of the mesophases of the molecules under discussion (measured as their clearing temperatures) should depend on the size of the distinct regions and on the degree of difference between them. Thus the mesophases should be stabilised either by enlarging the molecules, that is, on increasing the number of segments covalently bound to each other, and/or by increasing the intramolecular polarity contrast, that is, by enhancing the polarity in the polar region. At first we changed the intramolecular polarity contrast by structural variations in the central linking unit.

Molecules incorporating amide groups: In order to evaluate the importance of the polarity of the central regions, we at first replaced one of the carboxyl groups of the tetraester **1d** by an amide group (Table 2), which is more polar and provides additional cohesive forces by hydrogen bonding. The amide **2** and also compound **3**,[8c] which has the amide group directly attached to the central quaternary carbon atom, have enantiotropic liquid-crystalline phases. The mesophases of both compounds have the same spherulitic texture as the ester compounds **1**. However, only one (compound **2**) or two (compound **3**) equidistant reflections (see Table 3) were detected in the small-angle region of the X-ray diffraction pattern beside a diffuse scattering in the wide-angle range. These reflections do not allow an assignment of a

Table 2. Phase transition temperatures (T [°C]) and transition enthalpies ΔH [kJ mol^{-1}] (italics) of compounds **1d, 2** and **3**.



	X	K		Col		I
1d	$COOCH_2$	·	54	(·	47)	·
			102.3		*5.4*	
2	$CONHCH_2$	·	–[a]	·	72	·
					5.9	
3	CONH	·	47	·	66	·
			29.5		*7.6*	

[a] Crystallization has not yet been observed.

Table 3. Scattering vectors ($d_1 - d_3$ [nm]) and hexagonal lattice parameter (a_{hex}) of the mesophases of selected compounds; a_{hex} values in square brackets are calculated from the (10) reflection assuming a hexagonal lattice.

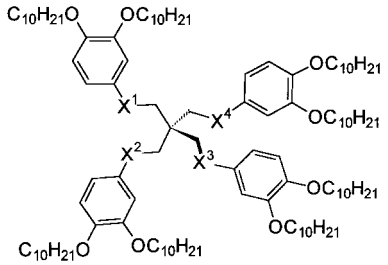
		d [nm]			
	T [°C]	(10)	(11)	(20)	a_{hex} [nm]
1d	25	2.89	1.65	1.43	3.33
2	25	2.88		1.47	[3.33]
3	25	2.82			[3.24]
4	25	2.89	1.70	1.46	3.40
5b	25	2.98	1.77	1.53	3.53
17	25	diffuse			
18	25	2.84			[3.35]
25	25	2.81			[3.24]
26	40	2.88			[3.32]

columnar mesophase from the X-ray results, but it should be emphasized that the $3^{0.5}$ reflection is often not observed in the scattering diagrams because of its low intensity. Therefore, on the basis of the observed textures and because of the complete miscibility of the mesophases of **2** and **3** with the Col_h phase of compound **1d**, we assume that the mesophases of the amides **2** and **3** are hexagonal columnar mesophases.

Both amides **2** and **3** show enhanced stabilities of their liquid-crystalline phases in comparison with the tetrabenzoate **1d**; this is in accordance with the proposed model. It shows that the mesophases of the pentaerythritol tetrabenzoates can indeed be stabilized by enhancing the intramolecular polarity contrast. However, in these amides intermolecular hydrogen bonding also contributes to the mesophase stabilization. Therefore we did not synthesize other molecules of this type with a further increased number of amide groups. Instead we asked what would happen, if we decrease the polarity in the central region.

Tetrahedral molecules incorporating ether groups: In order to achieve this the carboxyl groups of the tetrabenzoate **1d** were replaced step by step by less polar CH_2O groups. Compounds **4**–**7** (see Table 4) are all liquid-crystalline materials. The

Table 4. Comparison of the phase transition temperatures (T [°C]) of the pentaerythritol derivatives **1d, 4, 5b, 6** and **7** (italics refer to the transition enthalpies ΔH [kJ mol^{-1}]).



	X^1	X^2	X^3	X^4	K		Col		I
1d	COO	COO	OOC	OOC	·	54	(·	47)	·
						102.3		*5.4*	
4	COO	COO	OOC	OCH_2	·	7	·	32	·
						10.6		*5.1*	
5b	COO	COO	OCH_2	OCH_2	·	10	·	24	·
						34.5		*5.0*	
6	COO	CH_2O	OCH_2	OCH_2	·	11	·	23	·
						59.7		*6.1*	
7	CH_2O	CH_2O	OCH_2	OCH_2	·	14	·	21	·
						54.1		*6.8*	

polarized-light optical microscopic textures of their mesophases are again spherulitic textures as observed for the other tetrahedral molecules. As a typical example, the texture of **4** is shown in Figure 4. X-Ray diffraction proved the hexagonal

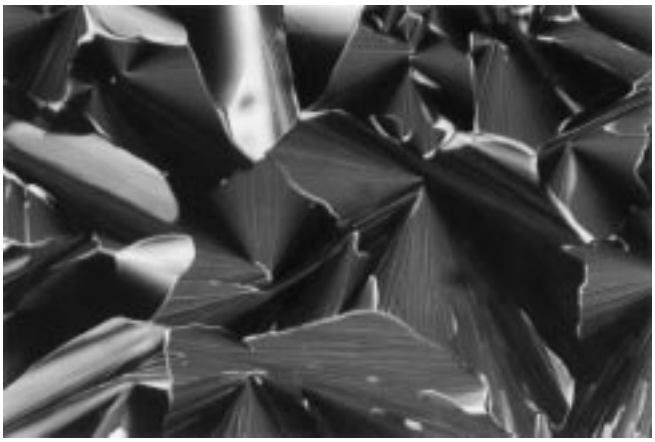


Figure 4. Optical texture of the hexagonal columnar mesophase of compound **4** as obtained by cooling from the isotropic melt (crossed polarizers) at 30 °C.

columnar structure (see Table 3) of the mesophases of compounds **4** and **5b**.

Replacement of only one carboxyl group of the tetrabenzoate **1d** by a CH_2O group lowers the mesophase stability considerably. The effect of the second ether group is less pronounced (compound **5b**). The diether **5b** and the triether **6** have nearly the same clearing temperature as the tetraether **7**, in which all ester group are replaced by the less-polar ether groups. The more-polar ester groups clearly stabilize the mesophases, but they are not necessary for mesogenity. Obviously, the intramolecular polarity contrast provided by the aromatic units, together with the ether oxygens (both benzyl ethers and phenyl ethers) is sufficient to enable micro

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segregation for these molecules. Though the observed dependence of the mesophase stability on the polarity of the central core unit is in line with the proposed model based on micro segregation, we have to take into account that also other molecular parameter are changed by these structural variations that can also influence the mesomorphic properties. This is discussed in the next section.

The interplay of polarity and rigidity: In order to evaluate the cohesive energy provided by the distinct molecular parts we have estimated the solubility parameter of the central units by using the group contributions and equations proposed by Hoy for amorphous polymers (Table 5).[31] The solubility parameter δ_t represents the square root of the total cohesive energy density, whereas δ_d, δ_p, and δ_h represent the dispersion, polar, and hydrogen bonding components, respectively. Clearly the cohesive forces between the alkyl chains are exclusively dispersion forces, whereas dispersion and polar forces are found in the region of the benzoate groups. Because the 3,4-didecyloxyphenyl groups are identical constituents of the molecules **1d, 2**, and **4–7**, their contribution should be constant. Therefore, we have considered only the central $C(CH_2–X)_4$ units (X = OOC, NHCO, OCH_2) without the aromatic rings. The δ_p values of the central units decrease in the same way as the stability of their liquid-crystalline phases decreases; this is in agreement with the proposed model. The especially strong increase of mesophase stability by introduction of the amide group should largely be caused by the additional hydrogen bonding.

Table 5. Solubility parameter δ_t and their polar (δ_p), hydrogen bonding (δ_h) and dispersion (δ_d) components of the central building blocks of the compounds **1d, 2** and **4–7** as calculated according to the method of Hoy [$J^{0.5}cm^{-1.5}$].[31]

central unit	δ_t	δ_p	δ_h	δ_d
$-CONHCH_2C(CH_2OOC-)_3$	26.6	15.7	16.6	13.7
$C(CH_2OOC-)_4$	24.2	14.3	–	13.2
$-CH_2OCH_2C(CH_2OOC-)_3$	23.5	13.3	–	13.8
$(-CH_2OCH_2)_2C(CH_2OOC-)_2$	22.9	12.2	–	14.6
$(-CH_2OCH_2)_3CCH_2OOC-$	22.2	10.9	–	15.1
$C(CH_2OCH_2-)_4$	21.5	9.4	–	15.8

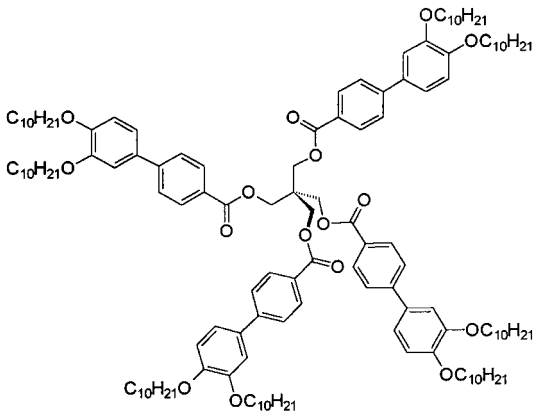
As mentioned above, by means of structure variations it is impossible to change one parameter exclusively. Also other molecular parameters, such as bond angles, bond lengths, the rotational barriers, and the conformational energies, are changed. Therefore these effects can additionally contribute to the total effect. The rigidity of the connecting units between the central tetrahedral core and the aromatic rings, for example, should increase in the order $CH_2OCH_2 < COOCH_2 < CONHCH_2 < CONH$. In this order tetrahedral shaped conformers that inhibit mesophase formation (Figure 2a) should be favored, whereas deformation of the molecules to give a more disclike shape becomes increasingly more difficult. Because the adaptation of a disclike shape facilitates molecular self-organization in columns, columnar mesophases should be stabilized by reducing the rigidity of the connecting units. Since the polarity of the connecting units rises in the same direction as the rigidity increases, the mesophase stabilization gained by increased polarity competes with the mesophase destabilizing effect of the increased rigidity. Thus, polarity and rigidity compete with each other in these molecules. The decreased mesophase stability of the amide **3** in comparison with the amide **2** is probably a result of the increased rigidity of the $-CONH-$ connecting unit (compound **2**) in comparison with the $-CONHCH_2-$ unit of **3**. It is also possible that the plateau like behavior of the clearing temperatures of the ether compounds **4–7** could be the result of a competition between rigidity (and other molecular parameter) and micro segregation. In any case, segregation tendency and rigidity act in different directions in these pentaerythritol derivatives.

In contrast to these molecules with tetrahedral cores, in classical disclike mesogens increased rigidity of the disc-shaped central units favors mesophase formation. There are also some cases of mesogens with a rather flexible central core forming columnar mesophases. One example is provided by the mesogenic azacrown derivatives.[32] Acylated azacrowns form columnar mesophases, whereas the related alkyl derivatives do not. Here, rigidification of the molecules by the amide groups is assumed to stabilize disclike conformers and thus stabilizes columnar mesophases. However, not only the rigidity, but also the polarity contrast is much larger in the acylated azacrowns (amides) than in the alkylated azacrowns (amines), and therefore micro segregation should also contribute to mesophase formation. Here, both effects act in the same direction and therefore no decision can be made concerning the importance of micro segregation in these molecules. However, in the tetrahedral molecules described herein, both effects are in competition to each other, uncovering the importance of micro segregation for their mesophase formation.

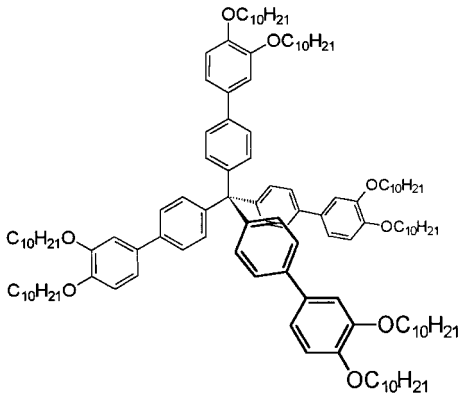
Tetrahedral biphenyl derivatives: We have tried to further evaluate the influence of rigidity on mesophase formation. Therefore the ester compound **8** (Figure 5), in which the phenyl rings of the tetrabenzoate **1d** are replaced by rodlike biphenyl units, was synthesized.[33] This compound displays a monotropic mesophase with a nonspecific texture. It occurs on cooling at 72 °C and immediately crystallizes. Due to the rapid crystallization no X-ray studies could be performed. In the contact region with the hexagonal columnar phase of the pentaerythritol tetrabenzoate **1d**, a broad isotropic region occurs. This indicates the incompatibility of the hexagonal columnar phase of **1d** with the unknown phase of **8**.

The tetraphenylmethane derivative **9**, in which the rather flexible CH_2OOC groups of **1d** are formally replaced by rigid 1,4-phenylene units, is only a crystalline solid (m.p. 74 °C).[34, 35] The isotropic melt can be supercooled to 42 °C without formation of a mesophase.

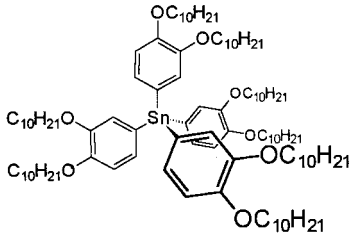
Additionally we have synthesized compound **10**, in which the tetrahedral central unit is directly connected to the phenyl rings. For preparative reasons a tetrahedral tin atom instead of a tetrahedral carbon was used. This compound is also nonmesogenic. Another example of a rigid tetrahedral molecule is provided by the zinc acetylacetonate **11**. Here, rigidity is combined with a polar center, but this compound is also only a crystalline solid. It seems, that indeed no mesophases can be obtained in rigid tetrahedral molecules.[36]



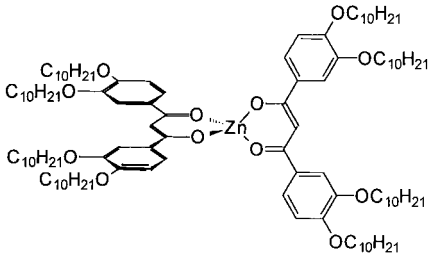
8: K 92 (X 72) I



9: K 74 I



10: K 60 I

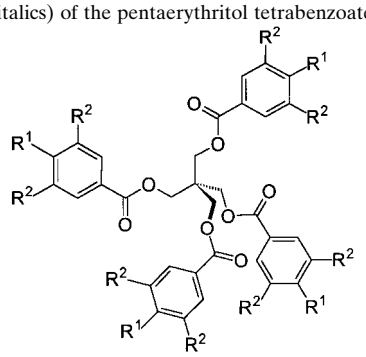


11: K 118 I

Figure 5. Phase transition temperatures (T [°C]) of the tetrahedral compounds **8**–**11.**

Influence of the number and position of the chains: As mentioned above, the mesomorphic properties of the pentaerythritol tetrakis(2,3-dialkoxybenzoates) occur at a certain length of the alkyl chains. The reason may be that in short-chain compounds the number of repeat units (CH_2) in the lipophilic regions is not large enough for micro segregation, but additionally space filling effects are responsible. In order to clarify this we have changed the number of alky chains attached to the polar central regions. Grafting additional alkyl chains to the phenyl benzoate moieties of the pentaerythritol tetrabenzoates **1** decreases the mesophase stability (Table 6). Compound **12b** with twelve lipophilic decyloxy chains has a considerably lower mesophase stability than **1d** bearing only eight of these chains. Obviously the space required by the twelve alkyl chains is larger than necessary for the efficient surrounding of the polar cylindrical regions. Thus, the polar interactions between the central regions of neighboring molecules are disturbed for steric reasons. This shows, that the molecules must be able to interact efficiently through both of their incompatible parts in order to form liquid-crystalline phases.

Table 6. Phase transition temperatures (T [°C]) and transition enthalpies ΔH [kJ mol^{-1}] (italics) of the pentaerythritol tetrabenzoates **12**–**14.**



	R^1	R^2	K		Col		I
12a	OC_6H_{13}	OC_6H_{13}	·	< 20	–	–	·
12b	$OC_{10}H_{21}$	$OC_{10}H_{21}$	·	41	(·	8)	·
				121.9		*5.9*	
12c	$OC_{16}H_{33}$	$OC_{16}H_{33}$	·	50	–	–	·
				236.1			
13a	$OC_{10}H_{21}$	H	·	42	–	–	·
				72.7			
13b	$OC_{16}H_{33}$	H	·	72	–	–	·
				180.1			
14	H	$OC_{10}H_{21}$	·	35	(·	7)	·
				96.3		*9.3*	

Also the 4-alkoxybenzoates **13**, which carry only four instead of eight alkoxy chains, are not mesomorphic (**13a** can be supercooled to −25 °C, **13b** to +25 °C). Interestingly, no smectic phases were found as could be expected from the nearly equivalent space filling of polar and lipophilic regions in these molecules. Probably the tetrahedral preorganization of the substituents around the pentaerythritol central units disfavors the formation of layer structures and instead mesomorphic properties get lost.

In the following we have combined different building blocks. In the series **5a**–**c** the length of four alkyl chains was changed keeping the other four chains constant. Compound **5a** which combines hexyl and decyl chains has a significantly lower mesophase stability than compound **5b** with eight decyl chains (Table 7). Again, the hexadecyl substituted compound **5c** is a rather high-melting crystalline solid which cannot be supercooled.

In compound **15** two double chain and two triple chain units are combined, whereas in compound **16** double chain and

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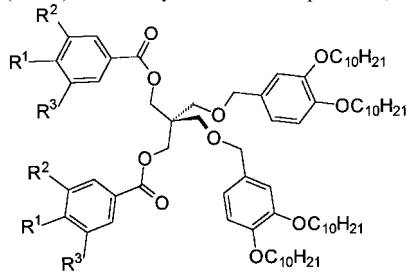
Table 7. Phase transition temperatures (T/°C) and transition enthalpies ΔH/ kJ mol^{-1} (italics) of the desymmetrized compounds **5, 15** and **16**.



	R^1	R^2	R^3	K		Col		I
5a	$C_6H_{13}O$	$C_6H_{13}O$	H	·	–[a]	·	5	·
					3.2			
5b	$C_{10}H_{21}O$	$C_{10}H_{21}O$	H	·	10	·	24	·
					34.5		*5.0*	
5c	$C_{16}H_{33}O$	$C_{16}H_{33}O$	H	·	42	–	–	·
					112.2			
15	$C_{10}H_{21}O$	$C_{10}H_{21}O$	$C_{10}H_{21}O$	·	–8	·	14	·
					12.6		*7.6*	
16	$C_{10}H_{21}O$	H	H	·	1	·	3	·
					26.9		*2.9*	

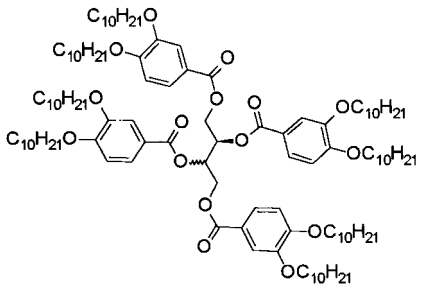
[a] Crystallization has not yet been observed.

single chain units are connected. In both cases the mesophase stability is lower than that one of the compound **5b** with four 3,4-didecyloxyphenyl groups. It seems, that in this class of compounds a number of eight alkyl chains grafted to the central core represents an optimum for mesophase formation.

Interestingly, the optimal number of alkyl chains can also be realized very simply by mixing two pentaerythritol derivatives that have a different number of alkyl chains. In the contact region between the 3,4,5-tridecyloxybenzoate **12b** and the nonmesogenic 4-decyloxybenzoate **13a** the columnar mesophase of **12b** is slightly stabilized ($T_{cl,max} = 12\,^{\circ}C$). This means that in the contact region the optimal conditions for mesophase formation is realized. This behavior is reminiscent of lyotropic systems and of thermotropic phases of mixed systems of amphiphilic polyhydroxy compounds.[25]

These results show that an appropriate number and length of the aliphatic chains is important for mesophase formation in this class of compounds. However, the position of the alkoxy chains is also of importance. The 3,5-didecyloxybenzoate **14**, which is an isomer of the 3,4-didecyloxybenzoate **1d** that differs exclusively in the position of the alkyl chains to each other, has a clearing temperature similar to the 3,4,5-trisubstituted compound **12b**. One explanation could be that the space required by the two chains in 3,5-position is approximately the same as that required by the three chains of the trialkoxy benzoates. On the other hand, it is often observed that 3,5-dialkoxybenzoates have lower mesophase stabilities than the corresponding 3,4-dialkoxybenzoates.[25c, 37]

Linear tetrabenzoates: In a next step we investigated the influence of the topology of connection of the 3,4-dialkoxybenzoate units. For this purpose the tetrahedral pentaerythritol linking unit was replaced by central units that allow the 3,4-dialkoxybenzoate groups to be fixed in a more linear fashion. The tetrakis(3,4-didecyloxybenzoates) of erythritol **17** and D-threitol **18**[8c] (Figure 6) form monotropic mesophases. The clearing points are slightly decreased in comparison with the pentaerythritol derivative **1d**.



17 (erythro): K 57 (Col 39) I
102.2 6.5

18 (D-threo): K 44 (Col 40) I
86.7 6.5

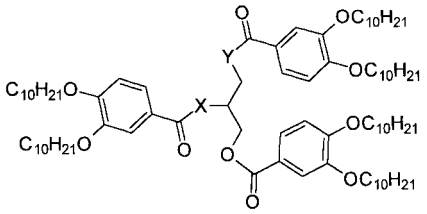
Figure 6. Phase transition temperatures (T [°C]) and transition enthalpies ΔH [kJ mol^{-1}] (italics) of the erythritol and D-threitol tetrabenzoates **17** and **18.**

In the X-ray diffraction pattern of the mesophases of both compounds a diffuse scattering in the wide-angle region indicates the liquidlike organization of the alkyl chains. Only one reflection corresponding to a d value of 2.84 nm is found in the small-angle region of the diffraction pattern of the threitol derivative **18** (see Table 3). Therefore the assignment of the mesophase is based on the spherulitic texture and the uninterrupted miscibility with the pentaerythritol tetrabenzoate **1d**; these both point to a hexagonal columnar mesophase. In the case of the erythritol tetrabenzoate **17**, only a diffuse scattering is found in the small-angle region. Its position corresponds to that found in the small-angle scattering of the diastereomer **18**. Though this diffraction pattern is reminiscent of nematic phases, this can be excluded from the observed spherulithic texture. Additionally, there is an uninterrupted miscibility with the columnar phase of the proven hexagonal columnar mesophase of the pentaerythritol tetrabenzoate **1d**. Probably, the unusual X-ray pattern of this compound can be explained by a partial loss of long-range positional order of the columns due to the slightly elongated shape of the molecules.[38]

Tribenzoates: In a next step we asked, what would happen if the number of 3,4-dialkoxybenzoyl groups connected with each other is changed. In compound **19** one of the 3,4-dialkoxybenzoyl units of the pentaerythritol tetrabenzoate **1d** is removed. The tribenzoate of tris(hydroxymethyl)methane is a rather high melting solid without mesomorphic properties (supercooled to 55 °C). Also on cooling the glycerol ester **20** to 30 °C no liquid crystalline phases were found (see Table 8). It seems, that in this class of compounds a minimum number of at least four 3,4-dialkoxybenzoyl groups must be connected with each other to observe liquid-crystalline properties.

Interestingly, the replacement of one carboxyl group of the glycerol ester **20** by an amide group (increased polarity and additional hydrogen bonding) can produce liquid crystallinity (compound **21**, see Table 8).[8c] However, only the amide **21** can be supercooled to sufficiently low temperatures that allows the observation of the mesophase.

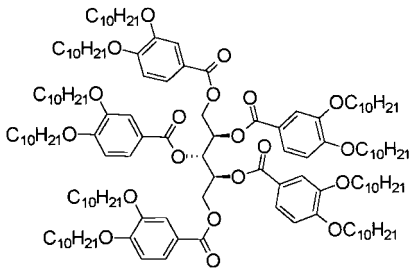
Table 8. Phase transition temperatures (T [°C]) and transition enthalpies ΔH [kJ mol^{-1}] (italics) of tris(3,4-didecyloxybenzoates) **19–22.**



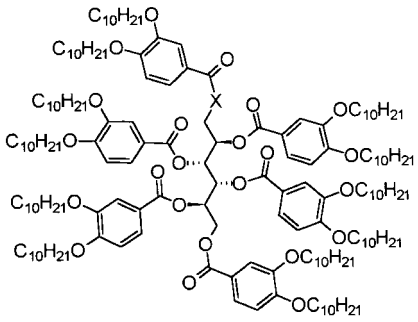
	X	Y	K		Col		I
19	OCH_2	O	·	75	–	–	·
				95.4			
20	O	O	·	98	–	–	·
				103.9			
21	O	NH	·	97	(·	64)	·
				85.6		*2.6*	
22	NH	O	·	94	–	–	·
				87.7			

Pentabenzoates and hexabenzoates: The adonitol derivative **23**, the D-mannitol derivative **24**,[8c] and the dipentaerythritol derivative **26** are molecules in which five or six 3,4-didecyloxybenzoate units are connected (Figure 7). All three compounds exhibit liquid crystalline properties. The highest mesophase stability is found for compounds **24** and **26** with the largest number of phenyl benzoate units. The increased clearing temperature of the D-mannitol derivative **24** in comparison with the D-threitol derivative **18** indicates, that the mesophases can be stabilized by increasing the number of 3,4-dialkoxybenzoyl groups connected with each other (i.e., by increasing the number of nonmesogenic repeat units). An especially high clearing temperature was found for the dipentaerythritol derivative **26**. Compound **26** was investigated by X-ray diffraction. As in the cases of other polybenzoates with nontetrahedral central linking units its X-ray diffraction pattern is characterized by a diffuse scattering in the wide-angle range and only two equidistant reflections in the small-angle region. Again, the optical textures (spherulitic textures) of the mesophases of compounds **23, 24**, and **26** and the uninterrupted miscibility of the mesophases of these compounds with the Col_h phase of the pentaerythritol tetrabenzoate **1 d** suggest that the mesophases of these compounds are also hexagonal columnar phases.

As expected, replacing one carboxyl group of the mannitol hexabenzoate **24** by an amide group (compound **25**) significantly stabilizes the liquid crystalline phase.

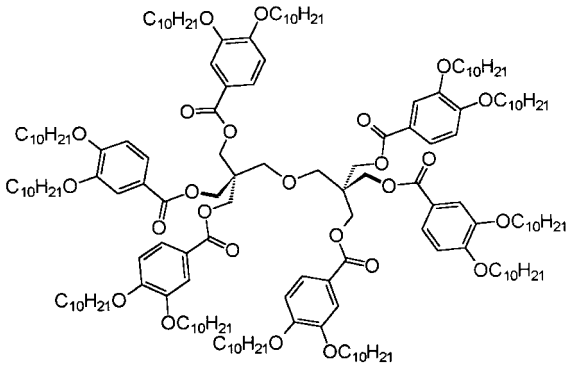


23: K 54 (Col 36) I
33.3 5.5



24: X = O K ? Col 55 I
9.1

25: X = NH K ? Col 78 I
8.0



26: K ? Col 79 I
11.6

Figure 7. Phase transition temperatures (T [°C]) and transition enthalpies ΔH [kJ mol^{-1}] (italics) of the compounds **23–26.**

Conclusion

The compounds described herein belong to a novel class of thermotropic liquid-crystalline compounds forming columnar mesophases. Their mesogenic properties are neither caused by a specific anisometric shape of these molecules as known from classical disc-shaped mesogens nor by a strong amphiphilicity as known from ionic amphiphiles and polyhydroxy amphiphiles. Instead their mesogenity is mainly driven by micro segregation of incompatible molecular parts.[27] As in block copolymers[28] the incompatibility of different molecular parts gives rise to the segregation of the chemically slightly different segments into well-organized different microdomains. The micro segregation can be observed below a certain order–disorder temperature, the clearing temperature, and depends on the size of the incompatible segments and on the degree of incompatibility between them. For example, the ethyl 3,4-didecyloxybenzoate **27** (see Figure 8), which represents a monomeric segment of the liquid crystalline compound **1 d**, is a nonmesomorphic compound. If the ester group of **27** is replaced by more polar groups, such as a polyhydroxy group[24a–d, 25] in the pentaerythritol ether **V** (an intermediate in the synthesis of compound **4**) a stronger amphiphilicity is generated and columnar liquid-crystalline properties can be found for this small but strongly amphiphilic tapered molecule (Figure 8). Another way to reinforce micro segregation

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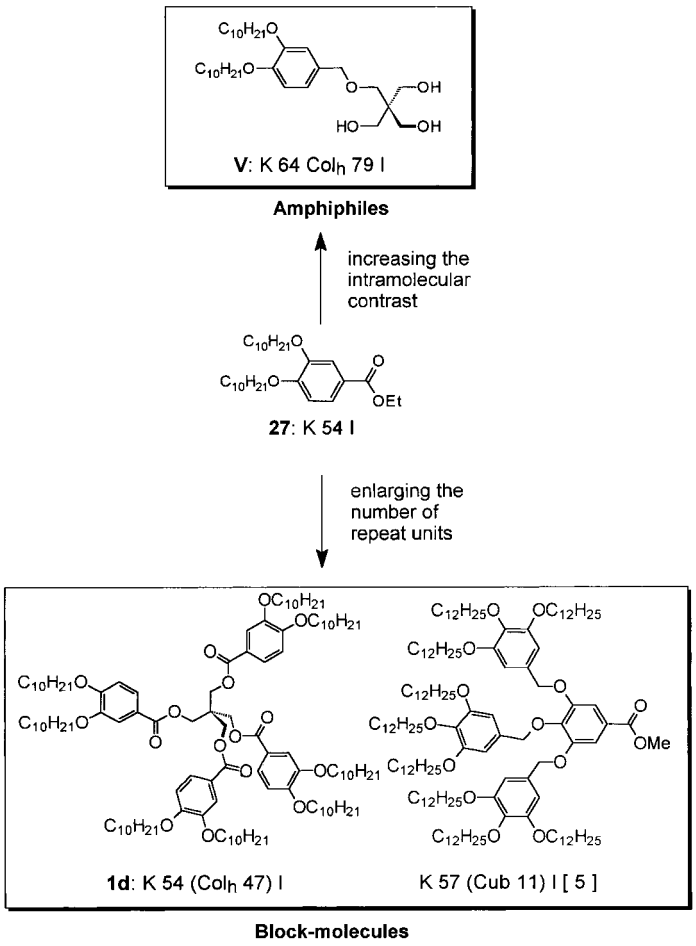

Figure 8. Structural variations at the nonmesogenic dialkoxybenzoate **27** which could lead to mesomorphic properties (Cub = cubic mesophase).

consists in the enlargement of the antagonistic molecular parts by linking them together covalently. This is realized in the compounds described herein. In this way the phenyl benzoate units become preorganized; this enables them to interact cooperatively forming a polar region that is able to segregate from the regions of the lipophilic alkyl chains. The relative space filling of the segregated regions and the preorganization of the lipophilic chains around the central linking units favor columnar aggregates.

The compounds reported in this paper are related to other nonconventional mesogens reported recently, such as open chain oligoamides[2, 3, 4], some DOBOB-esters of 2-hydroxymethyl-2-nitro-1,3-propanediol[39] and pentaerythritol,[40] and diabolo mesogens.[7] Cone-shaped dendritic 3,4,5-tris-(3,4,5-trialkoxybenzyloxy)benzene derivatives and related dendrons of higher generation also can self-organize to columnar and cubic mesophases and provide an alternative approach to reinforce micro segregation (see Figure 8).[5] Here the polar regions are enlarged by dendritic branching. Also higher generation dendrimers consisting of branched oligoamine polar regions, peripherally surrounded by 3,4-dialkoxybenzoate groups, have recently been reported.[4]

In summary, the molecules described herein can be regarded as the most simple starlike low-aspect-ratio block molecules that form liquid-crystalline phases. They bridge the gap between classical amphiphilic mesogens, several nonconventional dendritic and oligomeric liquid crystals, and mesomorphic block copolymers. Most importantly, they provide a novel designing principle for liquid crystals that could lead to interesting new materials in the near future.

Experimental Section

General: ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were obtained on Varian Gemini 200, Varian Unity 400, and Varian Unity 500 spectrometers. Mass spectra were recorded on an AMD 402 Intectra (70 eV) instrument and on a Hewlett–Packard LD-TOF-system G2025A. Microanalyses were performed with a CHNF-932 (Leco) elemental analyzer. Infrared spectroscopy was performed with a Perkin-Elmer Spektrum 1000 spectrometer. Thin-layer chromatography was performed on aluminium TLC plates (silica gel 60 F_{254}) from Merck. For the preparative centrifugal thin-layer chromatography a Chromatotron from Harrison Research Europe (Muttenz) was used. Transition temperatures were measured by the use of a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarizing microscope, and these were confirmed from differential scanning calorimetry (Perkin Elmer DSC-7). Tetrahydrofuran, diethyl ether, and benzene were distilled from sodium/benzophenone ketyl; dichlormethane was distilled from P_4O_{10}; DMF was distilled from CaH_2; ethanol and glyme were used as obtained. Adonitol (Acros), 1-amino-1-deoxy-D-sorbitol (Aldrich), 2-amino-1,3-propanediol (Aldrich), 1-amino-2,3-propanediol (Merck), ethyl 4-bromobenzoate (Aldrich), *N*-cyclohexyl-*N'*-(2-morpholinoethyl)carbodiimide methyl-*p*-toluenesulfonate (CMC, Fluka), 4-(dimethylamino)pyridine (Merck), dipentaerythritol (Aldrich), meso-erythritol (Acros), glycerol (Ferak Berlin), 2-(hydroxymethyl)-1,3-propanediol (Aldrich), D-mannitol, pentaerythritol (Merck), phosphorus tribromide (Merck), pyridinium 4-toluenesulfonate (Merck), 4-toluene sulfonic acid (Chemapol), D-threitol (Fluka), trifluoro acetic acid (Merck), and tris(hydroxymethyl)aminomethane (Serva) were used without further purification. Sodium hydride (80 % suspension in paraffin) was washed three times with dry hexane under an argon atmosphere and dried under a stream of argon. Substituted benzoic acids[25c], 3,4-didecyloxybenzaldehyde,[41] 3,4-didecyloxybenzyl bromide,[15] 3,4-didecyloxyphenylboronic acid,[20] 4-(hydroxymethyl)-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane,[12] tetrakis(4-bromophenyl)methane,[19] 3,4-didecyloxybromobenzene,[20, 42] 1,3-bis(3,4-didecyloxyphenyl)-1,3-propanedione,[22] and $Pd(PPh_3)_4$[43] were synthesized according to literature procedures.

Acylation of polyhydroxy compounds and amino alkohols—general procedure: At 20 °C a suspension of the appropriate polyhydroxy compound or amino alcohol was stirred in dry CH_2Cl_2 (70 mL per mmol). Two equivalents of the appropriately substituted benzoic acid, 2.4 equivalents of CMC per XH group to be acylated, and a catalytic amount of DMAP (20 mg) were added, and the mixture was stirred for 72 hours at 20 °C. The reaction mixture was washed once with water (70 mL). The aqueous phase was extracted with $CHCl_3$ (20 mL), and the organic layer was dried over Na_2SO_4. The solvent was removed in vacuo to give the crude product, which was purified by preparative centrifugal thin-layer chromatography (Chromatotron). The complete acylation was proved by infrared spectroscopy of the final products (absence of $\tilde{\nu}_{O-H}$).

1,3-Bis(3,4-dihexyloxybenzoyloxy)-2,2-bis(3,4-dihexyloxybenzoyloxymethyl)-propane (1a): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4-dihexyloxybenzoic acid (2.6 g, 8 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:1.5–2). Yield: 0.27 g (20 %); m.p. 45 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86-0.90$ (m, 24H; CH_3), 1.31–1.36 (m, 32H; CH_2), 1.43–1.47 (m, 16H; $O(CH_2)_2CH_2$), 1.76–1.84 (m, 16H; OCH_2CH_2), 3.98 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.60 (s, 8H; CCH_2), 6.77 (d, $^3J(H,H) = 8.5$ Hz, 4H; Ar–H), 7.47 (d, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H), 7.56 (dd, $^3J(H,H) = 8.5$ Hz, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1375.5 $[M+Na]^+$, 1392.1 $[M+K]^+$; $C_{81}H_{124}O_{16}$ (1353.7): calcd C 71.87, H 9.22; found C 71.91, H 9.33.

1,3-Bis(3,4-dioctyloxybenzoyloxy)-2,2-bis(3,4-dioctyloxybenzoyloxymethyl)-propane (1b): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4-dioctyloxybenzoic acid (3.1 g, 8 mmol). Purified twice by chromatography

with petroleum ether/ethyl acetate (10:1.5). Yield: 0.46 g (29%); K 55°C Col 31°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 7.0$ Hz, 12H; CH_3), 0.87 (t, $^3J(H,H) = 7.0$ Hz, 12H; CH_3), 1.26–1.34 (m, 64H; CH_2), 1.42–1.48 (m, 16H; $O(CH_2)_2CH_2$), 1.76–1.84 (m, 16H; OCH_2CH_2), 3.97 (t, $^3J(H,H) = 7.0$ Hz, 8H; OCH_2), 4.00 (t, $^3J(H,H) = 7.0$ Hz, 8H; OCH_2), 4.60 (s, 8H; CCH_2), 6.77 (d, $^3J(H,H) = 8.6$ Hz, 4H; Ar–H), 7.47 (d, $^4J(H,H) = 2.1$ Hz, 4H; Ar–H), 7.55 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.1$ Hz, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1579.3 $[M+H]^+$, 1602.2 $[M+Na]^+$, 1618.7 $[M+K]^+$; $C_{97}H_{156}O_{16}$ (1578.1): calcd C 73.83, H 9.95; found C 73.81, H 9.96.

1,3-Bis(3,4-dinonyloxybenzoyloxy)-2,2-bis(3,4-dinonyloxybenzoyloxymethyl)-propane (1c): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4-dinonyloxybenzoic acid (3.2 g, 8 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:1.5). Yield: 0.39 g (23%); K 55°C Col 42°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 7.1$ Hz, 12H; CH_3), 0.87 (t, $^3J(H,H) = 6.8$ Hz, 12H; CH_3), 1.25–1.34 (m, 80H; CH_2), 1.42–1.47 (m, 16H; $O(CH_2)_2CH_2$), 1.76–1.84 (m, 16H; OCH_2CH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 8H; CH_2), 4.60 (s, 8H; CCH_2), 6.76 (d, $^3J(H,H) = 8.6$ Hz, 4H; Ar–H), 7.47 (d, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H), 7.55 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H); MS (MALDI-TOF, CHC): *m/z*: 1712.0 $[M+Na]^+$, 1728.2 $[M+K]^+$; $C_{105}H_{172}O_{16}$ (1690.3): calcd C 74.61, H 10.25; found C 74.42, H 10.20.

1,3-Bis(3,4-didecyloxybenzoyloxy)-2,2-bis(3,4-didecyloxybenzoyloxymethyl)-propane (1d): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4-didecyloxybenzoic acid (3.5 g, 8 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:0.7–1.5). Yield: 0.41 g (22%); K 54°C Col 47°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.85-0.87$ (m, 24H; CH_3), 1.25–1.34 (m, 96H; CH_2), 1.42–1.48 (m, 16H; $O(CH_2)_2CH_2$), 1.76–1.83 (m, 16H; OCH_2CH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.60 (s, 8H; CCH_2), 6.77 (d, $^3J(H,H) = 8.5$ Hz, 4H; Ar–H), 7.48 (d, $^4J(H,H) = 1.9$ Hz, 4H; Ar–H), 7.57 (dd, $^3J(H,H) = 8.5$ Hz, $^4J(H,H) = 1.9$ Hz, 4H; Ar–H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.07$, 22.67, 25.99, 26.05, 29.11, 29.25, 29.34, 29.35, 29.40, 29.45, 29.56, 29.59, 29.61, 29.64, 31.91, 43.23 (CCH_2), 63.34 (CCH_2), 69.08, 69.35, 112.06, 114.44, 121.75, 123.68, 148.73, 153.58, 165.94 (C=O); IR (Nujol): $\tilde{\nu} = 1721$ cm^{-1} (C=O); MS (MALDI-TOF, DHB): *m/z*: 1803.5 $[M+H]^+$, 1826.3 $[M+Na]^+$, 1843.2 $[M+K]^+$; $C_{113}H_{188}O_{16}$ (1802.5): calcd C 75.30, H 10.50; found C 75.19, H 10.41.

1,3-Bis(3,4-diundecyloxybenzoyloxy)-2,2-bis(3,4-diundecyloxybenzoyloxy-methyl)propane (1e): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4-diundecyloxybenzoic acid (3.7 g, 8 mmol). Purified twice by chromatography with petroleum ether/$CHCl_3$ (1:1–2). Yield: 0.59 g (31%); K 14°C Col 53°C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.87$ (t, $^3J(H,H) = 7.1$ Hz, 12H; CH_3), 0.88 (t, $^3J(H,H) = 7.3$ Hz, 12H; CH_3), 1.26–1.33 (m, 112H; CH_2), 1.42–1.48 (m, 16H; $O(CH_2)_2CH_2$), 1.77–1.86 (m, 16H; OCH_2CH_2), 3.99 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.02 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.62 (s, 8H; CCH_2), 6.78 (d, $^3J(H,H) = 8.5$ Hz, 4H; Ar–H), 7.48 (d, $^4J(H,H) = 1.9$ Hz, 4H; Ar–H), 7.57 (dd, $^3J(H,H) = 8.5$ Hz, $^4J(H,H) = 1.9$ Hz, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1914.5 $[M+H]^+$, 1936.1 $[M+Na]^+$, 1952.7 $[M+K]^+$; $C_{121}H_{204}O_{16}$ (1914.7): calcd C 75.90, H 10.73; found C 75.96, H 10.85.

1,3-Bis(3,4-didodecyloxybenzoyloxy)-2,2-bis(3,4-didodecyloxybenzoyloxy-methyl)propane (1f): Synthesized from pentaerythritol (0.102 g, 0.75 mmol) and 3,4-didodecyloxybenzoic acid 2.9 g (6 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:0.7–1.5). Yield: 0.18 g (12%); K 24°C Col 53°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.84-0.87$ (m, 24H; CH_3), 1.24–1.33 (m, 128H; CH_2), 1.42–1.47 (m, 16H; $O(CH_2)_2CH_2$), 1.76–1.83 (m, 16H; OCH_2CH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.60 (s, 8H; CCH_2), 6.76 (d, $^3J(H,H) = 8.6$ Hz, 4H; Ar–H), 7.46 (d, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H), 7.55 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2049.7 $[M+Na]^+$, 2066.5 $[M+K]^+$; $C_{129}H_{220}O_{16}$ (2026.9): calcd C 76.44, H 10.93; found C 76.15, H 10.94.

1,3-Bis(3,4-dihexadecyloxybenzoyloxy)-2,2-bis(3,4-dihexadecyloxybenzoyl-oxymethyl)propane (1g): Synthesized from pentaerythritol (0.102 g, 0.75 mmol) and 3,4-dihexadecyloxybenzoic acid (3.6 g, 6 mmol). Purified by chromatography with $CHCl_3$ and recrystallization from ethyl acetate. Yield: 0.15 g (8%); m.p. 58°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.87$ (t, $^3J(H,H) = 6.8$ Hz, 24H; CH_3), 1.21–1.46 (m, 208H; CH_2), 1.76–1.86 (m, 16H; OCH_2CH_2), 3.98 (t, $^3J(H,H) = 6.4$ Hz, 8H; CH_2), 4.01 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.61 (s, 8H; CCH_2), 6.78 (d, $^3J(H,H) = 8.6$ Hz, 4H; Ar–H), 7.48 (d, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H), 7.57 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.0$ Hz, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2475.7 $[M+H]^+$, 2496.3 $[M+Na]^+$, 2512.8 $[M+K]^+$; $C_{161}H_{284}O_{16}$ (2475.7) calcd C 78.10, H 11.55; found C 77.75, H 11.35.

1,3-Bis(3,4,5-trihexyloxybenzoyloxy)-2,2-bis(3,4,5-trihexyloxybenzoyloxy-methyl)propane (12a): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4,5-trihexyloxybenzoic acid (3.4 g, 8 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:1). Yield: 0.55 g (31%); m.p. < -20°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.85-0.89$ (m, 36H; CH_3), 1.27–1.35 (m, 48H; CH_2), 1.42–1.48 (m, 24H; $O(CH_2)_2CH_2$), 1.68–1.80 (m, 24H; OCH_2CH_2), 3.94 (t, $^3J(H,H) = 6.6$ Hz, 16H; OCH_2), 3.98 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.58 (s, 8H; CCH_2), 7.19 (s, 8H; Ar–H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.84$, 22.48, 22.54, 25.59, 25.67, 29.24 29.59, 30.21, 31.50, 43.39 (CCH_2), 63.02 (CCH_2), 69.27, 73.52, 108.33, 123.99, 143.18, 153.11, 165.98 (C=O); MS (MALDI-TOF, DHB): *m/z*: 1755.0 $[M]^+$, 1777.1 $[M+Na]^+$, 1794.1 $[M+K]^+$; $C_{105}H_{172}O_{20}$ (1754.3).

1,3-Bis(3,4,5-tridecyloxybenzoyloxy)-2,2-bis(3,4,5-tridecyloxybenzoyloxy-methyl)propane (12b): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,4,5-tridecyloxybenzoic acid (4.7 g, 8 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:0.7). Yield: 0.43 g (18%); K 41°C Col 8°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 7.1$ Hz, 24H; CH_3), 0.87 (t, $^3J(H,H) = 7.1$ Hz, 12H; CH_3), 1.25–1.33 (m, 144H; CH_2), 1.42–1.48 (m, 24H; $O(CH_2)_2CH_2$), 1.68–1.79 (m, 24H; OCH_2CH_2), 3.93 (t, $^3J(H,H) = 6.4$ Hz, 16H; OCH_2), 3.97 (t, $^3J(H,H) = 6.4$ Hz, 8H; OCH_2), 4.58 (s, 8H; CCH_2), 7.18 (s, 8H; Ar–H); MS (MALDI-TOF, CHC): *m/z*: 2449.0 $[M+Na]^+$, 2465.7 $[M+K]^+$; $C_{153}H_{268}O_{20}$ (2427.5): calcd C 75.70, H 11.12; found C 75.93, H 11.18.

1,3-Bis(3,4,5-trihexadecyloxybenzoyloxy)-2,2-bis(3,4,5-trihexadecyloxy-benzoyloxymethyl)propane (12c): Synthesized from pentaerythritol (0.068 g, 0.5 mmol) and 3,4,5-trihexadecyloxybenzoic acid (3.7 g, 4 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (6:10–0) and recrystallization from ethyl acetate. Yield: 0.47 g (27%); m.p. 50°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 6.8$ Hz, 36H; CH_3), 1.24–1.31 (m, 288H; CH_2), 1.41–1.50 (m, 24H; $O(CH_2)_2CH_2$), 1.68–1.79 (m, 24H; OCH_2CH_2), 3.93 (t, $^3J(H,H) = 6.6$ Hz, 16H; OCH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.57 (s, 8H; CCH_2), 7.18 (s, 8H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 3457.6 $[M+Na]^+$; $C_{225}H_{412}O_{20}$ (3437.3): calcd C 78.62, H 12.07; found C 78.72, H 12.24.

1,3-Bis(4-decyloxybenzoyloxy)-2,2-bis(4-decyloxybenzoyloxymethyl)propane (13a): Synthesized from pentaerythritol (0.204 g, 1.5 mmol) and 4-decyloxybenzoic acid (3.4 g, 12 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:0.2–1). Yield: 0.31 g (18%); m.p. 42°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 6.8$ Hz, 12H; CH_3), 1.26–1.40 (m, 48H; CH_2), 1.42–1.46 (m, 8H; $O(CH_2)_2CH_2$), 1.74–1.80 (m, 8H; OCH_2CH_2), 3.96 (t, $^3J(H,H) = 6.4$ Hz, 8H; OCH_2), 4.62 (s, 8H; CCH_2), 6.82 (d, $^3J(H,H) = 8.8$ Hz, 8H; Ar–H), 7.91 (d, $^3J(H,H) = 8.8$ Hz, 8H; Ar–H); MS (MALDI-TOF, CHC): *m/z*: 1199.5 $[M+Na]^+$, 1216.2 $[M+K]^+$; $C_{73}H_{108}O_{12}$ (1177.5): calcd C 74.46, H 9.24; found C 74.10, H 9.14.

1,3-Bis(4-hexadecyloxybenzoyloxy)-2,2-bis(4-hexadecyloxybenzoyloxy-methyl)propane (13b): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 4-hexadecyloxybenzoic acid (2.9 g, 8 mmol). Purified by chromatography with petroleum ether/ethyl acetate (10:1) and recrystallization from ethyl acetate. Yield: 0.33 g (22%); m.p. 72°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 6.9$ Hz, 12H; CH_3), 1.24–1.40 (m, 96H; CH_2), 1.42–1.46 (m, 8H; $O(CH_2)_2CH_2$), 1.74–1.80 (m, 8H; OCH_2CH_2), 3.96 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.62 (s, 8H; CCH_2), 6.83 (d, $^3J(H,H) = 8.8$ Hz, 8H; Ar–H), 7.91 (d, $^3J(H,H) = 8.8$ Hz, 8H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1536.0 $[M+Na]^+$, 1552.9 $[M+K]^+$; $C_{97}H_{156}O_{12}$ (1514.1): calcd C 76.94, H 10.37; found C 76.74, H 10.20.

1,3-Bis(3,5-didecyloxybenzoyloxy)-2,2-bis(3,5-didecyloxybenzoyloxymethyl)-propane (14): Synthesized from pentaerythritol (0.136 g, 1 mmol) and 3,5-didecyloxybenzoic acid (3.5 g, 8 mmol). Purified twice by chromatography with petroleum ether/ethyl acetate (10:0.4–0.6). Yield: 0.74 g (41%); K 35°C Col 7°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H;H) = 7.1$ Hz, 24H; CH_3), 1.24–1.38 (m, 96H; CH_2), 1.40–1.43 (m, 16H; $O(CH_2)_2CH_2$), 1.71–1.76 (m, 16H; OCH_2CH_2), 3.89 (t, $^3J(H,H) =$

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6.4 Hz, 16H; OCH_2), 4.60 (s, 8H; CCH_2), 6.58 (t, ^4J(H,H) = 2.2 Hz, 4H; Ar–H), 7.06 (d, ^4J(H,H) = 2.2 Hz, 8H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1801.9 $[M]^+$, 1824.2 $[M+Na]^+$, 1840.6 $[M+K]^+$; $C_{113}H_{188}O_{16}$ (1802.5): calcd C 75.30, H 10.50; found C 75.24, H 10.63.

2-(3,4-Didecyloxybenzoylamino)-1,3-bis(3,4-didecyloxybenzoyloxy)-2-(3,4-didecyloxybenzoyloxymethyl)propane (3): Synthesized from tris(hydroxymethyl)aminomethane (0.121 g, 1 mmol) and 3,4-didecyloxybenzoic acid (3.5 g, 8 mmol). Purified twice by chromatography with $CHCl_3$/methanol (10:0–0.5). Yield: 0.3 g (17%); K 47 °C Col 66 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J(H,H) = 6.8 Hz, 24H; CH_3), 1.26–1.40 (m, 96H; CH_2), 1.42–1.45 (m, 16H; $O(CH_2)_2CH_2$), 1.73–1.82 (m, 16H; OCH_2CH_2), 3.91 (t, ^3J(H,H) = 6.4 Hz, 6H; OCH_2), 3.98–4.02 (m, 10H; OCH_2), 4.94 (s, 6H; CCH_2), 6.76 (d, ^3J(H,H) = 8.5 Hz, 3H; Ar–H), 6.83 (d, ^3J(H,H) = 8.6 Hz, 1H; Ar–H), 7.31 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 2.2 Hz, 1H; Ar–H), 7.36 (s, 1H; NH), 7.38 (d, ^4J(H,H) = 2.2 Hz, 1H; Ar–H), 7.46 (d, ^4J(H,H) = 2.0 Hz, 3H; Ar–H), 7.56 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 3H; Ar–H); ^{13}C NMR (200 MHz, $CDCl_3$): δ = 14.08, 22.67, 25.97, 26.07, 29.08, 29.22, 29.37, 29.48, 29.57, 29. 62, 31.91, 59.94 (CCH_2), 63.94 (CCH_2), 69.05, 69.20, 111.93, 112.29, 114.30, 119.76, 121.52, 123.80, 126.53, 148.64, 148.98, 152.09, 153.63, 166.51 (COO), 167.17 (CONH); IR (Nujol): $\tilde{\nu}$ = (N–H), 1714 (C=O), 1667 (C=O), 1513 cm^{-1} (N–H); MS (MALDI-TOF, DHAP): *m/z*: 1788.7 $[M+H]^+$; $C_{112}H_{187}NO_{15}$ (1787.5): calcd C 75.26, H 10.53, N 0.78; found C 75.30, H 10.70, N 0.76.

Tetrakis-*O*-(3,4-didecyloxybenzoyl)erythritol (17): Synthesized from meso-erythritol (0.122 g, 1 mmol) and 3,4-didecyloxybenzoic acid (3.5 g, 8 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (1:1–0). Yield: 0.42 g (24%); K 57 °C Col 39 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.83–0.88 (m, 24H; CH_3), 1.26–1.34 (m, 96H; CH_2), 1.40–1.47 (m, 16H; $O(CH_2)_2CH_2$), 1.74–1.84 (m, 16H; OCH_2CH_2), 3.91–3.96 (m, 8H; OCH_2), 3.97–4.02 (m, 8H; OCH_2), 4.52 (dd, ^2J(H,H) = 12.1 Hz, ^3J(H,H) = 5.8 Hz, 2H; $CHCH_AH_B$), 4.82 (dd, ^2J(H,H) = 11.8 Hz, ^3J(H,H) = 2.9 Hz, 2H; $CHCH_AH_B$), 5.85–5.87 (m, 2H; CH), 6.79 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 6.80 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 7.46 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.47 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.58 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.60 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1789.4 $[M+H]^+$, 1812.0 $[M+Na]^+$, 1828.3 $[M+K]^+$; $C_{112}H_{186}O_{16}$ (1788.5): calcd C 75.21, H 10.47; found C 75.48, H 10.43.

Tetrakis-*O*-(3,4-didecyloxybenzoyl)-D-threitol (18): Synthesized from D-threitol (0.122 g, 1 mmol) and 3,4-didecyloxybenzoic acid (3.5 g, 8 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (1:1–0). Yield: 0.35 g (20%); K 44 °C Col 40 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J(H,H) = 6.1 Hz, 24H; CH_3), 1.25–1.33 (m, 96H; CH_2), 1.40–1.45 (m, 16H; $O(CH_2)_2CH_2$), 1.73–1.83 (m, 16H; OCH_2CH_2), 3.93 (t, ^3J(H,H) = 7.1 Hz, 4H; OCH_2), 3.95 (t, ^3J(H,H) = 6.4 Hz, 4H; OCH_2), 3.99 (t, ^3J(H,H) = 6.6 Hz, 8H; OCH_2), 4.59 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 6.1 Hz, 2H; $CHCH_AH_B$), 4.68 (dd, ^2J(H,H) = 11.8 Hz, ^3J(H,H) = 3.9 Hz, 2H; $CHCH_AH_B$), 5.84–5.88 (m, 2H; CH), 6.78 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 6.79 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 7.45 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.49 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.56 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.61 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1790.9 $[M+H]^+$, 1812.9 $[M+Na]^+$, 1829.5 $[M+K]^+$; $C_{112}H_{186}O_{16}$ (1788.5): calcd C 75.21, H 10.47; found C 75.05, H 10.31.

1,3-Bis(3,4-didecyloxybenzoyloxy)-2-(3,4-didecyloxybenzoyloxymethyl)-propane (19): Synthesized from 2-(hydroxymethyl)-1,3-propanediol (0.16 g, 1.5 mmol) and 3,4-didecyloxybenzoic acid (3.9 g, 9 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (1:1–0). Yield: 0.56 g (28%); m.p. 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84–0.87 (m, 18H; CH_3), 1.25–1.41 (m, 72H; CH_2), 1.43–1.46 (m, 12H; $O(CH_2)_2CH_2$), 1.76–1.85 (m, 12H; OCH_2CH_2), 2.80 (t, ^3J(H,H) = 5.7 Hz, 1H; CH), 3.97–4.03 (m, 12H; OCH_2), 4.51 (d, ^3J(H,H) = 5.8 Hz, 6H; CCH_2), 6.80 (d, ^3J(H,H) = 8.6 Hz, 3H; Ar–H), 7.50 (d, ^4J(H,H) = 2.0 Hz, 3H; Ar–H), 7.59 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 2.0 Hz, 3H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1356.5 $[M]^+$, 1379.7 $[M+Na]^+$; $C_{85}H_{142}O_{12}$ (1355.9): calcd C 75.29, H 10.54; found C 75.31, H 10.49.

1,2,3-Tris(3,4-didecyloxybenzoyloxy)propane (20): Synthesized from dry glycerol (freshly destilled, 0.138 g, 1.5 mmol) and 3,4-didecyloxybenzoic acid (3.9 g, 9 mmol). Purified twice by chromatography with $CHCl_3$ and crystallized once from ethyl acetate. Yield: 0.55 g (27%); m.p. 98 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J(H,H) = 6.8 Hz, 18H; CH_3), 1.25–1.33 (m, 72H; CH_2), 1.40–1.45 (m, 12H; $O(CH_2)_2CH_2$), 1.74–1.84 (m, 12H; OCH_2CH_2), 3.95 (t, ^3J(H,H) = 6.6 Hz, 2H; OCH_2), 3.96 (t, ^3J(H,H) = 6.8 Hz, 4H; OCH_2), 3.99, 4.02 (m, 6H; OCH_2), 4.57 (dd, ^2J(H,H) = 11.7 Hz, ^3J(H,H) = 6.1 Hz, 2H; $CHCH_AH_B$), 4.67 (dd, ^2J(H,H) = 11.7 Hz, ^3J(H,H) = 4.6 Hz, 2H; $CHCH_AH_B$), 5.71–5.76 (m, 1H; CH), 6.81 (d, ^3J(H,H) = 8.5 Hz, 3H; Ar–H), 7.49 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.50 (d, ^4J(H,H) = 2.2 Hz, 1H; Ar–H), 7.60 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.62 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.2 Hz, 1H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1363.8 $[M+Na]^+$, 1380.4 $[M+K]^+$; $C_{84}H_{140}O_{12}$ (1341.8): calcd C 75.19, H 10.51; found C 75.19, H 10.52.

3-(3,4-Didecyloxybenzoylamino)-1,2-bis(3,4-didecyloxybenzoyloxy)propane (21): Synthesized from 3-amino-1,2-propanediol (0.136 g, 1.5 mmol) and 3,4-didecyloxybenzoic acid (3.9 g, 9 mmol). Purified twice by chromatography with $CHCl_3$/methanol (10:0–0.05) and recrystallization from ethyl acetate. Yield: 0.22 g (11%); K 97 °C M 65 °C I; ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 0.85–0.88 (m, 18H; CH_3), 1.28–1.36 (m, 72H; CH_2), 1.45–1.53 (m, 12H; $O(CH_2)_2CH_2$), 1.71–1.82 (m, 12H; OCH_2CH_2), 3.82–3.99 (m, 8H; OCH_2, CH_2NH), 4.01–4.06 (m, 6H; OCH_2), 4.48 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 6.6 Hz, 1H; $CHCH_AH_B$), 4.71 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 3.7 Hz, 1H; $CHCH_AH_B$), 5.55–5.60 (m, 1H; CH), 6.93 (d, ^3J(H,H) = 9.0 Hz, 1H; Ar–H), 6.96 (d, ^3J(H,H) = 8.5 Hz, 1H; Ar–H), 6.98 (d, ^3J(H,H) = 8.5 Hz, 1H; Ar–H), 7.44 (d, ^4J(H,H) = 2 Hz, 1H; Ar–H), 7.44 (dd, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 2 Hz, 1H; Ar–H), 7.47 (d, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.51 (d, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.58 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.62 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.97 (t, ^3J(H,H) = 6.1 Hz, 1H; N–H); MS (MALDI-TOF, DHAP): *m/z*: 1340.8 $[M]^+$; $C_{84}H_{141}NO_{11}$ (1340.9): calcd C 75.24, H 10.59, N 1.04; found C 75.45, H 10.58, N 0.95.

2-(3,4-Didecyloxybenzoylamino)-1,3-bis(3,4-didecyloxybenzoyloxy)propane (22): Synthesized from 2-amino-1,3-propanediol (0.136 g, 1.5 mmol) and 3,4-didecyloxybenzoic acid (3.9 g, 9 mmol). Purified twice by chromatography with $CHCl_3$/methanol (10:0–0.05) and recrystallization from ethyl acetate. Yield: 0.47 g (23%); m.p. 94 °C; ^{1}H NMR (500 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 0.88 (t, ^3J(H,H) = 6.4 Hz, 18H; CH_3), 1.30–1.41 (m, 72H; CH_2), 1.47–1.51 (m, 12H; $O(CH_2)_2CH_2$), 1.73–1.83 (m, 12H; OCH_2CH_2), 3.95–3.98 (m, 6H; OCH_2), 4.04 (t, ^3J(H,H) = 6.4 Hz, 2H; OCH_2), 4.07 (t, ^3J(H,H) = 6.3 Hz, 4H; OCH_2), 4.55 (dd, ^2J(H,H) = 11.2 Hz, ^3J(H,H) = 6.6 Hz, 2H; $CHCH_AH_B$), 4.62 (dd, ^2J(H,H) = 11.4 Hz, ^3J(H,H) = 5.6 Hz, 2H; $CHCH_AH_B$), 4.91–4.92 (m, 1H; CH), 6.95 (d, ^3J(H,H) = 8.8 Hz, 1H; Ar–H), 6.97 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 7.46 (s, 1H; Ar–H), 7.47 (d, ^3J(H,H) = 2 Hz, 1H; N–H), 7.54 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.62 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.68 (d, ^3J(H,H) = 8.8 Hz, 1H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1343.3 $[M+H]^+$, 1364.9 $[M+Na]^+$, 1381.3 $[M+K]^+$; $C_{84}H_{141}NO_{11}$ (1340.9): calcd C 75.24, H 10.59, N 1.04; found C 75.24, H 10.58, N 0.89.

Pentakis-*O*-(3,4-didecyloxybenzoyl)adonitol (23): Synthesized from adonitol (0.076 g, 0.5 mmol) and 3,4-didecyloxybenzoic acid (2.2 g, 5 mmol); Purified twice by chromatography with $CHCl_3$/petroleum ether (1:1–0). Yield: 0.09 g (8%); K 54 °C Col 36 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS, 25 °C, TMS): δ = 0.82–0.88 (m, 30H; CH_3), 1.24–1.38 (m, 120H; CH_2), 1.42–1.44 (m, 20H; $O(CH_2)_2CH_2$), 1.71–1.83 (m, 20H; OCH_2CH_2), 3.89–3.93 (m, 10H; OCH_2), 3.95–4.02 (m, 10H; OCH_2), 4.49 (dd, ^2J(H,H) = 12.0 Hz, ^3J(H,H) = 6.6 Hz, 2H; $CHCH_AH_B$), 4.85 (dd, ^2J(H,H) = 12.1 Hz, ^3J(H,H) = 3.9 Hz, 2H; $CHCH_AH_B$), 5.91–5.94 (m, 2H; *CH*CH*CH*), 6.04 (t, ^3J(H,H) = 5.4 Hz, 1H; CH*CH*CH), 6.72 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 6.79 (d, ^3J(H,H) = 8.5 Hz, 1H; Ar–H), 6.80 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 7.43 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.46 (d, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.47 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.53 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.59 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.61 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2234.9 $[M]^+$, 2257.7 $[M+Na]^+$, 2273.0 $[M+K]^+$; $C_{140}H_{232}O_{20}$ (2235.1): calcd C 75.23, H 10.45; found C 75.31, H 10.44.

Hexakis-*O*-(3,4-didecyloxybenzoyl)-D-mannitol (24): Synthesized from D-mannitol (0.091 g, 0.5 mmol) and 3,4-didecyloxybenzoic acid (2.6 g, 6 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (1,5:1). Yield: 0.35 g (26%); K ? Col 55 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84–0.88 (m, 36H; CH_3), 1.25–1.48 (m, 168H; CH_2),

1.67 – 1.83 (m, 24H; OCH_2CH_2), 3.82 – 3.93 (m, 20H; OCH_2), 3.98 (t, ^3J(H,H) = 6.6 Hz, 4H; OCH_2), 4.45 (dd, ^2J(H,H) = 12.3 Hz, ^3J(H,H) = 5.7 Hz, 2H; $CHCH_AH_B$), 4.86 (dd, ^2J(H,H) = 12.2 Hz, ^3J(H,H) = 3.4 Hz, 2H; $CHCH_AH_B$), 5.75 – 5.77 (m, 2H; CHCHCH), 6.10 (virtual br d, 2H; CHCHCH), 6.59 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 6.60 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 6.73 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar–H), 7.38 (d, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.42 (d, ^4J(H,H) = 2.0 Hz, 4H; Ar–H), 7.45 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.49 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H), 7.56 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.0 Hz, 2H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2682.2 $[M]^+$, 2705.2 $[M+Na]^+$; $C_{168}H_{278}O_{24}$ (2681.7): calcd C 75.24, H 10.44; found C 74.86, H 10.21.

1-(3,4-Didecyloxybenzoylamino)-1-deoxypentakis-*O*-(3,4-didecyloxybenzoyl)-D-sorbitol (25): Synthesized from 1-amino-1-deoxy-D-sorbitol (0.135 g, 0.75 mmol) and 3,4-didecyloxybenzoic acid (3.9 g, 9 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (1,5:1). Yield: 0.71 g (35 %); K ? Col 78 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 – 0.89 (m, 36H; CH_3), 1.27 – 1.53 (m, 168H; CH_2), 1.70 – 1.86 (m, 24H; OCH_2CH_2), 3.63 – 3.66 (m, 1H; CH_AH_BNH), 3.84 – 4.02 (m, 24H; OCH_2), 4.16 – 4.23 (m, 1H; CH_AH_BNH), 4.42 (dd, ^2J(H,H) = 12.2 Hz, ^3J(H,H) = 5.6 Hz, 1H; CH_AH_BCH), 4.78 (dd, ^2J(H,H) = 12.1 Hz, ^3J(H,H) = 3.5 Hz, 1H; CH_AH_BCH), 5.62 – 5.64 (m, 1H; CH), 5.74 – 5.78 (m, 1H; CH), 5.96 (dd, ^2J(H,H) = 5.3 Hz, ^3J(H,H) = 3.9 Hz, 1H; CH), 6.18 (dd, ^2J(H,H) = 6.9 Hz, ^3J(H,H) = 3.7 Hz, 1H; CH), 6.52 (d, ^3J(H,H) = 8.6 Hz, 1H; Ar–H), 6.60 (d, ^3J(H,H) = 8.6 Hz, 1H; Ar–H), 6.71 – 6.77 (m, 5H; Ar–H), 7.16 – 7.19 (m, 1H; NH), 7.37 – 7.60 (m, 11H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2683.5 $[M]^+$; 2705.3 $[M+Na]^+$; $C_{168}H_{279}NO_{23}$ (2680.7): calcd C 75.27, H 10.48, N 0.52; found C 75.15, H 10.50, N 0.50.

Bis[3-(3,4-didecyloxybenzoyloxy)-2,2-(3,4-didecyloxybenzoyloxymethyl)-propyl]ether (26): Synthesized from dipentaerythritol (0.19 g, 0.75 mmol) and 3,4-didecyloxybenzoic acid (3.9 g, 9 mmol). Purified twice by chromatography with $CHCl_3$/petroleum ether (1:1 – 0). Yield: 0.27 g (13 %); K ? Col 79 °C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J(H,H) = 7.0 Hz, 18H; CH_3), 0.87 (t, ^3J(H,H) = 7.3 Hz, 18H; CH_3), 1.25 – 1.34 (m, 144H; CH_2), 1.40 – 1.47 (m, 24H; $O(CH_2)_2CH_2$), 1.74 – 1.82 (m, 24H; OCH_2CH_2), 3.67 (s, 4H; CH_2OCH_2), 3.94 (t, ^3J(H,H) = 6.7 Hz, 12H; OCH_2), 3.95 (t, ^3J(H,H) = 6.5 Hz, 12H; OCH_2), 4.50 (s, 12H; CCH_2), 6.68 (d, ^3J(H,H) = 8.6 Hz, 6H; Ar–H), 7.42 (d, ^4J(H,H) = 2.1 Hz, 6H; Ar–H), 7.46 (dd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 2.1 Hz, 6H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2776.8 $[M+Na]^+$, 2791.7 $[M+K]^+$; $C_{172}H_{286}O_{25}$ (2753.8): calcd C 75.02, H 10.46; found C 75.07, H 10.59.

Synthesis of 2

5-Aminomethyl-5-hydroxymethyl-2-nonyl-1,3-dioxane (II): A solution of **I**[11] (6.2 g, 20 mmol) in dry diethyl ether (50 mL) was slowly added at 20 °C under an argon atmosphere to a stirred suspension of $LiAlH_4$ (0.9 g, 23.6 mmol) in dry diethyl ether (30 mL). The mixture was stirred for 4 h at this temperature. Afterwards water (30 mL) was slowly added drop by drop at 0 – 5 °C (CAUTION, exothermic reaction). The white precipitate formed was removed and washed with diethyl ether (30 mL). The combined organic phases were dried over Na_2SO_4. The solvent was removed in vacuo and the residue was recrystallisized from ethyl acetate/petroleum ether (10:1). Yield: 3.2 g (51 %); m.p. 148 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 1.24 – 1.37 (m, 14H; CH_2), 1.56 – 1.60 (m, 2H; CH_2CH), 3.24 (s, 2H; CH_2NH_2), 3.46 (s, 2H; CH_2OH), 3.47 (d, ^2J(H,H) = 11.9 Hz, 2H; $CH–4,6_{ax}$), 3.93 (d, ^2J(H,H) = 11.9 Hz, 2H; $CH–4,6_{eq}$), 4.42 (t, ^3J(H,H) = 5.1 Hz, 1H; CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.90, 22.53, 23.80, 29.18, 29.04, 29.43, 31.78, 34.78, 36.99 (CCH_2), 44.47 (CH_2NH_2), 67.67 (CH_2OH), 70.81 ($CHOCH_2$), 103.08 (CH); IR (Nujol): $\tilde{\nu}$ = 3371 (OH), 3134 cm^{-1} (NH); MS: *m/z* (%): 273 (6) $[M]^+$, 230 (40), 146 (56), 115 (37), 100 (30), 88 (44), 82 (46), 70 (78), 57 (100); $C_{15}H_{31}NO_3$ (273.3).

2-(3,4-Didecyloxybenzoylaminomethyl)-2-(3,4-didecyloxybenzoyloxymethyl)-1,3-propanediol (III): 5-(3,4-Didecyloxybenzoylaminomethyl)-5-(3,4-didecyloxybenzoyloxymethyl)-2-nonyl-1,3-dioxane was synthesized from **II** (0.82 g, 3 mmol) and 3,4-didecyloxybenzoic acid (5.2 g, 12 mmol) according to the general procedure. Purified by chromatography with $CHCl_3$/methanol (10:0.5). Yield: 1.54 g (46 %); m.p. 15 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 – 0.89 (m, 15H; CH_3), 1.27 – 1.49 (m, 70H; CH_2), 1.62 – 1.68 (m, 2H; CH_2CH), 1.79 – 1.88 (m, 8H; OCH_2CH_2), 3.15 (d, ^3J(H,H) = 6.4 Hz, 2H; CH_2NH), 3.73 (d, ^2J(H,H) = 11.9 Hz, 2H; $CH–4,6_{ax}$), 3.98 (d, ^2J(H,H) = 11.9 Hz, 2H; $CH–4,6_{eq}$), 4.01 – 4.08 (m, 8H; OCH_2), 4.50 (t, ^3J(H,H) = 5.1 Hz, 1H; CH), 4.77 (s, 2H; CH_2OOC), 6.86 (d, ^3J(H,H) = 8.4 Hz, 1H; Ar–H), 6.89 (d, ^3J(H,H) = 8.4 Hz, 1H; Ar–H), 7.24 (t, ^3J(H,H) = 6.4 Hz, 1H; N–H), 7.37 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.2 Hz, 1H; Ar–H), 7.47 (d, ^4J(H,H) = 2.2 Hz, 1H; Ar–H), 7.56 (d, ^4J(H,H) = 2.0 Hz, 1H; Ar–H), 7.69 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar–H); MS: *m/z* (%): 1105 (8) $[M]^+$, 487 (25), 447 (17), 434 (25), 417 (100), 277 (43), 154 (47), 137 (30), 71 (17), 57 (37); $C_{69}H_{119}NO_9$ (1106.5): calcd C 74.89, H 10.82, N 1.26; found C 74.75, H 10.52, N 1.25.

The obtained 5-(3,4-didecyloxybenzoylaminomethyl)-5-(3,4-didecyloxybenzoyloxymethyl)-2-nonyl-1,3-dioxane (1.24 g, 1.12 mmol) was dissolved in ethanol (70 mL). After addition of water (1 mL) and a catalytic amount of PPTS (20 mg) the solution was heated at reflux temperature for 5 h. The solution cooled to 0 – 5 °C and the white precipitat formed was removed and recrystallisized twice from methanol. Yield: 0.84 g (77 %); K 72 °C Col 97 °C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84 – 0.88 (m, 12H; CH_3), 1.25 – 1.34 (m, 48H; CH_2), 1.42 – 1.46 (m, 8H; $O(CH_2)_2CH_2$), 1.79 – 1.86 (m, 8H; OCH_2CH_2), 3.48 (d, ^3J(H,H) = 6.4 Hz, 2H; CH_2NH), 3.53 (s, 4H; CH_2OH), 4.00 – 4.06 (m, 8H; OCH_2), 4.23 (s, 2H; CH_2OOC), 6.85 (d, ^3J(H,H) = 8.5 Hz, 1H; Ar–H), 6.88 (d, ^3J(H,H) = 8.5 Hz, 1H; Ar–H), 7.14 (br t, ^3J(H,H) = 6.4 Hz, 1H; N–H), 7.35 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.1 Hz, 1H; Ar–H), 7.44 (d, ^4J(H,H) = 2.1 Hz, 1H; Ar–H), 7.52 (d, ^4J(H,H) = 2.1 Hz, 1H; Ar–H), 7.64 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.1 Hz, 1H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.95, 22.55, 25.85, 25.90, 28.94, 29.01, 29.12, 29.22, 29.24, 29.28, 29.31, 29.47, 29.52, 31.81, 38.09 (CCH_2), 46.62 (CH_2NH), 62.24 (CH_2OH), 62.70 (CH_2OOC), 69.08, 69.17, 69.35, 69.43, 112.06, 112.47, 112.87, 114.58, 120.04, 121.30, 124.20, 125.40, 148.91, 149.26, 152.73, 154.17, 167.95 (COO), 169.30 (CONH); IR (Nujol): $\tilde{\nu}$ = 3389 cm^{-1} (OH, NH), 1698 (C=O), 1575 cm^{-1} (NH); MS: *m/z* (%): 967 (12) $[M]^+$, 840 (32), 533 (31), 434 (45), 417 (88), 294 (28), 277 (42), 154 (100), 137 (34), 57 (29); $C_{59}H_{101}NO_9$ (968.3).

2-(3,4-Didecyloxybenzoylaminomethyl)-1,3-bis(3,4-didecyloxybenzoyloxy)-2-(3,4-didecyloxybenzoyloxymethyl)propane (2): Synthesized from **III** (0.29 g, 0.3 mmol) and 3,4-didecyloxybenzoic acid (0.52 g, 1.2 mmol) according to the general procedure. Purified by chromatography with $CHCl_3$/methanol (10:0 – 0.1). Yield: 0.46 g (85 %); K ? Col 72 °C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84 – 0.88 (m, 24H; CH_3), 1.25 – 1.46 (m, 112H; CH_2), 1.75 – 1.84 (m, 16H; OCH_2CH_2), 3.70 (d, ^3J(H,H) = 6.4 Hz, 2H; CH_2NH), 3.97 – 4.03 (m, 16H; OCH_2), 4.54 (s, 6H; CH_2O), 6.78 (d, ^3J(H,H) = 8.7 Hz, 3H; Ar–H), 6.84 (d, ^3J(H,H) = 8.5 Hz, 1H; Ar–H), 7.23 (t, ^3J(H,H) = 6.4 Hz, 1H; N–H), 7.35 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.3 Hz, 1H; Ar–H), 7.45 (d, ^4J(H,H) = 2.3 Hz, 1H; Ar–H), 7.51 (d, ^4J(H,H) = 1.9 Hz, 3H; Ar–H), 7.60 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 1.9 Hz, 3H; Ar–H); MS (MALDI-TOF, DHAP): *m/z*: 1801.6 $[M]^+$; $C_{113}H_{189}NO_{15}$ (1801.2): calcd C 75.35, H 10.55, N 0.78; found C 75.25, H 10.47, N 0.79.

Synthesis of 4

2-(3,4-Didecyloxybenzyloxymethyl)-2-hydroxymethyl-1,3-propanediol (V): A suspension of **IV**[12] (1.12 g, 7 mmol) and NaH (0.19 g, 7.9 mmol) in dry DMF (30 mL) was stirred for 2 h at 20 °C. 3,4-Didecyloxybenzyl bromide [crude product as obtained from 3,4-didecyloxybenzyl alkohol (4.2 g, 10 mmol) by treatment with PBr_3 in dry benzene[15]] dissolved in dry DMF (70 mL) was added dropwise. The mixture was stirred for 5 h at 50 °C and for 12 h at 20 °C and then poured into ice water (100 mL). The mixture was extracted three times with diethyl ether (70 mL), and the organic extracts were washed with water (40 mL) and brine (40 mL). The solvent was removed in vacuo, and the residue was dissolved in ethanol (100 mL). After addition of hydrochloric acid (0.01M; 20 mL) the solution was stirred for 1 h at 20 °C. Then $NaHCO_3$ (0.7 g) was added, and the mixture was stirred for an additional 1 h at 20 °C. The solvent was removed in vacuo and the residue was purified by chromatography with $CHCl_3$/methanol (10:0.2 – 50). Yield: 0.3 g (8 %); K 64 °C Col 79 °C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.86 (t, ^3J(H,H) = 6.8 Hz, 6H; CH_3), 1.25 – 1.44 (m, 28H; CH_2), 1.75 – 1.82 (m, 4H; OCH_2CH_2), 3.46 (s, 2H; CH_2OCH_2Ph), 3.70 (s, 6H; CH_2OH), 3.96 (t, ^3J(H,H) = 6.5 Hz, 4H; OCH_2), 4.40 (s, 2H; CH_2Ph), 6.77 – 6.83 (m, 3H; Ar–H); IR (Nujol): $\tilde{\nu}$ = 3345 cm^{-1} (OH); MS: *m/z* (%): 538 (100) $[M]^+$, 419 (33), 404 (12), 279 (64), 263 (13), 139 (37), 123 (53), 111 (10), 83 (16), 71 (14), 57 (26); $C_{32}H_{58}O_6$ (538.7): calcd C 71.34, H 10.84; found C 71.13, H 10.82.

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1,3-Bis(3,4-didecyloxybenzoyloxy)-2-(3,4-didecyloxybenzoyloxymethyl)-2-(3,4-didecyloxybenzyloxymethyl)propane (4): Synthesized from **V** (0.134 g, 0.25 mmol) and 3,4-didecyloxybenzoic acid (0.65 g, 1.5 mmol) according to the general procedure. Purified by chromatography with $CHCl_3$/petroleum ether (1:1–0). Yield: 0.165 g (37%); K 7°C Col 32°C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.84-0.87$ (m, 24H; CH_3), 1.25–1.44 (m, 112H; CH_2), 1.70–1.84 (m, 16H; OCH_2CH_2), 3.64 (s, 2H; CH_2OCH_2Ph), 3.84 (t, $^3J(H,H) = 6.6$ Hz, 2H; CH_2OPhCH_2), 3.85 (t, $^3J(H,H) = 6.5$ Hz, 2H; CH_2OPhCH_2), 3.96 (t, $^3J(H,H) = 6.4$ Hz, 6H; $CH_2OPhCOO$), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 6H; $CH_2OPhCOO$), 4.40 (s, 2H; $PhCH_2$), 4.51 (s, 6H; CH_2OOC), 6.67 (d, $^3J(H,H) = 8.0$ Hz, 1H; Ar–H), 6.73–6.77 (m, 5H; Ar–H), 7.45 (d, $^4J(H,H) = 2.0$ Hz, 3H; Ar–H), 7.49 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 2.0$ Hz, 3H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.94$, 22.57, 25.91, 25.96, 29.05, 29.17, 29.24, 29.26, 29.32, 29.37, 29.41, 29.48, 29.50, 29.52, 29.55, 29.58, 31.83, 43.65 (CCH_2), 63.58 (CCH_2OOC), 68.65 (CCH_2OCH_2), 69.06, 69.16, 69.33, 69.40, 73.62, 112.13, 113.65, 113.90, 114.53, 120.40, 122.18, 123.66, 130.62, 148.83, 148.97, 149.47, 153.60, 166.20 (C=O); IR (Nujol): $\tilde{\nu} = 1714$ cm^{-1} (C=O); MS (MALDI-TOF, CHC): *m/z*: 1810.8 $[M+Na]^+$, 1827.4 $[M+K]^+$; $C_{113}H_{190}O_{15}$ (1788.5): calcd C 75.88, H 10.69; found C 75.79, H 10.76.

Synthesis of the pentaerythritol ethers 5, 6, 7, 15, and 16

3,9-Bis(3,4-didecyloxyphenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (VI): A mixture of pentaerythritol (1.36 g, 0.01 mol), 3,4-didecyloxybenzaldehyde (8.4 g, 0.02 mol) and a catalytic amount of PPTS (20 mg) was refluxed in benzene (80 mL) for 20 h with a water separator. The solution was cooled to 20°C and was washed with saturated aqueous solution of $NaHCO_3$ (30 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was recrystallisized from acetone. Yield: 6.5 g (69%); K 40°C S_A 48°C I; ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 6.4$ Hz, 12H; CH_3), 1.25–1.43 (m, 56H; CH_2), 1.70–1.83 (m, 8H; OCH_2CH_2), 3.61 (d, $^2J(H,H) = 11.5$ Hz, 2H; CH–5_{ax}, CH–11_{ax}), 3.78 (br d, $^2J(H,H) = 11.5$ Hz, 2H; CH–5_{eq}, CH–11_{eq}), 3.80 (d, $^2J(H,H) = 11.7$ Hz, 2H; CH–1_{ax}, CH–7_{ax}), 3.96 (t, $^3J(H,H) = 6.8$ Hz, 4H; OCH_2), 3.98 (t, $^3J(H,H) = 6.6$ Hz, 4H; OCH_2), 4.84 (br d, $^2J(H,H) = 10.2$ Hz, 2H; CH–1_{eq}, CH–7_{eq}), 5.37 (s, 2H; Ph–CH), 6.84 (d, $^3J(H,H) = 8.2$ Hz, 2H; Ar–H), 6.98 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 7.01 (d, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H); MS: *m/z* (%): 936 $[M]^+$ (100), 796 (10), 138 (15), 85 (16), 71 (18), 57 (38); $C_{59}H_{100}O_8$ (937.3): calcd C 75.60, H 10.74; found C 75.68, H 10.51.

2,2-Bis(3,4-didecyloxybenzyloxymethyl)-1,3-propanediol (VII): Compound **VI** (4.7 g, 5mmol) was dissolved in dry THF (100 mL) and cooled to 5°C. $NaBH_4$ (2 g, 52 mmol) was added and a solution of trifluoro acetic acid (40 mL, 52 mmol) in dry THF (50 mL) was added dropwise with stirring over 1.5 h at this temperature. The mixture was allowed to warm to 20°C within 4 h while stirring and then it was poured into 10% aqueous KOH (300 mL). The solution was extracted three times with diethyl ether (100 mL). The organic extracts were washed with brine (50 mL) und dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by recrystallization from ethanol and chromatography with $CHCl_3$/methanol (10:0.1). Yield: 3,7 g (79%); K 40°C Col 51°C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 6.8$ Hz, 12H; CH_3), 1.25–1.29 (m, 48H; CH_2), 1.40–1.45 (m, 8H; $O(CH_2)_2CH_2$), 1.75–1.82 (m, 8H; OCH_2CH_2), 3.49 (s, 4H; CCH_2), 3.64 (s, 4H; CH_2OH), 3.95 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.38 (s, 4H; OCH_2Ph), 6.76 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 6.79 (d, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 6.80 (d, $^3J(H,H) = 8.2$ Hz, 2H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.08$, 22.67, 26.06, 26.08, 29.35, 29.38, 29.44, 29.46, 29.58, 29.64, 31.91, 44.84 (CCH_2), 65.08 (CH_2OH), 69.38, 69.41, 71.84 (CCH_2OCH_2), 73.68 (CCH_2OCH_2), 113.66, 113.80, 120.41, 130.49, 148.98, 149.30; IR (Nujol): $\tilde{\nu} = 3362$ cm^{-1} (OH); MS: *m/z* (%): 940 (6) $[M]^+$, 537 (100), 419 (47), 279 (37), 263 (18), 139 (25), 123 (38), 83 (17), 57 (27).

1,3-Bis(3,4-dihexyloxybenzoyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)-propane (5a): Synthesized from **VII** (0.376 g, 0.4 mmol) and 3,4-dihexyloxybenzoic acid (0.52 g, 1.61 mmol) according to the general procedure. Purified twice by chromatography with $CHCl_3$. Yield: 0.29 g (46%); K ? Col 5°C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.86-0.92$ (m, 24H; CH_3), 1.26–1.49 (m, 80H; CH_2), 1.70–1.87 (m, 16H; OCH_2CH_2), 3.61 (s, 4H; CH_2OCH_2Ph), 3.88 (t, $^3J(H,H) = 6.6$ Hz, 4H; CH_2OPhCH_2), 3.90 (t, $^3J(H,H) = 6.8$ Hz, 4H; CH_2OPhCH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.02 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.40 (s, 4H; $PhCH_2$), 4.45 (s, 4H; CH_2OOC), 6.72 (d, $^3J(H,H) = 8.1$ Hz, 2H; Ar–H), 6.75 (dd, $^3J(H,H) = 8.1$ Hz, $^4J(H,H) = 1.7$ Hz, 2H; Ar–H), 6.78 (d, $^3J(H,H) = 8.3$ Hz, 2H; Ar–H), 6.79 (d, $^4J(H,H) = 1.7$ Hz, 2H; Ar–H), 7.45 (dd, $^3J(H,H) = 8.3$ Hz, $^4J(H,H) = 2.1$ Hz, 2H; Ar–H), 7.47 (d, $^4J(H,H) = 2.1$ Hz, 2H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1571.7 $[M+Na]^+$, 1588.3 $[M+K]^+$; $C_{97}H_{160}O_{14}$ (1550.1): calcd C 75.16, H 10.39; found C 74.84, H 10.37.

1,3-Bis(3,4-didecyloxybenzoyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)-propane (5b): Synthesized from **VII** (0.282 g, 0.3 mmol) and 3,4-didecyloxybenzoic acid (0.52 g, 1.2 mmol) according to the general procedure. Purified twice by chromatography with $CHCl_3$/methanol (10:0–0.2). Yield 0.42 g (79%); K 10°C Col 24°C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.87$ (t, $^3J(H,H) = 6.4$ Hz, 12H; CH_3), 0.88 (t, $^3J(H,H) = 7.1$ Hz, 12H; CH_3), 1.27–1.49 (m, 112H; CH_2), 1.70–1.86 (m, 16H; OCH_2CH_2), 3.61 (s, 4H; CH_2OCH_2Ph), 3.88 (t, $^3J(H,H) = 6.6$ Hz, 4H; CH_2OPhCH_2), 3.89 (t, $^3J(H,H) = 6.6$ Hz, 4H; CH_2OPhCH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.02 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.40 (s, 4H; $PhCH_2$), 4.45 (s, 4H; CH_2OOC), 6.71 (d, $^3J(H,H) = 8.2$ Hz, 2H; Ar–H), 6.75 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 1.6$ Hz, 2H; Ar–H), 6.77 (d, $^3J(H,H) = 8.4$ Hz, 2H; Ar–H), 6.79 (d, $^4J(H,H) = 1.6$ Hz, 2H; Ar–H), 7.44 (dd, $^3J(H,H) = 8.4$ Hz, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 7.47 (d, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.94$, 22.56, 25.93, 25.96, 26.00, 29.08, 29.17, 29.26, 29.34, 29.38, 29.40, 29.42, 29.49, 29.52, 29.53, 29.57, 31.83, 44.20 (CCH_2), 63.85 (CCH_2OOC), 68.91 (CCH_2OCH_2), 69.04, 69.18, 69.30, 69.41, 73.50, 112.11, 113.63, 113.91, 114.52, 120.27, 122.50, 123.55, 131.04, 148.77, 148.87, 149.42, 153.46, 166.26 (C=O); IR (Nujol): $\tilde{\nu} = 1714$ cm^{-1} (C=O); MS (MALDI-TOF, DHB): *m/z*: 1797.0 $[M+Na]^+$, 1813.7 $[M+K]^+$; $C_{113}H_{192}O_{14}$ (1774.5): calcd C 76.48, H 10.89; found C 76.33, H 10.82.

1,3-Bis(3,4-dihexadecyloxybenzoyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)propane (5c): Synthesized from **VII** (0.312 g; 0.33 mmol) and 3,4-dihexadecyloxybenzoic acid (0.8 g, 1.33 mmol) according to the general procedure. Purified twice by chromatography with $CHCl_3$/petroleum ether (1:1–0). Yield: 0.37 g (53%); m.p. 42°C; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.85-0.88$ (m, 24H; CH_3), 1.24–1.47 (m, 160H; CH_2), 1.70–1.83 (m, 16H; OCH_2CH_2), 3.59 (s, 4H; CH_2OCH_2Ph), 3.86 (t, $^3J(H,H) = 6.7$ Hz, 4H; CH_2OPhCH_2), 3.88 (t, $^3J(H,H) = 6.7$ Hz, 4H; CH_2OPhCH_2), 3.95 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.38 (s, 4H; $PhCH_2$), 4.43 (s, 4H; CH_2OOC), 6.70 (d, $^3J(H,H) = 8.3$ Hz, 2H; Ar–H), 6.73 (dd, $^3J(H,H) = 8.3$ Hz, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 6.75 (d, $^3J(H,H) = 8.6$ Hz, 2H; Ar–H), 6.77 (d, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 7.43 (dd, $^3J(H,H) = 8.6$ Hz, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 7.45 (d, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2132.1 $[M+Na]^+$, 2149.1 $[M+K]^+$; $C_{137}H_{240}O_{14}$ (2111.1): calcd C 77.94, H 11.45; found C 77.92, H 11.42.

1,3-Bis(3,4,5-tridecyloxybenzoyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)-propane (15): Synthesized from **VII** (0.29 g, 0.31 mmol) and 3,4,5-tridecyloxybenzoic acid (0.73 g, 1.24 mmol) according to the general procedure. Purified twice by chromatography with $CHCl_3$/petroleum ether (1:2–0). Yield: 0.56 g (87%); K –8°C Col 14°C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.84-0.87$ (m, 30H; CH_3), 1.25–1.43 (m, 140H; CH_2), 1.68–1.79 (m, 20H; OCH_2CH_2), 3.59 (s, 4H; CH_2OCH_2Ph), 3.84–3.91 (m, 16H; $CH_2OPhCOO$, CH_2OPhCH_2), 3.97 (t, $^3J(H,H) = 6.6$ Hz, 4H; $CH_2OPhCOO$), 4.38 (s, 4H; $PhCH_2$), 4.45 (s, 4H; CH_2OOC), 6.69 (d, $^3J(H,H) = 8.2$ Hz, 2H; Ar–H), 6.72 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 1.6$ Hz, 2H; Ar–H), 6.76 (d, $^4J(H,H) = 1.6$ Hz, 2H; Ar–H), 7.15 (s, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 2108.8 $[M+Na]^+$, 2125.5 $[M+K]^+$; $C_{113}H_{232}O_{16}$ (2087.0): calcd C 76.54, H 11.19; found C 76.56, H 11.34.

1,3-Bis(4-decyloxybenzoyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)-propane (16): Synthesized from **VII** (0.376 g, 0.4 mmol) and 4-decyloxybenzoic acid (0.45 g, 1.6 mmol) according to the general procedure. Purified twice by chromatography with $CHCl_3$/petroleum ether(1:1–0). Yield: 0.36 g (62%); K 1°C Col 3°C I; ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 0.85-0.88$ (m, 18H; CH_3), 1.25–1.47 (m, 84H; CH_2), 1.69–1.80 (m, 12H; OCH_2CH_2), 3.58 (s, 4H; CH_2OCH_2Ph), 3.86 (t, $^3J(H,H) = 6.5$ Hz, 4H; CH_2OPhCH_2), 3.88 (t, $^3J(H,H) = 6.7$ Hz, 4H; CH_2OPhCH_2), 3.96 (t, $^3J(H,H) = 6.5$ Hz, 2H; $CH_2OPhCOO$), 4.38 (s, 4H; $PhCH_2$), 4.43 (s, 4H; CH_2OOC), 6.69 (d, $^3J(H,H) = 8.3$ Hz, 2H; Ar–H), 6.74 (dd, $^3J(H,H) = 8.3$ Hz, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 6.77 (d, $^4J(H,H) = 1.8$ Hz, 2H; Ar–H), 6.81 (d, $^3J(H,H) = 8.8$ Hz, 4H; Ar–H), 7.81 (d, $^3J(H,H) = 8.8$ Hz, 4H; Ar–H); MS (MALDI-TOF, DHB): *m/z*: 1484.1 $[M+Na]^+$, 1500.8

$[M+K]^+$; $C_{93}H_{152}O_{12}$ (1462.0): calcd C 76.40, H 10.47; found C 76.22, H 10.44.

3-(3,4-Didecyloxybenzyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)propanol (VIII): A suspension of **VII** (0.94 g, 1 mmol) and NaH (53 mg, 2.2 mmol) in dry DMF (15 mL) was stirred 2 h at 20 °C under an argon atmosphere. 3,4-Didecyloxybenzyl bromide [crude product as obtained from 3,4-didecyloxybenzyl alkohol (1.3 g, 3 mmol) by treatment with PBr_3 in dry benzene[15]] dissolved in dry DMF (40 mL) was added drop by drop. The mixture was stirred for 5 h at 50 °C and 12 h by 20 °C and then poured into ice water (50 mL). The solution was extracted three times with diethyl ether (30 mL), and the organic extracts were washed with water (30 mL) and brine (30 mL), and dried over Na_2SO_4. The solvent was removed in vacuo and the purification of the residue by chromatography with $CHCl_3$ gave the crude products **VIII** and **7**. **VIII** was further purified by chromatography with $CHCl_3$/petroleum ether (1:1.0); Yield: 0.33 g (24 %); K 11 °C Col 29 °C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.84-0.87$ (m, 18H; CH_3), 1.25–1.40 (m, 72H; CH_2), 1.42–1.45 (m, 12H; $O(CH_2)_2CH_2$), 1.73–1.81 (m, 12H; OCH_2CH_2), 3.50 (s, 6H; CH_2OCH_2Ph), 3.72 (s, 2H; CH_2OH), 3.93 (t, $^3J(H,H) = 6.6$ Hz, 4H; OCH_2), 3.94 (t, $^3J(H,H) = 6.6$ Hz, 4H; OCH_2), 4.36 (s, 6H; CH_2Ph), 6.75 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 1.6$ Hz, 3H; Ar–H), 6.78 (d, $^3J(H,H) = 8.2$ Hz, 3H; Ar–H), 6.79 (d, $^4J(H,H) = 1.6$ Hz, 3H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.94$, 22.56, 25.97, 26.00, 29.24, 29.25, 29.31, 29.36, 29.38, 29.50, 29.49, 29.54, 31.82, 44.96 (CCH_2), 66.19 (CCH_2OH), 69.34, 69.44, 70.84 (CCH_2OCH_2), 73.50 (CCH_2OCH_2), 113.71, 113.95, 120.27, 131.21, 148.94, 149.39; IR (Nujol): $\tilde{\nu} = 3454$ cm^{-1} (OH).

1-(3,4-Didecyloxybenzoyloxy)-3-(3,4-didecyloxybenzyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)propane (6): Synthesized from **VIII** (0.208 g, 0.155 mmol) and 3,4-didecyloxybenzoic acid (0.13 g, 0.31 mmol) according to the general procedure. Purified by chromatography with $CHCl_3$/petroleum ether (10:2–0). Yield: 0.198 g (75 %); K 10 °C Col 23 °C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.84-0.87$ (m, 24H; CH_3), 1.25–1.42 (m, 112H; CH_2), 1.70–1.85 (m, 16H; OCH_2CH_2), 3.54 (s, 6H; CH_2OCH_2Ph), 3.88 (t, $^3J(H,H) = 6.6$ Hz, 6H; CH_2OPhCH_2), 3.90 (t, $^3J(H,H) = 6.6$ Hz, 6H; CH_2OPhCH_2), 3.95 (t, $^3J(H,H) = 6.6$ Hz, 2H; $CH_2OPhCOO$), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 2H; $CH_2OPhCOO$), 4.36 (s, 8H; CH_2OOC, $PhCH_2$), 6.71–6.78 (m, 10H; Ar–H), 7.36 (dd, $^3J(H,H) = 8.4$ Hz, $^4J(H,H) = 1.9$ Hz, 1H; Ar–H), 7.45 (d, $^4J(H,H) = 1.9$ Hz, 1H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.97$, 22.58, 25.98, 26.01, 29.10, 29.17, 29.27, 29.33, 29.37, 29.40, 29.42, 29.52, 29.58, 31.84, 44.84 (CCH_2), 64.13 (CCH_2OCH_2), 68.99 (CCH_2OCH_2), 69.18, 69.39, 73.38, 111.98, 113.53, 113.82, 114.40, 120.12, 122.74, 123.42, 131.38, 148.64, 148.72, 149.29, 153.26, 166.28 (C=O); IR (Nujol): $\tilde{\nu} = 1713$ cm^{-1} (C=O); MS (MALDI-TOF, DHB): m/z: 1782.4 $[M+Na]^+$, 1798.7 $[M+K]^+$; $C_{113}H_{194}O_{13}$ (1760.5): calcd C 77.09, H 11.10; found C 76.98, H 11.03.

1,3-Bis(3,4-didecyloxybenzyloxy)-2,2-bis(3,4-didecyloxybenzyloxymethyl)-propane (7): Purified by chromatography with petroleum ether/ethyl acetate (10:0.05); Yield: 90 mg (5 %); K 14 °C Col 21 °C I; ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 0.91-0.96$ (m, 24H; CH_3), 1.29–1.34 (m, 96H; CH_2), 1.44–1.48 (m, 16H; $O(CH_2)_2CH_2$), 1.71–1.78 (m, 16H; OCH_2CH_2), 3.84 (t, $^3J(H,H) = 6.4$ Hz, 8H; OCH_2), 3.87 (t, $^3J(H,H) = 6.4$ Hz, 8H; OCH_2), 3.97 (s, 8H; CCH_2), 4.54 (s, 8H; CH_2Ph), 6.81 (d, $^3J(H;H) = 8.2$ Hz, 4H; Ar–H), 6.98 (dd, $^3J(H;H) = 8.2$ Hz, $^4J(H;H) = 1.8$ Hz, 4H; Ar–H), 7.03 (d, $^4J(H;H) = 1.8$ Hz, 4H; Ar–H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.11$, 22.89, 26.42, 26.45, 29.61, 29.64, 29.73, 29.76, 29.84, 29.87, 29.89, 29.93, 29.96, 32.14, 32.16, 46.26 (CCH_2), 69.17, 69.27, 69.90 (CCH_2), 73.72, 114.04, 114.26, 120.45, 132.22, 149.54, 150.15; MS (MALDI-TOF, DHAP): m/z: 1745.8 $[M]^+$; $C_{113}H_{196}O_{12}$ (1746.6): calcd C 77.71, H 11.30; found C 77.60, H 11.22.

Synthesis of 8

4-(3,4-Didecyloxyphenyl)benzoic acid: Ethyl 4-bromobenzoate (2.5 g, 11.5 mmol) was dissolved in glyme (25 mL) at 20 °C. After addition of $Pd(PPh_3)_4$ (0.4 g, 35 mmol) the mixture was stirred for 15 min. 3,4-Didecyloxyphenylboronic acid (4.0 g, 9.2 mmol) dissolved in glyme (100 mL) and saturated aqueous solution of $NaHCO_3$ (35 mL) was added, while stirring was continued. The reaction mixture was heated at reflux temperature under an argon atmosphere for 8 h and then it was cooled to 0–5 °C. The ethyl 4-(3,4-didecyloxyphenyl)benzoate precipitated and was removed and recrystallisized twice from methanol. Yield: 3.2 g (65 %); m.p. 63–65 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.85-0.92$ (m, 6H; CH_3), 1.28–1.52 (m, 31H; CH_2, OCH_2CH_3), 1.81–1.88 (m, 4H; OCH_2CH_2), 4.01–4.11 (m, 4H; OCH_2CH_2), 4.40 (q, 2H; OCH_2CH_3), 6.96 (d, $^3J(H,H) = 8.8$ Hz, 1H; Ar–H), 7.15–7.19 (m, 2H; Ar–H), 7.61 (d, $^3J(H,H) = 8.6$ Hz, 2H; Ar–H), 8.08 (d, $^3J(H,H) = 8.6$ Hz, 2H; Ar–H); IR (Nujol): $\tilde{\nu} = 1706$ cm^{-1} (C=O); MS: m/z (%): 538 (58) $[M]^+$, 398 (15), 258 (60), 213 (10), 57 (20), 43 (100); $C_{35}H_{54}O_4$ (538.7): calcd C 78.03, H 10.09; found C 78.15, H 10.29.

A suspension of ethyl 4-(3,4-didecyloxyphenyl)benzoate (3.0 g, 5.5 mmol) and KOH (0.7 g, 11 mmol) in ethanol (100 mL) was heated at reflux for 3 h, during which the mixture became clear. After acidification of the hot solution with hydrochloric acid (2 M; 15 mL), the mixture was cooled to 0–5 °C. The white precipitat was removed and recrystallisized twice from acetone. Yield: 2.6 g (93 %); M.p 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.87-0.90$ (m, 6H; CH_3), 1.28–1.37 (m, 24H; CH_2), 1.46–1.51 (m, 4H; $O(CH_2)_2CH_2$), 1.81–1.89 (m, 4H; OCH_2CH_2), 4.05 (t, $^3J(H,H) = 6.6$ Hz, 2H; OCH_2), 4.08 (t, $^3J(H,H) = 6.6$ Hz, 2H; OCH_2), 6.97 (d, $^3J(H,H) = 8.2$ Hz, 1H; Ar–H), 7.16–7.20 (m, 2H; Ar–H), 7.65 (d, $^3J(H,H) = 8.4$ Hz, 2H; Ar–H), 8.14 (d, $^3J(H,H) = 8.4$ Hz, 2H; Ar–H); IR (Nujol): $\tilde{\nu} = 3250$ (OH), 1841 cm^{-1} (C=O); MS: m/z (%): 510 (63) $[M]^+$, 370 (18), 230 (100), 71 (15), 57 (40), 43 (68); $C_{33}H_{50}O_4$ (510.7): calcd C 77.61, H 9.86; found C 77.80, H 10.00.

1,3-Bis[4-(3,4-didecyloxyphenyl)benzoyloxy]-2,2-bis[4-(3,4-didecyloxyphenyl)benzoyloxymethyl]propane (8): Synthesized from pentaerythritol (0.068 g, 0.5 mmol) and 4-(3,4-didecyloxyphenyl)benzoic acid (2.04 g, 4 mmol) according to the general procedure. Purified by chromatography with $CHCl_3$/methanol (1:0–0.05). Yield: 0.52 g (49 %); K 92 °C M 72 °C I; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.84-0.88$ (m, 24H; CH_3), 1.25–1.34 (m, 96H; CH_2), 1.42–1.48 (m, 16H; $O(CH_2)_2CH_2$), 1.77–1.85 (m, 16H; OCH_2CH_2), 4.00 (t, $^3J(H,H) = 6.6$ Hz, 8H; OCH_2), 4.01 (t, $^3J(H,H) = 6.6$ Hz, 2H; OCH_2), 4.74 (s, 8H; CCH_2), 6.89 (d, $^3J(H,H) = 8.2$ Hz, 4H; Ar–H), 7.06–7.09 (m, 8H; Ar–H), 7.54 (d, $^3J(H,H) = 8.4$ Hz, 8H; Ar–H), 8.02 (d, $^3J(H,H) = 8.4$ Hz, 8H; Ar–H); MS (MALDI-TOF, DHB): m/z: 2108.5 $[M+H]^+$; $C_{137}H_{204}O_{16}$ (2106.9): calcd C 78.10, H 9.75; found C 78.13, H 9.87.

Tetrakis[4-(3,4-didecyloxyphenyl)phenyl]methane (9): Tetrakis(4-bromophenyl)methane[19] (0.16 g, 0.25 mmol) was dissolved at 20 °C in Glyme (20 mL). After addition of $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) the mixture was stirred for 15 min. 3,4-Didecyloxyphenylboronic acid[20] (0.6 g, 1.38 mmol) dissolved in glyme (30 mL) and saturated aqueous solution of $NaHCO_3$ (5 mL) were added while stirring was continued. The reaction mixture was heated at reflux under an argon atmosphere for 8 h. The solvent was removed in vacuo and $CHCl_3$ (50 mL) was added. The organic phase was separated, washed with water (20 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. The residue was purified by chromatography with petroleum ether/$CHCl_3$ (2:0.5–2); Yield: 0.04 g (8 %); m.p. 74 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.84-0.88$ (m, 24H; CH_3), 1.25–1.34 (m, 96H; CH_2), 1.43–1.47 (m, 16H; $O(CH_2)_2CH_2$), 1.78–1.84 (m, 16H; OCH_2CH_2), 4.01 (t, $^3J(H,H) = 6.8$ Hz, 8H; OCH_2), 4.02 (t, $^3J(H,H) = 6.8$ Hz, 8H; OCH_2), 6.91 (d, $^3J(H,H) = 8.3$ Hz, 4H; Ar–H), 7.10–7.12 (m, 8H; Ar–H), 7.33 (d, $^3J(H,H) = 8.5$ Hz, 8H; Ar–H), 7.46 (d, $^3J(H,H) = 8.5$ Hz, 8H; Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.11$, 22.68, 26.04, 27.00, 29.31, 29.34, 29.43, 29.58, 29.63, 30.94, 31.90, 41.94, 69.37, 69.43, 112.92, 114.05, 119.44, 125.78, 131.42, 133.64, 138.44, 145.32, 148.72, 149.22; MS (MALDI-TOF, DHB): m/z: 1873.3 $[M]^+$; 1897.0 $[M+Na]^+$; $C_{129}H_{196}O_8$ (1874.7).

Tetrakis(3,4-didecyloxyphenyl)stannane (10): 3,4-Didecyloxybromobenzene (5.2 g, 11 mmol) was dissolved in dry diethyl ether (100 mL) and cooled to −20 °C. Under an argon atmosphere butyllithium (6.8 mL of a 1.6 molar solution in *n*-hexane, 11 mmol) was added slowly with stirring. The mixture was stirred at this temperature for 2 h. A solution of $SnCl_4$ (0.3 mL, 2.5 mmol) in dry benzene (20 mL) was added slowly. When addition was complete the mixture was allowed to warm to 20 °C, while stirring was continued. Afterwards the mixture was heated at reflux for 5 h. After cooling to 0 °C a saturated aqueous solution of NH_4Cl (50 mL) was added at 0–5 °C. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo to give the crude product, which was purified by chromatography with petroleum ether/ethyl acetate (10:1.5) and recrystallization from acetone. Yield: 170 mg (4 %); m.p. 53 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C, TMS): $\delta = 0.91$ (t, $^3J(H,H) = 6.8$ Hz, 12H; CH_3), 0.92 (t, $^3J(H,H) = 7.0$ Hz, 12H; CH_3), 1.27–1.44 (m, 112H; CH_2), 1.64–1.74 (m, 16H; OCH_2CH_2), 3.82 (t, $^3J(H,H) = 6.4$ Hz,

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8H; OCH_2), 3.86 (t, $^3J(H,H) = 6.2$ Hz, 8H; OCH_2), 6.98 (d, $^3J(H,H) = 7.6$ Hz, 4H; Ar–H), 7.60 (d, $^3J(H,H) = 7.6$ Hz, 4H; Ar–H), 7.65 (s, 4H; Ar–H); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.47$, 23.22, 26.67, 29.96, 30.04, 30.16, 32.45, 69.06, 69.41, 114.94, 122.70, 130.04, 131.10, 150.80, 151.42; ^{119}Sn NMR (149 MHz, C_6D_6): $\delta = -108.12$; MS (MALDI-TOF, DHAP): m/z: 1677.8 $[M]^+$; $C_{104}H_{180}O_8Sn$ (1677.0): calcd C 74.48, H 10.81; found C 74.42, H 10.57.

Zinc bis[1,3-bis(3,4-didecyloxyphenyl)-1,3-propanedionate] (11): A solution of sodium hydride (0.28 mg, 80 per cent dispersion in mineral oil, 0.0118 mmol) in dimethoxyethane (1 mL) was added dropwise to an solution of 1,3-bis(3,4-didecyloxyphenyl)-1,3-propanedione[22] (10.0 mg, 0.0118 mmol) and $ZnCl_2$ (0.81 mg, 0.0059 mmol) in dimethoxyethane (5 mL). The mixture was refluxed for 6 h, during which a white precipitate was formed. The precipitate was filtered off and washed with cold dimethoxyethane. Column chromatography (chloroform/ethanol 10:0.3–1) afforded a white solid in 19% yield (2 mg). M.p. 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86$ (t, $^3J(H,H) = 6.9$ Hz, 24H; CH_3), 1.49–1.25 (m, 112H; CH_2), 1.84–1.77 (m, 16H; OCH_2CH_2), 3.44 (s, 2H; CH), 4.03 (2t, 16H; OCH_2), 6.87 (d, $^3J(H,H) = 8.5$ Hz, 4H; Ar–H), 7.56 (d, $^4J(H,H) = 2$ Hz, 4H; Ar–H), 7.69 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 2$ Hz, 4H; Ar–H).

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