

New Mesophase Morphologies Formed by Facial T-shaped Ternary Amphiphiles

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Numbering of the substance in this work:

I, II, ...	compounds quote from literature
1, 2, ...	intermediates
H10/2, H10/3, ...	carboxylic acid derivatives (final products)
Na10/2, Li10/3, ...	metal carboxylates (final products)
A10/2, A10/3, ...	polyhydroxy alkyl amides (final products)

Abbreviations

Chemical Material

Ar	Aromatic
n-Bu	n-Butyl
Me	Methyl
Et	Ethyl
DMAP	4-Dimethylaminopyridine
EtOH	Ethanol
MeOH	Methanol
DME	Dimethoxyethylene
Ph	Phenyl
THF	Tetrahydrofuran
DCC	<i>N,N'</i> -Dicyclohexylcarbodiimide
HCl	Hydrochloric acid
Tos	p-Toluenesulfonyl

Spectroscopy

DSC	Differential scanning calorimetry
δ	Chemical shift
NMR	Nuclear magnetic resonance
s	Singlet
d	Doublet
t	Triplet
dd	Doubled doublet
m	Complex multiplet
<i>J</i>	Coupling constant
br s	Broad singlet

Phase Name

SmA _{frm}	Filled random mesh phase
Col	Columnar mesophase
Col _r	Rectangular columnar phase
Col _{sq}	Square columnar phase
Col _h	Hexagonal columnar phase (<i>p6mm</i>)
Col _h (//)	“Non-segregation” hexagonal columnar phase with aromatic cores perpendicular to the polar columns

Col _{h(⊥)}	“Non-segregation” hexagonal columnar phase with aromatic cores parallel to the polar columns
Col _{h(Δ)}	Hexagonal columnar phase where the aromatic cores are arranged in triangular shell surrounding the polar columns
Rho	Rhombohedral phase ($R3m$)
Lam _{Sm}	Laminated smectic phase where the aromatic cores have a SmA arrangement
Lam _N	Laminated nematic phase where the aromatic cores have a Nematic arrangement
Lam _{iso}	Laminated isotropic phase where the aromatic cores have a isotropic arrangement
Cr	Crystalline phase
G	Glass phase
Cub _v	Bicontinuous cubic phase
Cub _I	Discontinuous cubic phases
Iso	Isotropic liquid phase
N	Nematic phase
N _D	Discotic nematic phase
SmA or S _A	Smectic A phase
Sm	Smectic phase
SmA ⁺	Disordered SmA-phase
LLC	Lyotropic liquid crystal

Other

<i>a</i>	Lattice parameter
<i>c</i>	Lattice parameter
<i>L</i>	Length of molecule (the distance of two ends of the terminal alkyl chains in its most extended conformation)
<i>d</i>	Layer periodicity distance
<i>D</i>	Distance between alkyl chains or aromatic cores
<i>T</i>	Temperature
ΔH	Transition enthalpy
TLC	Thin-layer chromatography
r.t.	Room temperature (25 °C)
2D	Two dimensional
3D	Three dimensional

Contents

1	INTRODUCTION.....	1
1.1	GENERAL CONCEPTS OF LIQUID CRYSTALS.....	1
1.2	MESOPHASE MORPHOLOGIES OF AB BINARY COMPOUNDS.....	3
1.3	MESOPHASE MORPHOLOGIES OF AB BINARY COPOLYMERS.....	5
1.4	MESOPHASE MORPHOLOGIES OF ABC TERNARY COPOLYMERS.....	5
1.5	MESOPHASE MORPHOLOGIES OF LOW MOLECULAR WEIGHT TERNARY BLOCK MOLECULES.....	7
1.5.1	Linear triblock molecules with a rod-like central core.....	7
1.5.2	T-shaped ternary tetrablock molecules with a rod-like central core.....	8
1.5.2.1	Bolaamphiphiles with lateral nonpolar chains.....	8
1.5.2.2	T-shaped amphiphiles with a polar lateral chain ("facial amphiphiles").....	10
1.6	OBJECTIVE.....	12
2	SYNTHESIS.....	13
2.1	SYNTHESIS OF METHYL ω -(4,4''-DIALKOXY-p-TERPHENYL-2'-YLOXY)OLIGO- (OXYETHYLENE)-YL ACETATES 7/m/n	14
2.1.1	Synthesis of methyl ω -tosyloxyloligo(oxyethylene)yl acetates 2/n	14
2.1.2	Synthesis of p-alkoxylbenzeneboronic acids 5/m	15
2.1.3	Synthesis of methyl ω -(2,5-dichlorophenyl)[oligo(oxyethylene)yl] acetates 3/n	15
2.1.4	Synthesis of methyl ω -(4,4''-diakoxy-p-terphenyl-2'-yloxy)oligo- (oxyethylene)yl acetates 7/m/n	15
2.2	SYNTHESIS OF METHYL ω -(4,4''-DIDECYLOXY-p-TERPHENYL-3-YL)- OLIGO(OXYETHYLENE)YL ACETATES (17/10/n).....	17
2.3	SYNTHESIS OF METHYL ω -(4,4''-DIALKOXY-p-TERPHENYL-2'-YL)-OLIGO- (OXYETHYLENE)YL ACETATES 22/m'/m/n WITH TWO DIFFERENT TERMINAL ALKOXY CHAINS.....	18
2.4	SYNTHESES OF SODIUM CARBOXYLATES (Nam/n , Nam'/m/n , Na*10/n) AND THE CARBOXYLIC ACIDS (Hm/n , Hm'/m/n , H*10/n).....	19
2.5	SYNTHESIS OF CARBOXYLATES WITH DIFFERENT CATIONS Mm/n ($M^+ = Li^+, K^+, Cs^+, Ba^{2+}, Cu^{2+}, La^{3+}, Eu^{3+}$).....	20
2.6	SYNTHESIS OF FACIAL AMPHIPHILES WITH POLYHYDROXY GROUP AT THE END OF THE LATERAL CHAIN (A , A¹ AND A²).....	21

MESOPHASE BEHAVIOUR OF THE SYNTHESIZED COMPOUNDS

3	LIQUID CRYSTALLINE PROPERTIES OF THE METAL CARBOXYLATES.....	24
3.1	SODIUM CARBOXYLATES.....	24
3.1.1	Influence of the length of the terminal alkoxy chains.....	24
3.1.2	Influence of the length of the oligo(oxyethylene) chain.....	28
3.2	FACIAL AMPHIPHILES WITH DIFFERENT CATIONS.....	32
3.2.1	Alkali metal carboxylates.....	32
3.2.2	Rear earth metal, transition metal and alkaline earth metal carboxylates.....	34
3.3	FACIAL AMPHIPHILES WITH TWO DIFFERENT TERMINAL ALKOXY CHAINS.....	35
3.4	INFLUENCE OF THE POSITION OF THE LATERAL CHAIN.....	37

3.5	SUMMARY OF THE MESOPHASE BEHAVIOUR OF THE METAL CARBOXYLATES.....	39
4	LIQUID CRYSTALLINE PROPERTIES OF FACIAL AMPHIPHILES WITH A LATERAL CHAIN CONTAINING AN AMIDE GROUP.....	40
4.1	1-ACYLAMINO-1-DEOXY-D-SORBITOL UNIT AT THE END OF THE LATERAL POLAR CHAIN.....	40
4.1.1	Influence of the length of the alkoxy chains.....	40
4.1.2	Influence of the length of oligo(oxyethylene) chains.....	42
4.1.3	Influence of the position of the lateral chain (Y-shaped amphiphiles).....	51
4.1.4	Facial amphiphiles with different terminal alkoxy chains.....	51
4.2	MOLECULES INCORPORATING POLAR CHAINS WITH DIOLS END GROUPS.....	52
4.3	MESOPHASES OF A4/4 WITH FORMAMIDE.....	52
4.4	SUMMARY OF THE MESOPHASE BEHAVIOUR OF THE AMIDES.....	54
5	LIQUID CRYSTALLINE PROPERTIES OF THE CARBOXYLIC ACIDS.....	56
5.1	INFLUENCE OF THE LENGTH OF TERMINAL ALKOXY CHAINS.....	56
5.2	INFLUENCE OF THE LENGTH OF THE LATERAL POLAR CHAIN.....	57
5.3	INFLUENCE OF THE POSITION OF THE LATERAL CHAIN (Y-SHAPED AMPHIPHILES).....	63
5.4	COMPOUNDS WITH TWO DIFFERENT TERMINAL ALKOXY CHAINS.....	64
5.5	SUMMARY OF THE MESOPHASE BEHAVIOUR OF THE CARBOXYLIC ACIDS.....	67
6	BINARY SYSTEMS.....	68
7	SUMMARY.....	71
8	EXPERIMENTAL SECTION.....	77
8.1	GENERAL CONSIDERATIONS.....	77
8.2	SYNTHESIS AND ANALYTICAL DATA OF THE FINAL COMPOUNDS.....	79
8.2.1	Sodium salts (Nam/n , Na*10/n , Na6.16/n and Na16.6/n).....	79
8.2.2	Carboxylic acids (Hm/n , H*10/n , H6.16/n and H16.6/n).....	90
8.2.3	Amides (Am/n , A*10/n , A6.16/n , A16.6/n , A¹10/n and A²10/n).....	100
8.2.4	Alkali metal and alkali earth metal carboxylates (Li10/n , K10/n , Csm/n and Ba10/n).....	114
8.2.5	Copper carboxylates (Cu10/n).....	118
8.2.6	Rear earth metal carboxylates (La10/n and Eu10/3).....	118
9	SYNTHESIS AND ANALYTICAL DATA OF INTERMEDIATES.....	120
9.1	SYNTHESIS OF METHYL ω -HYDROXY[OLIGO(OXYETHYLENE)YL]ACETATES (1/n).....	120
9.2	SYNTHESIS OF METHYL 20-HYDROXY-3,6,9,12,15,18-HEXAOXAECOSANOATE (1/6).....	121
9.3	SYNTHESIS OF METHYL ω -TOSYLOXY[OLIGO(OXYETHYLENE)YL]ACETATES (2/n).....	122
9.4	SYNTHESIS OF METHYL ω -(2,5-DICHLOROPHENYLOXY)[OLIGO(OXYETHYLENE)-YL]ACETATES (3/n).....	123
9.5	SYNTHESIS OF 2,5-DICHLOROPHENYLACETATE (4)	124

9.6	SYNTHESIS OF METHYL ω -(4,4''-DIALKOXY-p-TERPHENYL-2'-YLOXY)[OLIGO-(OXYETHYLENE)-YL]ACETATES (7/m/n).....	125
9.6.1	Procedure (I)	125
9.6.2	Procedure (II).....	130
9.6.3	Procedure (III).....	132
9.6.4	Procedure (IV).....	133
9.7	SYNTHESIS OF 3-SUBSTITUTED P-TERPHENYL DERIVATIVES 17/10/n	133
9.8	SYNTHESIS OF 2'-SUSTITUTED 4-HEXADECYLOXY-4''-HEXYLOXY-p-TERPHENYL DERIVERATIVES AND 2'-SUSTITUTED 4''-HEXADECYLOXY-4-HEXYLOXY-p-TERPHENYL DERIVERATIVES (22/m'/m/n).....	136
9.8.1	Synthesis of intermediates.....	136
9.8.2	Synthesis of 2'-sustituted 4-hexadecyloxy-4''-hexyloxy-p-terphenyl derivatives and 2'-sustituted 4''-hexadecyloxy-4-hexyloxy-p-terphenyl derivatives (22/m'/m/n).....	140
10	APPENDIX.....	143
11	REFERENCES.....	145

ZUSAMMENFASSUNG

1 Introduction

1.1 General concepts of liquid crystals

Liquid crystalline phases (or mesophases) occur as intermediates between the ordered solid crystalline state and the disordered liquid state or the isotropic solution.^[1] Combination of order (orientational and/or positional order) and mobility on a molecular level is a typical feature of liquid crystals.

There are two different ways to form a mesophase, which give rise to two main classes of liquid crystals: (a) Thermotropic liquid crystals which form mesophases by the influence of temperature. (b) Lyotropic liquid crystals which form mesophases in the presence of a solvent. A great number of materials have been found to be thermotropic or lyotropic liquid crystals, and some of them exhibit both types of behaviour (amphotropic liquid crystals).^[2]

Thermotropic liquid crystals are usually classified into two main groups depending on their structural characters: calamitic (rod-like) and discotic (disc-like) molecules. Because of the anisometric geometry, these molecules prefer to have a parallel alignment (orientational order). Depending on the degree of positional order, different liquid crystalline phases can be distinguished. The least ordered phase is the nematic phase,^[3] where the molecules have exclusively long-range orientational order. If the molecules are confined into subspaces, which gives rise to positional orders, more ordered phases can be formed. The shape of the subspaces is dominantly depending on the geometry of the molecules. In the case of calamitic molecules, layer structures could be formed (smectic phases, Sm),^[4] while the discotic molecules prefer an organisation in columns (columnar phases, Col)^[5] (Figure 1.1).

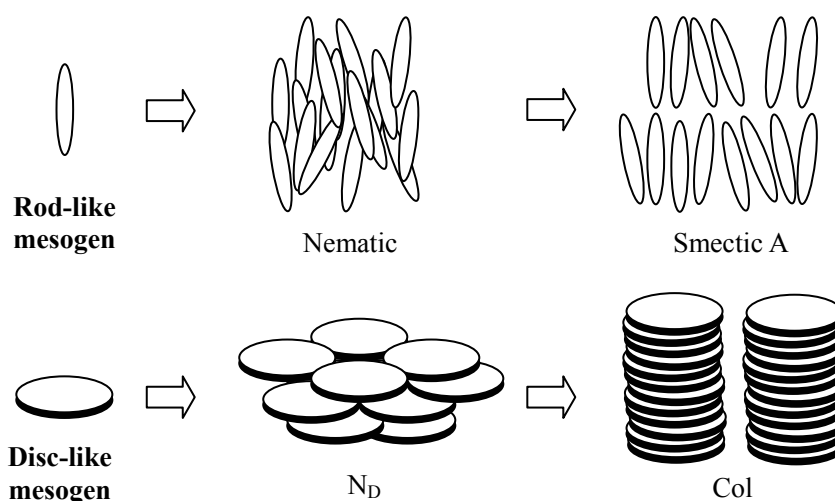


Figure 1.1. Fundamental mesophases formed by the organisation of rod-like molecules and disc-like molecules.

Lyotropic liquid crystals (LLC) are another important class of mesophase forming materials. In the case of LLC, not only the temperature but also the type of solvent as well as the concentration are decisive factors for the appearance of the lyotropic mesophases.

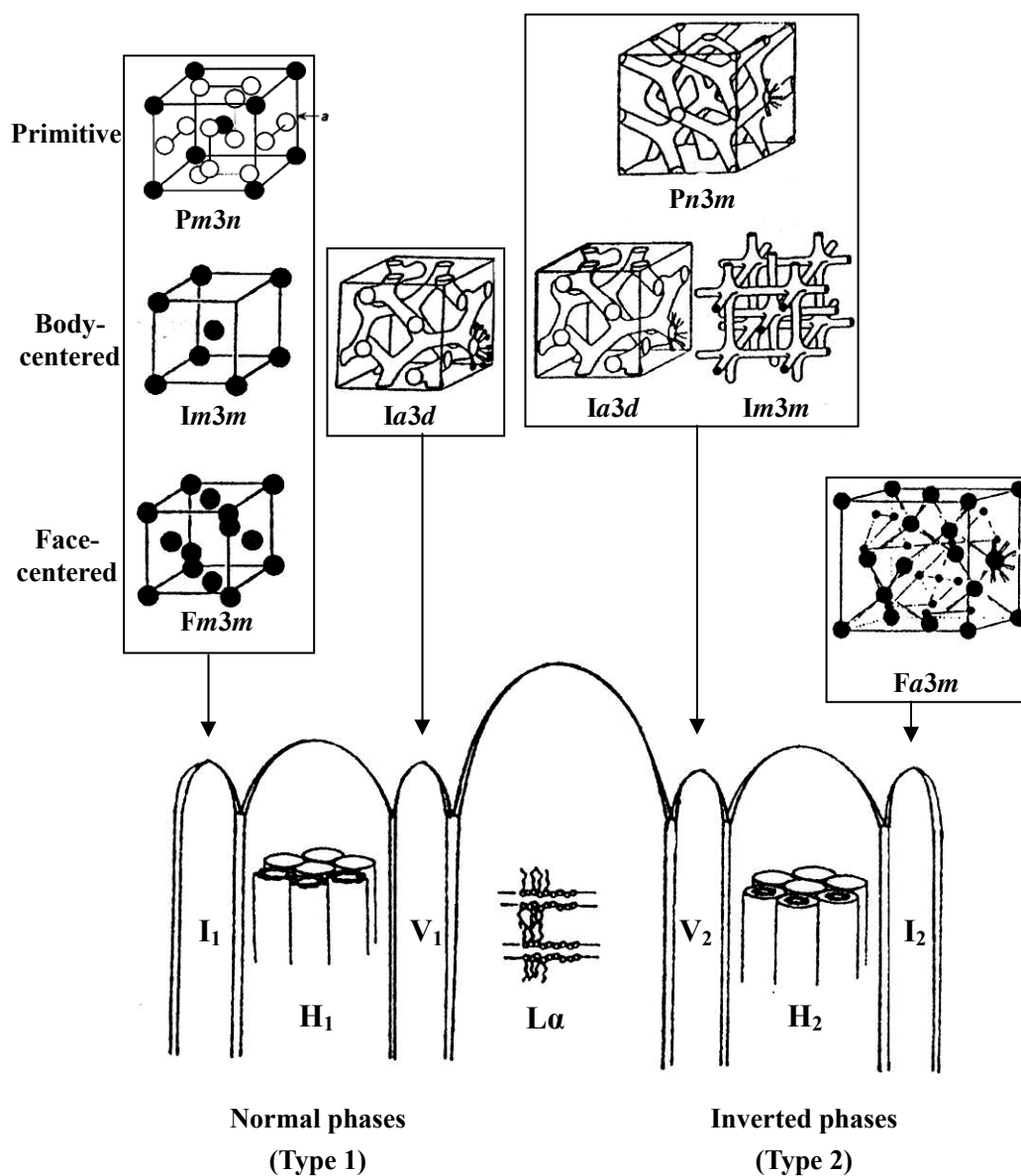


Figure 1.2. Main types of lyotropic mesophases and their occurrence in dependence of the volume fraction of the lipophilic part (increasing from left to right).^[8c]

Generally, lyotropic mesophases are formed by amphiphilic molecules. Amphiphiles containing a hydrophilic head group and a hydrophobic tails are the most explored lyotropic liquid crystals.^[6] LLC aggregate structures vary from closed micellar systems (Cub_I) via anisotropic assemblies composed of ordered arrays of cylinders (columnar hexagonal phase, Col_h), interwoven networks of branched cylinders (bicontinuous cubic phases, Cub_V) to bilayers (lamellar phases, $L\alpha$). Depending on whether the hydrophobic/hydrophilic interface has a net positive mean curvature (curves toward the hydrophobic domains) or a net negative mean curvature (curves toward the hydrophilic domains), these phases can be further classified as Type I (oil-in-water or “normal”) or Type II (water-in-oil or “inverted”)

phases. The lamellar phase is considered to have zero mean curvature and serves as a midpoint in an idealized progression of LLC phases with the increase of the volume fraction of the lipophilic part or the polar part.^[7] A number of bicontinuous cubic (Cub_V) phases have also been identified, which can exist as an intermediate between the lamellar and columnar phases. These cubic phases are termed bicontinuous because they consist of two unconnected but interpenetrating hydrophobic or hydrophilic networks with overall cubic symmetry. Depending on where they appear in the phase diagram relative to the central lamellar phase, these cubic phases can also be classified as type I or type II (they have the same cubic symmetries but inverted locations of the polar and hydrocarbon domains). Besides the cubic phases, several noncubic intermediate phases, for example mesh phases,^[8] tetragonal,^[9] and rhombohedral 3D-phases,^[10] have also been found at the transition from lamellar to columnar organisations. These intermediate phases usually occur in very small temperature and/or concentration ranges.

1.2 Mesophase morphologies of AB binary compounds

Hydrophilic and hydrophobic are the most common combination in AB binary molecules (amphiphiles). Amphiphilic molecules can self-organize into lamellar, cylindrical or spherical structures in water to form lyotropic mesophases (Figure 1.2). Many of the amphiphiles (ionic amphiphiles, amphiphilic carbohydrate derivatives and polyhydroxy amphiphiles) can also form thermotropic liquid crystalline phases in the absence of any solvent. Recently, investigations of polyhydroxy^[11] and carbohydrate^[12] derivatives have shown that the same sequence of mesophases found for lyotropic mesophases can also be realized in thermotropic systems by controlling the volume ratio of the polar part with respect to the apolar part (Figure 1.3).

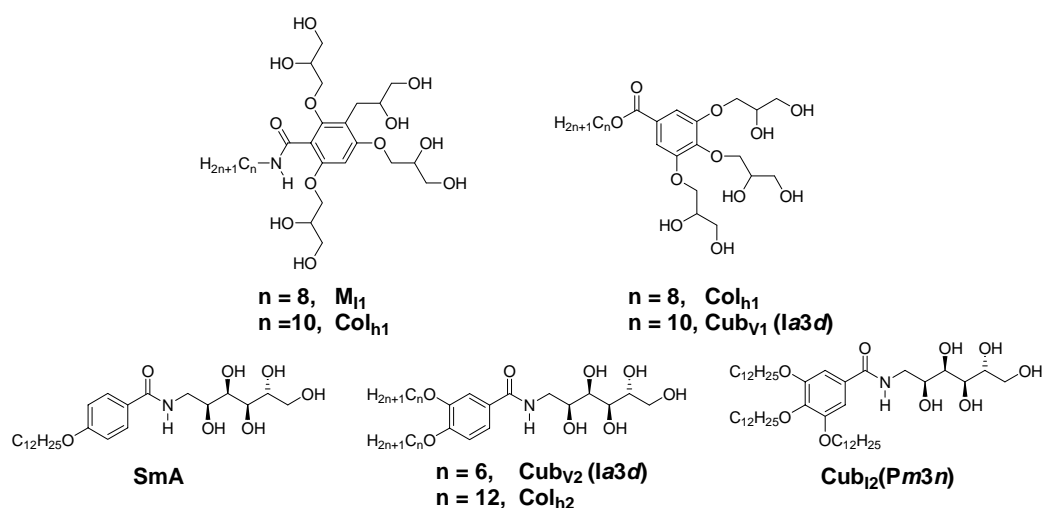


Figure 1.3. Dependence of the mesophase type of the polyhydroxy amphiphiles on the molecule structure (polar/apolar volume ratio). $\text{M}_{\text{I}1}$ = optically isotropic mesophase comprised of discrete direct micelles with unknown lattice.

Besides the well explored polar/apolar groups, perfluoroalkyl chains^[13-17] as well as oligosiloxane groups^[18] are becoming more and more important building blocks in low

molecular weight amphiphilic liquid crystals. Another important type of incompatibility comes from the flexible/rigid amphiphilicity, which has been found for calamitic mesogens^[19], polycatenars^[20] and rod-coil molecules.^[21] The advantage of these compounds is that the rigid part has an anisometric shape which gives rise to an additional orientational order. For example, the rod-coil molecules show not only lamellar phases but also mesophases comprised of cylindrical or spherical micro-segregated domains depending on the volume fraction of the coil segment in the molecule.^[22-26] Furthermore, if the rigid core is elongated, 3D body-centred tetragonal (3D-Tet, $I4mm$) and 3D hexagonal structures (3D-Hex, AB stacking, $P6_3/mmc$) can be formed (Figure 1.4),^[25] which is unusual for the flexible amphiphiles. The oblate shape of the supramolecular aggregates which can pack more densely into an optical anisotropic 3D tetragonal lattice is believed to be responsible for the formation of this unusual 3D-Tet phase.

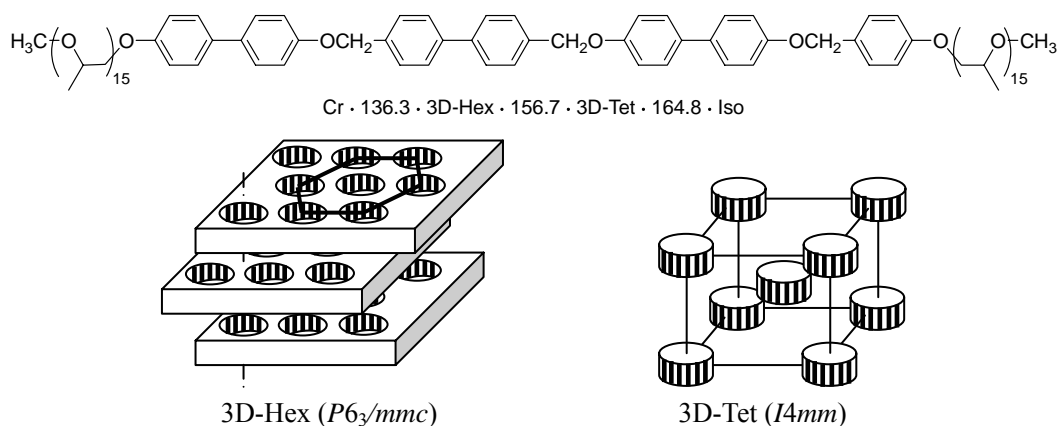


Figure 1.4. A representative example of a binary coil-rod-coil molecule forming 3D-Hex and 3D-Tet mesophases. (3D-Hex: AB arrangement of hexagonal perforated layers; 3D-Tet: body-centred tetragonal mesophase.)

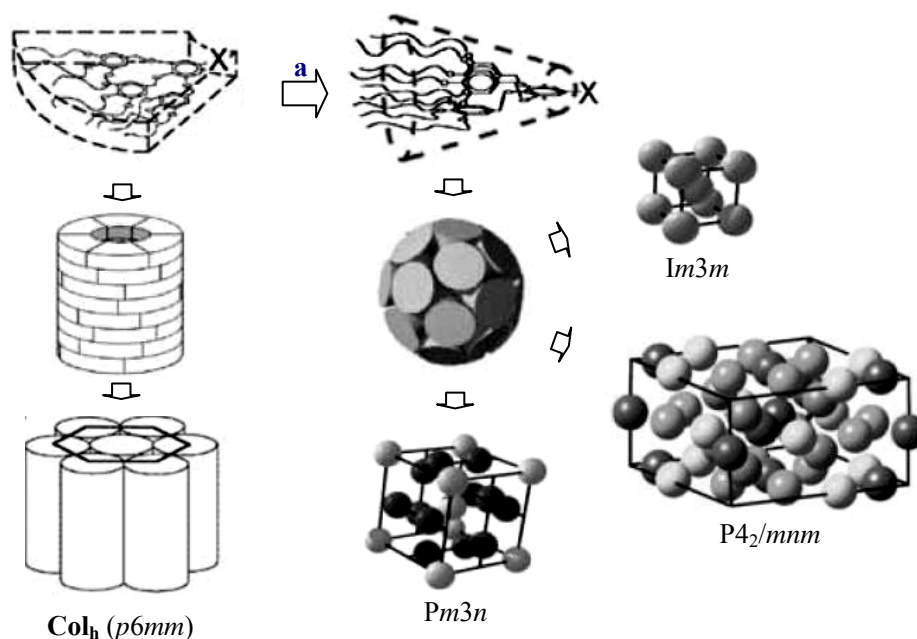


Figure 1.5. Self-assembly of benzyl ether dendrons in 2D (columnar) and 3D mesophases. (a: increase the volume of aliphatic parts.)

In the benzyl ether dendrons,^[27, 28, 15b] the micro-segregation of aliphatic and aromatic segments as one of the self-organisation forces is investigated.^[29, 13e] As shown in Figure 1.5, the mono-dendron with fewer aliphatic chains adopts tapered shape and stacks up to form a hexagonal columnar phase (Col_h). Dendrons with more aliphatic chains are assumed to be conical. The cones assemble into spheres which lead to three different 3D organisations. Very recently, a micellar liquid quasi-crystal phase with 12-fold rotational symmetry has been discovered.^[28]

1.3 Mesophase morphologies of AB binary copolymers

In recent decades, it has been found that AB binary block copolymers, which are made up of chemically distinct polymer blocks joined by covalent bond, can also produce well-developed mesostructures. The most characteristic feature of a block copolymer is the strong incompatibility between the unlike polymer segments even when the chemical difference between the unlike monomers is relatively weak. Depending on the segregation strength between the distinct blocks, the variation of the composition, the conformation of the molecule, and the stiffness of the polymer chains, various well-ordered mesostructures have been found.^[30] The associated bulk state phase behaviour is quite similar to that exhibited by certain low molecular weight amphiphiles. Even in the simplest case of AB diblock copolymers which consist of two chemical distinct chains connected with each other, lamellar phases ($\text{L}\alpha$), hexagonal packed cylinders (Col_h), a bicontinuous cubic structure (Cub_V) with $\text{Ia}3d$ space group symmetry and spheres packed in a bcc lattice (Cub_I , $\text{Im}3m$) can be formed in the same sequence as known for low molecular weight surfactants.^[31-36] Besides the classical mesophases mentioned above, additional complex structures such as hexagonally modulate layers (HML), hexagonal perforated layers (HPL, a hexagonal mesh phase) have been found as metastable phases between the lamellar and the columnar morphology near the order-disorder transition.^[37,38] Furthermore, various AB binary multiblock copolymers with complex architectures have been investigated (Figure 1.6). The ordered microphase-separated morphologies of such copolymers are quite different from what occurred in the corresponding linear diblock copolymer systems.^[39-43]

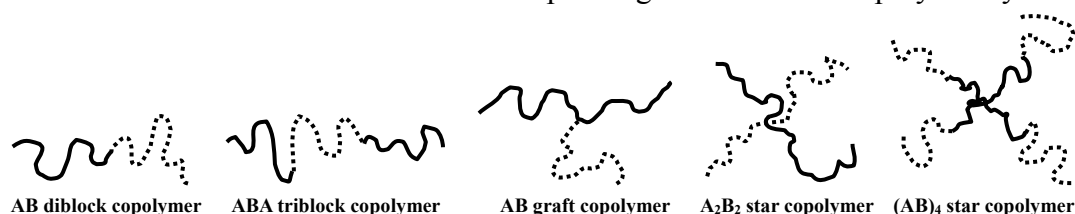


Figure 1.6. Schematic representation of five types of copolymers with two chemical distinct blocks.

1.4 Mesophase morphologies of ABC ternary copolymers

With the improvement of the polymerization techniques, it is now possible to prepare ABC ternary copolymers with well-controlled molecular architecture, that is, with well-controlled block lengths. Such macromolecules consist of three incompatible segments, and as a result, more complicated phase behaviour has been found.^[44] Compared with the

AB binary copolymers, the mesophase morphologies of ABC ternary copolymers are dictated not only by the two independent volume fractions (f_A , f_B), the three interaction parameters between the distinct blocks (χ_{AB} , χ_{BC} , χ_{AC}), the overall number of monomers per chain (N), but also by the architecture of the molecule (linear, star-shaped or cyclic). In the case of the linear triblock copolymers, the sequence of the blocks (ABC, ACB or BAC) is an additional variable.^[45]

Figure 1.7 shows a phase sequence of linear ABC triblock copolymers, where $\chi_{AB} \approx \chi_{BC} < \chi_{AC}$,^[46-50] by increasing the volume fraction of the middle block (f_B) while keeping the volume fraction of the two end segments equal ($f_A = f_C$).

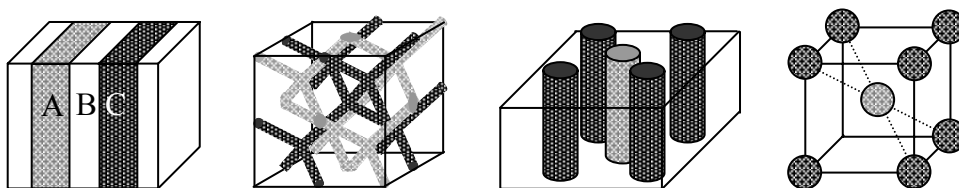


Figure 1.7. Selected morphologies of linear ABC triblock copolymers. From left to right the volume fraction of the middle block (white) is increased.

In another case of linear triblock copolymers, where the incompatibilities between the end blocks and the middle block are more unfavourable than, or comparable to, the interaction between the end components (χ_{AB} , $\chi_{BC} > \chi_{AC}$), a number of novel morphologies can be formed (Figure 1.8).^[51-57]

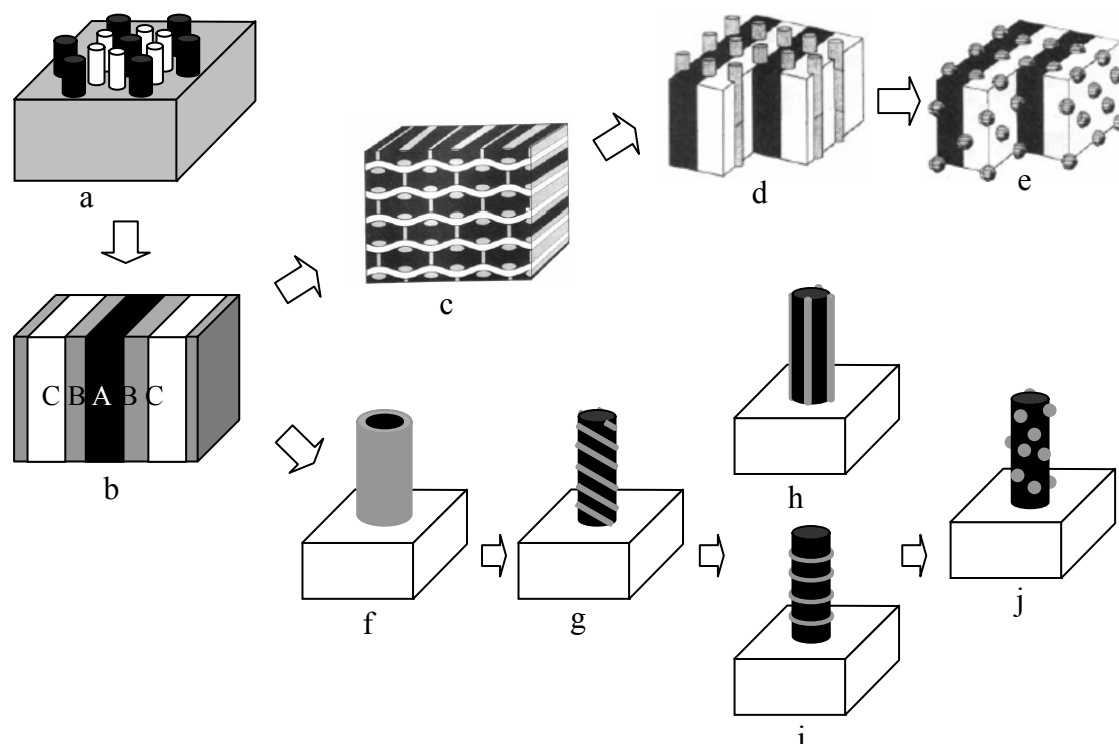


Figure 1.8. Selected morphologies of ABC linear triblock copolymers: (a) hexagonal morphology with A and C forming two kinds of cylindrical microdomains in a B matrix; (b) triple layer structure; (c) “knitting pattern” morphology; (d) B cylinders located at the interface between A/C lamellae; (e) B spheres located at the interface between A/C lamellae; (f) core-shell columnar morphology; (g) helical morphology; (h, i) cylinders on cylinder morphology; (j) spheres on cylinder morphology.

While a lot of work concerning linear ABC triblock copolymers has been published, only relatively few studies on ternary star-shaped triblock copolymers have been carried out.^[58-60] In contrast to the linear analogues,^[40] the star-shaped topology of such copolymers leads to square (Figure 1.9a) and hexagonal morphologies (Figure 1.9b) composed of three sets of columns. Each column contains one of the distinct components. In such morphologies the junction points of the three components are located along lines. This is significantly different from the linear triblock copolymers which have the junction points located in planes. However, under some special conditions, core-shell morphologies^[60] and lamellar structures with cylinders embedded in one of the lamellae (Figure 1.9c)^[58] can also be formed.

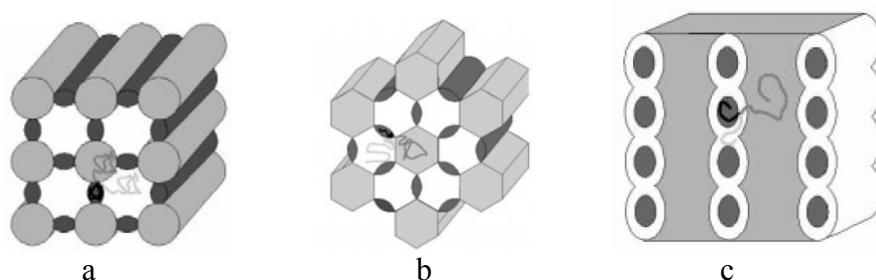


Figure 1.9. Selected morphologies of ABC star-shaped copolymers: (a) square morphology; (b) hexagonal morphology; (c) lamellar morphology.

1.5 Mesophase morphologies of low molecular weight ternary block molecules

Recently, several efforts have been made to combine rod-like (calamitic) segments and amphiphilicity to form new types of amphotropic molecules. These molecules consist of three distinct components, i.e., a hydrophilic part, a flexible hydrophobic part and a rod-like core.^[6a] Depending on the way of the combination of these three parts, three different linear and T-shaped molecular topologies have been reported.

1.5.1 Linear triblock molecules with a rod-like central core

In such molecules, a hydrophilic group is grafted to one terminal of the rigid core, and a hydrophobic group is grafted to the other. Smectic A, smectic C bilayer structures, where the hydrophilic groups are confined between the layers as well as an oblique columnar phase have been recognized.^[61-63] The linear combination of the distinct incompatible parts favours the parallel alignment of the rigid core. The segregation of the rigid cores from the hydrophilic and hydrophobic parts of the molecules additionally stabilises the lamellar organisation. Consequently, the smectic bilayer structure is stabilised significantly. Up to now, the columnar phases have only been found for compounds with long hydrophobic chains. It was supposed that the large volume of these chains caused the collapse of the smectic layers with formation of ribbons arranged in an oblique lattice.^[64]

1.5.2 T-shaped ternary tetrablock molecules with a rod-like central core

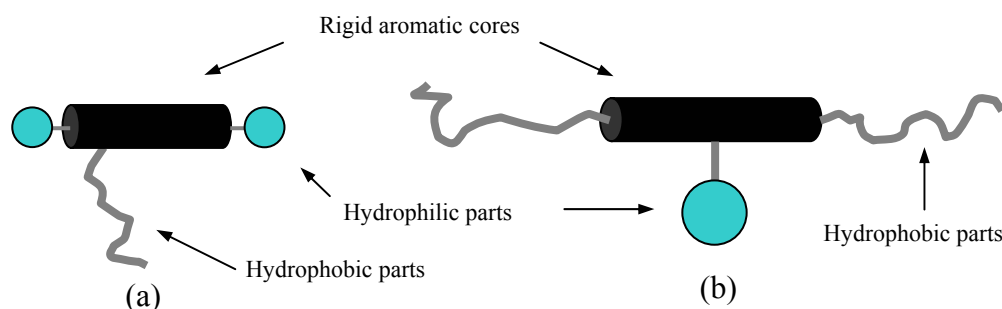


Figure 1.10. Schematic view of two topologies of ternary block molecules: (a) bolaamphiphiles with lateral lipophilic chains; (b) T-shaped facial amphiphiles with lateral polar chains.

Molecules consisting of a rigid and linear p-terphenyl or biphenyl unit, and two types of incompatible (hydrophilic and hydrophobic) groups attached to the termini and to a lateral position can be considered as ternary block molecules. There are two possible combinations:

1. The hydrophobic group is grafted to the lateral position and the hydrophilic groups are grafted to the terminal positions of the rod-like core (bolaamphiphile with a nonpolar lateral chain, Figure 1.10a).
2. The hydrophobic groups are grafted to both terminal positions of the calamitic core while the hydrophilic group is in the lateral position (facial amphiphiles, Figure 1.10b).

In both cases two important self-organisation forces, the parallel alignment of the rigid cores and the segregation of the hydrophilic and hydrophobic parts, are combined in such a manner that they are in competition with each other, and as a result, novel mesophases are expected.

1.5.2.1 Bolaamphiphiles with lateral nonpolar chains

Compounds **I/n** (Figure 1.10) are the first reported samples of the type 1 molecules (bolaamphiphiles).^[65-67] Herein, the strongest attractive forces are positioned at both terminal ends of the rigid calamitic core. The strong segregation of the polar groups from the biphenyl cores into different sub-layers leads to a dramatic stabilization of smectic A phase. Hence, compound **I/0** without any lateral substituents forms an extremely stable SmA phase. Introduction of a lateral alkyl chain and successive increase of its length leads to the disturbance of the layer structure. The stability of the SmA phase is significantly reduced for the methyl and propyl substituted compounds ($n \leq 3$). A SmA phase with a strongly disturbed layer structure (SmA^+) has been identified for compounds with longer lateral chains ($3 \leq n \leq 7$). Further elongation of the lateral alkyl chain leads to a complete collapse of the layer structure and to the formation of a sequence of novel mesophases. A phase sequence $\text{Col}_r (c2mm) - \text{Col}_r (p2gg) - \text{Col}_h (p6mm)$ has been observed (Figure 1.11).

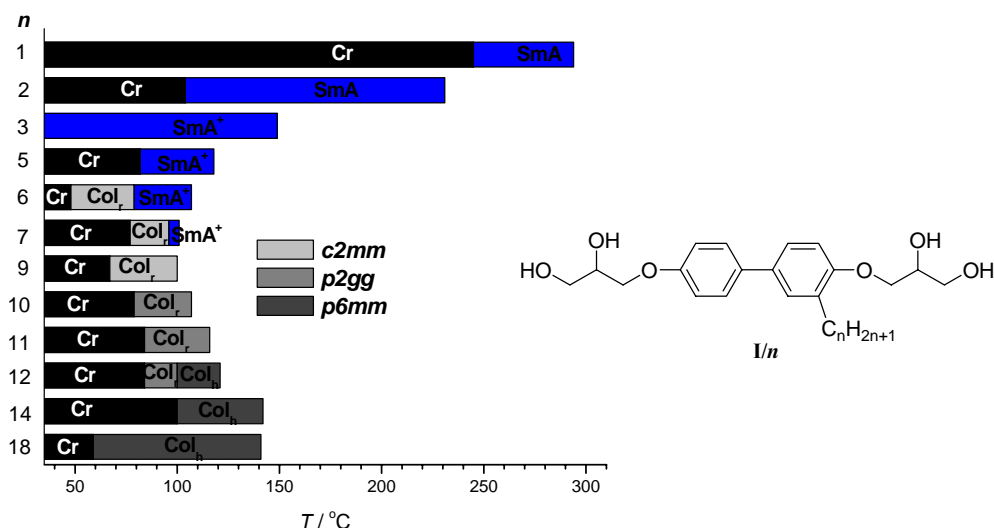


Figure 1.11. Mesophase types and transition temperatures ($T/^{\circ}\text{C}$) of the bolaamphiphiles **I/n**.

More recently fluorinated lateral alkyl chains were introduced to replace the hydrocarbon chains.^[67-70] The stronger incompatibility of the fluorinated chains with the other parts of the molecule gives rise to higher mesophase stabilities. Furthermore the larger volume of the CF_2 groups with respect to the CH_2 groups leads to the occurrence of additional mesophases. Besides the mesophases found in the hydrocarbon compounds, Col_{sq} ($p4mm$) and different Col_r ($c2mm$, $p2gg$) phases, a novel type of lamellar phases (Lam_{iso} , Lam_{N} , Lam_{Sm}) have been recognized (Figure 1.11). In the columnar mesophases the bolaamphiphilic cores and the terminal polar groups form networks of cylinder walls which enclose the columns formed by the lipophilic lateral chains. Hence, the alkyl chains are confined into a constrained environment and the space required by them with respect to the length of the bolaamphiphilic cores is limited. Therefore, enlarging the volume fraction of the lateral chains leads to a change of the cross-section shape of the cylinders (rhomb -- square -- pentagon -- hexagon -- stretched hexagon -- giant pentagon) which leads to the observed columnar mesophases. In these columnar mesophases, the space is divided into three distinct sets of columns (non-polar columns,¹ ribbons formed by the aromatic units and hydrophilic columns) which is similar to the morphologies of the star-shaped ABC triblock copolymers. These columnar mesophases are also distinct from those observed for the other low molecular weight molecules (the conventional amphiphiles, disc-like molecules and polycatenar molecules) where the columns are surrounded by a continuum of the solvent (lyotropic systems) or by a continuum of the fluid alkyl chains (thermotropic liquid crystals). Upon further enlarging the volume fraction of the lateral chains, the lipophilic cylinders expand and fuse with formation of infinite layers. The bolaamphiphilic cores are organized into separate layers in which the aromatic cores are aligned parallel to the layer planes. The stepwise inset of orientational and positional order within these sublayers leads to different subtypes of these lamellar phases (Lam_{iso} , Lam_{N} , Lam_{Sm}).

¹ In the case of semi-perfluorinated alkyl chains, an additional segregation of the hydrocarbon part and the fluorocarbon segment can be discussed.

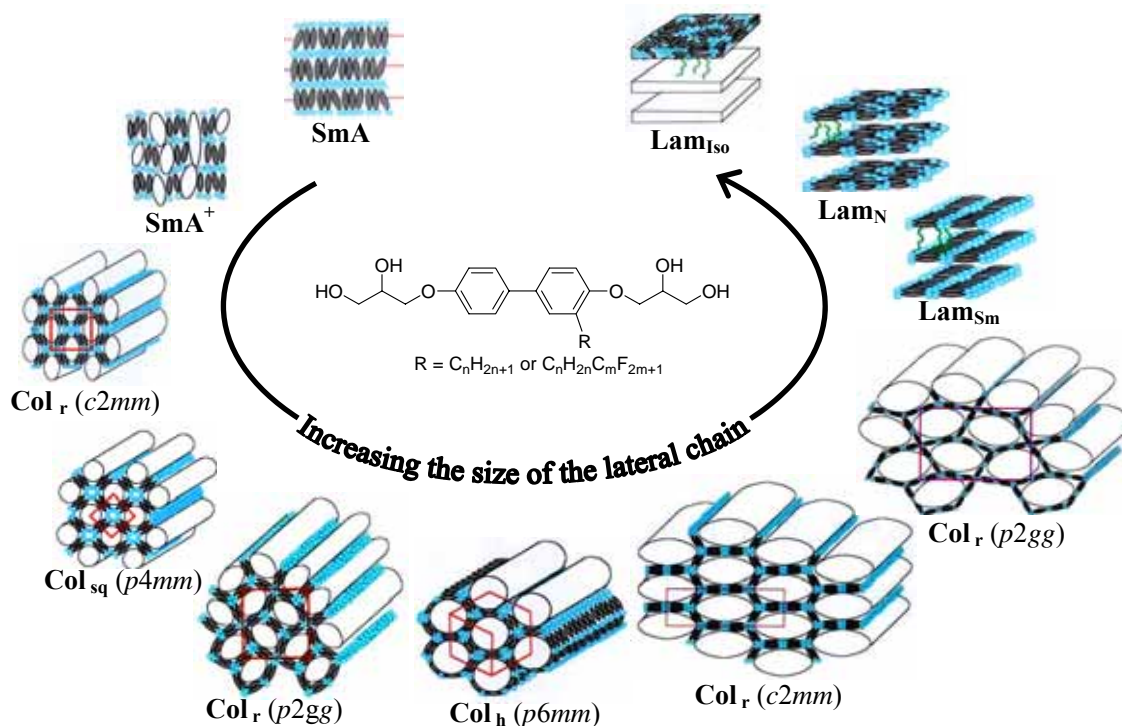


Figure 1.12. Transition between two different types of layer structures (SmA and Lam_{iso}) with columnar phases as intermediate phases as observed for rigid bolaamphiphiles with nonpolar lateral chains.

1.5.2.2 T-shaped amphiphiles with a polar lateral chain (“facial amphiphiles”)

This type of multiblock amphiphiles has reversed positions of nonpolar and polar chains with respect to the bolaamphiphiles discussed above. At first, a stabilisation effect was found for the attachment of a small lateral polar group to a calamitic terphenyl unit with two terminal alkyl chains.^[71] Recently, a variety of such compounds which contain polyether chains, crown ether units, amide groups and 1,2-diol units as polar groups have been synthesised. Alkyl chains as well as semi-perfluorinated alkyl chains were used as non-polar terminal chains; biphenyl, p-terphenyl, m-terphenyl and p-quinquiphenyl units were explored as rigid cores.^[72] The series of diol compounds **II/n** (Figure 1.13) is one representative example.^[67, 73-75]

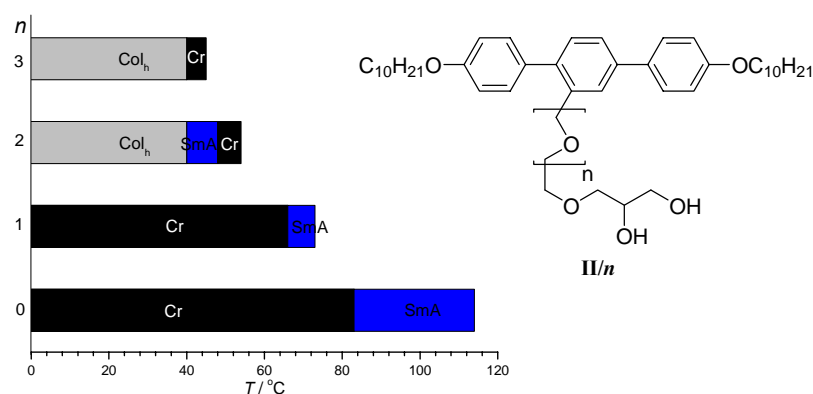


Figure 1.13. Mesomorphic properties of compounds **II/n** as a function of the length of the lateral polar chain.

Figure 1.13 summarises the liquid crystalline properties of compounds **II**/*n* depending on the length of the lateral hydrophilic chain. Compounds **II**/0 and **II**/1 only have a SmA mesophase. The stability of this SmA phase is reduced when the number of oxyethylene unit is increased. For molecules with three or four oxyethylene units within the lateral chain, new mesophases were observed. In compound **II**/2, for the low temperature columnar phase, a non-centred rectangular columnar structure was proposed on the basis of power X-ray diffraction and microscopic investigation. The formation of the columnar phase upon elongating the polar lateral chain was suggested to be due to the increased steric hindrance of the lateral groups which destabilizes the smectic layer structure and leads to a strong segregation of the hydrophilic and hydrophobic groups. Therefore, the polar groups organise in separate cylindrical regions, which leads to the collapse of the smectic layers. The regular packing of the polar groups affords a two dimensional lattice (columnar mesophase) as shown in Figure 1.14. Recent reinvestigation of the mesophases of compound **II**/2 by X-ray diffraction of aligned samples, however, indicated the presence of a hexagonal columnar phase.^[76]

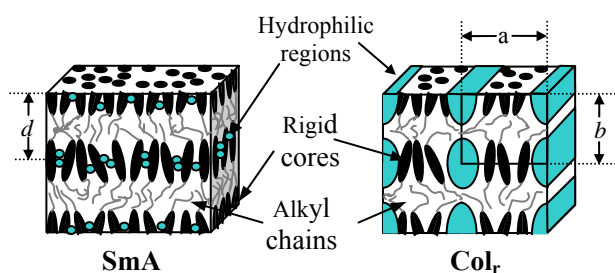
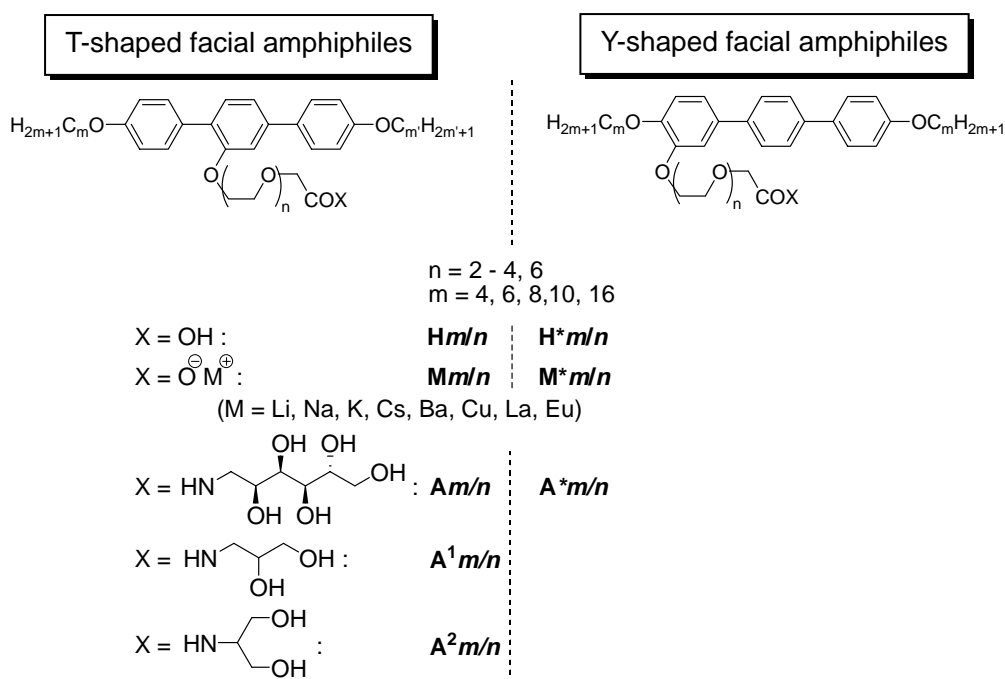


Figure 1.14. Schematic illustration of the structures of the SmA phase and Col_r phase of compound **II**/2 as proposed in ref. ^[57, 62-64]

Further investigations of compound **II**/2 shows that three different solvent-induced mesophases (lyotropic mesophases) can be formed by the addition of protic solvents (H₂O or formamide). On the other hand, the addition of a lipophilic solvent (dodecane) destabilises the columnar phases and replaces them by a smectic layer structure (SmA phase). The addition of protic solvents is expected to lead to an increased volume of the hydrophilic groups and to an enhancement of the attractive interactions between these groups as well. Both facilitate the formation of novel mesophases. The lipophilic solvent increases the volume of the hydrophobic parts which stabilize the smectic layer structure. However, due to several experimental difficulties (inhomogeneity of the sample, evaporation of solvent or taking up of water during investigation of the aligned samples), it was impossible to investigate these lyotropic mesophases in more detail.

1.6 Objective

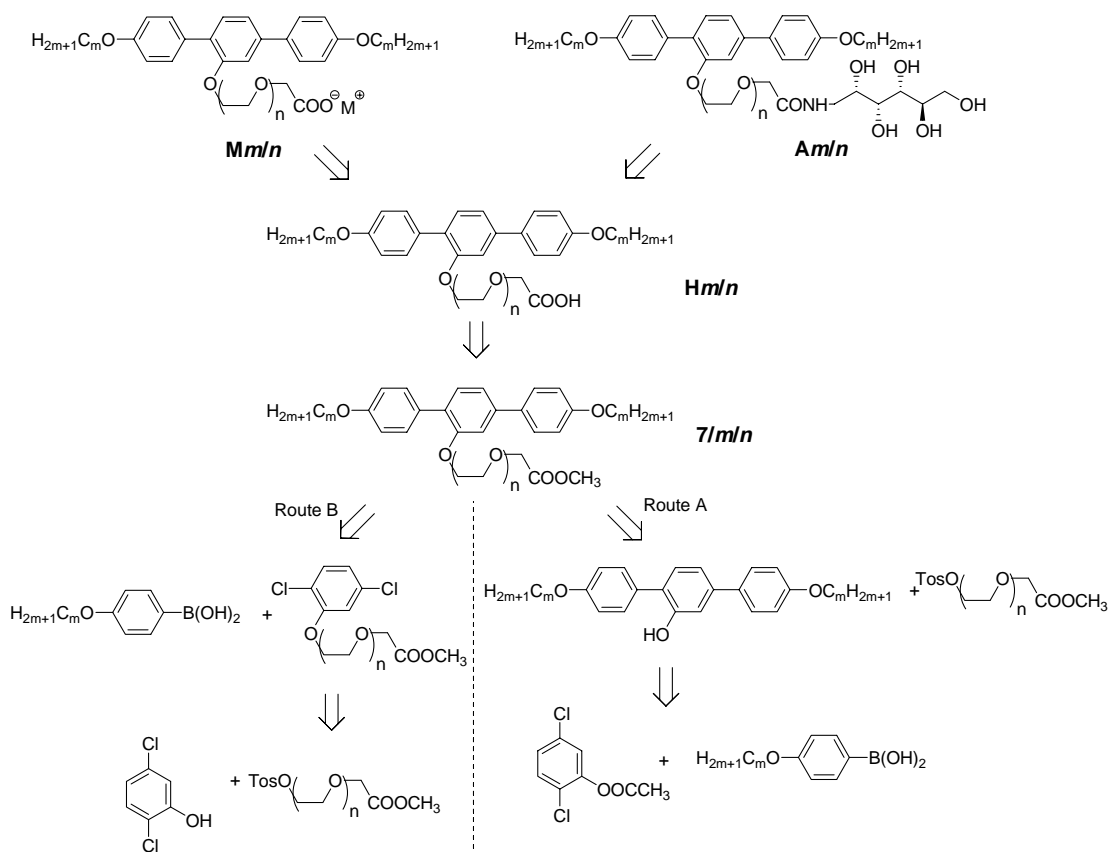
In order to clarify the structures of these liquid crystalline phases (protic solvent-induced mesophases of **II/n**), series of novel T-shaped and Y-shaped facial amphiphiles are synthesised and investigated. The main aim is to increase the size of the polar lateral group to get the mesophases related to those of the solvent-induced mesophases of compounds **II/2** and **II/3** in the mixed systems with protic solvents. Therefore, series of facial amphiphiles with polar lateral groups consisting of long oligo(oxyethylene) units, carboxylate end groups as well as carboxylic acids and carbohydrate derivatives (1-acylamino-1-deoxy-D-sorbitol derivatives) are synthesised. The influence of the length of the oligo(oxyethylene) segments and the type of cations on the mesophase behaviour is studied systematically. Furthermore, the position of the lateral substituents is changed (Y-shaped facial amphiphiles) and some variation is made for the terminal alkyl chains (different length, branched chains, non-symmetric distribution of the alkyl chains). In this way, the influence of the amphiphilic segregation and the parallel arrangement of the rigid p-terphenyl cores on the mesophase self-organisation behaviour are investigated in detail.



Scheme 1.1. General formula of the target molecules and their designation.

2 Synthesis

The synthetic strategy to obtain the T-shaped amphiphiles with a lateral polar chain attached to the central benzene ring is outlined in Scheme 2.1. Two synthetic routes were used to synthesize the p-terphenyl¹ derivatives **7/m/n**. In both synthetic routes, the key step is a Suzuki coupling reaction.^[86, 92] Due to the recent developments of the C-C coupling reaction, arylchlorides, which are commercially available at relatively low cost can, nowadays, be used.^[82] In route A, a p-terphenyl core was built up at first by the reaction of 2,5-dichlorophenyl acetate with appropriate 4-alkoxybenzene boronic acids. After deprotection, the lateral chain was attached by an etherification reaction. In route B, the polar chain was attached to the 2,5-dichlorobenzene unit at first, then the Suzuki cross coupling was carried out. In this way, the methylesters **7/m/n** were obtained, which were then hydrolysed to the corresponding carboxylic acids **Hm/n**. The obtained carboxylic acids were used to produce the alkali metal (**Li**, **K**, **Cs**), alkali-earth metal (**Ba**), transition metal (**Cu**) and rare earth metal (**La**, **Eu**) carboxylates (Scheme 2.13). The carboxylic acids **Hm/n** were also used to synthesize the amides (**A**, **A**¹, **A**²) (Scheme 2.14).



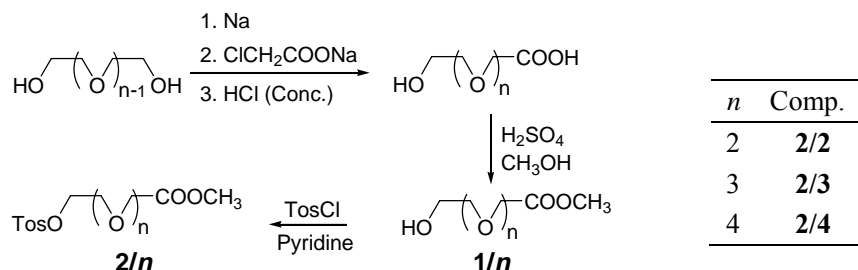
Scheme 2.1. Retrosynthetic route of the target molecules.

¹ p-Terphenyl is always (1,1',4',1'')-terphenyl.

The Y-shaped amphiphiles **M^{*}m/n**, **H^{*}m/n** and **A^{*}m/n** having the lateral polar chain at an outer benzene ring of the p-terphenyl core were obtained in a similar way as route A, but 4-alkoxy-3-benzyloxy-iodobenzene and 4'-alkoxybiphenyl-4-boronic acid were used as the starting materials to build up the p-terphenyl unit *via* Suzuki coupling reaction.

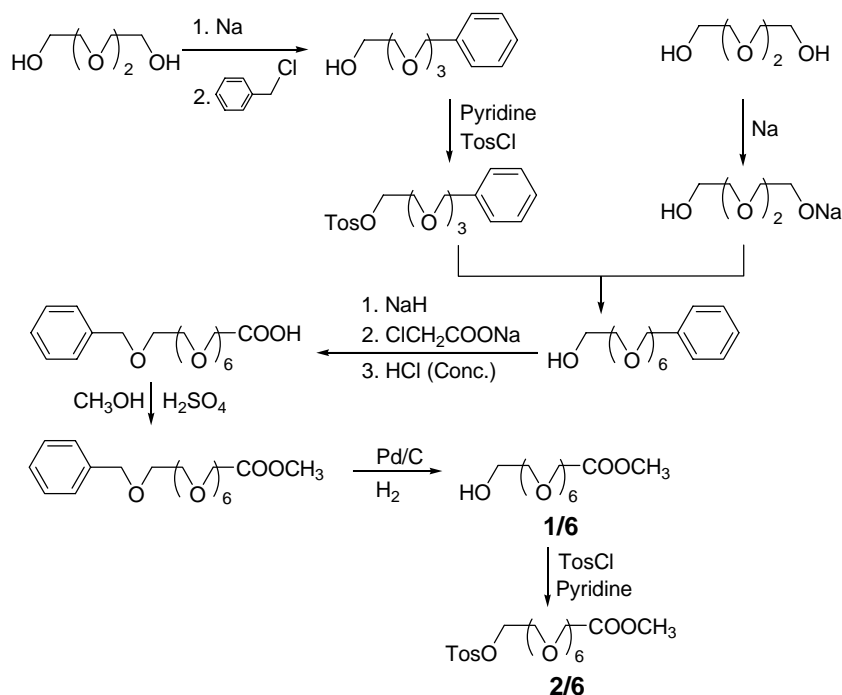
2.1 Synthesis of methyl ω-(4,4''-dialkoxy-p-terphenyl-2'-yloxy)oligo(oxyethylene)yl acetates **7/m/n**

2.1.1 Synthesis of methyl ω-tosyloxyoligo(oxyethylene)yl acetates **2/n**



Scheme 2.2. Synthesis of methyl ω-tosyloxyoligo(oxyethylene)yl acetates **2/n** ($n = 2 - 4$).

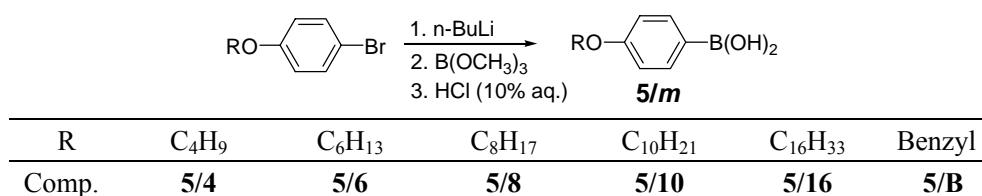
The methyl ω-hydroxyoligo(oxyethylene)yl acetates **1/2** - **1/4** were synthesized according to the literature method with slight modifications.^[77] Sodium was dissolved in an excess of the appropriate oligoethylene glycol to form the mono sodium alcoholate, which reacted with sodium chloroacetate to give the sodium ω-hydroxy[oligo(oxyethylene)yl]acetate. The excess oligoethylene glycol was removed in vacuum. After acidification with concentrated HCl, the carboxylic acid group was protected by formation of the methyl esters **1/n**. The target methyl ω-tosyloxy[oligo(oxyethylene)yl] acetates **2/n** were obtained by the tosylation of the hydroxy group of **1/n** in the presence of pyridine.^[78]



Scheme 2.3. Synthesis of the methyl ω -tosyloxy[sexi(oxyethylene)yl] acetate **2/6**.

Another synthetic route (Scheme 2.3) was used to synthesize compound **1/6** which has six oxyethylene units within the chain. At first, triethylene glycol was mono-protected by the reaction of the mono sodium alcoholate of triethylene glycol with benzyl chloride. The free hydroxyl group was tosylated^[78] and the resulting tosylate reacted with the mono sodium alcoholate of triethylene glycol to yield the mono benzyl protected hexaethylene glycol. The corresponding sodium alcoholate was obtained by addition of sodium hydride. After that, sodium chloroacetate was used to afford the sodium ω -benzyloxy[sexi(oxyethylene)yl] acetate which was further acidified with concentrated HCl and the resulting carboxylic acid was esterified to give the methyl ester. Then the benzyl group was removed by palladium catalyzed hydrogenation reaction to form compound **1/6**^[79] which was used for the tosylation reaction to afford compound **2/6**.

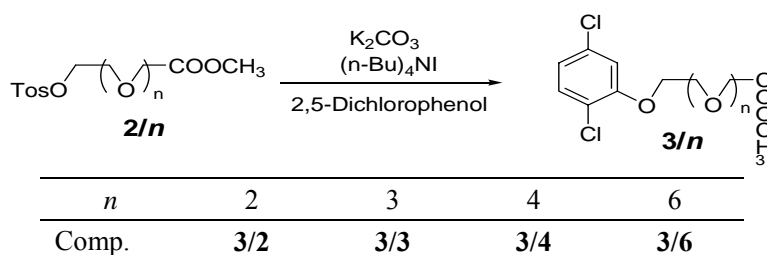
2.1.2 Synthesis of p-alkoxybenzeneboronic acids **5/m**



Scheme 2.4. Synthesis of p-alkoxybenzeneboronic acids **5/m**.

The p-alkoxybenzeneboronic acids **5/m** and p-benzyloxybenzeneboronic acid **5/B** were synthesized from the corresponding 4-bromoalkoxybenzenes and 4-benzyloxybromobenzene respectively by the standard method of halogen-metal-exchange reaction using n-BuLi,^[80] followed by reaction with trimethylborate and hydrolysis with hydrochloric acid (Scheme 2.4).

2.1.3 Synthesis of methyl ω -(2,5-dichlorophenyl)[oligo(oxyethylene)yl] acetates **3/n**



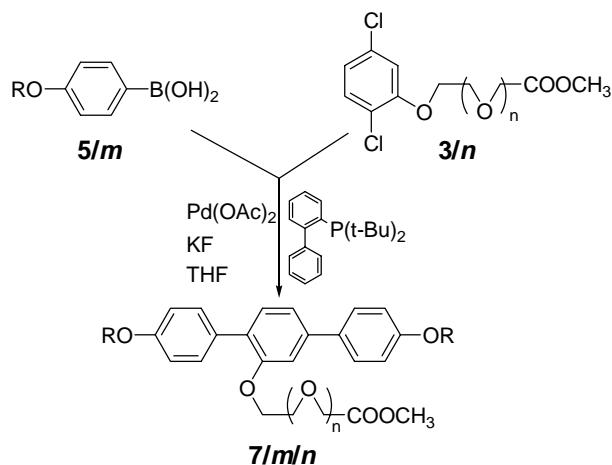
Scheme 2.5. Synthesis of the methyl ω -(2,5-dichlorophenyl)[oligo(oxyethylene)yl] acetates **3/n**.

The etherification^[81] of **2/n** with 2,5-dichlorophenol in the presence of K₂CO₃ as the base gave the methyl ω -(2,5-dichlorophenyl)[oligo(oxyethylene)yl] acetates **3/n**.

2.1.4 Synthesis of methyl ω -(4,4''-dialkoxy-p-terphenyl-2'-yloxy)oligo(oxyethylene)yl acetates **7/m/n**

Three synthetic routes were employed to synthesize the methyl acetates **7/m/n**. The key

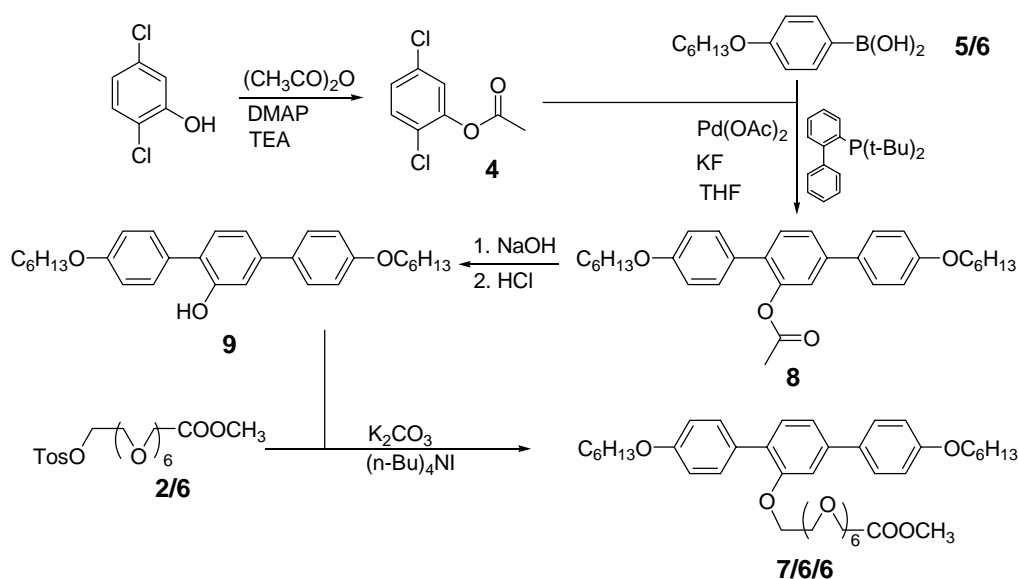
reaction was the palladium catalysed C-C coupling reaction of the 1,4-dichlorobenzene derivatives **3/n** (Scheme 2.5) or **4** (Scheme 2.7) with the p-alkoxybenzeneboronic acids **5/m** which was carried out with Pd(OAc)₂, 2-(di-*tert*-butylphosphino)biphenyl and KF in THF. The yield of this reaction varied between 70 % to 80 %.^[82]



R	n	Comp.
C ₄ H ₉	2	7/4/2
C ₄ H ₉	3	7/4/3
C ₄ H ₉	4	7/4/4
C ₆ H ₉	3	7/6/3
C ₆ H ₉	4	7/6/4
C ₆ H ₉	6	7/6/6
C ₈ H ₁₇	3	7/8/3
C ₁₀ H ₂₁	2	7/10/2
C ₁₀ H ₂₁	3	7/10/3
C ₁₀ H ₂₁	4	7/10/4
C ₁₀ H ₂₁	6	7/10/6
Benzyl	3	7/B/3
Benzyl	4	7/B/4

Scheme 2.6. Synthesis of T-shaped compounds **7/m/n** (m = 4, 6, 8, 10) and the corresponding 4,4''-dibenzyl-p-terphenyl derivatives **7/B/n** (R = benzyl).

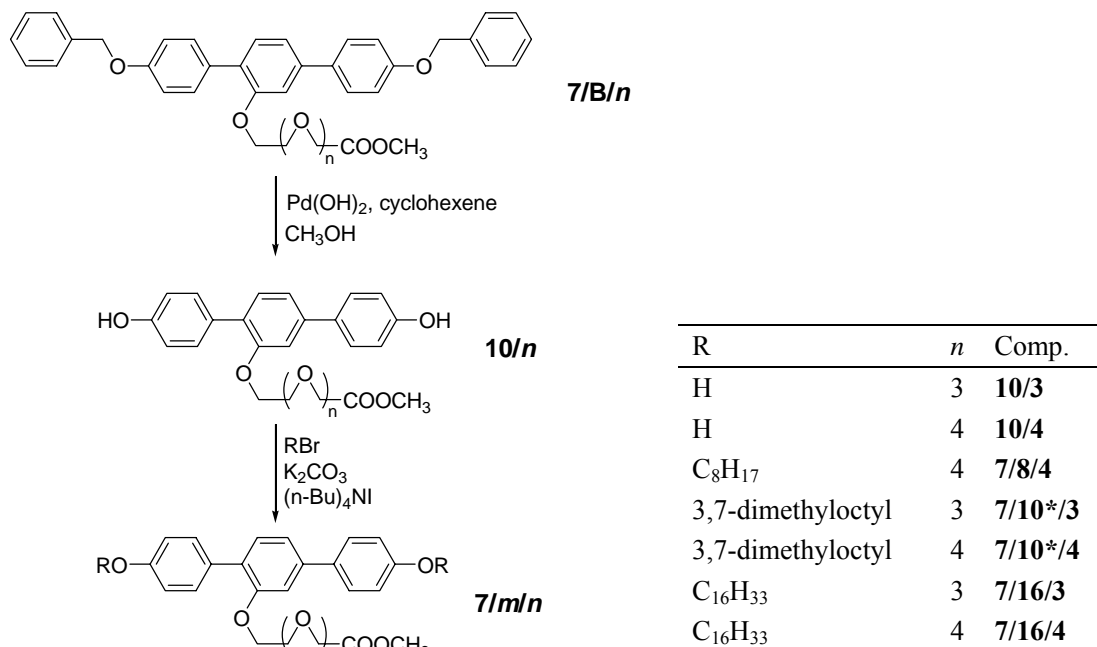
Most compounds of series **7/m/n** were synthesized according to Scheme 2.6. The hexaethylene glycol derivative **7/6/6** was synthesized according to Scheme 2.7. 4-Hexyloxybenzeneboronic acid (**5/6**) and 2,5-dichlorophenyl acetate (**4**) were coupled, and the resulting p-terphenyl compound **8** was hydrolysed by NaOH, sequentially acidified by HCl to remove the acetyl protecting group. Afterwards the obtained phenol **9** was etherified with the tosylate **2/6** to give the target molecule **7/6/6**.



Scheme 2.7. Synthesis of compound **7/6/6**.

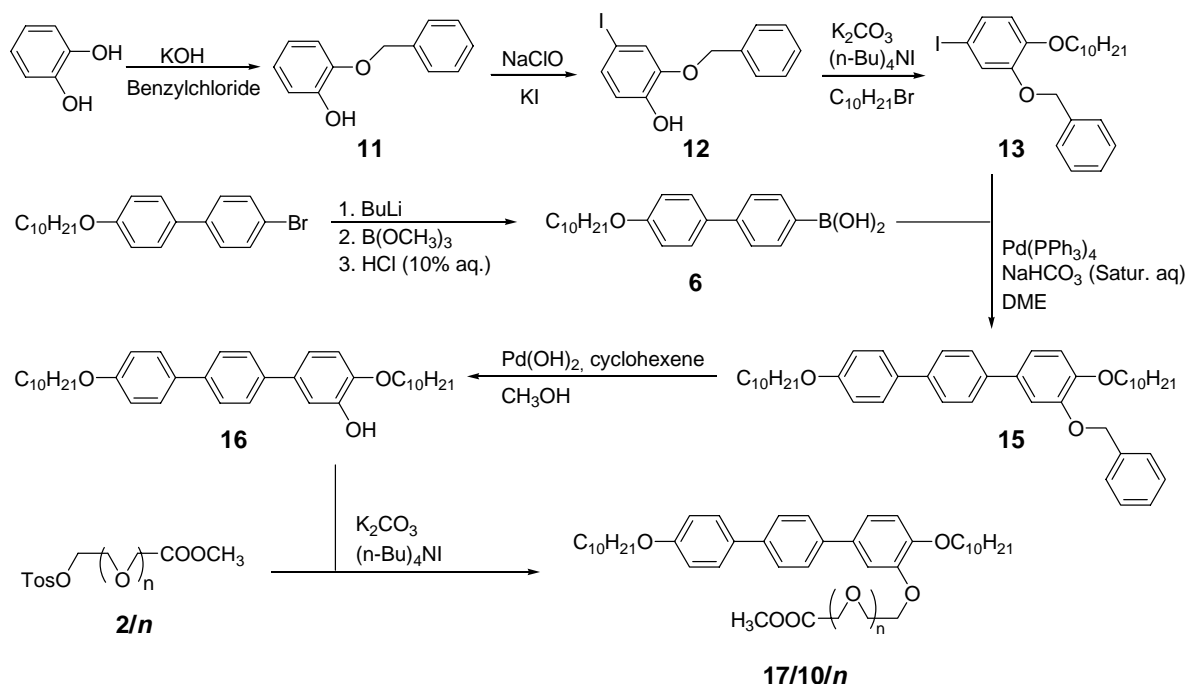
The coupling reactions between 4-hexadecyloxybenzeneboronic acid (**5/16**) and the

dichlorobenzene derivatives **3/n** were unsuccessful. Thus, the dibenzyl protected p-terphenyl derivatives **7/B/n** were synthesized at first. After removal of the protecting benzyl groups, the resulting 2'-substituted p-terphenyl-4,4''-diol derivatives **10/n** were etherified with 1-bromohexadecane (Scheme 2.8). In the same way, the 3,7-dimethyloctyloxy substituted compounds **7/10*/n** and one octaoxy substituted compound **7/8/4** were also synthesized.



Scheme 2.8. Synthesis of methyl acetates **7/m/n** with $m = 8, 16$ and $R = 3,7$ -dimethyloctyl.

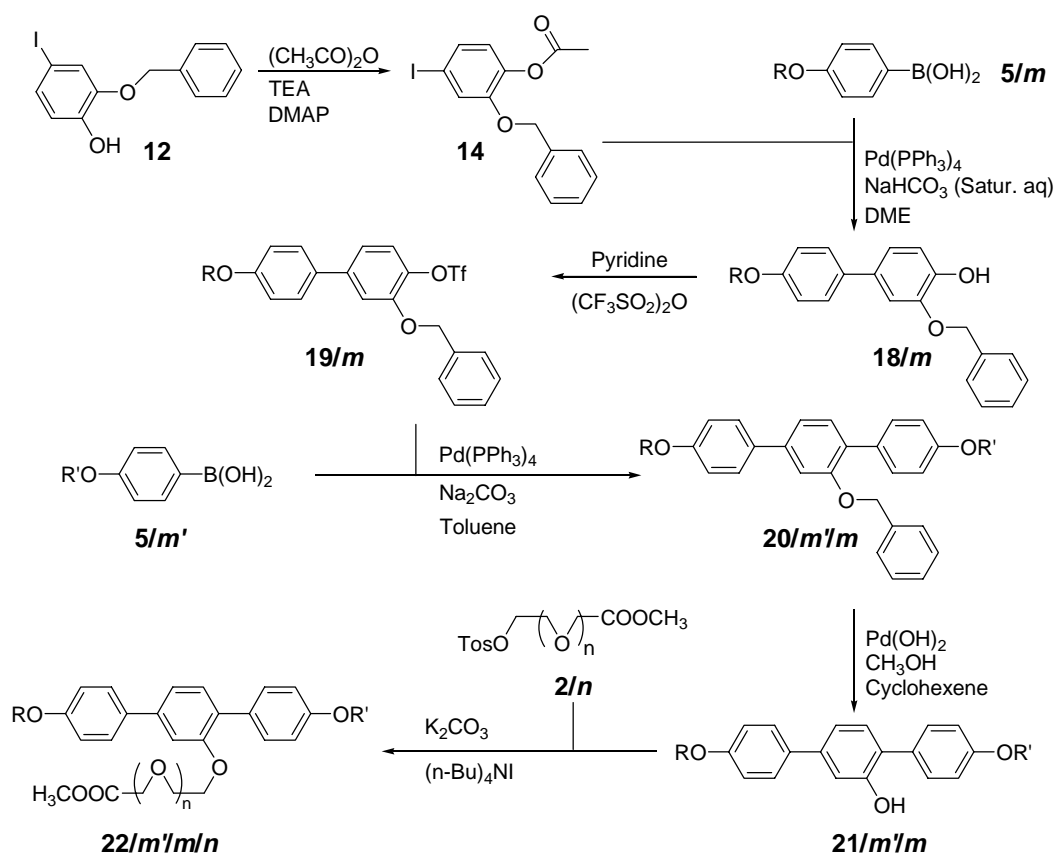
2.2 Synthesis of methyl ω -(4,4''-didecyloxy-p-terphenyl-3-yl)oligo(oxyethyl-ene)yl acetates (**17/10/n**)



Scheme 2.9. Synthesis of the methyl ω -(4,4''-didecyloxy-p-terphenyl-3-yl)oligo(oxyethylene)yl acetates **17/10/n** with $n = 3, 4$.

As shown in Scheme 2.9, the 2-benzyloxyphenol **11** was iodinated in the para position to give compound **12**.^[83] Sequentially the decyl chain was introduced by etherification reaction to yield compound **13**. The 4-decyloxybiphenyl-4'-boronic acid **6** was synthesized from 4-bromo-4'-decyloxybiphenyl by halogen-metal-exchange reaction as described for compound **5/m** (Scheme 2.4). The $\text{Pd}(\text{PPh}_3)_4$ catalysed coupling reaction^[84] of the iodide **13** with the boronic acid **6** afforded 3-benzyloxy substituted p-terphenyl compound **15**. After removal of the protecting benzyl group by hydrogenation. The obtained phenol **16** was reacted with the tosylates **2/n** to give the products **17/10/n**.

2.3 Synthesis of methyl ω -(4,4''-dialkoxy-p-terphenyl-2'-yl)oligo(oxyethylene)yl acetates **22/m'/m/n** with two different terminal alkoxy chains



R	Comp.	Comp.
C ₆ H ₉	18/6	19/6
C ₁₆ H ₃₃	18/16	19/16

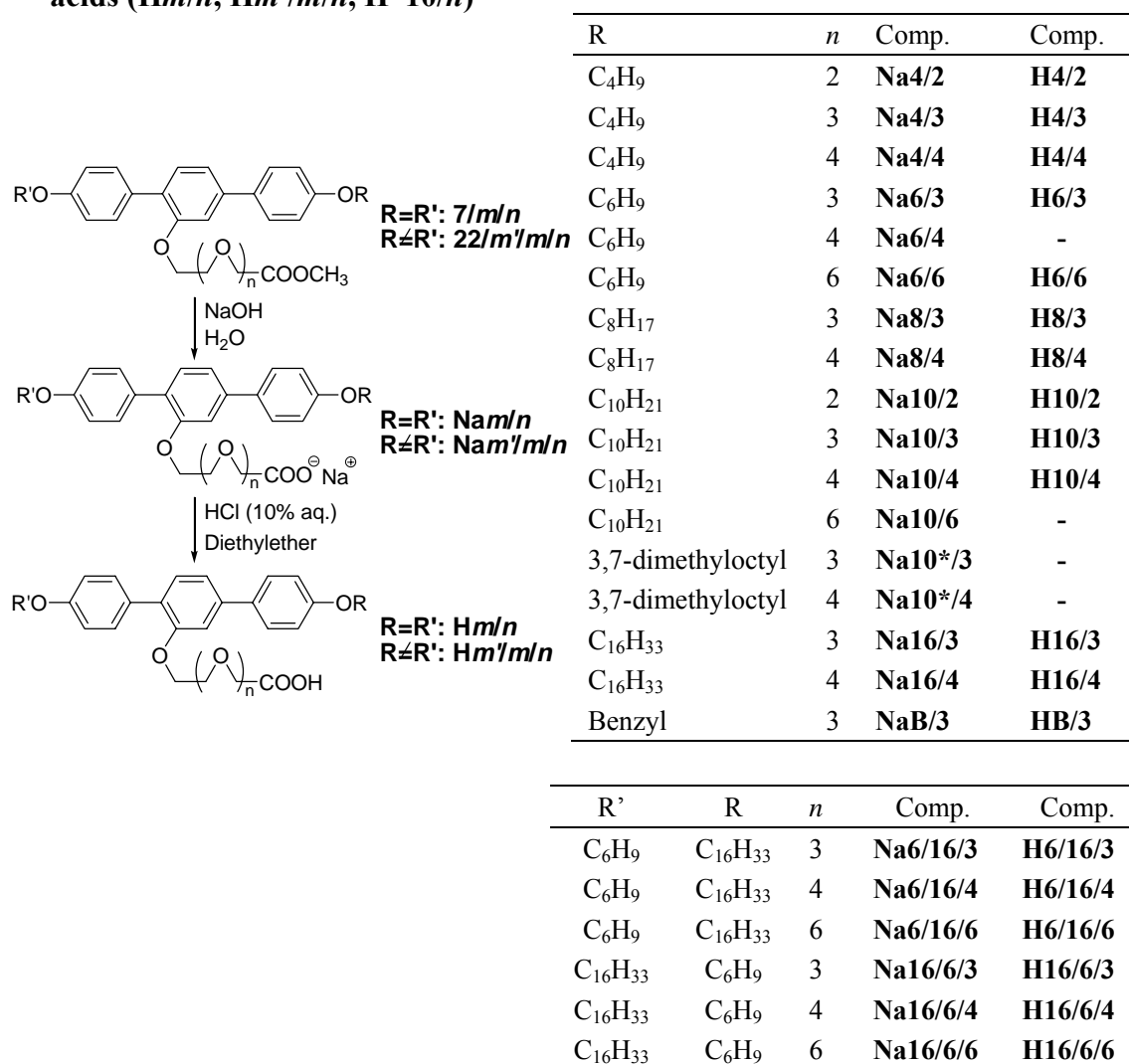
R	R	Comp.	Comp.
C ₆ H ₉	C ₁₆ H ₃₃	20/6/16	21/6/16
C ₁₆ H ₃₃	C ₆ H ₉	20/16/6	21/16/6

R'	R	n	Comp.
C ₆ H ₉	C ₁₆ H ₃₃	3	22/6/16/3
C ₆ H ₉	C ₁₆ H ₃₃	4	22/6/16/4
C ₆ H ₉	C ₁₆ H ₃₃	6	22/6/16/6
C ₁₆ H ₃₃	C ₆ H ₉	3	22/16/6/3
C ₁₆ H ₃₃	C ₆ H ₉	4	22/16/6/4
C ₁₆ H ₃₃	C ₆ H ₉	6	22/16/6/6

Scheme 2.10. Synthesis of the methyl ω -(4,4''-dialkoxy-p-terphenyl-2'-yl)oligo(oxyethylene)yl acetates **22/m'/m/n**.

As shown in Scheme 2.10, the synthesis of compounds **22/m'/m/n** also started from the iodide **12**, however the hydroxyl group was protected as acetate ester to give compound **14**. The palladium catalyzed Suzuki coupling reaction of **14** and the p-alkoxybenzeneboronic acids **5/m** gave the biphenylols **18/m** (in most cases the acetyl protecting group was removed during the coupling reaction; otherwise, it was removed by alkaline hydrolysis by means of NaOH and ethanol). Then, compounds **18/m** reacted with trifluoromethanesulfonic acid anhydride in dry pyridine to form the triflates **19/m**.^[85] The p-terphenyl compounds **20/m'/m** were obtained by C-C coupling reaction of the triflates **19/m** with the p-alkoxybenzeneboronic acids **5/m'**, with Na₂CO₃ as base, Pd(PPh₃)₄ as catalyst and dry toluene as solvent.^[86] After removal of the protecting benzyl group, the 4,4''-dialkoxy-p-terphenyl-2'-ols **21/m'/m** were obtained which further reacted with the tosylates **2/n** to afford the products **22/m'/m/n**.

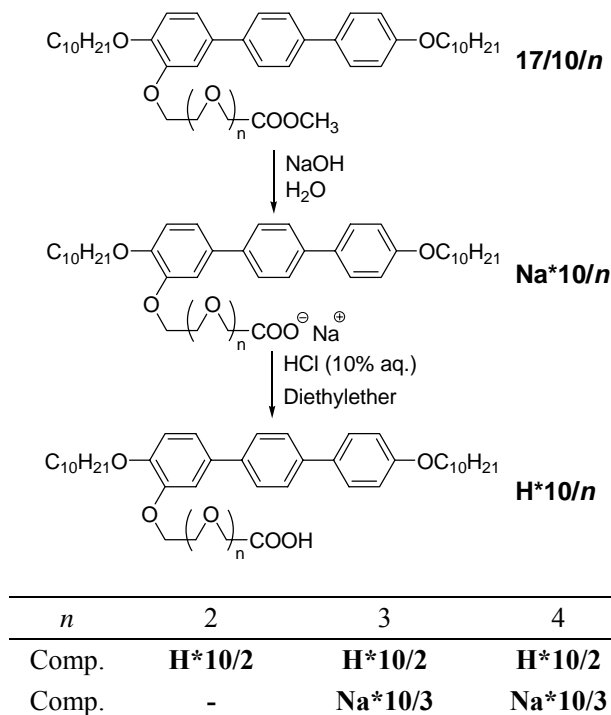
2.4 Syntheses of sodium carboxylates (Na*m/n*, Na*m'/m/n*, Na*10/*n*) and the carboxylic acids (H*m/n*, H*m'/m/n*, H*10/*n*)



Scheme 2.11. Hydrolysis of compounds **7/m/n** and **22/m'/m/n**.

The methyl esters obtained according to Schemes 2.6 to 2.10 were hydrolysed with

aqueous NaOH solution to afford the sodium carboxylates (**Nam/n**, **Nam'/m/n**, **Na*10/n**). (In the beginning, ethanol was used as solvent. However, transesterification reaction occurred instead of the hydrolysis reaction. Afterwards, water was proven to be a good solvent for the reaction.) The resulting waxy sodium salts were insoluble in water. Therefore, they were separated by filtration. In most cases, the obtained sodium salts contained traces of NaOH which could not be removed by recrystallization. Hence column chromatography on silicone gel was used to purify these sodium salts. In order to obtain the carboxylic acids (**Hm/n**, **Hm'/m/n**, **H*10/n**), the crude sodium salts were further acidified with aqueous HCl in diethylether and purified by recrystallization.

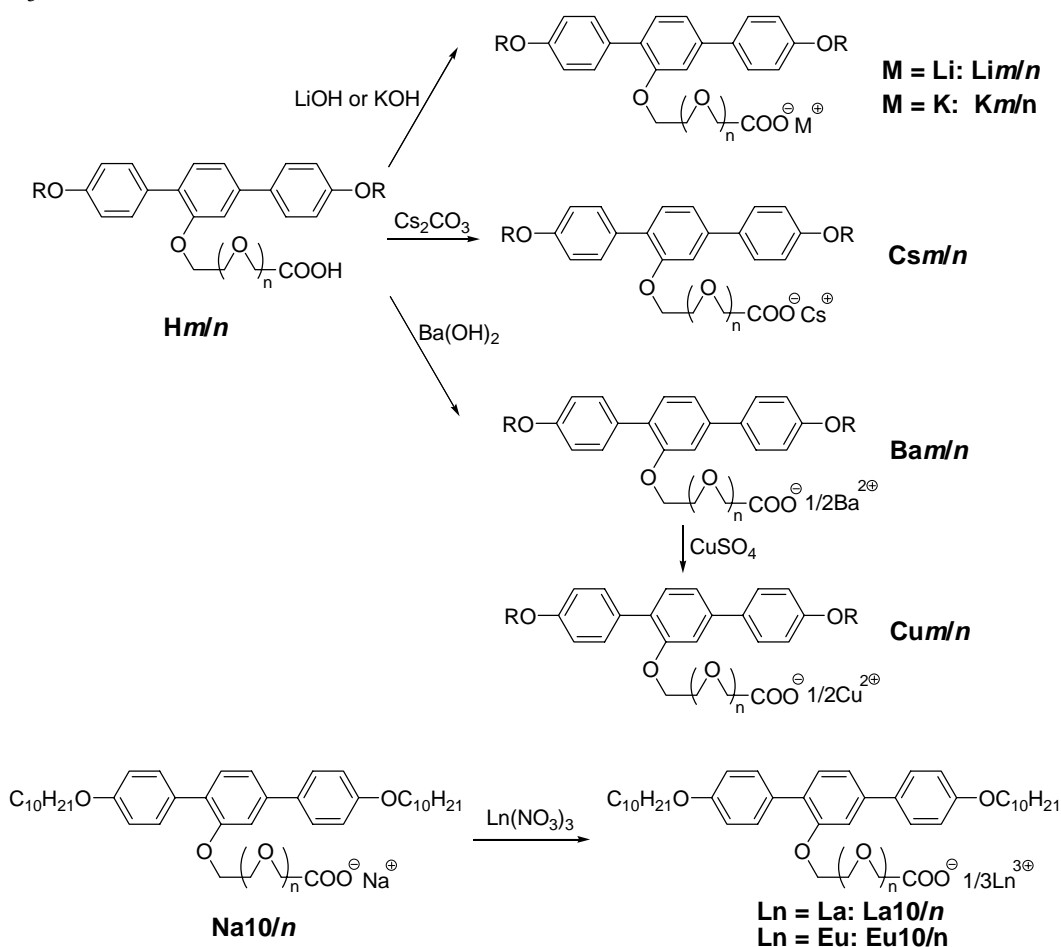


Scheme 2.12. Hydrolysis of compounds **17/10/n**.

2.5 Synthesis of carboxylates with different cations **Mm/n** ($M^+ = Li^+, K^+, Cs^+, Ba^{2+}, Cu^{2+}, La^{3+}, Eu^{3+}$)

The metal carboxylates were synthesized according to Scheme 2.13. To a solution of the carboxylic acid in diethylether, an aqueous solution of LiOH (100 % by mol), KOH (100 % by mol), Cs_2CO_3 (50 % by mol), or $Ba(OH)_2$ (50 % by mol) was added, which led to the immediate deposition of a white solid, and the reactants were kept overnight at room temperature in order to complete the reaction. In most cases stirring was avoided, because after stirring the solid became too finely distributed to be filtered upon stirring. Thus, the lithium salts (**Li10/n**), potassium salts (**K10/n**), cesium salts (**Csm/n**) and barium salts (**Ba10/n**) were synthesised. The copper(II) salts (**Cu10/n**) were obtained from the reactions of the barium salts (**Ba10/n**) with $CuSO_4$ in THF at room temperature. The lanthanum salts (**La10/n**) and one europium salt (**Eu10/3**) were formed by reactions of the sodium salts with lanthanum nitrate or europium nitrate in ethanol upon refluxing, respectively. Since, the resulting rare earth metal salts always contained traces of $NaNO_3$, the crude rare earth metal

crboxylates were dissolved in chloroform and washed with distilled water to remove the NaNO_3 .

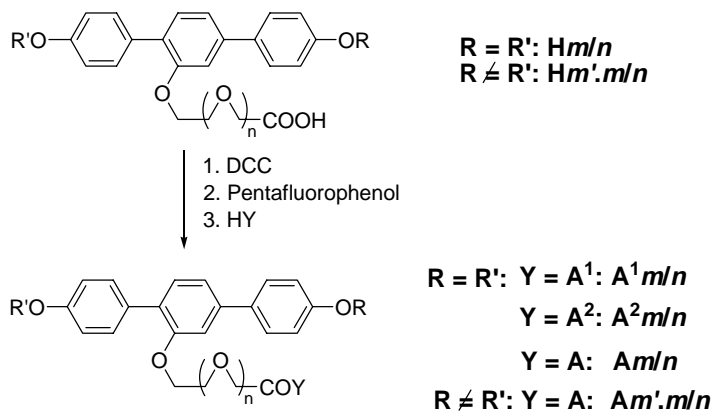


R	<i>n</i>	Comp.	Comp.	Comp.	Comp.	Comp.	Comp.	Comp.
C_6H_{13}	4	-	-	Cs6/4	-	-	-	-
$\text{C}_{10}\text{H}_{21}$	2	-	-	Cs10/2	-	-	-	-
$\text{C}_{10}\text{H}_{21}$	3	Li10/3	K10/3	Cs10/3	Ba10/3	Cu10/3	La10/3	Eu10/3
$\text{C}_{10}\text{H}_{21}$	4	Li10/4	K10/4	Cs10/4	Ba10/4	Cu10/4	La10/4	-
$\text{C}_{16}\text{H}_{33}$	3	-	-	Cs16/3	-	-	-	-

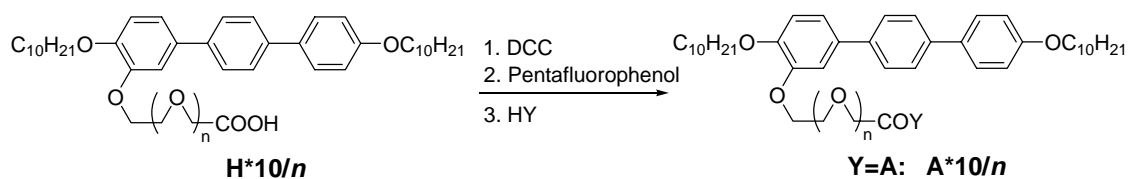
Scheme 2.13. Synthesis of the lithium salts (**Li10/*n***), potassium salts (**K10/*n***), cesium salts (**Csm/*n***), barium salts (**Ba10/*n***), copper(II) salts (**Cu10/*n***), lanthanum(III) salts (**La10/*n***) and europium(III) salt (**Eu10/3**).

2.6 Synthesis of facial amphiphiles with polyhydroxy group at the end of the lateral chain (**A**, **A¹** and **A²**)

The carboxyl group of the acid derivatives was activated by the formation of pentafluorophenyl esters, which easily underwent amidolysis with the appropriate amino alcohols added *in situ* to afford the amides. Three different amino alcohol groups (**A**, **A¹** and **A²**) were introduced in this way (Scheme 2.14).



$R = R'$	n	Y	Comp.	R'	R	n	Y	Comp.
C_4H_9	2	A	A4/2	C_6H_9	$C_{16}H_{33}$	3	A	A6.16/3
C_4H_9	3	A	A4/3	C_6H_9	$C_{16}H_{33}$	4	A	A6.16/4
C_4H_9	4	A	A4/4	C_6H_9	$C_{16}H_{33}$	6	A	A6.16/6
C_6H_{13}	3	A	A6/3	$C_{16}H_{33}$	C_6H_9	3	A	A16.6/3
C_6H_{13}	4	A	A6/4	$C_{16}H_{33}$	C_6H_9	4	A	A16.6/4
C_6H_{13}	6	A	A6/6	$C_{16}H_{33}$	C_6H_9	6	A	A16.6/6
C_8H_{17}	3	A	A8/3					
$C_{10}H_{21}$	2	A	A10/2					
$C_{10}H_{21}$	3	A ¹	A ¹ 10/3					
$C_{10}H_{21}$	3	A ²	A ² 10/3					
$C_{10}H_{21}$	3	A	A10/3					
$C_{10}H_{21}$	4	A ¹	A ¹ 10/4					
$C_{10}H_{21}$	4	A ²	A ² 10/4					
$C_{10}H_{21}$	4	A	A10/4					
$C_{10}H_{21}$	6	A	A10/6					
3,7-dimethyloctyl	3	A	A10*/3					
3,7-dimethyloctyl	4	A	A10*/4					
$C_{16}H_{33}$	3	A	A16/3					
$C_{16}H_{33}$	4	A	A16/4					



n	Y	Comp.
3	A	A [*] 10/3
4	A	A [*] 10/4

Scheme 2.14. Synthesis of facial amphiphiles with polyhydroxy groups as the end group of the lateral chain (A, A¹ and A²).

Mesophase behaviour of the synthesized compounds

In the following chapters (Chapter 3, 4, 5 and 6), the mesophase properties of the metal carboxylates (Chapter 3) followed by the molecules containing polyhydroxy groups (Chapter 4) and the carboxylic acids (Chapter 5) will be discussed. At the end, the mesophase properties of some selected binary systems will be also reported. The mesophase properties were investigated by polarising optical microscopy at first. The transition temperatures were determined by differential scanning calorimetry (DSC) and cross checked by investigation with polarising optical microscopy. Most compounds were studied by X-ray diffraction (Guinier method), and aligned samples were also investigated by X-ray diffraction using a 2D detector.

3 Liquid crystalline properties of the metal carboxylates

In this chapter, the mesophase properties of the sodium carboxylates with two identical terminal alkoxy chains will be discussed. After that will be the discussion of the mesophase properties of the alkali metal carboxylates, the alkali-earth metal carboxylates, the transition metal carboxylates and the rare earth metal carboxylates. As well as the mesophase properties of the sodium carboxylates with two different terminal alkoxy chains and the compounds with lateral polar chain attached at one of the outer benzene ring will be reported.

3.1 Sodium carboxylates

For the series of sodium carboxylates **Nam/n**, the influence of the length of the terminal alkoxy chains, the length of the lateral polar chain and the position of the lateral chain upon the mesophase properties will be scanned.

3.1.1 Influence of the length of the terminal alkoxy chains

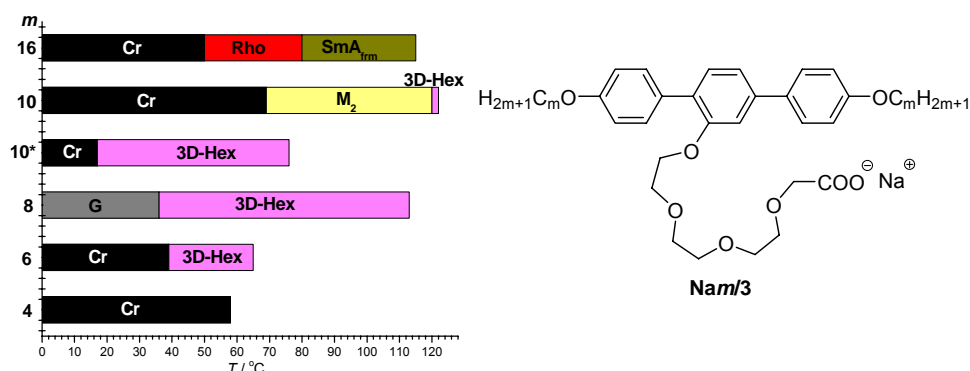


Figure 3.1. Transition temperatures ($T/^\circ\text{C}$) and mesophase types of compounds **Nam/3** depending on the length of the terminal alkyl chains (10*: 3, 7-dimethyloctyl chain).

Figure 3.1 summarises the mesophase properties of the homologous compounds **Nam/3**, which incorporate a ter(oxyethylene) unit within the lateral chain.

Compound **Na16/3** with two rather long hexadecyloxy chains shows a SmA phase as characterised by the polarising microscopy (small fan-like texture and homeotropic alignment after shearing). In comparison with the parent free carboxylic acid (compound **H16/3**, see chapter 5), the SmA phase in compound **Na16/3** is significantly stabilised by about 45°C. This is in line with the fact that the attractive forces provided by Coulomb forces are stronger than the hydrogen bonding between carboxylic acid groups. SmA phases are very often found for calamitic molecules. In these SmA phases, the calamitic cores segregate into layers which are separated by the layers of the terminal alkyl chains. Within the sub-layers of the rod-like cores, the molecules are arranged in average perpendicularly to the layer plane. It seems that the SmA phase of compound **Na16/3** has a similar smectic layer structure. However, due to the strong incompatibility between the lateral polar chain

and the other parts of the molecule, it is reasonable to assume that the polar groups will segregate into separate domains. This is confirmed by the X-ray diffraction investigations of aligned samples of compound **Na16/3** (Figure 3.2a). In the wide angle region, the diffuse scattering has maximal intensity on the equator, which indicates that the long axes of the aromatic cores have a preferred direction perpendicular to the layer plane. In the small angle region, a sharp reflection and its second order reflection are found on the meridian confirming the presence of a SmA phase with a layer distance $d = 4.0$ nm. However, there is an additional diffuse scattering on the equator. This might be due to the organisation of the hydrophilic regions (Figure 3.2b). The reflection is diffused, which indicates that these hydrophilic regions distribute randomly within the “aromatic” sub-layers. Hence, this SmA phase is distinct from conventional SmA phases. It can be considered as a random mesh phase,^[8] in which the “mesh-holes” are filled by the polar regions (i.e., SmA_{frm}, filled random mesh phase).

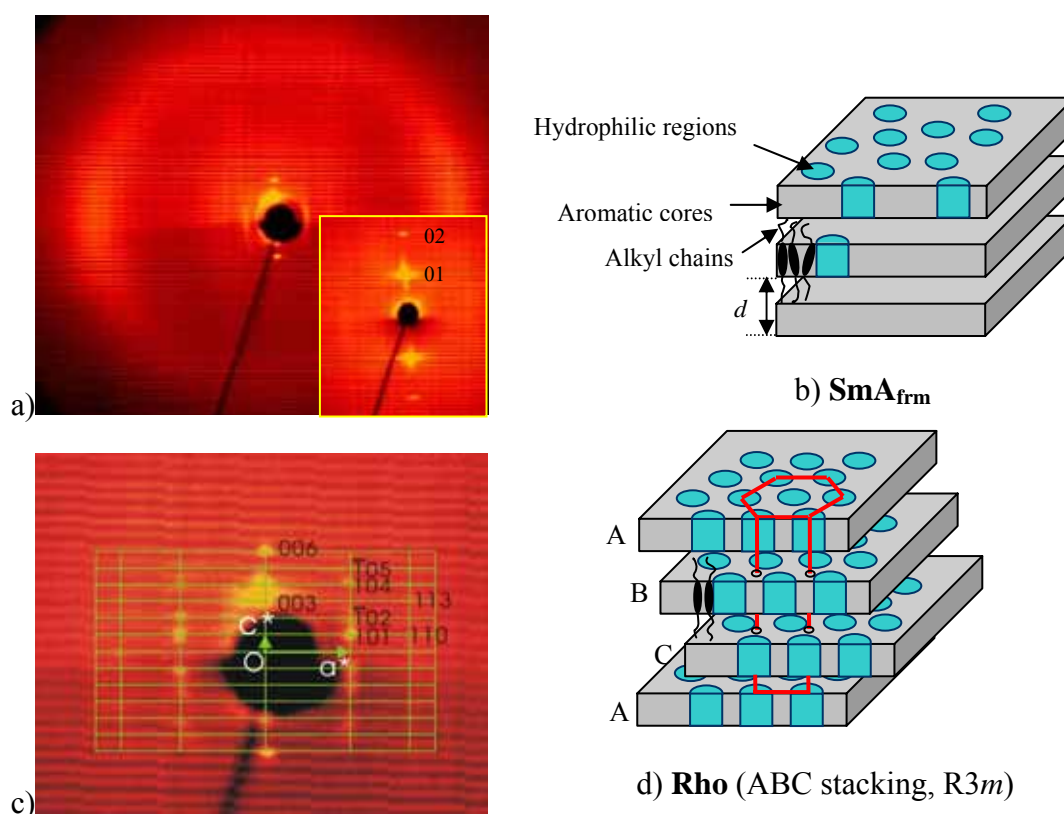


Figure 3.2. (a) X-ray diffraction pattern of the SmA_{frm} (filled random mesh) phase of compound **Na16/3** at 90°C; (b) model of the SmA_{frm} phase of **Na16/3**; (c) X-ray diffraction pattern of the rhombohedral (ABC stacking, R3m) phase of compound **Na16/3** at 50°C; (d) model of the rhombohedral phase of compound **Na16/3**.

Upon cooling of an aligned sample of compound **Na16/3**, a phase transition is observed by X-ray scattering. The diffuse scattering in the small angle region splits off into a series of sharp reflections (Figure 3.2c). This X-ray diffraction pattern can be indexed on the basis of a 3D **R**hombohedral phase (Rho, space group R3m) with the lattice parameters $a = 2.98$ nm, $c = 12.53$ nm. However, under the polarising microscope, no significant change of the texture can be observed at the transition from the SmA_{frm} phase to the Rho phase. Only the

viscosity increases significantly between 90 – 70°C. All the experiment observations indicate that the polar domains become ordered in a 2D hexagonal lattice. The occurrence of the order within the layers is associated with a correlation of the layers in an ABC sequence. The parameter c corresponds to the distance between two identical layers and it is about three times as long as the layer distance d in the high temperature SmA_{fm} phase. The parameter a corresponds to the distance between the hexagonal ordered polar regions within the “aromatic” sub-layers. It can be calculated that in average about 23 polar chains are organized in each of the polar domains (see appendix 1). Rhombohedral phases, which represent ordered mesh phases, have been reported for some lyotropic systems in narrow concentration ranges^[10] and for several diblock copolymer systems.^[37,87] In those Rho phases, the holes are filled by an excess of the component in the second sub-layer. But the Rho phase reported here is different from that have been determined before. In the Rho phase reported herein, the mesh holes are filled by the third incompatible component. So, with respect to the precise structure, the Rho and SmA_{fm} phases reported here are new mesophases.

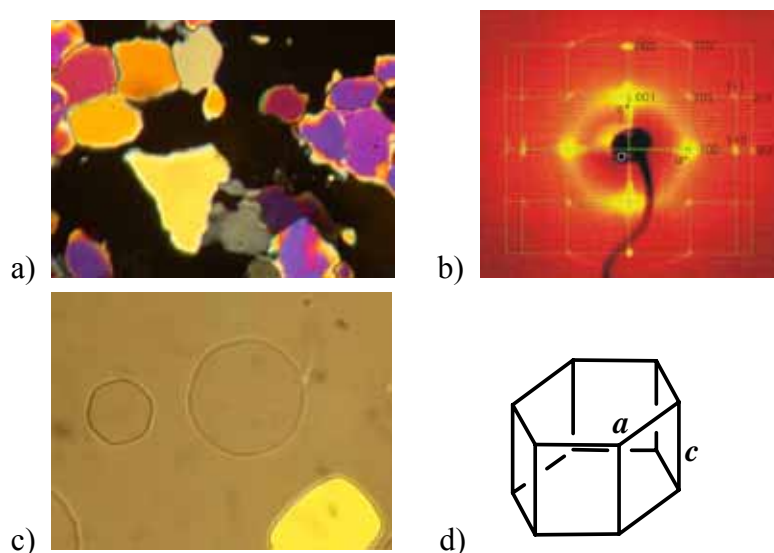


Figure 3.3. Textures and X-ray diffraction pattern of the 3D hexagonal phase of compound **Na10/3**: (a) texture of the 3D-Hex phase at 122°C; (b) X-ray diffraction pattern of an aligned sample of the 3D-Hex phase at 122°C (small angle region); (c) growing of optically isotropic hexagons of the 3D-Hex phase of compound **Na10/3** at the transition from the isotropic liquid state to the 3D-Hex phase (uncrossed polarisers); (d) the 3D-Hex lattice as discussed for the mesophase of **Na10/3**.

For the decyloxy substituted compound **Na10/3**, no SmA phase can be observed. When the sample was cooled down from the isotropic liquid, birefringent mosaic like domains grew and finally, texture containing highly birefringent mosaic like domains together with optically isotropic regions was formed (Figure 3.3a). These optically isotropic regions indicate that this mesophase should be optically uniaxial. Additionally, this mesophase has a high viscosity related to cubic mesophases, which points to a mesophase with a three dimensional lattice. X-ray diffraction studies (Guinier method) show a diffuse scattering in the wide angle region besides several sharp reflections in the small angle region, which confirms the liquid crystalline property of this phase. Aligned samples were obtained and

investigated by X-ray diffraction. The diffraction pattern (Figure 3.3b) shows reflections on the meridian, on the equator as well as cross reflections. These reflections can be indexed on the basis of a 3D hexagonal lattice. The diffraction pattern shown in Figure 3.3b results from a homogeneously aligned sample of which the X-ray beam is applied perpendicularly to the c -axis. Careful investigation of the growing process of this mesophase with polarising optical microscopy (Figure 3.3c), indicates that the homeotropic regions grow with circular or hexagonal shapes which is in line with the 3D-Hex lattice (Figure 3.3d). This 3D-Hex lattice seems to be resulted from an AA correlation of the filled mesh layers, which is probably due to an interconnection of the polar domains between the adjacent layers.

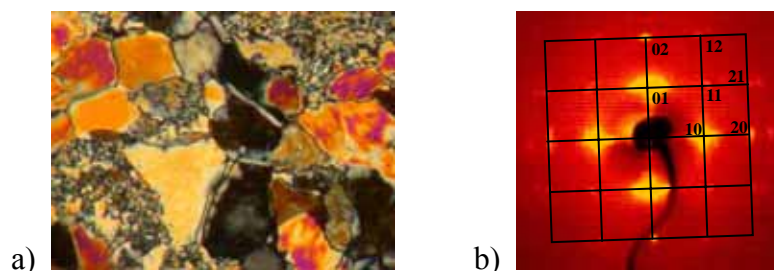


Figure 3.4. (a) Texture of the low temperature phase of **Na10/3** at 75°C (the same region as in Figure 3.3a); (b) X-ray diffraction pattern of **Na10/3** at 75°C (indexed as a Col_{sq} lattice, the reflections which are not indexed could be the residue reflection of the high temperature 3D-Hex phase).

On cooling between *ca.* 86°C - 93°C (depending on the cooling rate) a phase transition is observed. Optically it can be seen by the occurrence of a birefringence within the homeotropically aligned (optically isotropic) regions of the 3D-Hex phase (Figure 3.4a) and the colour of the birefringent mosaics changes as well. On heating, the transition from this low temperature phase to the 3D-Hex phase occurs between 115°C - 120°C. This transition cannot be detected by DSC probably because it is very slow. Also, the X-ray diffraction pattern does not change significantly at this transition. Only the intensity of the 100 reflection is reduced and a new reflection can be observed at a slightly smaller angle on the equator (Figure 3.4b). This reflection corresponds to a distance of 3.5 nm which is identical to the distance in the c -direction. A possible explanation could be, that the low temperature phase is a Col_{sq} phase, but the phase transition is not complete, so that the reflections of the 3D-Hex phase can be observed in the diffraction pattern, too. Nevertheless, further investigations are necessary to confirm the structure of this low temperature mesophase. A further discussion of this 3D-Hex mesophase and the low temperature phases will be done in Chapter 3.2 for the corresponding lithium and cesium salts.

Compounds **Na10*/3**, **Na8/3** and **Na6/3** have similar textures which correspond to those of the 3D-Hex phase of **Na10/3**. Additionally, the same hexagonal or circular growth of the optically isotropic regions is observed at the transition from isotropic state to liquid crystalline state. Thus, these three compounds have the same 3D-Hex organisation. The 3D-Hex lattice was also confirmed by X-ray diffraction investigation. Compound **Na10/3** has lattice parameters $a = 3.39$ nm and $c = 3.50$ nm, **Na8/3** has $a = 3.38$ nm and $c = 3.36$ nm, and **Na6/3** has $a = 3.38$ nm and $c = 3.07$ nm. By the comparison of the lattice parameters, it

can be concluded that reduction of the terminal alkoxy chain length only reduces the parameter c , whereas the parameter a remains constant. This suggests that the long axes of the molecules (i.e., the 4,4''-dialkoxy-p-terphenyl units) should be parallel to the c direction. Reduction of the length of the terminal alkoxy chains leads to the destabilisation of this 3D-Hex phase. And this destabilisation effect becomes stronger when branched terminal alkoxy chains are introduced (compound **Na8/3** with n-octyl chains vs. compound **Na10*/3** with 3,7-dimethyloctyl chains). Unlike **Na10/3**, no low temperature phases have been found for these three sodium carboxylates according to the optical investigations.

Compound **Na4/3** with short terminal butyloxy chains has no liquid crystalline properties. It can be deduced that the alkyl chains with a certain minimum length are essential for the formation of mesophase in this class of compounds.

In summary, the phase sequence $\text{SmA}_{\text{frm}} \rightarrow \text{Rho (R3m)} \rightarrow \text{3D hexagonal}$ has been found by reduction of the length of the terminal alkoxy chains (whereby the Rho phase occurs as a low temperature mesophase below the SmA_{frm} phase). All these three mesophases have not been observed in the related carboxylic acid compounds **Hm/3** (see chapter 5). It seems that the strength of the attractive intermolecular actions (Coulomb interactions vs. H-bonding) has strong influence on the mesophase stability and upon the mesophase morphology.

3.1.2 Influence of the length of the oligo(oxyethylene) chain

The influence of the length of the lateral oligo(oxyethylene) chains on the mesomorphic behaviour of the sodium salts is summarised in Table 1. Figure 3.5 summarises the transition temperatures and the mesophase types which have been observed upon increasing the length of the lateral chain of a series of analogous compounds **Na10/n**.

In the series of the compounds **Na10/n** with two decyloxy terminal chains, compound **Na10/2**, which incorporates a relatively short bi(oxyethylene) unit, shows a SmA mesophase according to the optical investigations. Same as the SmA_{frm} phase of compound **Na16/3**, there is a diffuse scattering besides the layer reflections in the powder X-ray diffraction pattern (Guinier method). This means that this SmA phase is a randomly filled mesh phase. A transition to another (3D ordered) mesophase, however, could not be detected down to room temperature.

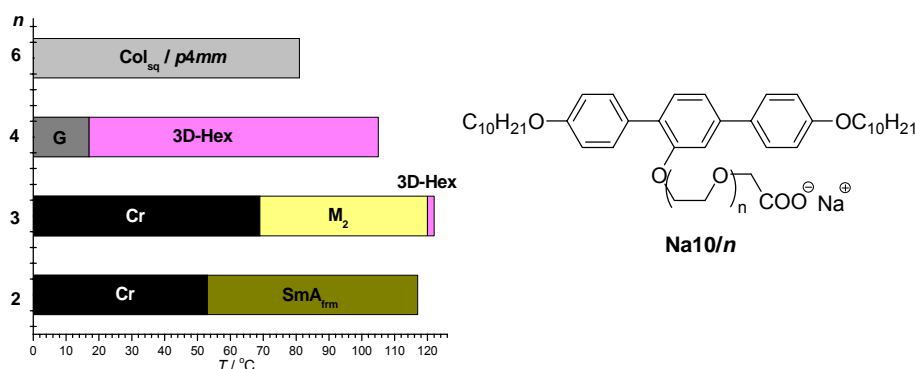
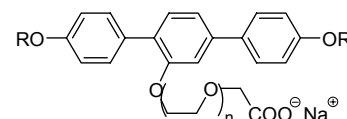


Figure 3.5. Transition temperatures ($T/^\circ\text{C}$) and mesophase types of compounds **Na10/n** depending on the number of oxyethylene units in the polar lateral chain.

Compounds **Na10/3** and **Na10/4** have mosaic like textures with large optically isotropic domains and exhibit a high viscosity. Hence, it can be assumed that they have the same type of 3D-Hex mesophases. And this has been confirmed by X-ray scattering with aligned samples. Compound **Na10/6** with six oxyethylene units in the lateral chain shows spherulitic textures, which has a rather low viscosity if compared with the 3D-Hex phase. X-ray diffraction (Guinier method) indicates a square columnar mesophase (three small angle reflections with a ratio of $1:\sqrt{2}:2$ of the d values). The lattice parameter amounts $a_{sq} = 3.9$ nm. Hence, a phase sequence $SmA_{rm} - 3D-Hex - Col_{sq} (p4mm)$ was found by increasing the number of oxyethylene units in the lateral chain in the series of compounds **Na10/n**.

Table 1. Transition temperatures ($T/^\circ C$), corresponding enthalpy values ($\Delta H/kJ \cdot mol^{-1}$, lower lines in italics), lattice parameters (nm) and volume fraction values of terminal alkoxy chains (f_R), middle aromatic core (f_{Ar}) and lateral polar chain (f_P) of compounds **Na m/n** .



Comp.	R	n	Phase transitions ($T/^\circ C$) $\Delta H/kJ \cdot mol^{-1}$	Lattice parameter (nm)	f_R	f_{Ar}	f_P
Na4/2	C ₄ H ₉	2	Cr 83 Iso <i>9.0</i>		0.31	0.41	0.28
Na4/3	C ₄ H ₉	3	Cr 58 Iso <i>15</i>		0.29	0.38	0.33
Na4/4	C ₄ H ₉	4	Cr 15 Iso <i>2.0</i>		0.27	0.35	0.38
Na6/3	C ₆ H ₁₃	3	Cr 39 3D-Hex 60 Iso <i>0.29</i> <i>1.1</i>	$a = 3.38, c = 3.07$	0.37	0.34	0.29
Na6/4	C ₆ H ₁₃	4	Cr < 20 Col _{sq} ($p4mm$) 50 Iso <i>2.3</i>	$a_{sq} = 3.29$ (50°C)	0.35	0.31	0.34
Na6/6	C ₆ H ₁₃	6	Cr < 20 Col _{sq} ($p4gm$) 33 Iso <i>1.8</i>	$a_{sq} = 7.85$	0.24	0.31	0.45
Na8/3	C ₈ H ₁₇	3	G 36 3D-Hex 112 Iso <i>1.7</i>	$a = 3.38, c = 3.36$	0.43	0.31	0.26
Na8/4	C ₈ H ₁₇	4	Cr < 20 Col _{sq} ($p4mm$) 99 Iso <i>3.1</i>	$a_{sq} = 3.50$	0.41	0.29	0.30
Na10/2	C ₁₀ H ₂₁	2	Cr 53 SmA _{fm} 119 Iso <i>0.78</i> <i>0.98</i>	$d = 3.36$	0.51	0.29	0.20
Na10/3	C ₁₀ H ₂₁	3	Cr 69 M ₂ 120 3D-Hex 122 Iso <i>7.8</i> <i>1.7</i>	$a = 3.39, c = 3.50$	0.48	0.28	0.24
Na10/4	C ₁₀ H ₂₁	4	G 17 3D-Hex 105 Iso <i>1.8</i>	$a = 3.92, c = 3.66$	0.46	0.26	0.28
Na10/6	C ₁₀ H ₂₁	6	Cr < 20 Col _{sq} ($p4mm$) 71 Iso <i>3.3</i>	$a_{sq} = 4.0$	0.42	0.23	0.35
Na10*/3	C ₁₀ H ₂₁	3	Cr 17 3D-Hex 73 Iso <i>0.82</i> <i>1.6</i>		0.48	0.28	0.24
Na10*/4	C ₁₀ H ₂₁	4	Cr < 20 M ₂ 47 3D-Hex 56 Iso <i>1.6</i>	$a = 3.67, c = 3.40$	0.46	0.26	0.28
Na16/3	C ₁₆ H ₃₃	3	Cr 50 Rho 90 SmA _{fm} 116 Iso <i>43</i> <i>3.7</i>	$d = 4.0$ (90°C); $a = 2.98, c = 12.5$ (50°C)	0.59	0.22	0.19
Na16/4	C ₁₆ H ₃₃	4	Cr ₁ 37 Cr ₂ 52 Rho 61 SmA _{fm} 108 Iso <i>17</i> <i>75</i> <i>0.11</i> <i>2.0</i>	$d = 4.0$ (90°C); $a = 3.4, c = 12.8$ (50°C)	0.57	0.21	0.22
NaB/3	Benzyl	3	Cr 126 Iso <i>13</i>		0.34	0.35	0.31

According to the X-ray diffraction investigation, the phase transition temperature is between 70 to 90°C. Branched 3,7-dimethyloctyl chains are used. In some cases, only partial crystallization was observed.

Three different mesophases were observed for the series of hexyloxy substituted compounds **Na6/n**. As reported in the previous section, compound **Na6/3** has a 3D-Hex mesophase. According to the X-ray diffraction studies (Guinier method) which indicate three sharp reflections with d spacings with a ratio of $1:\sqrt{2}:\sqrt{4}$ as well as the textural

observations (Figure 3.6a), compound **Na6/4** has a square columnar mesophase (Col_{sq} , $p4mm$). The lattice parameter was estimated to be $a_{\text{sq}} = 3.3$ nm. Compound **Na6/6** which has a long lateral chain incorporating a sexi(oxyethylene) unit has textures with some small isotropic regions (Figure 3.6b). The low viscosity of the mesophase indicates that there is no 3D arrangement. X-ray investigation indicates a Col_{sq} ($p4gm$) phase with lattice parameter $a_{\text{sq}} = 7.85$ nm. The lattice parameter is nearly three times as large as the length of the molecule in its most extended conformation from the ends of the terminal alkyl chains ($L = 3.0$ nm, $a_{\text{sq}} \approx 2.6 L$). A detailed discussion of this Col_{sq} ($p4gm$) phase will be carried out in Chapter 4 for the polyhydroxy alkyl amides.

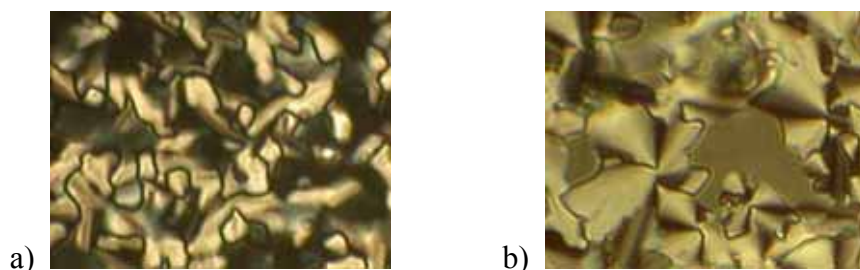


Figure 3.6. (a) Texture of the Col_{sq} ($p4mm$) phase of compound **Na6/4** at 56°C; (b) texture of the Col_{sq} ($p4gm$) of compound **Na6/6** at 33°C.

Compound **Na8/4** with two terminal octyloxy chains shows textures (Figure 3.7a) similar to those of the Col_{sq} ($p4mm$) phase of compound **Na6/4** (filament texture with optical isotropic regions). Additionally, X-ray diffraction studies also indicate a liquid crystal phase (diffuse wide angle scattering with a maximum at $D = 0.45$ nm) with a square columnar lattice [Col_{sq} ($p4mm$), $a_{\text{sq}} = 3.5$ nm].

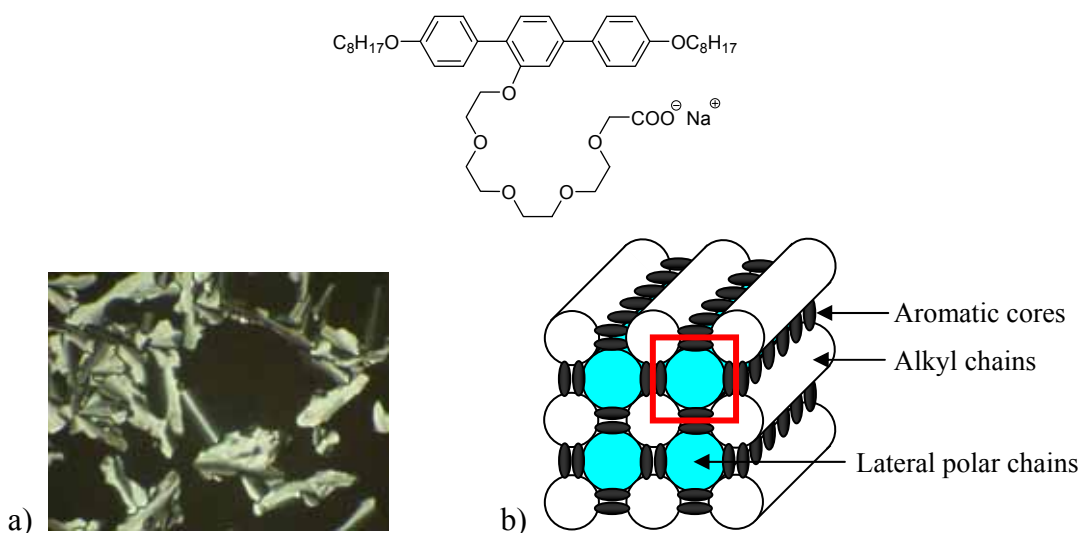


Figure 3.7. (a) Texture of the Col_{sq} phase of compound **Na8/4** at 80°C; (b) model of the organisation of the molecules in the square columnar phases.

A model of this Col_{sq} ($p4mm$) phase is shown in Figure 3.7b. According to this model, the aromatic cores form hollow cylinders with a square cross-section and the polar groups are segregated into columns inside the “aromatic” square shells. Also, the non-polar alkyl chains are segregated into columns which are located at the corners of the “aromatic”

squares. This model is similar to the model proposed for the square columnar phase of calamitic bolaamphiphiles with lateral lipophilic chains.^[88] The main difference between these square columnar phases and those reported for the bolaamphiphiles is, that the locations of the polar and the apolar cylinders are exchanged. The lattice parameters of the square columnar phases decrease with decreasing the length of the terminal alkoxy chains (**Na8/4**: $a_{sq} = 3.5$ nm and **Na6/4**: $a_{sq} = 3.3$ nm). Furthermore, the lattice parameters are close to the molecular length of these compounds (most extended conformation of the molecules, as measured between the ends of the terminal alkyl chains, $L = 3.5$ nm for **Na8/4** and $L = 3.0$ nm for **Na6/4**). These observations are accord with the proposed model.

Calculations based on this model using the lattice parameters as obtained from X-ray investigations were carried out for **Na10/6**, **Na8/4** and **Na6/4**. The results are summarised in Table 2. The calculated numbers of molecules in one unit cell with a height of $h = 0.45$ nm is about five molecules. This means that in average 2.25 aromatic cores are arranged in the cross-section of one cylinder wall. According to the model shown in Figure 3.7b, the space available for the alkyl chains must allow the organisation of *ca.* ten alkyl chains. The calculations in Table 2 show that this is indeed the case which indicates that the proposed model of the Col_{sq} ($p4mm$) phase is a reasonable structure for these three carboxylates.

Table 2. Calculations based on the model of the Col_{sq} ($p4mm$) phase for **Na10/6**, **Na8/4** and **Na6/4**. The volume values of the molecules and the alkoxy chains were calculated using the crystal volume increments of Immirzi.^[89] The height of the cell is assumed to be 0.45 nm. The length of the aromatic p-terphenyl core is 1.25 nm. The shape of the lipophilic columns is assumed to be either circular or square.

Comp.	Na10/6	Na8/4	Na6/4
Lattice parameter a_{sq} (nm)	3.9	3.50	3.29
$V_{cell} = 0.45 \times a_{sq}^2$ (nm ³)	6.84	5.51	4.87
$V_{molecule}$ (nm ³)	1.27	1.05	0.95
Volume of one terminal alkyl chain (V_R , nm ³)	0.255	0.206	0.156
Number of molecules in one cell = $V_{cell}/V_{molecule}$	5.39	5.25	5.13
Width of the lipophilic column: $d = a_{sq} - 1.25$ (nm)	2.65	2.25	2.04
Volume of the lipophilic column in one cell			
$V_{circular} = 0.45 \times \pi d^2/4$ (nm ³)	2.48	1.78	1.47
$V_{square} = 0.45 \times d^2$ (nm ³)	3.16	2.28	1.87
Number of alkyl chains in one cell = V/V_R			
in circular	9.7	8.6	9.4
in square	12.4	11.1	12.0

It seems that increasing the volume of the lateral polar chain has a similar effect upon the mesophase morphology as shortening the terminal alkyl chains. The compounds with short terminal alkoxy chains or a long lateral chain form Col_{sq} phases whereas the compounds with long alkoxy chains or a short lateral chain form SmA_{frm} phases (filled random mesh phase). However, there is a minimum length for the terminal alkyl chains. All compounds **Na4/n** with very short butyloxy chains have no liquid crystalline properties. Also the benzyloxy substituted compound **NaB/3** is not a liquid crystal. The other compounds mentioned in Table 1 show mesophase behaviour which are in line with the above mentioned guidelines, i.e., compound **Na10*/4** has a 3D-Hex mesophases and compound **Na16/4** with two long terminal hexadecyloxy chains has a SmA_{frm} high temperature mesophase and a Rho (R3*m*) phase at lower temperature.

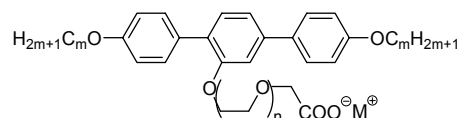
3.2 Facial amphiphiles with different cations

Herein, the influence of cations upon the self-organisation of the facial amphiphiles will be discussed. The mesophase properties of these compounds are summarised in Table 3 and Table 4.

3.2.1 Alkali metal carboxylates

Generally, a significant stabilization of the mesophases for all series **Mm/n** has been observed in the sequence of $\text{Li} < \text{Na} < \text{K} < \text{Cs}$, i.e., with increasing size of the cation. At the first glance, the influence of the cations upon the mesophase type seems to be marginal. All compounds **M10/3** and **M10/4** show optically uniaxial 3D-Hex phases, and Col_{sq} phases were observed for **Na6/4** as well as **Cs6/4**. However, there is a strong influence on the stability of the SmA_{frm} phase with respect to the 3D-Hex phase. Hence, the SmA_{frm} phase of **Na16/3** and **Na10/2** is replaced by a 3D-Hex phase in the corresponding cesium salts **Cs16/3** and **Cs10/2** (for **Cs16/3**, the SmA_{frm} phase can still be observed as a metastable phase on cooling from the isotropic liquid state. On heating only a direct transition from 3D-Hex phase to Iso was observed).

Table 3. Transition temperatures ($T/^{\circ}\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics), lattice parameters and volume fraction values of terminal alkoxy chains (f_{R}), middle aromatic core (f_{Ar}) and lateral polar chain (f_{P}) of the alkali metal salts.



Comp.	<i>m</i>	<i>n</i>	M^+	Phase transitions ($T/^{\circ}\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameters (nm)	f_{R}	f_{Ar}	f_{P}
Na6/4	6	4	Na^+	Cr < 20 Col_{sq} (<i>p4mm</i>) 50 Iso 2.3	$a_{\text{sq}} = 3.29$ (50 $^{\circ}\text{C}$)	0.35	0.32	0.34
Cs6/4	6	4	Cs^+	Cr < 20 Col_{sq} (<i>p4mm</i>) 104 Iso 2.9		0.26	0.34	0.40
Na10/2	10	2	Na^+	Cr 53 SmA_{frm} 119 Iso 0.78 0.98	$d = 3.36$	0.51	0.29	0.20
Cs10/2	10	2	Cs^+	Cr < 20 M_2 118 3D-Hex 140 Iso 1.7	$a = 3.46, c = 3.46$	0.50	0.28	0.22
Li10/3	10	3	Li^+	Cr 84 M_2 111 (3D-Hex 111) Iso 14.3 1.9 1.5		0.49	0.28	0.23
Na10/3	10	3	Na^+	Cr 69 M_2 120 3D-Hex 122 Iso 7.8 1.7	$a = 3.39, c = 3.50$	0.48	0.28	0.24
K10/3	10	3	K^+	Cr 106 3D-Hex 140 Iso 2.3 2.1	$a = 3.60, c = 3.55$	0.48	0.27	0.25
Cs10/3	10	3	Cs^+	Cr ₁ 68 Cr ₂ 80 M_1 122 3D-Hex 140 Iso 13 2.5 2.3	$a = 3.87, c = 3.59$	0.47	0.27	0.26
Li10/4	10	4	Li^+	Cr 11 3D-Hex 99 Iso 1.2 1.9	$a = 3.78, c = 3.61$	0.46	0.27	0.27
Na10/4	10	4	Na^+	G 17 3D-Hex 105 Iso 1.8	$a = 3.92, c = 3.66$	0.46	0.26	0.28
K10/4	10	4	K^+	G 4 M_1 107 3D-Hex 123 Iso 0.97 2.1	$a = 3.81, c = 3.61$	0.45	0.26	0.29
Cs10/4	10	4	Cs^+	Cr ₁ 51 Cr ₂ 71 (G-8) Col_{sq} (<i>p4mm</i>) 120 3D-Hex 127 Iso 20 3.2 2.3	$a = 4.00, c = 3.62$	0.45	0.25	0.30
Na16/3	16	3	Na^+	Cr 50 Rho 90 SmA_{frm} 116 Iso 43 3.7	$d = 4.0$ (90 $^{\circ}\text{C}$); $a = 2.98, c = 12.5$ (50 $^{\circ}\text{C}$)	0.59	0.22	0.19
Cs16/3	16	3	Cs^+	Cr 40 3D-Hex 117 (SmA_{frm} 117) Iso 35 2.4	$a = 3.58, c = 4.26$	0.58	0.21	0.21

On heating, an additional cubic phase occurs before the transition to the 3D-Hex phase. 3D-Hex phase.

Compounds **Li10/4** and **Cs10/4** were investigated in more detail by X-ray diffraction using a synchrotron X-ray source.^[90] Compound **Li10/4** has only one mesophase which is in accordance with the observation under the microscope. Compound **Cs10/4** has the same 3D-Hex phase when cooled down from the isotropic state. The reconstructed electron density map shown in Figure 3.8b gives a definite confirmation of a 3D hexagonal structure. In this electron density map, the undulating columns represent the high electron density areas which correspond to the lateral polar chains of the molecules. These columns penetrate the sub-layers formed by the aromatic and aliphatic parts of the molecules, which leads to mesh like layers of the aromatic p-terphenyl parts of the molecules and mesh layers of the aliphatic chains (Figure 3.8c). These perforated layers are penetrated by the columns of the polar lateral chains which are organized in a hexagonal 2D lattice. Hence, this 3D mesophase can be regarded as mesophase built up by AA correlated hexagonal filled mesh layers. This AA packing is possible due to the fusion of the polar domains in adjacent layers. Therefore, there are two different correlations of hexagonal filled mesh layers in this class of compounds. For compounds **Na16/n** there is an ABC packing leading to the Rho phase. This packing occurs if the terminal alkyl chains are long and, therefore, a fusion of the polar regions in adjacent layers is impossible. In this case, the ABC packing is favoured for steric reasons. For compounds with shorter alkyl chains, the fusion becomes possible and the 3D-Hex phase is formed. Thus, the lithium salt **Li10/4** and the cesium salt **Cs10/4** have the same type of 3D hexagonal phase. Because the diffraction patterns (Guinier method, in some cases also aligned samples) of all the 3D mesophases of compounds **Mm/n**, which show an optically uniaxial mosaic like texture, are in line with such a 3D-Hex structure, the 3D mesophase of all these compounds should be 3D hexagonal phases, too.

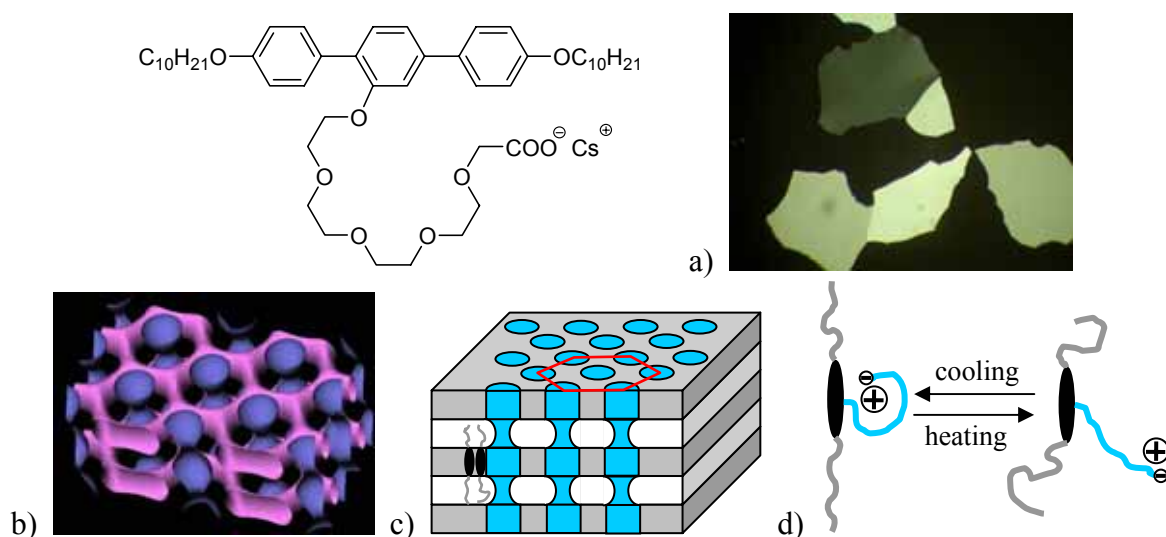


Figure 3.8. (a) Texture of the 3D-Hex phase of compound **Cs10/4** at 118°C; (b) electron density map of the 3D-Hex phase of compound **Cs10/4**; (c) model of the 3D-Hex phase; (d) two possible conformations of the lateral chains.

By cooling of **Cs10/4**, a transition from the 3D-Hex to a square columnar mesophase [$\text{Col}_{\text{sq}}(p4mm)$] has been observed, however the transition is very slow, it does not proceed to a completion even over a weekend. This $\text{Col}_{\text{sq}}(p4mm)$ phase has the same structure as

that of the sodium salts, e.g., **Na8/4**. A possible explanation of this phase sequence could be the following. Upon cooling down from the 3D-Hex phase, the thermal motion of the terminal alkyl chains is reduced, which reduces the space demanded by the alkyl chains. In other words, the volume required by the lipophilic domains is decreased by cooling. However, the conformation of the lateral polar chain might also play an important role. Figure 3.8d shows two extreme conformations. At high temperature the lateral polar chain might prefer a stretched conformation, and upon cooling, the polar chains become more coiled around the metal cation. This concentrates the polar chains into the “aromatic” sub-layers. Hence, upon cooling the size of the lipophilic layers is reduced and the size of the “aromatic” layers is increased simultaneously (due to the increased size of the polar domains within the “aromatic” sub-layers), which could lead to the transition from the layer structure to the columnar phase structure.

Upon heating, an additional cubic ($Pm3m$) phase is formed above the $Col_{sq}(p4mm)$ phase, and then changes to the 3D-Hex phase. It seems that the 3D-Hex phase is the thermodynamically stable mesophase and the Cub phase is a metastable intermediate phase at the transition from the $Col_{sq}(p4mm)$ to the 3D-Hex phase. The electron density map of this cubic phase is shown in Figure 3.9a. The yellow domains represent the high electron density areas (i.e., polar part), the green domains represent the low electron density areas (i.e., alkyl chains). Therefore, the aromatic cores should be organized on the frame of the cube, the polar groups are segregated inside these cubes and the alkyl chains are segregated into spheroids located at the corners. The polar domains of the neighbouring cubes seem to be interconnected (Figure 3.9b).

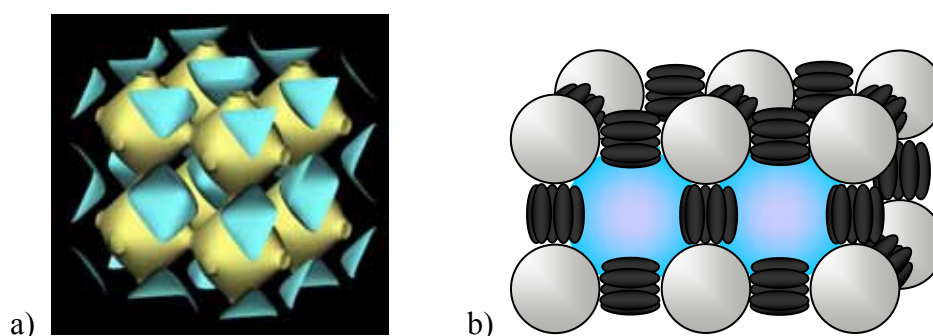


Figure 3.9. (a) Electron density map of the cubic ($Pm3m$) phase of **Cs10/4**; (b) model for the cubic ($Pm3m$) phase of **Cs10/4**.

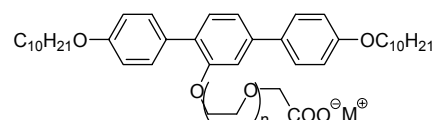
The appearance of additional low temperature phases can be also seen for most of the other compounds with 3D-Hex mesophase. However, only **Li10/4** and **Cs10/4** could be investigated in such details. Therefore, the precise structures of the other low temperature mesophases are not clear.

3.2.2 Rear earth metal, transition metal and alkaline earth metal carboxylates

For nearly all these salts, 3D-Hex phase has been found according to the textural investigation at the transition from the isotropic liquid state to the liquid crystalline state (optical uniaxiality, high viscosity, growth as circles or hexagons). Except that the **Cu10/3**

shows optically isotropic squares. The similar optical textures have also been found for the Y-shaped facial amphiphiles, so this mesophase will be discussed in Chapter 3.4. For **Cu10/4** the 3D-Hex phase was confirmed by the X-ray diffraction pattern (Guinier method). Of course, some of them have not only the 3D-Hex phase, there are some other low temperature phases like those in the series of alkali metal salts. The copper(II) salts have extremely low clearing temperatures, possibly because of the small radius of the copper(II) cation [the radius of Cu(II) is 0.087 nm which is even smaller than 0.09 nm of the Li cation^[93]]. Otherwise the low electropositivity of Cu(II) could lead to a higher contribution of the covalent interaction in the Cu-carboxylates. This would lead to a reduced segregation which might reduce the mesophase stabilities.

Table 4. Transition temperatures ($T/^{\circ}\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics), and lattice parameters of the rare earth metal, alkali metal and the alkali-earth metal salts.



Comp.	<i>n</i>	M^+	Phase transitions ($T/^{\circ}\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameters (nm)
Ba10/3	3	$\frac{1}{2}\text{Ba}^{2+}$	Cr < 20 M_2 123 3D-Hex 135 Iso <i>0.17</i> <i>4.0</i>	
Cu10/3	3	$\frac{1}{2}\text{Cu}^{2+}$	G 27 M_3 63 3D-M 79 Iso <i>3.2</i>	
La10/3	3	$\frac{1}{3}\text{La}^{3+}$	Cr 86 M_2 116 (99 3D-Hex 113) Iso <i>5.4</i> <i>4.7</i> <i>4.7</i>	
Eu10/3	3	$\frac{1}{3}\text{Eu}^{3+}$	Cr 34 M_2 116 (104 3D-Hex 114) Iso <i>1.8</i> <i>5.7</i>	
Ba10/4	4	$\frac{1}{2}\text{Ba}^{2+}$	Cr < 20 M_2 114 3D-Hex 118 Iso <i>4.1</i> <i>4.0</i>	
Cu10/4	4	$\frac{1}{2}\text{Cu}^{2+}$	Cr 53 (M_2 47 3D-Hex 53) Iso <i>1.5</i> <i>1.2</i>	$a = 3.85, c = 3.68$
La10/4	4	$\frac{1}{3}\text{La}^{3+}$	Cr 97 3D-Hex 123 Iso <i>3.6</i> <i>12</i>	

Observed on cooling. Unknown phase M_2 as a low temperature phase of the 3D-Hex phase which shows high birefringence in the optically isotropic areas of the textures of the 3D-Hex phase and also changes the colour of the mosaics. Mesophase M_3 as a low temperature phase of the 3D-M phase where non-specific birefringent textures grow both in the optically isotropic areas and the bright mosaics of the texture of the 3D-M phase. The unknown 3D-M phase which shows optically isotropic squares at the transition from the isotropic state to the liquid crystalline state.

3.3 Facial amphiphiles with two different terminal alkoxy chains

Table 5 summarises the transition temperatures of the series of compounds **Na6.16/*n*** and **Na16.6/*n***, which consist a hexyloxy chain at one terminal position and a hexadecyloxy chain at another.



Figure 3.10. Textures of the columnar phases of: (a) compound **Na6.16/3** at 87 °C; (b) compound **Na6.16/4** at 73 °C; (c) compound **Na6.16/6** at 78 °C.

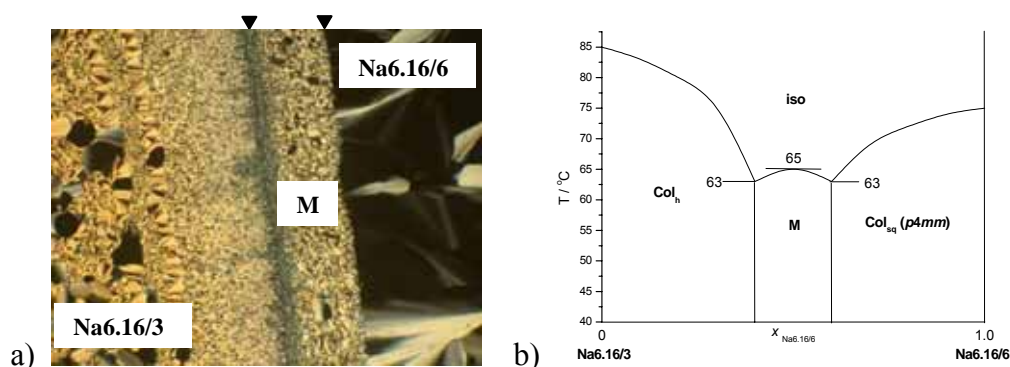
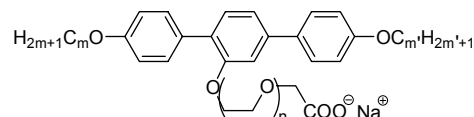


Figure 3.11. (a) Contact region of **Na6.16/3** and **Na6.16/6** at 62°C; (b) qualitative binary phase diagram of **Na6.16/3** and **Na6.16/6**.

Based on texture investigations, all of the three compounds **Na6.16/*n*** appear to have optically uniaxial mesophases (filament textures or spherulitic texture with optically isotropic areas, Figure 3.10). All these mesophases have a significantly lower viscosity in comparison with the 3D mesophase and therefore represent columnar phases. Hence, these mesophases could be Col_{sq} or Col_{h} phases. In the contact region between compounds **Na6.16/3** and **Na6.16/6** (Figure 3.11a), an additional new mesophase is induced which is separated from the mesophases of **Na6.16/3** and **Na6.16/6** by sharp phase boundaries (Figure 3.11a). It seems that the columnar mesophases of these three compounds are all different from each other. X-ray studies indicate a hexagonal columnar phase for **Na6.16/3** with lattice parameter $a_{\text{hex}} = 5.08$ nm, a hexagonal columnar phase for **Na6.16/4** with lattice parameter $a_{\text{hex}} = 10.5$ nm and a Col_{sq} ($p4mm$) phase **Na6.16/6** with lattice parameter $a_{\text{sq}} = 4.2$ nm. The similar hexagonal columnar phases are also found for the carboxylic acid derivatives which will be discussed in Chapter 5.

Table 5. Transition temperatures ($T/^\circ\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics), lattice parameters and volume fraction values of terminal alkoxy chains (f_{R}), middle aromatic core (f_{Ar}) and lateral polar chain (f_{P}) of compounds **Na*m.m*'/*n***.



Comp.	<i>m</i>	<i>m</i> '	<i>n</i>	Phase transitions ($T/^\circ\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameter (nm)	f_{R}	f_{Ar}	f_{P}
Na6.16/3	6	16	3	Cr 40 Col_{h} 89 Iso 33 1.8	$a_{\text{hex}} = 5.08$	0.51	0.26	0.23
Na6.16/4	6	16	4	Cr 54 Col_{h} 74 Iso 31 1.2	$a_{\text{hex}} = 10.5$	0.48	0.25	0.27
Na6.16/6	6	16	6	Cr ₁ -5 Cr ₂ 28 Col_{sq} ($p4mm$) 70 Iso 2.0 1.1 2.0	$a_{\text{sq}} = 4.2$	0.44	0.23	0.33
Na16.6/3	16	6	3	Cr < 20 Col_{h} 100 (92 3D-Hex 100) Iso 2.3 0.96	$a = 3.35$, $c = 3.7$ (95 °C); $a_{\text{hex}} = 5.0$ (75 °C)	0.51	0.26	0.23
Na16.6/4	16	6	4	Cr < 20 Col_{h} 66 3D-Hex 79 Iso 0.90 0.64	$a_{\text{hex}} = 5.11$	0.48	0.25	0.27
Na16.6/6	16	6	6	Cr 55 Col_{sq} ($p4mm$) 80 Iso 41 0.81	$a_{\text{sq}} = 4.1$	0.44	0.23	0.33

Observed on cooling.

In the isomeric compounds **Na16.6/*n***, the position of the alkoxy chains are exchanged. Compounds **Na16.6/3** and **Na16.6/4** have the typical textures of 3D-Hex mesophases (Figure 3.12a, b) with birefringent mosaic like domains and optically isotropic areas. The phase assignment is also confirmed by X-ray investigations. By cooling the 3D-Hex phase

of **Na16.6/4**, the whole sample becomes birefringent (Figure 3.12c). X-ray studies (Guinier method) indicate that the low temperature phase is a hexagonal columnar phase. The texture of compound **Na16.6/6** (Figure 3.12d), which consist a long lateral chain incorporating a sexi(oxyethylene) unit, is similar to that of **Na6.16/6** and also in this case, it is likely that this phase is a Col_{sq} phase. X-ray investigation also confirms a Col_{sq} (*p4mm*) phase for **Na16.6/6**.

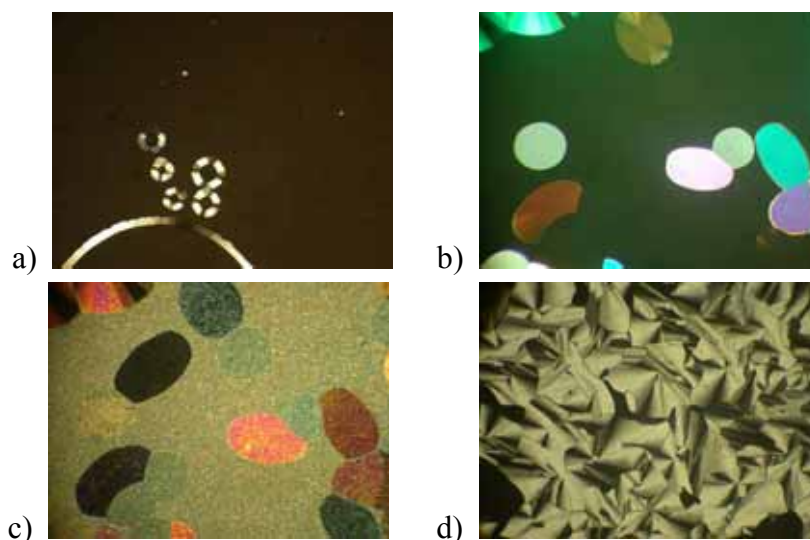


Figure 3.12. Textures of: (a) the 3D-Hex phase of **Na16.6/3** at 99 °C; (b) the 3D-Hex phase of **Na16.6/4** at 87 °C; (c) the Col_h phase of **Na16.6/4** at 60 °C obtained upon cooling down from the 3D-Hex phase (same region as b); (d) the columnar phase of **Na16.6/6** at 80 °C.

This shows that exchange of the terminal alkoxy chains leads to quite different mesophase behaviour. Only columnar mesophases have been observed in the series of compounds **Na6.16/*n*** which have the lateral polar chain grafted close to the shorter hexyloxy chain. However, in the series of compounds **Na16.6/*n***, which have the lateral chain grafted close to the long hexadecyloxy chain, the 3D-Hex phase is additionally observed. Compounds **Na6.16/*n*** and **Na16.6/*n*** can roughly be regarded as non-symmetric analogues of the symmetric compounds **Na10/*n*** (see chapter 3.1) because the average length of the terminal alkyl chains is nearly the same (C₁₀ vs. C₁₁) in these series of compounds. The series of compounds **Na16.6/*n*** behave similarly to compounds **Na10/*n***, whereas the columnar phases are more dominant in the series of compounds **Na6.16/*n***.

3.4 Influence of the position of the lateral chain

Table 6. Transition temperatures (*T*/°C), corresponding enthalpy values (ΔH /kJ·mol⁻¹, lower lines in italics) and volume fraction values of terminal alkoxy chains (*f_R*), middle aromatic core (*f_{Ar}*) and lateral polar chain (*f_P*) of the series of compounds **Na*10/*n***.

<chem>CCCCCCCCCCCCOC1=CC=C(C=C1)-C2=CC=C(C=C2)-C3=CC=C(C=C3)OCCCCCCCCC</chem> <chem>[O-]C(=O)O[Na+]</chem>	Comp.	<i>n</i>	Phase transitions (<i>T</i> /°C) ΔH /kJ·mol ⁻¹	<i>f_R</i>	<i>f_{Ar}</i>	<i>f_P</i>
	Na*10/3	2	Cr ₁ 60 Cr ₂ 77 Col 99 3D-M 128 Iso <i>1.4 4.9 0.30 1.9</i>	0.48	0.28	0.24
	Na*10/4	3	Cr 90 (Col 95) 3D-M 113 Iso <i>16 1.7 1.5</i>	0.46	0.26	0.28

Table 6 summarises the transition temperatures of the two compounds **Na*10/3** and **Na*10/4**, which have the lateral chain grafted to one of the ortho-positions with respect to the terminal alkoxy chain. Two different textures were found. At higher temperature, the typical textures of the optically uniaxial 3D mesophase have been observed for both compounds (Figure 3.13a, c). The growing process of the mesophase from the isotropic liquid state was carefully observed by polarising optical microscopy (Figure 3.13b). In contrast to the textures of carboxylates **Mm/n** (the lateral chains are at the central position of the p-terphenyl cores) which all grow with hexagonal (or circular) shapes, the optically isotropic regions of compounds **Na*10/n** grow with square shapes. Miscibility studies of **Na10/4** and **Na*10/4** confirm the difference of the mesophase structures of these compounds as a phase boundary between these two mesophases has been observed. From these observations it is possible that this 3D ordered mesophase is a 3D tetragonal (3D-Tet) phase. However, the distance of reflections in the Guinier pattern is too small to unambiguously index the reflections to a tetragonal cell. The attempt to get a 2D X-ray diffraction pattern was failed because aligned samples could not be obtained. Upon cooling from the 3D mesophases of **Na*10/3** and **Na*10/4**, an additional phase transition can be identified by the transition of the optically isotropic regions into a birefringent texture. The low temperature mesophases have a lower viscosity than the high temperature phases. Therefore, it seems that these low temperature phases are columnar phases, probably Col_{sq} phases as observed for **Na10/3**.

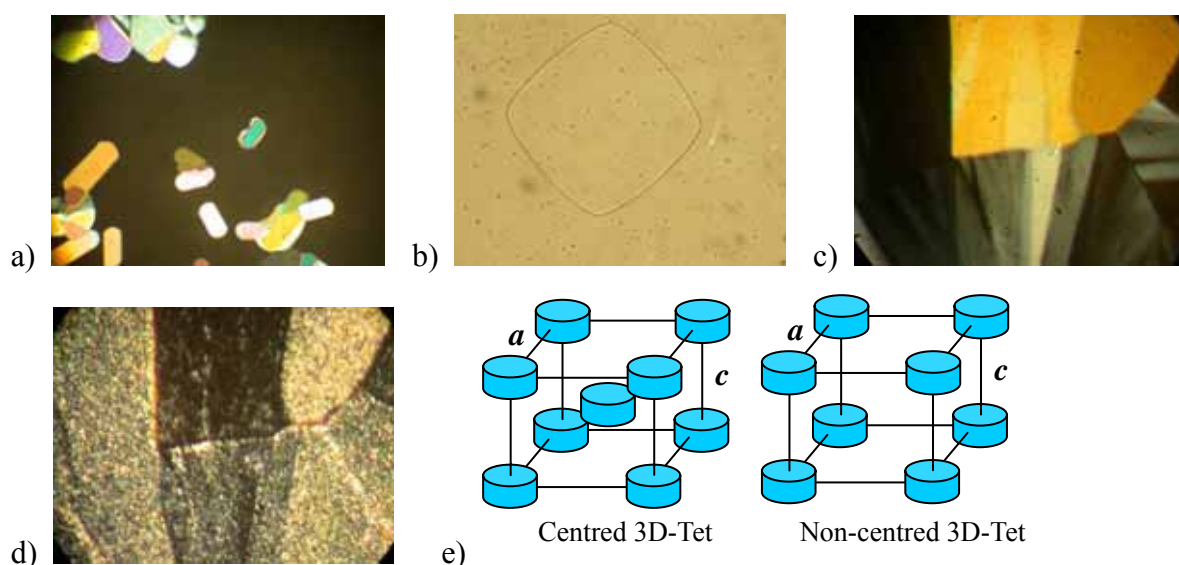


Figure 3.13. (a) Texture of the 3D mesophase of compound **Na*10/3** at 125°C; (b) growing of an optically isotropic square from the isotropic liquid state of **Na*10/4** at 113°C (uncrossed polarisers); (c) texture of the 3D mesophase of **Na*10/4** at 108°C; (d) low temperature mesophase of **Na*10/4** at 74°C as seen by cooling down from the 3D mesophase (the same region as in c); (e) a non centred and a centred 3D-Tet lattice as possible structures of the 3D mesophase of compounds **Na*10/n**.

3.5 Summary of the mesophase behaviour of the metal carboxylates

For the metal carboxylates, depending on the size of the lateral polar chain and the size of the terminal alkoxy chains, a SmA_{frm} (filled random mesh phase), a Rho (rhombohedral with space group $R3m$) phase, a 3D-Hex (3D hexagonal) phase, a Col_{sq} (square columnar with space group $p4mm$), a Col_{sq} (square columnar with space group $p4gm$) for symmetric compounds and two kinds of Col_{h} (hexagonal columnar) phases for asymmetric compounds have been identified. SmA layer structures are quite often found for calamitic liquid crystals. However, the SmA_{frm} phases of compounds **Na m/n** are different. The incompatibility of the lateral polar chains and the aromatic cores leads to the formation of segregated polar domains (filled meshes) within the “aromatic” sub-layers. With small volume fraction value of the lateral polar part, the polar domains have no correlation between each others. Thus, a SmA_{frm} phase is formed. Upon cooling, these polar domains (filled meshes) are organized in a 2D hexagonal lattice within the “aromatic” layers, and a closest ABC packing of the layers leads to the formation of a Rho ($R3m$) phase. Increasing the volume fraction value of the lateral polar part leads to the fusion of the polar domains in adjacent layers, thus a 3D-Hex phase is formed. Upon further increasing the volume fraction value of the lateral polar chain, the layer structure breaks up with formation of a square columnar phase ($p4mm$) via a metastable $\text{Pm}3m$ cubic phase. Figure 3.14 schematically shows the phase sequence of these metal carboxylates upon increasing the volume fraction value of the later polar chain.

Additionally, two kinds of Col_{h} phase are found for the asymmetric compounds **Na6.16/ n** . The 3D-Hex phase can be induced in compounds **Na16.6/ n** where the two terminal alkoxy chains are exchanged.

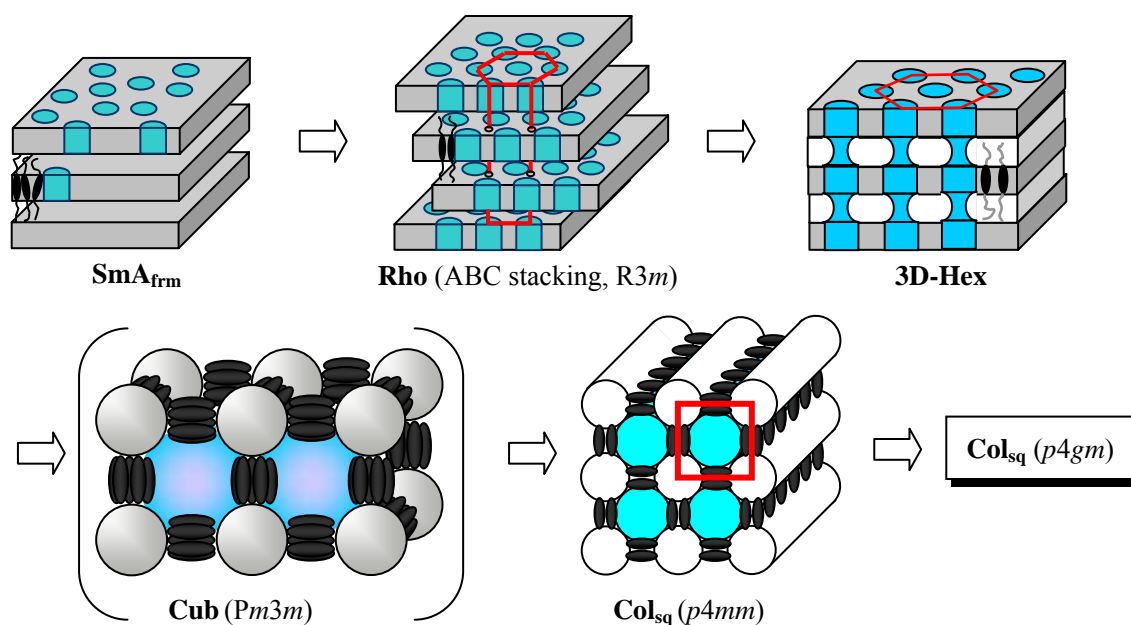


Figure 3.14. Phase sequence of the metal carboxylates. Along the arrows direction, the volume fraction value of the later polar chain is increased or the temperature is reduced (the cubic phase is observed as a metastable phase at the transition from the Col_{sq} phase to the 3D-Hex phase of **Cs10/4**; the structure of the Col_{sq} ($p4gm$) phase will be discussed in Chapter 4).

4 Liquid crystalline properties of facial amphiphiles with a lateral chain containing an amide group

Conventional amphiphiles, which consist of a hydrophilic part and a lipophilic part connected covalently, form various types of mesophases depending upon the relative size of polar and apolar molecular parts. In the facial amphiphiles discussed in Chapter 3, the same behaviour has also been observed. Compounds with long alkoxy chains prefer the SmA_{frm} (filled random mesh) organisation. Increasing the size of the hydrophilic group and/or reduction of the length of the alkoxy chains lead to a collapse of the smectic layer structure and the formation of novel mesophases with 2D or 3D organisation, namely, Rho ($\text{R}3m$), 3D-Hex and Col_{sq} phases. It seems that further increase of the volume of the hydrophilic group is a promising method to design new molecules for which novel types of mesophases could be expected. Thus, the 1-amido-1-deoxy-D-sorbitol unit is chosen as a segment of the polar group for its larger space requirement and because it can be easily obtained from the carboxylic acids **Hm/n** by amidation reaction. Additionally, it has six OH groups, that means there are six H donors for H-bonding which would give very strong intermolecular attractions.

4.1 1-Acylamino-1-deoxy-D-sorbitol unit at the end of the lateral polar chain

Different series of amides have been synthesized. Thus, the influences of the length of the terminal alkoxy chains, the length of the lateral chain and the position of the lateral chain upon the mesophase behaviour have been systematically investigated. Compounds with two different terminal alkoxy chains have been investigated as well.

4.1.1 Influence of the length of the alkoxy chains

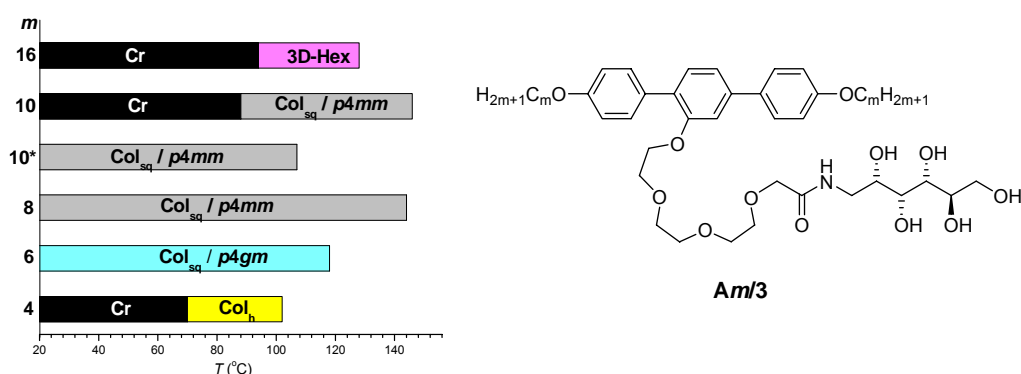


Figure 4.1. Mesophase types and transition temperatures ($T/^{\circ}\text{C}$) of compounds **Am/3** (all chains are linear alkoxy chains, except 10* which is a 3, 7-dimethyloctyloxy chain).

Figure 4.1 summarises the mesophase types and the transition temperatures of compounds **Am/3**, which have the same lateral polar group consisting of a 1-acylamino-1-deoxy-D-sorbitol group connected by a ter(oxyethylene) chain to the p-terphenyl core. Four different liquid crystalline phases have been observed in total. The mesophase of compound **A16/3**, which has two hexadecyloxy terminal chains, appears

almost completely black between crossed polarizers. Additionally, this mesophase has very high viscosity. Upon shearing, the sample becomes birefringent which excludes the possibility of a cubic mesophase. All these observations indicate an optically uniaxial 3D mesophase. The X-ray diffraction pattern (Guinier method) confirms a 3D hexagonal structure of this phase. This means that the 3D hexagonal phase of **A16/3** has the same structure as the 3D-Hex phase of the metal carboxylates (e.g., **Cs10/4**, section 3.2).

Reduction of the length of the alkoxy chains to decyloxy chains leads to a change of the phase type. The mesophase of compound **A10/3** has a lower viscosity than the 3D-Hex phase of **A16/3**. The optically isotropic regions in the texture shown in Figure 4.2a indicates an optically uniaxial columnar phase. Aligned samples were investigated by X-ray diffraction (Figure 4.2b). In the wide angle regions of the diffraction pattern, a diffuse scattering forms a closed ring indicating that this is a liquid crystalline phase. In the small angle region, the sharp reflections can be indexed on the basis of a Col_{sq} ($p4mm$) lattice with a lattice parameter $a_{\text{sq}} = 3.8$ nm. Additionally, the outer reflections have the maximal intensity on the meridian and on the equator which indicates that the long axes of the molecules (i.e., the aromatic core with two terminal alkoxy chains) are organised in two dominant directions which are perpendicular to each other. All these observations are in line with the model of the Col_{sq} ($p4mm$) phase (Chapter 3, Figure 3.5b) which has already been suggested for the carboxylates (e.g., **Na8/4**).

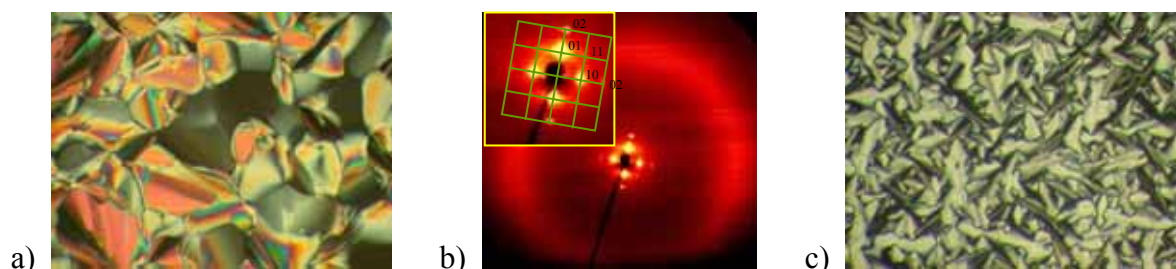


Figure 4.2. (a) Texture of the Col_{sq} ($p4mm$) phase of compound **A10/3** at 142°C; (b) X-ray diffraction pattern of the Col_{sq} ($p4mm$) phase of compound **A10/3** at 142°C; (c) texture of the Col_{sq} ($p4gm$) phase of compound **A6/3** at 115°C.

Compound **A10*/3** with two branched 3,7-dimethyloctyloxy chains and compound **A8/3** with two octyloxy chains show the same Col_{sq} ($p4mm$) phase according to their textures and X-ray diffraction patterns (Guinier method). The branched terminal chains depress the clearing temperature by about 40°C in comparison to compound **A10/3** with linear decyloxy chains (the same number of carbon atoms in the alkoxy chain). The melting point is even more depressed by replacing the linear chains with branched chains.

Hence, three different compounds have the same Col_{sq} ($p4mm$) mesophase (**A8/3**, $a_{\text{sq}} = 3.7$ nm, $L = 3.5$ nm; **A10/3**, $a_{\text{sq}} = 3.8$ nm, $L = 4.0$ nm; and **A10*/3**, $a_{\text{sq}} = 3.8$ nm, $L = 3.5$ nm, L is estimated by Chem3D). It can be seen that the lattice parameters are nearly the same for all three compounds, though their molecular lengths (L) are different.

Therefore, it can be deduced that the molecular length is not the only factor determining the lattice parameter a_{sq} . For short chain compound **A8/3**, more molecules are organised in the one unit cell than for compounds with a larger volume fraction of the alkyl chains

(**A10/3** and **A10*/3**). It seems that a certain minimum value of the cross section area of the lipophilic columns is required for the organisation in the Col_{sq} ($p4mm$) phase. This is achieved for the short chain compounds by increasing the number of molecules organised in the cross section of the columns (see Table 6). Such increase is possible by raising the number of p-terphenyl units in the cross section of the cylinder walls, while the square shape of the cylinders remains.

Compound **A6/3**, which has two terminal hexyloxy chains, has another texture (Figure 4.2c). The X-ray diffraction pattern (Guinier method) can be explained on the basis of a square columnar mesophase with the space group $p4gm$, and the lattice parameter $a_{\text{sq}} = 7.87$ nm. The structure of this Col_{sq} ($p4gm$) phase will be discussed in detail for the similar compound **A6/4** in the next section.

Further reduction of the alkoxy chain length to butyloxy changes the mesophase type again. Compound **A4/3** has a hexagonal lattice (Col_{h}) with a lattice parameter $a_{\text{hex}} = 4.1$ nm as found by X-ray diffraction investigations (Guinier method).

In summary, a phase sequence 3D hexagonal – Col_{sq} ($p4mm$) – Col_{sq} ($p4gm$) – Col_{h} has been found by reduction of the length of the terminal alkoxy chains. This phase sequence can be understood in the following way. If the alkyl chains are long (**A16/3**), the incompatibility between the alkyl chains and the other part of the molecule is strong. Additionally, the lipophilic parts have a rather large volume fraction. All these allow the organisation in a layer structure. The polar molecular segments are incompatible with both the p-terphenyl and the alkoxy chains. They organise in cylinders which organise in a hexagonal lattice and penetrate the layer structure in the same way as described for the carboxylates (e.g., **Cs10/4**). Thus a 3D-Hex structure is formed. When the length of the alkoxy chains is reduced, then the layer of the alkyl chains break up into columns. This leads to a square columnar phase, in which the polar cylinders are surrounded by the square-shaped cylinder shell of the aromatic cores, and the lipophilic groups are segregated into columns located at the corners of the squares as described for the carboxylates (e.g., **Na8/4**). Upon further decreasing the length of the alkoxy chains, the square-shaped cross section is broken up, thus, Col_{sq} ($p4gm$) phase and Col_{h} phase are formed. The structure of these two phases will be discussed in the next section.

4.1.2 Influence of the length of oligo(oxyethylene) chains

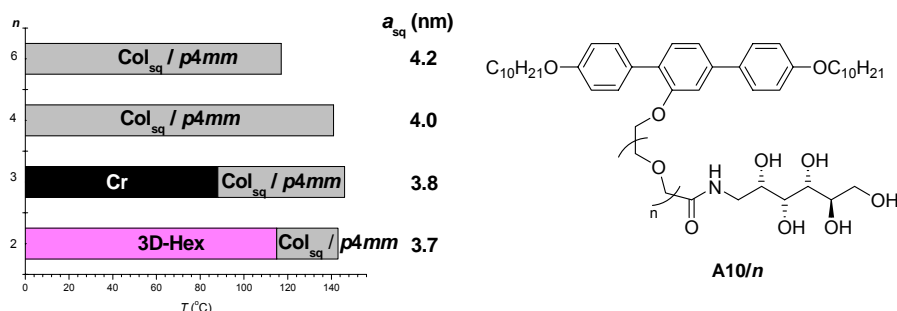


Figure 4.3. Mesophase types, transition temperatures ($T/^\circ\text{C}$) and lattice parameters (nm) of the Col_{sq} ($p4mm$) mesophases of compounds **A10/n** depending on the length of the lateral chain.

Table 6 summarises the transition temperatures of compounds **A m/n** , and the selected compounds are compared in Figure 4.3 graphically (compounds **A10/ n**).

For the series of the decyloxy compounds **A10/ n** , two different mesophases have been observed. All compounds **A10/2**, **A10/3**, **A10/4** and even **A10/6** which incorporate the long sexi(oxyethylene) connecting unit show the Col_{sq} ($p4mm$) phase as determined by the textures and the results of X-ray diffraction. The elongation of the lateral chain increases the lattice parameter (from $a_{sq} = 3.7$ nm to $a_{sq} = 4.2$ nm), which is achieved by reduction of the number of molecules in the cross section of the cylinders (from 5.1 to 5.5), i.e., by a stretching of the columns along the long axis direction. Comparison with Figure 4.1 shows that the length of the terminal alkoxy chains has a much larger influence upon the mesophase type than the size of the lateral polar chain.

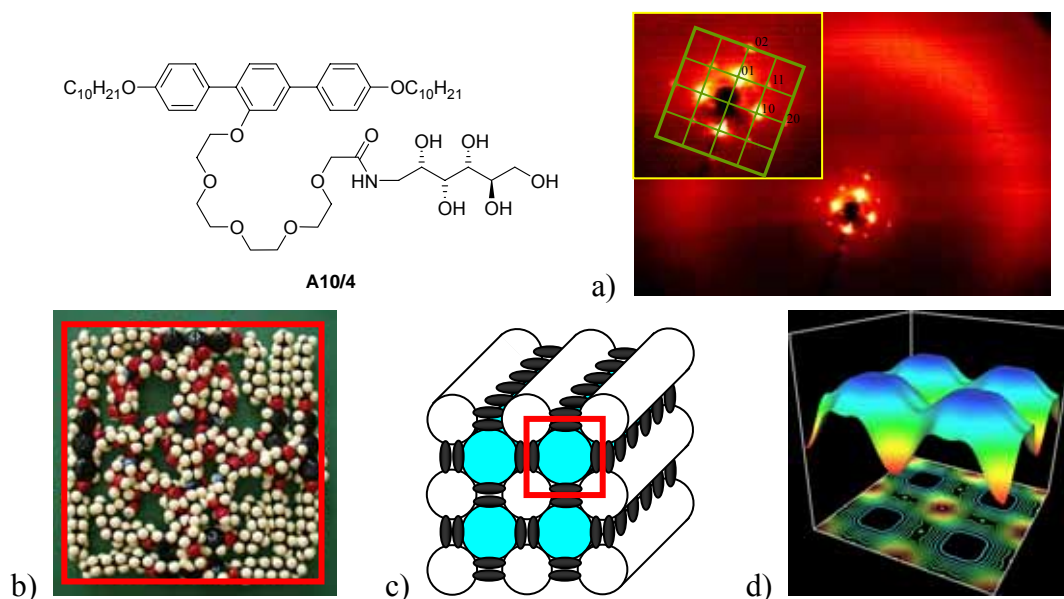


Figure 4.4. (a) X-diffraction pattern of the Col_{sq} ($p4mm$) phase of **A10/4** at 137°C; (b) CPK model of the Col_{sq} ($p4mm$) phase of **A10/4**; (c) model of the Col_{sq} ($p4mm$) phase; (d) electron density map of the Col_{sq} ($p4mm$) phase of **A10/4**.

For **A10/4**, an electron density map was obtained from the X-ray diffraction (synchrotron) results (Figure 4.4d). The blue regions are the high electron density domains (i.e., polar columns) and the red regions are the low electron density areas (i.e., alkyl columns). This electron density map gives a definite evidence of the structure of this Col_{sq} ($p4mm$) phase.

For compound **A10/2** which has a relatively short lateral chain, a second mesophase has been observed. When cooled down from the isotropic melt, a Col_{sq} ($p4mm$) phase is observed (Figure 4.5a). Upon further cooling of the sample, the bright textures disappear and the whole sample becomes optically isotropic (Figure 4.5b) at the transition to the low temperature mesophase. When another kind of glass plates, which provides a different alignment, is used, a different texture is observed for the Col_{sq} ($p4mm$) phase (Figure 4.5c). The characteristic feature of this texture is the presence of large homeotropically aligned regions which appear optically isotropic. At the transition to the low temperature mesophase, a birefringent mosaic texture develops, i.e., the optically isotropic areas become birefringent. This indicates that the direction of the optical axis changes at the phase transition. In

contrast to the Col_{sq} (*p4mm*) high temperature phase, which has a rather low viscosity, the low temperature phase was found to have a significantly higher viscosity. All of these observations point to an optically uniaxial 3D organisation in the low temperature mesophase which is most probably a 3D-Hex phase (though the $\sqrt{3}$ reflection cannot be detected in an X-ray experiment). Compared with the phase sequence of the carboxylate **Cs10/4**, which has a low temperature Col_{sq} (*p4mm*) phase and a high temperature 3D-Hex phase, in the amide **A10/2**, the phase sequence is reversed [low temperature 3D phase and high temperature Col_{sq} (*p4mm*) phase]. This might be due to the different structure of the polar groups, i.e., due to the different nature of the intermolecular interactions between metal carboxylates (ionic interactions: the oxyethylene chains coordinate to the metal cations) and carbohydrates (H-bonding).

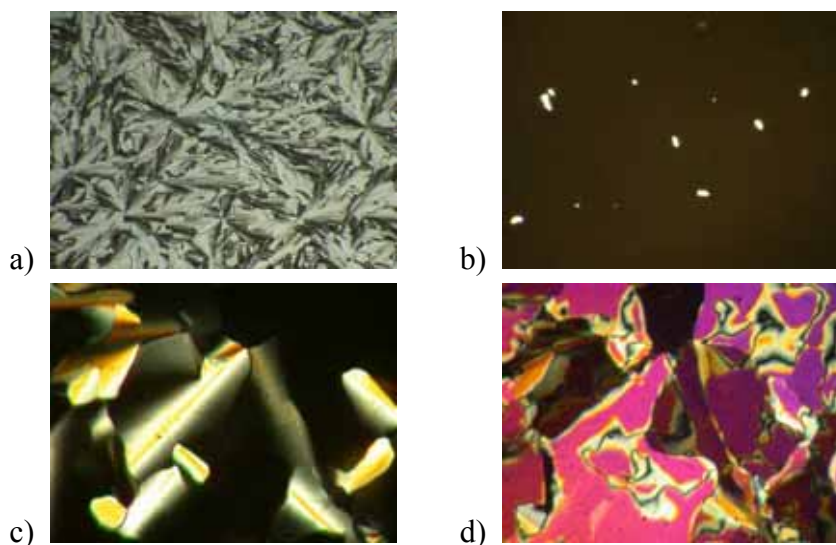


Figure 4.5. Representative textures of compound **A10/2** under different alignment conditions: a) the Col_{sq} (*p4mm*) phase at 146°C (homogeneous alignment, cooling into the 3D-Hex phase leads to the texture shown in b); b) the 3D-Hex phase at 53°C; c) the Col_{sq} (*p4mm*) phase at 146°C (predominating homeotropic alignment, cooling leads to the texture shown in d); d) the 3D-Hex phase at 53°C.

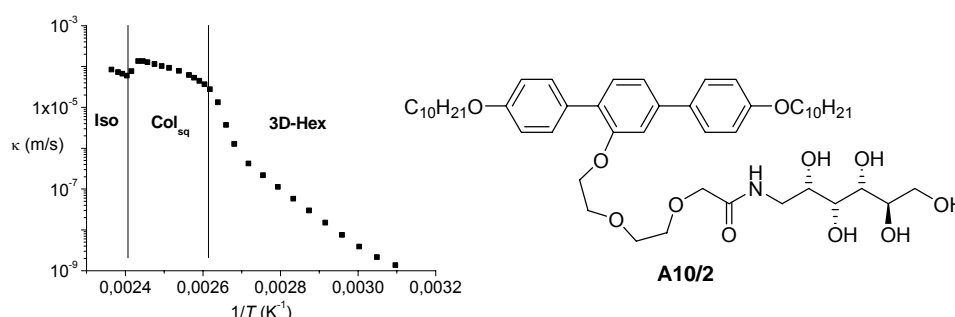
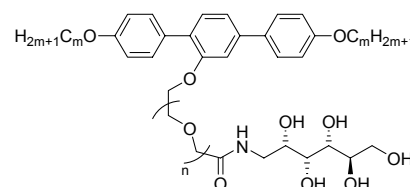


Figure 4.6. Conductivity measurements of compound **A10/2**.

Conductivity measurements have been carried out for **A10/2**. These experiments indicate that at the transition from the Col_{sq} (*p4mm*) phase to the 3D ordered phase, a reduction of the conductivity by a factor of about 100 takes place (Figure 4.6). This reduction of the conductivity is not expected, because the models of the Col_{sq} (*p4mm*) and the 3D-Hex phase

suggest the presence of polar (conductive) cylinders. It might result from the reorganisation of the polar columns at the phase transition. As indicated by the changes of the texture (Figure 4.5), the direction of the polar columns changed by 90° at the phase transition. If there would be a uniform homeotropic alignment of the Col_{sq} (*p4mm*) phase in the measurement cell, then the conductivity should be reduced, because the columns would be aligned parallel to the electrodes in the 3D-Hex phase and the conductive columns would be isolated by the nonpolar molecular parts.

Table 6. Transition temperatures ($T/^{\circ}\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics), lattice parameters (measured temperature in brackets, $^{\circ}\text{C}$), volumes of the unit cells (nm^3), number of molecules in the unit cell and volume fraction values of terminal alkoxy chains (f_R), central aromatic core (f_{Ar}) and lateral polar chain (f_P) of compounds **A***m*/*n*.



Comp.	<i>m</i>	<i>n</i>	Phase transitions ($T/^{\circ}\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameter (nm) (at $T/^{\circ}\text{C}$)	Volume of one unit cell (nm^3) ^b	Number of molecules in one unit cell ^d	f_R	f_{Ar}	f_P
A4/2	4	2	Cr 86 Col _{sq} (<i>p4gm</i>) 104 Col _h 108 Iso <i>18.7</i> <i>1.03</i> <i>0.63</i>	$a_{\text{hex}} = 3.7$ (105); $a_{\text{sq}} = 7.08$ (90)			0.25	0.33	0.42
A4/3	4	3	Cr 70 Col _h 102 Iso <i>21.6</i> <i>0.73</i>	$a_{\text{hex}} = 4.05$ (90), 4.18 (50)	6.39 6.81	6.6 7.0	0.24	0.31	0.45
A4/4	4	4	Cr 56 Col _h 88-92 Col _h 97 Iso <i>16.7</i> <i>0.46</i>	$a_{\text{hex}} = 4.25$ (85), 4.38 (55)	7.04 7.48	6.8 7.3	0.22	0.29	0.48
A6/3	6	3	Cr < 20 Col _{sq} (<i>p4gm</i>) 115 Iso <i>2.15</i>	$a_{\text{sq}} = 7.87$ (100)	27.87	26.0	0.31	0.28	0.41
A6/4	6	4	Cr < 20 Col _{sq} (<i>p4gm</i>) 104 Col _h 111 Iso <i>1.58</i> <i>0.75</i>	$a_{\text{sq}} = 8.05$ (98); $a_{\text{hex}} = 4.34$ (108)	29.16 7.34	27.2 6.8	0.29	0.27	0.44
A6/6	6	6	Cr < 20 Col _h 102 M ^a 113 Iso <i>0.69</i>	$a_{\text{hex}} = 4.86$ (80); $d = 4.02$ (100) ^c	9.17	7.3	0.26	0.24	0.49
A8/3	8	3	Cr < 20 Col _{sq} (<i>p4mm</i>) 148 Iso <i>4.10</i>	$a_{\text{sq}} = 3.72$ (140), 3.97 (25)	6.23 7.09	5.3 6.1	0.37	0.26	0.38
A10/2	10	2	Cr < 20 3D-Hex 115 Col _{sq} 143 Iso	$a_{\text{sq}} = 3.70$ (130)	6.16	5.1	0.44	0.25	0.32
A10/3	10	3	Cr 88 Col _{sq} (<i>p4mm</i>) 146 Iso <i>0.99</i> <i>3.84</i>	$a_{\text{sq}} = 3.9$ (130)	6.84	5.4	0.42	0.24	0.34
A10/4	10	4	Cr -6 Col _{sq} (<i>p4mm</i>) 139 Iso <i>2.11</i> <i>4.49</i>	$a_{\text{sq}} = 3.95$ (135), 4.02 (115)	7.02 7.27	5.3 5.5	0.40	0.23	0.38
A10/6	10	6	Cr -7 Col _{sq} (<i>p4mm</i>) 116 Iso <i>2.30</i> <i>4.01</i>	$a_{\text{sq}} = 4.16$ (90), 4.20 (50)	7.79 7.94	5.4 5.5	0.37	0.21	0.43
A10*/3	10* ^b	3	Cr <20 Col _{sq} (<i>p4mm</i>) 106 Iso <i>3.48</i>	$a_{\text{sq}} = 3.77$ (100), 3.86 (25)	6.40 6.70	5.0 5.3	0.42	0.24	0.35
A10*/4	10* ^b	4	Cr <20 Col _{sq} (<i>p4mm</i>) 94 Iso				0.40	0.23	0.38
A16/3	16	3	Cr ₁ 65 Cr ₂ 77 Cr ₃ 94 3D-Hex 127 Iso <i>5.71</i> <i>2.23</i> <i>1.00</i> <i>2.55</i>	$a = 4.75$, $c = 4.65$ (80)	90.86	58	0.53	0.19	0.28
A16/4	16	4	Cr 43 M ₁ 75 3D-Hex 122 Iso <i>56.6</i> <i>3.01</i>	$a = 5.04$, $c = 4.70$ (65)	103.4	64	0.51	0.19	0.31

^a The mesophase M is assumed to have an arrangement of columns without 2D lattice. ^b 3,7-dimethyloctyloxy. ^c The height of the unit cell is 0.45 nm. ^d The volume of the molecules are obtained by using Immirzi's crystal volume increments.^[89]

^e There could be a slight deviation of the temperatures calibration of the diffractometer.

For the series of compounds **A6**/*n* which have two hexyloxy chains, two different mesophases were observed depending on the size of the lateral polar chain (Figure 4.7). Compound **A6/3** has a Col_{sq} (*p4gm*) phase as discussed earlier.

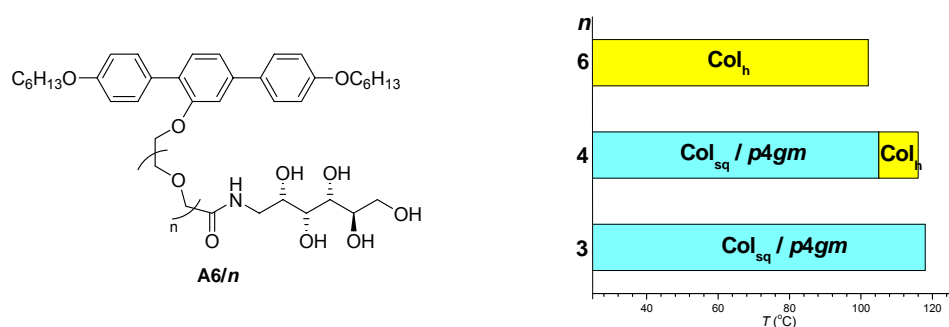


Figure 4.7. Mesophase types and transition temperatures ($T/^{\circ}\text{C}$) of compounds **A6/n** depending on the length of the lateral chain.

In compound **A6/4** which has a quater(oxyethylene) unit, two different mesophases were found. The low temperature phase (Figure 4.8a) has a more bright texture than the high temperature phase (Figure 4.8b). A square columnar phase ($p4gm$) at low temperature, and a hexagonal columnar phase at high temperature were identified on the basis of the X-ray diffraction pattern. It should be pointed out that the symmetry of the square columnar phase of **A6/4** is different from that of the Col_{sq} ($p4mm$) in compounds **A10/n**. Furthermore, the lattice parameter of the Col_{sq} ($p4gm$) phase is much larger than those typically found for the Col_{sq} ($p4mm$) phases. The lattice parameter of the Col_{sq} ($p4gm$) phase of **A6/4** amounts $a_{\text{sq}} = 8.0$ nm, while the length of the molecule (L) in its most extended conformation between the two ends of the terminal chains is only 3.0 nm (estimated by Chem3D). The lattice parameter is more than twice as large as the molecular length ($a_{\text{sq}} \approx 2.7 L$). About 29 molecules are arranged in a unit cell with a height of 0.45 nm, which is more than four times of the numbers found in the Col_{sq} ($p4mm$) phases (Table 6). This Col_{sq} ($p4gm$) phase can be considered as an intermediate phase between the Col_{sq} ($p4mm$) phases which have the polar columns surrounded by the square arranged aromatic cores and the Col_h phase. A similar phase sequence Col_{sq} ($p4mm$) – Col_r ($p2gg$) – Col_h has been found (see Chapter 1, Figure 1.12) for the bolaamphiphiles with lateral nonpolar chain by increasing the size of the lateral chain. For these bolaamphiphiles, it has been proven that the $p2gg$ lattice is resulted from a regular organisation of pentagons (slightly distorted) in a 2D lattice. The $p4gm$ lattice is formed if the two lattice parameters a and b of the $p2gg$ lattice become equivalent. So, a pentagonal cross section is also assumed for the columns forming this Col_{sq} ($p4gm$) phase as shown in Figure 4.8c. In this model, the polar chains segregate into elliptical columns and the aromatic cores surround these columns with a slightly distorted pentagonal shape, and two pentagons form a dimer. These dimers, arranged in a herring-bone pattern, can fill the space efficiently. By increasing the size of the lateral polar chain, the diameter of the polar columns is also increased. The larger the polar columns, the more aromatic cores are required to frame the columns, which changes from four in the Col_{sq} ($p4mm$) phase to five in the Col_{sq} ($p4gm$) phase. As a consequence, the shape of the cross section changes from a square to a pentagon.

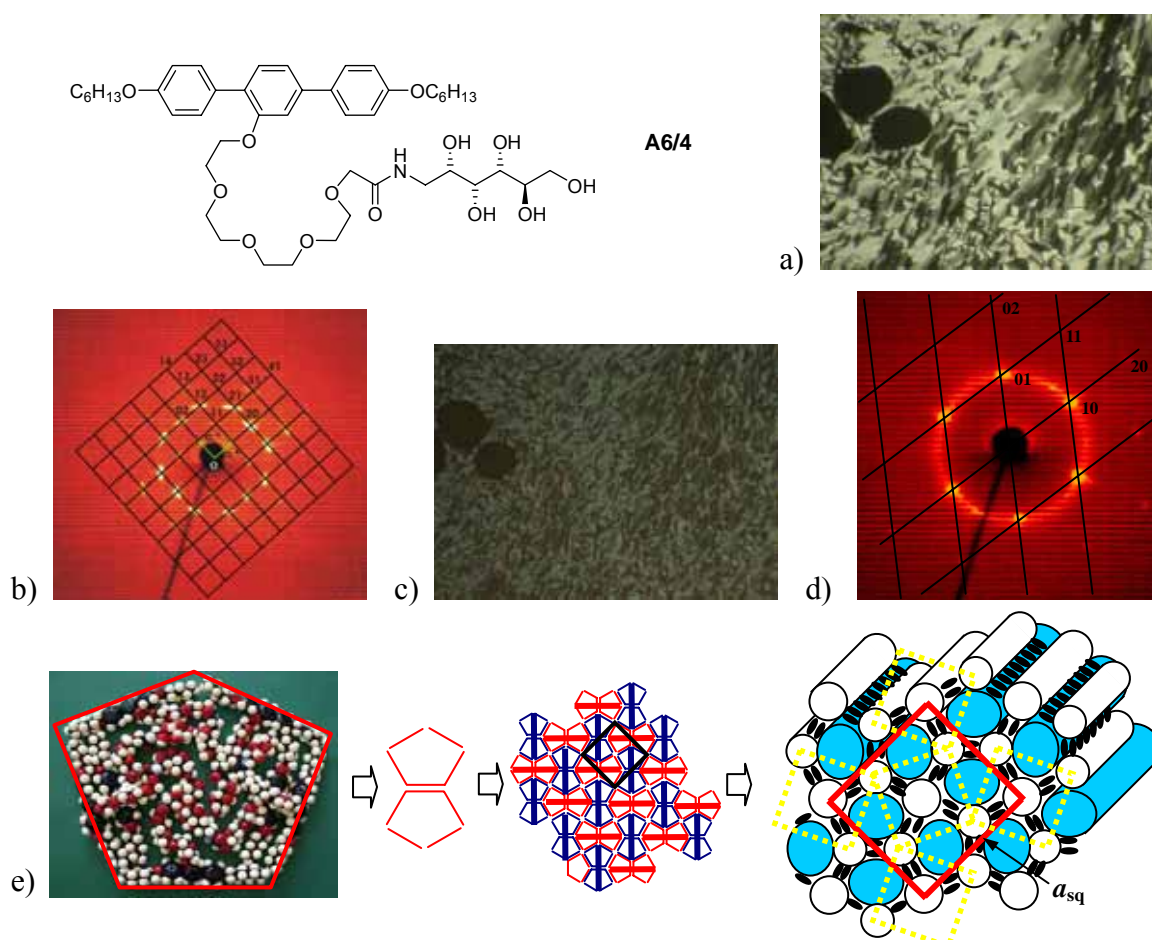


Figure 4.8. (a) Texture of the Col_{sq} ($p4gm$) of compound **A6/4** at 80°C; (b) X-ray diffraction pattern of the Col_{sq} ($p4gm$) phase of **A6/4** at 97°C; (c) texture of the Col_{h} phase of **A6/4** at 111°C; (d) X-ray diffraction pattern of the Col_{h} phase of **A6/4** at 102°C; (e) model for the organisation of the molecules in the Col_{sq} ($p4gm$) phase of **A6/4** (the distinct colours of the pentagonal frames and the bold lines are only guides for eyes to make it easier to see the symmetry).

It was expected at first that the high temperature Col_{h} phase of **A6/4** has the molecules arranged in hexagons and forms such a hexagonal columnar phase with the alkyl chains segregated into columns framed by six p-terphenyl cores as shown in Figure 4.8. However, the calculation shows that the volume occupied by the lipophilic chains mismatches with that required by the model (see Appendix 2). For example, based on the lattice parameter ($a_{\text{hex}} = 4.3 \text{ nm}$), it can be calculated that there are in average 6.4 molecules in one unit cell (see Table 6). If this segregated Col_{h} model would be right, the space available for the aliphatic chains in one unit cell can only accommodate 7.2 hexyl chains. However, the 6.4 molecules would require space for 12.8 alkyl chains. The disagreement indicates that the molecules might have another arrangement.

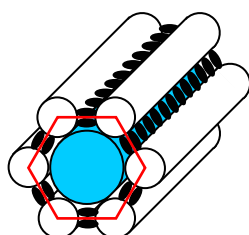


Figure 4.9. The model for the organisation of the molecules in the segregated Col_{h} phase.

The disagreement means that in contrast to the Col_{sq} ($p4mm$ and $p4gm$) phases, the segregation of the alkyl chains might be lost in this Col_{h} phase. This is in line with the fact that the enthalpy change at the Col_{sq} ($p4gm$) to Col_{h} transition amounts about twice as the value of the Col_{h} to Iso transition. This means that main change occurs at the Col_{sq} ($p4gm$) to Col_{h} transition. Therefore, the following model is suggested for this Col_{h} phase (Figure 4.10c). The polar groups segregate into cylinders which are organised in a 2D hexagonal lattice. These cylinders are surrounded by the aromatic cores and the alkoxy chains, and the aromatic cores and alkyl chains are not segregated. This “non-segregation” model is related to the organisation of the flexible amphiphiles in reversed Col_{h} phases. However, the lipophilic continuum also contains the rod-like p-terphenyl units. It is assumed that these rigid cores are organised parallel to each other (like those in the nematic phase) in order to minimize the excluded volume. This parallel organisation might be of short range order, leading to in total an isotropic distribution of the rigid cores, or it can have long range order. In the latter case, the long axis of the p-terphenyl units can be either organised parallel to the polar columns or perpendicular to them. The observed decrease of the birefringence at the phase transition of Col_{sq} ($p4gm$) to Col_{h} could be explained by the proposed loss of segregation. It is reasonable to assume that the main optical axis is determined by the p-terphenyl units. As the birefringence does not go through zero or a minimum at the phase transition, it is assumed that the direction of the p-terphenyl cores does not change at the phase transition. This means that the rod-like cores should be organised, in average, perpendicular to the long axis of the polar columns. Hence, a “nematic like” organisation of the p-terphenyl cores with the director perpendicular to the polar columns seems reasonable. This organisation could be favoured by a “residual partial segregation” of the alkyl chains in small domains probably positioned parallel to the polar cylinders in the regions between three polar cylinders (see Figure 4.10d, region A).

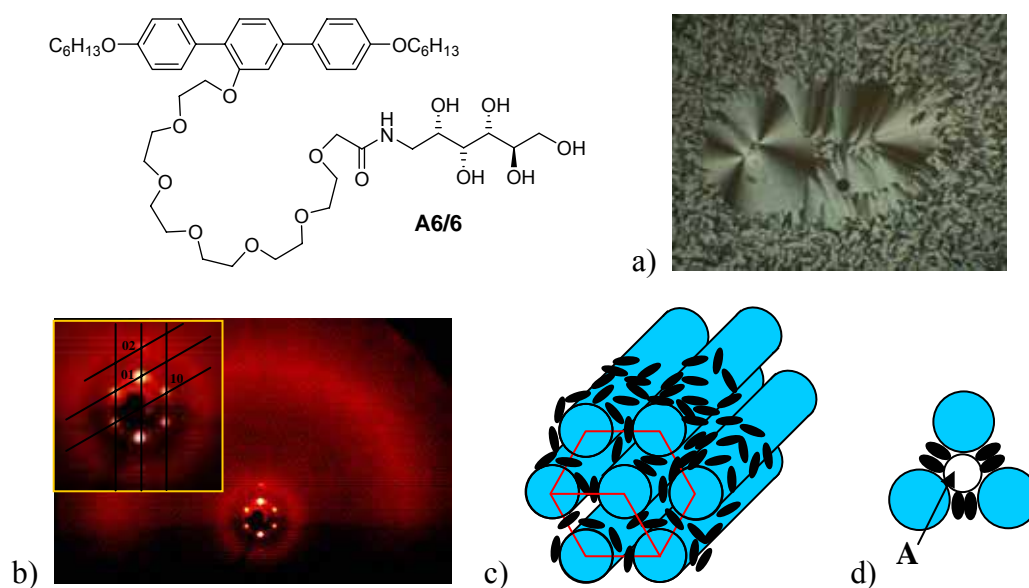


Figure 4.10. (a) Texture of the Col_{h} phase of compound **A6/6** at 80°C; (b) X-ray diffraction pattern of the Col_{h} phase of **A6/6** at 87°C; (c) model of the Col_{h} phase of **A6/4** and **A6/6** (the alkyl chains are omitted); (d) schematic sketch showing the “residual partial segregation” of the alkyl chains and the aromatic cores in the space between three polar cylinders (position A).

Compound **A6/6** which incorporates a sexi(oxyethylene) unit in the lateral polar chain shows a hexagonal columnar phase (Figure 4.10a). Aligned samples of this mesophase were obtained and investigated by X-ray diffraction (Figure 4.10b). In the wide angle region of the X-ray diffraction pattern, the diffuse scattering forms a closed ring, indicating an isotropic organisation of the aromatic terphenyl cores as well as the alkyl chains. In the small angle region the hexagonal arrangement of the spots confirms the Col_h phase of **A6/6** with the lattice parameter $a_{\text{hex}} = 4.85$ nm. The diffuse scattering in the small angle region of the X-ray diffraction pattern of **A6/6** (maximum at $D = 1.77$ nm) could be due to the average distance between the ends of the aromatic cores, and this would be in line with the organisation of the p-terphenyl perpendicular to the polar columns as proposed for the Col_h phase of **A6/4**.

Also for the butoxy compounds **A4/3** and **A4/4**, exclusively hexagonal columnar mesophases have been found (according to the calculation based on the lattice parameters, it is unlikely for these two compounds to have a Col_h phase with segregated lipophilic columns as shown in Figure 4.9, see Appendix 2). With increasing the size of the lateral polar group, the lattice parameter increases, and the clearing temperature decreases.

For compound **A4/4**, an additional phase transition was observed within the Col_h phase according to the texture investigation. When heated from the low temperature columnar phase (Figure 4.11a), the birefringence of the texture starts to decrease at about 89°C, and at about 90.5°C a texture with nearly no birefringence was formed (Figure 4.11b). Upon further heating, the birefringence increased again (Figure 4.11c). The birefringence changes continuously indicating that it is a second order phase transition. Also on the DSC curve, there is no peak correspondence to this transition. When cooled down, the same phenomena can be observed at the same temperatures, which indicate that these two mesophases are thermodynamic equilibrium mesophases. However, based on the X-ray diffraction pattern (Guinier method), no changes of the phase type could be observed. The low temperature phase and the high temperature phase have the same hexagonal columnar symmetry. The change of the optic axis of the mesophase is believed to give rise to this phase transition.^[94] It seems that the model shown in Figure 4.10c can also be used for the low temperature Col_h mesophase of **A4/4**, and a model shown in Figure 4.11e is assumed for the high temperature Col_h mesophase of **A4/4**. In both phases, the hexagonal lattice is due to a hexagonal order of the polar columns. The only difference between these two organisations is that the arrangement of the aromatic cores changes from perpendicular to the polar columns (low temperature Col_{h(⊥)} phase) to parallel to the polar columns (high temperature Col_{h(//)} phase). Based on these two models, the optical observations can be explained as shown in Figure 4.11d. In the low temperature phase, the aromatic cores are mainly arranged perpendicular to the polar columns. So, the main optical axis of the aromatic cores and the main optical axis of the polar columns (which is assumed to be parallel to the columns) are perpendicular to each other. The main contribution to the birefringence arises from the aromatic cores which are aligned perpendicular to the polar columns. When heated, the birefringence decreases at first. If it is assumed that the order of the parallel arrangement of the aromatic cores is reduced with rising the temperature, the distribution of the aromatic cores becomes

nearly isotropic, and then the birefringence will reach a minimum. The texture appears nearly isotropic and only the very weak “form birefringence” can be observed. Upon further heating, the birefringence increases again. This can be explained, if it is assumed that the p-terphenyl cores adopt an alignment parallel to the polar columns. This observation could be explained on the basis of the model shown in Figure 4.10c and d. It seems that with the raise of the temperature, the residual segregation of the alkyl chains become weaker. This means that the driving force for fixation of the aromatic cores perpendicular arranged to the polar columns also becomes weaker. At a certain temperature, the packing of the p-terphenyl cores parallel to the polar columns becomes favourable probably due to a closer possible packing which reduces the excluded volume.

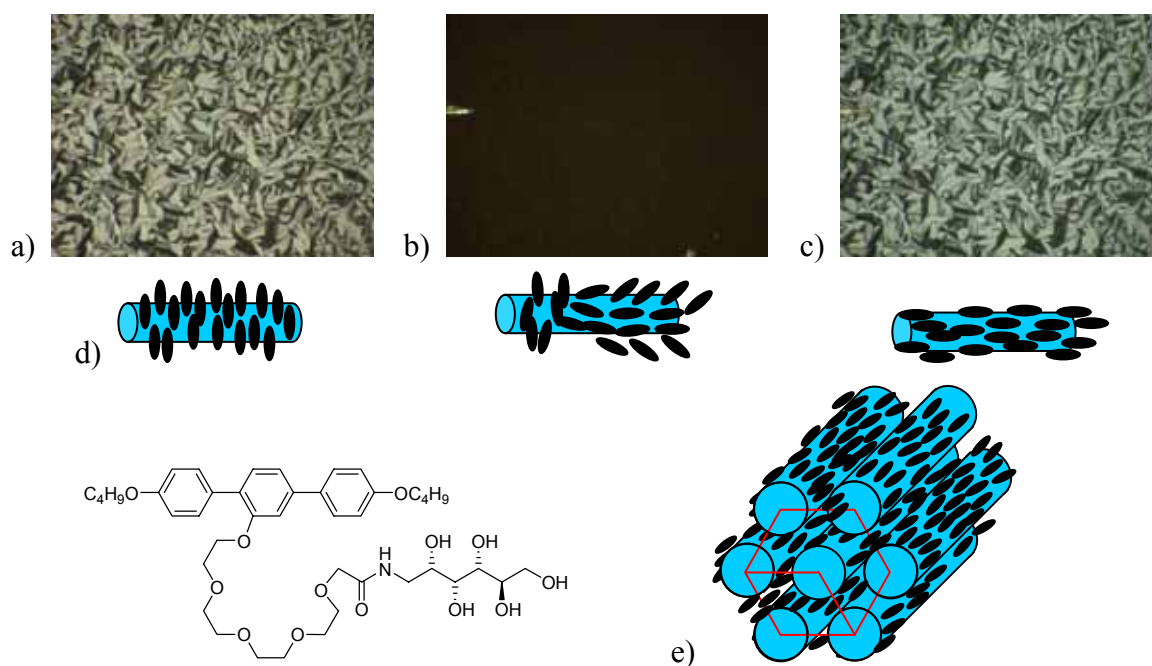


Figure 4.11. Textures of compound **A4/4**: (a) low temperature $\text{Col}_h(\perp)$ phase at 87 °C; (b) phase transition at 90.4 °C; (c) high temperature $\text{Col}_h(\parallel)$ phase at 95 °C; (d) schematic view of the phase transition of two different Col_h phases; (e) model of the organisation of the molecules in the high temperature $\text{Col}_h(\parallel)$ phase of **A4/4**.

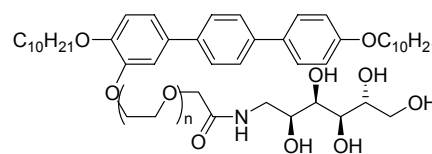
Compound **A4/2** has two optical uniaxial mesophases according to optical investigations. The X-ray studies indicate a low temperature $\text{Col}_{sq}(p4gm)$ phase and a high temperature Col_h phase. As the textures of compound **A4/2** as well as **A4/3** do not have a minimal birefringence upon cooling or heating, the Col_h phase of these two compounds are assumed to have the aromatic cores arranged perpendicular to the polar columns ($\text{Col}_h(\perp)$).

A typical feature of all columnar phases formed by these amides is that the lattice parameter increases with decreasing the temperature. This might be due to the increased contribution of the linear all-*trans*-conformation of the alkyl chains at reduced temperature, which increases the effective length of the dialkoxy p-terphenyl cores, and according to the proposed models of these mesophases, it is expected to increase the lattice parameters.

4.1.3 Influence of the position of the lateral chain (Y-shaped amphiphiles)

Table 7. Transition temperatures ($T/^\circ\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in *italics*), lattice parameters (nm, temperature in bracket $^\circ\text{C}$) and volume fraction values of terminal alkoxy chains (f_R), central aromatic core (f_{Ar}) and lateral polar chain (f_P) of compounds **A*10/*n***.

Comp.	n	Phase transitions ($T/^\circ\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameter (nm) (at $T/^\circ\text{C}$)	f_R	f_{Ar}	f_P
A*10/3	3	Cr 117 Col _{sq} (<i>p4mm</i>) 155 Iso <i>48.9</i> <i>4.09</i>	$a_{sq} = 4.00$ (130), 4.08 (90)	0.42	0.24	0.35
A*10/4	4	Cr 114 Col _{sq} (<i>p4mm</i>) 154 Iso <i>66.9</i> <i>5.59</i>		0.40	0.23	0.38

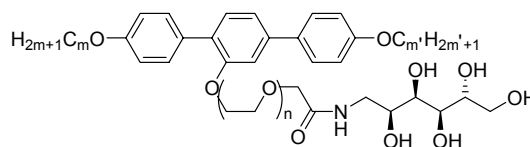


Only square columnar phases (*p4mm*) were found for the two compounds **A*10/3** and **A*10/4**, in which the polar groups are grafted to the ortho position adjacent to one of the terminal alkoxy chain. Comparison with the corresponding central substituted compounds **A10/3** and **A10/4** shows, that changing the position of the lateral chain does not change the mesophase type. The Col_{sq} (*p4mm*) phase is slightly stabilized by 10 $^\circ\text{C}$, however the melting points are also increased, so that the overall mesophase region is reduced.

4.1.4 Facial amphiphiles with different terminal alkoxy chains

Table 8. Transition temperatures ($T/^\circ\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in *italics*), lattice parameters (nm, measured temperatures in brackets, $^\circ\text{C}$) and volume fraction values of terminal alkoxy chains (f_R), central aromatic core (f_{Ar}) and lateral polar chain (f_P) of compounds **A6.16/*n*** and **A16.6/*n***.

Comp.	<i>m</i>	<i>m'</i>	<i>n</i>	Phase transitions ($T/^\circ\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameter (nm) (at $T/^\circ\text{C}$)	f_R	f_{Ar}	f_P
A6.16/3	6	16	3	Cr 49 Col _{sq} (<i>p4mm</i>) 137 Iso <i>29.6</i> <i>2.17</i>	$a_{sq} = 4.0$ (130), 4.15 (90)	0.44	0.23	0.33
A6.16/4	6	16	4	Cr 52 Col _{sq} (<i>p4mm</i>) 134 Iso <i>4.23</i> <i>2.54</i>	$a_{sq} = 4.15$ (130), 4.30 (90)	0.42	0.22	0.36
A6.16/6	6	16	6	Cr 56 Col _{sq} (<i>p4mm</i>) 120 Iso <i>46.9</i> <i>2.28</i>	$a_{sq} = 4.5$ (80)	0.39	0.20	0.41
A16.6/3	16	6	3	Cr 53 Col _{sq} (<i>p4mm</i>) 138 Iso <i>10.3</i> <i>2.52</i>		0.44	0.23	0.33
A16.6/4	16	6	4	Cr < 20 Col _{sq} (<i>p4mm</i>) 134 Iso <i>2.94</i>		0.42	0.22	0.36
A16.6/6	16	6	6	Cr 32 Col _{sq} (<i>p4mm</i>) 119 Iso <i>33.0</i> <i>3.04</i>		0.39	0.20	0.41



All these six compounds have the same Col_{sq} (*p4mm*) phase, which this is confirmed by the textures, X-ray diffraction pattern and by miscibility studies. In this case, it seems that there is no influence upon mesophase properties by exchanging the position of the different alkoxy chains. The difference between the asymmetric compounds and their symmetric analogous **A10/*n*** is also very small.

4.2 Molecules incorporating polar chains with diols end groups

Selected compounds with the smaller 1-amidopropane-2,3-diol group and 2-amidopropane-1,3-diol group at the end of the lateral polar chain were synthesized. Their mesophase properties are summarised in Table 9.

Table 9. Transition temperatures ($T/^\circ\text{C}$), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics) lattice parameters (nm, measured temperatures in brackets, $^\circ\text{C}$) and volume fractions of terminal alkoxy chain (f_R), central aromatic core (f_{Ar}) and lateral polar chain (f_P) of compounds **A¹10/*n*** and **A²10/*n***.

Comp.	<i>n</i>	X	Phase transitions ($T/^\circ\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameter(nm) (at $T/^\circ\text{C}$)	f_R	f_{Ar}	f_P
A¹10/3	3	A ¹	Cr 36 3D-Hex (Col _{sq}) 88 Iso <i>39</i> <i>2.3</i>	$a = 3.3, c = 3.5$ (78)	0.45	0.26	0.29
A¹10/4	4	A ¹	Cr 48 Col _{sq} (<i>p4mm</i>) 85 Iso <i>0.18</i> <i>2.6</i>	$a_{sq} = 3.8$ (32)	0.43	0.24	0.33
A²10/3	3	A ²	Cr 19 Col _{sq} (<i>p4mm</i>) 87 Iso <i>3.77</i> <i>2.3</i>		0.45	0.26	0.29
A²10/4	4	A ²	Cr < 20 Col 49 Col _{sq} (<i>p4mm</i>) 89 Iso <i>0.10</i> <i>3.3</i>	$a_{sq} = 3.8$	0.43	0.24	0.33

Upon fast cooling the Col_{sq} (*p4mm*) phase is formed, whereas slow cooling leads to the 3D-Hex phase. Lattice parameters of the 3D-Hex phase. Super cooled sample.

As expected, reduction of the number of OH groups depresses the clearing temperature. However, reduction of the number of the OH groups does not change the phase types, all four compounds have the same columnar square (*p4mm*) mesophase. Additionally, compound **A¹10/3** shows a 3D mesophase (most probably 3D-Hex) if cooled down from isotropic liquid very slowly (e.g., 0.1 $^\circ\text{C}/\text{min}$). The Col_{sq} (*p4mm*) only appears by fast cooling (e.g., 30 $^\circ\text{C}/\text{min}$). It seems that in this case, the Col_{sq} (*p4mm*) phase is metastable and the 3D phase is the thermodynamic stable mesophase. However, according to the optical investigation, if the Col_{sq} is once formed, then no transition to the 3D phase can be observed.

4.3 Mesophases of A4/4 with formamide

Actually, the compounds discussed above are amphotropic liquid crystals, because their mesomorphic properties can be influenced by specific interaction with one of the incompatible units. Herein, the liquid crystalline properties of **A4/4** in the presence of formamide are qualitatively studied by using the solvent-penetration technique (Appendix 3).

Formamide can form hydrogen bondings with the poly(oxyethylene) chains as well as with the OH groups and the amide group of compound **A4/4**. Thus it should have an influence upon the mesophase types and the mesophases stability (lyotropic mesophases). With increasing the concentration of formamide, the original Col_h phase of pure **A4/4** is destabilised and new types of mesophases are introduced. On cooling from the isotropic state, a texture with homeotropic alignment and some defects (small crosses and oily streaks)

is formed in the contact region between the solvent and the pure compound **A4/4** which is typical for SmA phases (Figure 4.12a). This SmA phase is separated from the Col_h phase of **A4/4** by an isotropic liquid ribbon. By further cooling, a schlieren texture with strong birefringence grows from the homeotropic SmA domains (Figure 4.12b). This indicates the formation of an optically biaxial mesophase. Crystallization occurs at 55°C and reheating gives a melting point of approximately 77°C. At the melting point, a phase transition from Cr to SmA phase was observed, hence, the biaxial mesophase seems to be monotropic. The biaxial mesophase has similar textures as a Lam_N phase which was recently found for bolaamphiphiles with large lateral perfluorinated alkyl chains.^[68-70,88] The model proposed for the bolaamphiphiles^[68-70,88] might also be suitable to explain the structure of this solvent induced (lyotropic) phase. When the concentration of formamide is increased, the effective size of the polar parts of the molecule increases due to the coordination of the solvent molecules to these polar groups. This leads to the fusion of the polar columns into layers. Thus, a layer structure is formed, in which the alkoxy chains and the p-terphenyl cores are segregated from the polar parts of the molecules. Within the apolar layers, the aromatic cores are arranged parallel to the layers. At high temperature they might have an isotropic arrangement within the layers and form the laminated isotropic phase (Lam_{iso}, Figure 4.12d), which is related to the L α phase and the SmA phase. On cooling, the p-terphenyl cores adopt a nematic like long range orientational order within the layers and a laminated nematic phase (Lam_N, Figure 4.12e) is formed. However, due to the monotropic character of this biaxial mesophase, more detailed investigations are not possible and therefore these are only tentative models.

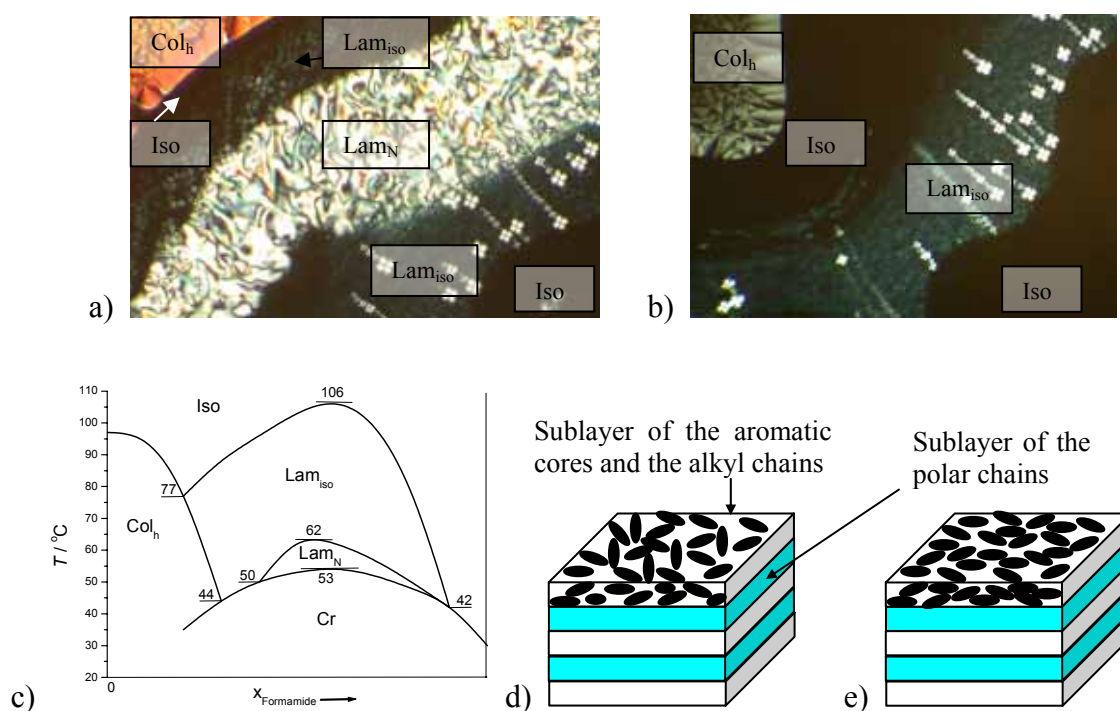


Figure 4.12. Contact region of **A4/4** (left top) and formamide (right bottom) as observed between crossed polarizers; (a) Lam_{iso} phase at 99°C; (b) growing of Lam_N phase from Lam_{iso} phase at 61°C; (c) qualitative phase diagram of **A4/4** with formamide as seen by cooling (as obtained from contact preparations, two phase regions are not shown); (d) model of Lam_{iso} phase; (e) model of Lam_N phase.

4.4 Summary of the mesophase behaviour of the amides

According to the previous discussion, it can be concluded that in the case of the facial amphiphiles with a lateral polar chain incorporating a polyhydroxy end group, a phase sequence 3D-Hex – Col_{sq} (*p4mm*) – Col_{sq} (*p4gm*) – Col_{h(⊥)} (aromatic cores perpendicular to the polar columns) – Col_{h(//)} (aromatic cores parallel to the polar columns) – Lam_{iso} (SmA) – Lam_N can be found by increasing the volume fraction of the lateral polar chain (or by heating, or by coordination of protic solvents to the polar chain) (Figure 4.13).

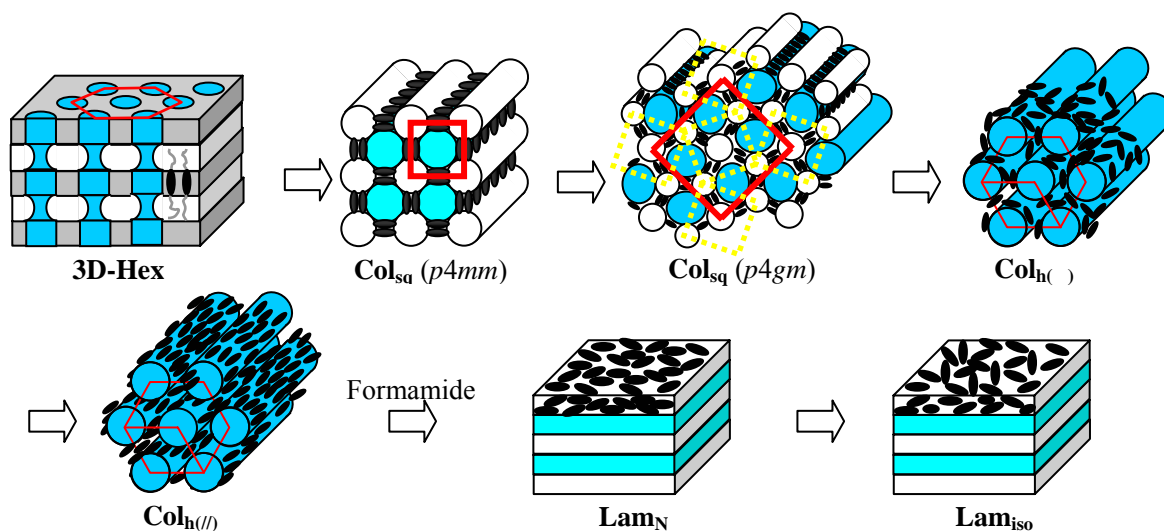


Figure 4.13. Schematic view of the phase sequence of the facial amphiphiles with lateral polyhydroxy groups. Along the arrows direction, the volume fraction of the lateral polar chain is increased or the temperature is risen.

As expected, the polyhydroxy groups also produce very strong intermolecular attractions similar to the metal carboxylates. The same mesophase morphologies can be formed by both amides and carboxylates which have similar volume fraction values of the polar and nonpolar parts: 3D-Hex: $f_p = 0.21 - 0.30$ (carboxylates), $f_p = 0.28 - 0.32$ (amides); Col_{sq} (*p4mm*): $f_p = 0.30 - 0.34$ (carboxylates), $f_p = 0.32 - 0.43$ (amides). However, larger volume fractions of the lateral polar chains are obtained with amides and therefore the Col_{sq} (*p4mm*) phase is dominating. Additional mesophases, Col_{sq} (*p4gm*) ($f_p = 0.41, 0.44$) and Col_h ($f_p = 0.44 - 0.49$), also could be observed.

Among these mesophases, the square columnar phases and the laminated phases (solvent induced phases) of the amides have their related mesophases in the bolaamphiphiles with nonpolar lateral chain. However, the location of the hydrophilic and lipophilic regions with respect to the rigid cores are exchanged in these two different classes of compounds.^[68-70,88] In contrast to bolaamphiphiles, the columns framed by five rigid cores represent the largest stable honeycomb like network structure of the synthesized facial amphiphiles, and also “non-segregation” Col_h phases are found. These Col_h phases are formed by losing the segregation of the terminal alkyl chains. This is due to the rather weak cohesive forces produced by the alkyl chains. In the case of bolaamphiphiles, the interactions between the terminal groups are strong H-bondings interactions which are more difficult to destroy. This makes it possible to observe larger polygons (hexagons, stretched hexagons, etc.).

However, if the terminal alkoxy chains were long enough, it might be possible that these facial amphiphiles also can form the segregated Col_h phase as shown in Figure 4.9, and probably also the other mesophases with giant cross sections could be observed.

5 Liquid crystalline properties of the carboxylic acids

These compounds were intermediates for the synthesis of the metal carboxylates (Chapter 3) and the amides (Chapter 4). They are structurally related to the diols **II/n** (Chapter 1) with the difference that the COOH group provides only one H-donor group for H-bonding. Their mesophase properties will be discussed here.

5.1 Influence of the length of terminal alkoxy chains

Table 10 summarises the transition temperatures of the compounds **Hm/n**. In Figure 5.1, the dependence of the mesomorphic behaviour on the length of the terminal alkoxy chains in the homologous series of compounds **Hm/3** is shown graphically.

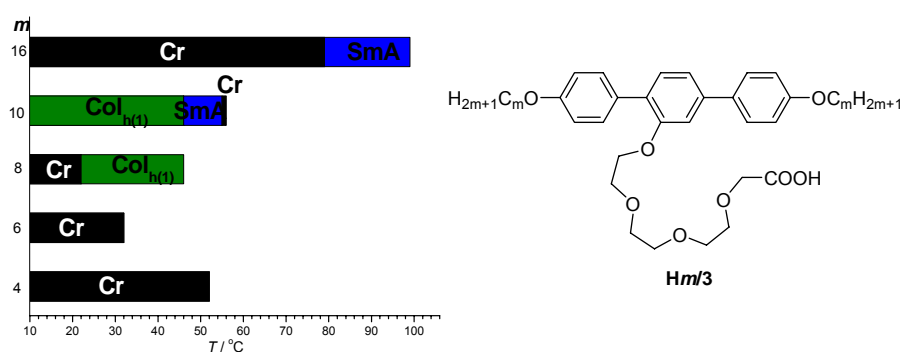


Figure 5.1. Transition temperatures ($T/^{\circ}\text{C}$) and mesophase types of the series of compounds **Hm/3** depending on the length of the terminal alkoxy chains ($\text{Col}_{h(1)}$: hexagonal columnar phase with large lattice parameter).

Compound **H4/3**, which has two butoxy terminal chains, does not exhibit any mesomorphic properties. Also compound **HB/3** (Table 10) which has two semi-rigid benzyloxy terminal groups is not a liquid crystal.

Compound **H6/3**, which has two hexyloxy terminal chains, also shows no liquid crystalline properties. However, further increasing the length of the terminal alkoxy chains leads to the appearance of liquid crystalline properties.

The octyloxy substituted compound **H8/3** is found to be liquid crystalline between 22 °C and 46 °C. It shows a texture with mosaic like domains, spherulitic domains and optically isotropic regions (Figure 5.2a), which indicates an optically uniaxial columnar mesophase (either Col_{sq} or Col_h). The X-ray scattering pattern can be indexed on the basis of a 2D hexagonal lattice with lattice parameter $a_{\text{hex}} = 8.9 \text{ nm}$.

Compound **H10/3**, which has two decyloxy chains, shows two monotropic liquid crystalline mesophases. On cooling from the isotropic melt, textures with pseudo-isotropic areas and oily streaks can be observed (Figure 5.2b), which indicates a SmA phase. The SmA phase was also confirmed by X-ray scattering studies. On further cooling, a phase transition appears at 46°C which is 10°C below the transition from the isotropic liquid to the SmA phase. The transition can be seen by the formation of a spherulitic texture (Figure 5.2c)

which grows from the optically isotropic regions of the SmA phase. X-ray diffraction investigation indicates a $\text{Col}_{\text{h}(1)}$ phase (lattice parameter $a_{\text{hex}} = 9.5 \text{ nm}$) which is nearly the same as that of compound **H8/3**.

Compound **H16/3**, which comprises two rather long hexadecyloxy chains, shows exclusively an enantiotropic SmA mesophase, and the melting point as well as the clearing temperature is much higher than those of the compounds with shorter alkoxy chains.

From the results shown above, a phase sequence $\text{Col}_{\text{h}(1)} - \text{SmA}$ can be observed by increasing the length of the terminal alkoxy chains.

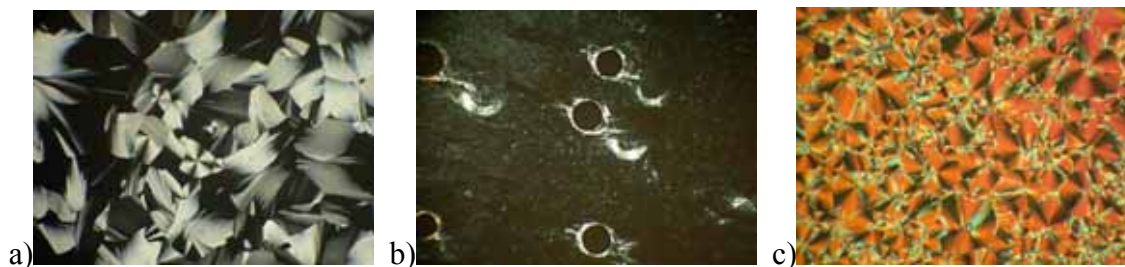


Figure 5.2. Textures of the: (a) columnar mesophase of compound **H8/3** at 44 °C; (b) SmA phase of compound **H10/3** at 46 °C; (c) Col_{h} phase of compound **H10/3** at 42 °C.

5.2 Influence of the length of the lateral polar chain

In the next step, a different number of oxyethylene units was introduced into the lateral polar chain and the influence of this change upon the liquid crystalline properties was examined. Not only the decyloxy substituted compounds **H10/n**, but also the compounds with other alkoxy chain lengths (compounds **H4/n**, **H6/n**, **H8/n**, **H16/n**), were investigated. The results are shown in Table 10. Figure 5.3 summarises the mesophase properties of the series of compounds **H10/n**.

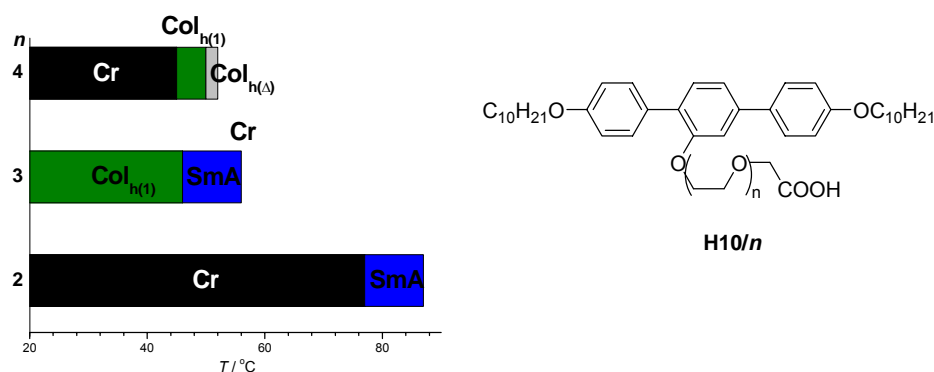


Figure 5.3. Transition temperatures ($T/^\circ\text{C}$) and mesophase types of the series of compounds **H10/n** depending on the length of the lateral chain ($\text{Col}_{\text{h}(1)}$: hexagonal columnar phase with large lattice parameter).

Similarly to the compounds **II/n** (see Chapter 1), the decyloxy substituted compounds **H10/n** show a transition from a SmA mesophase to a columnar phase by increasing the number of oxyethylene units in the lateral chain. Compound **H10/2**, which incorporates only two oxyethylene units, shows only a smectic layer structure. When one more oxyethylene unit is introduced, compound **H10/3**, a monotropic SmA phase and a Col phase

have been found as discussed previously. By further increasing the length of the lateral polar chain, the columnar phase is stabilised. Compound **H10/4** which has four oxyethylene units within the lateral chain shows an enantiotropic columnar phase, and the SmA phase has disappeared.

Aligned samples were obtained for the columnar phase of **H10/4** and investigated by X-ray diffraction with a 2D detector (Figure 5.4a). The outer diffuse scattering forms a closed ring (maximum at $2\theta = 21.0^\circ$, calculated distance $D = 0.42$ nm) corresponding to the average distance between fluid alkyl chains and the mean distance between the parallel arranged aromatic cores. The diffuse wide-angle scattering also indicates a strong deviation of the molecular long axis from a preferred direction. In the small-angle region, in addition to a diffuse scattering, some sharp reflections can be found, which can be indexed on the basis of a two dimensional hexagonal lattice with a lattice parameter of $a_{\text{hex}} = 4.7$ nm.

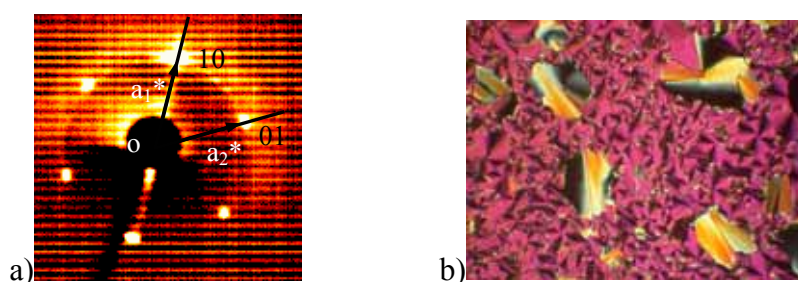


Figure 5.4. (a) X-ray diffraction pattern of the $\text{Col}_{\text{h}(\Delta)}$ phase of compound **H10/4** at 50 °C; (b) texture of the $\text{Col}_{\text{h}(\Delta)}$ mesophase of compound **H10/4** at 50 °C.

The observed phase sequence ($\text{SmA} - \text{Col}_{\text{h}(\Delta)} - \text{Col}_{\text{h}(1)}$) depending on the elongation of the lateral polar chain can be understood in the following way. The volume of the lateral polar chain is rather small and therefore the polar groups only weakly disturb the formation of the smectic layer structure. Additionally, the incompatibility between the aromatic cores and the lateral chains is reduced in comparison to the corresponding carboxylates. Therefore, no indication of a filled random mesh structure (additional small angle diffuse scattering on the equator) can be found. Hence, these smectic phases seem to represent conventional SmA phases. By increasing the volume of the lateral chain, the volume fraction value of the terminal lipophilic chains is reduced. It is reasonable to assume that the aliphatic layers break up with formation of cylinders. These cylinders are arranged in a 2D hexagonal lattice, i.e., a hexagonal columnar structure is formed (e.g., compound **H10/4**). In this Col_{h} phase (Figure 5.5a), the alkyl chains and the lateral polar chains are segregated into infinite cylinders, the aromatic cores surround the polar columns and connect two adjacent “alkyl” columns. Here, the aromatic cores are arranged in equilateral triangles around the polar columns. Calculations on the basis of this model using the lattice parameters (obtained from X-ray investigations) were carried out for compound **H10/4**.

$$\text{Volume of the unit cell: } V_{\text{cell}} = \frac{\sqrt{3}}{2} a_{\text{hex}}^2 \cdot h \quad (1)$$

$$\text{Number of molecules in one unit cell: } n = V_{\text{cell}} / V_{\text{molecule}} \quad (2)$$

$$\text{Calculated volume of the lipophilic columns within one unit cell: } V_{\text{alkyl}} = \pi \cdot r^2 \cdot h \quad (3)$$

Figure 5.5b shows one basic unit of the hexagonal lattice. It contains one lipophilic column and two hydrophilic columns. The lattice parameter is $a_{\text{hex}} = 4.7 \text{ nm}$ and the height of the unit cell is assumed to be 0.42 nm (maximum of the diffuse wide angle scattering). The volume of this unit cell can be calculated by equation (1) to be $V_{\text{cell}} = 8.0 \text{ nm}^3$. The volume of one molecule is 1.14 nm^3 as calculated using the crystal volume increments of Immirzi.^[89] According to equation (2), it can be calculated that there are in average 7 molecules in one unit cell ($n = 7$). Because the length of the p-terphenyl core is 1.25 nm , the diameter of the columns containing the alkyl chains is $(4.7 - 1.25) \text{ nm} = 3.45 \text{ nm}$. The volume of a 0.42 nm segment of this lipophilic column can be calculated by equation (3) to be 3.92 nm^3 . The volume of 14 ($2n$) decyloxy chains amounts to $14 \times 0.264 \text{ nm}^3 = 3.7 \text{ nm}^3$ (calculated using the crystal volume increments). These two values are in quite good agreement suggesting that the assumed organisation of the molecules is reasonable.

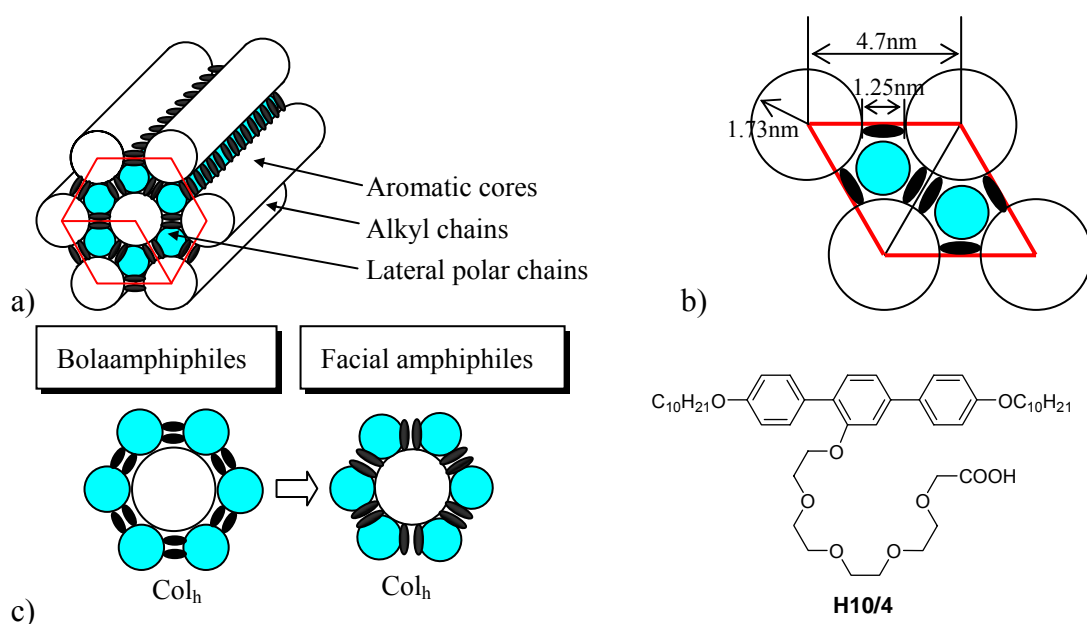


Figure 5.5. (a) Model for the Col_h phase of **H10/4**; (b) schematic view of one unit cell of the $\text{Col}_h(\Delta)$ lattice; (c) comparison of two types of Col_h phases of bolaamphiphiles and facial amphiphiles.

In the organisation shown in Figure 5.5, the aromatic cores form triangular walls around the polar columns. Regarding the lipophilic columns, each of them is framed by six aromatic walls, whereby the ends of the rigid cores are directed toward these lipophilic columns. When this arrangement is compared with the Col_h organisation of the bolaamphiphiles (see Chapter 1, Figure 1.12) then it can be seen that the long axes of the rigid cores within the cylinder walls are changed by 90° (Figure 5.5c).

It must be pointed out here, that these mesophases represent ordered liquid, which means that there is a high dynamic of the molecules (conformational, rotational, translational disorder). Therefore, the alignment of the p-terphenyl cores is by far not as perfect as suggested by the model shown in Figure 5.5a (and the other models shown in this work). In reality there is a high degree of local disorder which is also proved by the fact that the wide angle scattering is diffused.

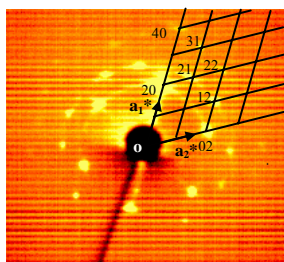
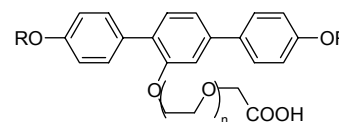


Figure 5.6. X-ray diffraction pattern of the low temperature $\text{Col}_{h(1)}$ phase of **H10/4** at 39 °C.

By further cooling from the Col_h phase of **H10/4** (1°C lower), a phase transition is indicated by the changes of the colour of the texture. The phase transition was also confirmed by X-ray scattering investigation. Some additional scatterings appeared in the X-ray diffraction pattern of the original Col_h phase at the phase transition (Figure 5.6). The reflections can be indexed on the basis of a 2D hexagonal lattice with lattice parameter $a_{\text{hex}} = 9.5$ nm, which is twice the value of the high temperature $\text{Col}_{h(\Delta)}$ phase ($a_{\text{hex}} = 4.7$ nm). By reducing the temperature, not only the strength of the H-bonding between the lateral polar chains but also the degree of the incompatibility between the later polar chain and the aromatic core increases. All these effects might lead to an increase of the size of the polar columns. However, the structure of this $\text{Col}_{h(1)}$ phase is still not clear.

Table 10. Transition temperatures ($T/^\circ\text{C}$, as detected by DSC and cross checked by polarizing microscopy), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics), lattice parameters (nm) and volume fraction values of terminal alkoxy chains (f_R), middle aromatic core (f_{Ar}) and lateral polar chain (f_P) of the series of compounds **Hm/n**, **HB/3**.



Comp.	R	n	Phase transitions ($T/^\circ\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameters (nm)	f_R	f_{Ar}	f_P
H4/2	C_4H_9	2	Cr 76 Iso 27.4		0.32	0.41	0.27
H4/3	C_4H_9	3	Cr 53 Iso 21.1		0.29	0.39	0.32
H4/4	C_4H_9	4	Cr ₁ 41 Cr ₂ 46 Iso 21.4 2.06		0.27	0.37	0.36
H6/3	C_6H_{13}	3	Cr 32 Iso 18.9		0.37	0.35	0.28
H6/6	C_6H_{13}	6	Cr 15 ($\text{Col}_{h(1)}$ 13) Iso 13.5 2.17		0.35	0.32	0.33
H8/3	C_8H_{17}	3	Cr 22 $\text{Col}_{h(1)}$ 43 Iso 27.0 2.24	$a_{\text{hex}} = 8.9$	0.44	0.32	0.26
H8/4	C_8H_{17}	4	Cr 21 Col_{sq} (<i>p4gm</i>) 30 (M 30) Iso 17.4 1.20	$a_{sq} = 7.9$	0.41	0.29	0.30
H10/2	$\text{C}_{10}\text{H}_{21}$	2	Cr 77 SmA 90 Iso 56.0 3.04		0.52	0.29	0.19
H10/3	$\text{C}_{10}\text{H}_{21}$	3	Cr ₁ 8 Cr ₂ 23 Cr ₃ 40 Cr ₄ 56 ($\text{Col}_{h(1)}$ 46 SmA 56) Iso 16.0 42.8 24.6 42.7 1.94	$d = 3.4$ (50 °C); $a_{\text{hex}} = 9.5$ (40 °C)	0.49	0.28	0.23
H10/4	$\text{C}_{10}\text{H}_{21}$	4	Cr 45 $\text{Col}_{h(1)}$ 50 $\text{Col}_{h(\Delta)}$ 51 Iso 47.05 1.74	$a_{\text{hex}} = 4.7$ (50 °C); $a_{\text{hex}} = 9.5$ (39 °C)	0.46	0.27	0.27
H16/3	$\text{C}_{16}\text{H}_{33}$	3	Cr 79 SmA 100 Iso 91.2 5.50		0.60	0.18	0.22
H16/4	$\text{C}_{16}\text{H}_{33}$	4	Cr 74 SmA 89 Iso 93.4 3.88		0.57	0.21	0.22
HB/3	Benzyl	3	Cr 105 Iso 39.7		0.34	0.35	0.31

The transition temperatures as observed by polarising microscopy. The mesophase M is an unknown mesophase, and the phase transition from M to Col_{sq} (*p4mm*) is observed as soon as the M phase is formed, but it is slow, it takes several minutes to hours to complete this phase transition.

In the series of the octyloxy substituted compounds **H8/*n***, three different liquid crystalline phases have been observed according to the textures. Compound **H8/3** has been discussed in section 5.1. Elongation of the lateral chain by one oxyethylene unit leads to compound **H8/4** for which a phase transition between two different liquid crystalline phases has been observed. At higher temperature, a non-specific sandy texture (Figure 5.7a) was observed (unknown mesophase M). On cooling, the formation of a spherulitic texture (Figure 5.7c) was observed which points to the formation of a columnar phase. For this columnar phase, aligned samples were obtained and investigated by X-ray diffraction (Figure 5.7d). According to the positions of the reflections, the diffraction pattern can be indexed on the basis of a non-centred square columnar mesophase with a $p4gm$ space group. The lattice parameter is $a_{sq} = 7.9$ nm. The length of the molecule (L) in its most extended conformation between the ends of the terminal chains is only 3.5 nm (estimated by Chem3D). Hence, the lattice parameter is more than twice as large as the molecular length ($a_{sq} \approx 2.3 L$).

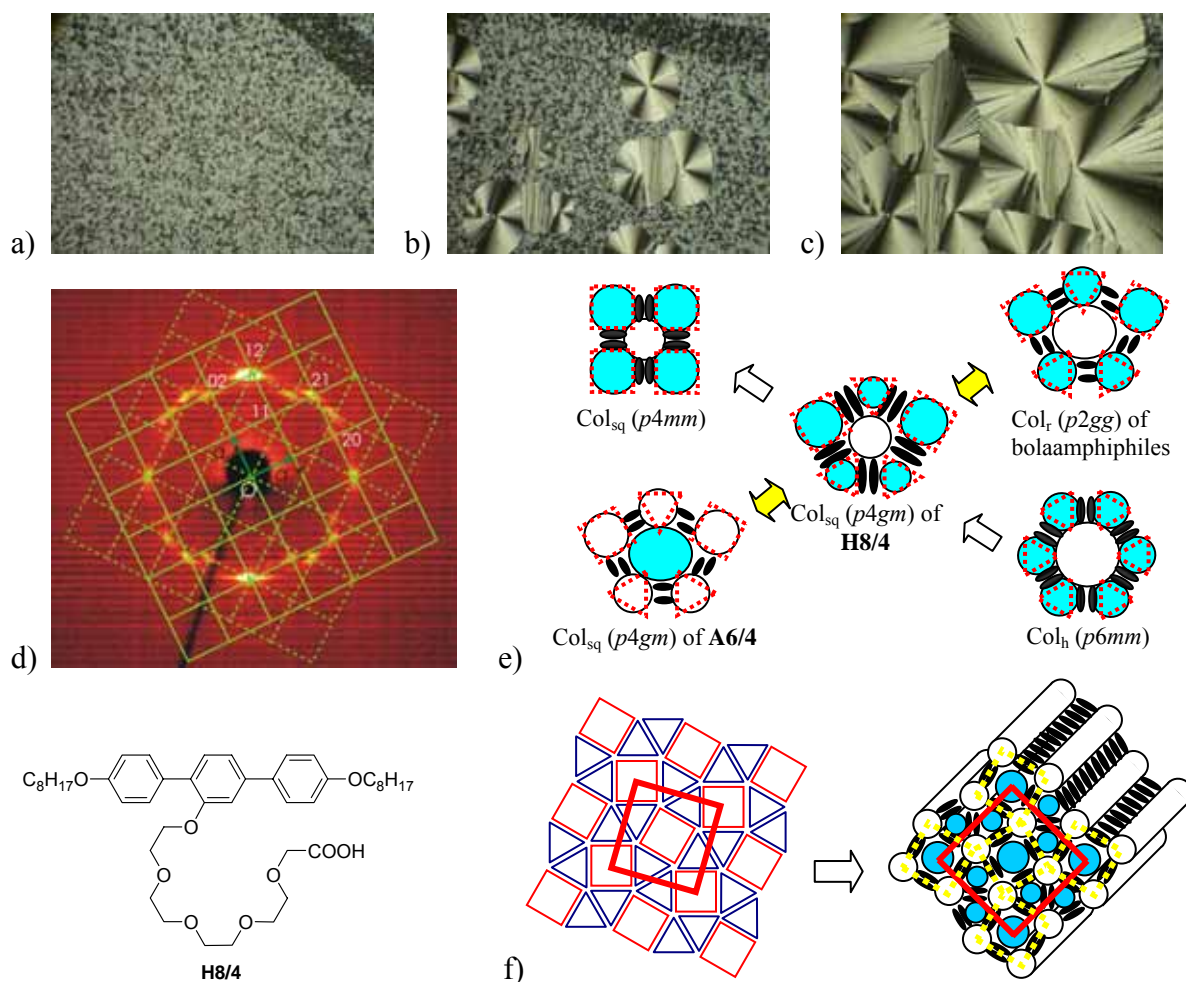


Figure 5.7. (a) Texture of the high temperature phase M of compound **H8/4** at 30 °C; (b) growing of the $Col_{sq} (p4gm)$ phase from the high temperature phase at 30 °C; (c) texture of the $Col_{sq} (p4gm)$ phase of compound **H8/4** at 30 °C; (d) X-ray diffraction pattern of the $Col_{sq} (p4gm)$ phase of compound **H8/4** at 30 °C; (e) schematic view of the comparison between the $Col_h (p6mm)$, $Col_{sq} (p4gm)$ of **H8/4**, $Col_{sq} (p4mm)$, $Col_{sq} (p4gm)$ of **A6/4** and $Col_r (p2gg)$ of bolaamphiphiles (along white arrow, the volume fraction of the polar chain is increased); (f) model of the $Col_{sq} (p4gm)$ phase of **H8/4** (the colour of the frames are only for guide of eyes).

A similar X-ray diffraction pattern has been found for the low temperature phase of the amide **A6/4** [$\text{Col}_{\text{sq}}(p4gm)$]. However, these two compounds have quite different volume fraction value of the lateral polar chain (for **H8/4** $f_p = 0.30$ and for **A6/4** $f_p = 0.44$). In the contact region of these two compounds, at least one additional new mesophase was induced (see Appendix 4). This indicates that the $\text{Col}_{\text{sq}}(p4gm)$ phase of **H8/4** must be different from the $\text{Col}_{\text{sq}}(p4gm)$ phase of **A6/4**. The volume fraction of the lateral polar chain for **H8/4** ($f_p = 0.30$) is even smaller than that of the lateral polar chain in compound **A10/4** ($f_p = 0.38$) which has a $\text{Col}_{\text{sq}}(p4mm)$ phase (see Chapter 4, Figure 4.4). It seems that the $\text{Col}_{\text{sq}}(p4gm)$ phase of **H8/4** is an intermediate phase between the $\text{Col}_{\text{sq}}(p4mm)$ phase and the $\text{Col}_{\text{h}(\Delta)}$ phase of **H10/4** ($f_p = 0.27$). Comparison of the structures of these columnar phases shows, that in the $\text{Col}_{\text{h}(\Delta)}$ phase, one lipophilic column is surrounded by six aromatic walls, and in the $\text{Col}_{\text{sq}}(p4mm)$ phase, four aromatic walls surround one lipophilic column (these aromatic walls point with the ends of the aromatic cores towards the lipophilic regions). So, it is reasonable to suggest that in the $\text{Col}_{\text{sq}}(p4gm)$ phase of **H8/4** there are five aromatic walls surrounding one lipophilic column (the ends of the aromatic cores pointing toward the lipophilic columns, see Figure 5.7e). Based on this idea, the model shown in Figure 5.7f was developed. In this model the aromatic cores form triangular and square frames around the polar cylinders (the sides of the cores are directed towards the polar regions). If this model is compared with the model of the $\text{Col}_{\text{sq}}(p4gm)$ phase of **A6/4** (Figure 4.8), in these two organisations the locations of the lipophilic columns and the hydrophilic columns are exchanged, and the direction of the aromatic cores is changed by 90° . The calculation based on this model shows, that there are in average 28.1 molecules in one unit cell (the height of the unit cell is 0.45 nm), and the calculated volume of the lipophilic columns in one unit cell can accommodate 55.3 octyl chains (see Appendix 5). These two numbers are in quite good agreement with each other suggesting that the model proposed here is reasonable.

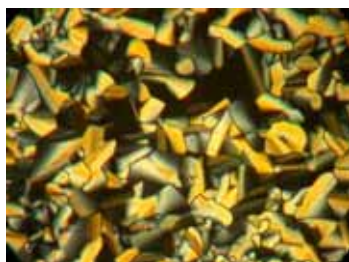


Figure 5.8. Texture of the columnar phase of compound **H6/6** at 13°C .

As discussed earlier, the hexyloxy substituted compound **H6/3** is a crystalline solid without liquid crystalline properties. If the polar lateral group is enlarged by three additional oxyethylene units, that is compound **H6/6**, a liquid crystalline mesophase is introduced. Compound **H6/6** has textures (Figure 5.8) with fern like domains and optically isotropic regions, which indicates an optically uniaxial columnar mesophase (Col_{h} or Col_{sq} phase). However, X-ray investigation is not possible with our equipment due to the low clearing point of this mesophase. This mesophase is immiscible with the square columnar phase of compound **H8/4** (see Appendix 6). When a protic solvent (water or formamide) was added to **H6/6**, no phase transition was found. Only the clearing temperature was drastically increased by increasing the concentration of the solvent (water: higher than 100°C ,

formamide: higher than 110 °C). It seems that the coordination of solvent has no influence upon the mesophase type, while it stabilises the mesophase. It is amazing that increasing the volume of the polar lateral chains by coordination of solvent molecules does not change the mesophase type. The model proposed for the “non-segregation” Col_h phase of amides could be one possible organisation for this mesophase. Accordingly, the cylinders containing the polar lateral chains are surrounded by the “nematic-like” ordered dialkoxy p-terphenyl units which are arranged perpendicular or parallel to the polar columns (“non-segregation” model, see Figure 4.10 and 4.11). In this case, there is no limitation for the size of the cross section of the polar columns as in the case of the mesophases in which the polar regions are framed by the terphenyl cores (segregation model). If this would be the case then for the carboxylic acids **Hm/n**, the segregation would already be lost at the transition from the Col_{sq} ($p4gm$) phase (the polar regions are framed by triangles and squares) to the next mesophase, i.e., before the polar regions can be framed by five p-terphenyl cores.

Independent on the length of the lateral chains, all three compounds **H4/n** have no liquid crystalline properties. This indicates again that a certain length of the terminal alkyl chains is required for the occurrence of liquid crystalline properties.

For compounds **H16/n** with long alkoxy chains, only smectic-A phases were observed. The clearing temperatures and the melting points decrease with increasing the number of oxyethylene units in the lateral polar chain. Also in these SmA phases no additional diffuse small angle scattering on the equator were found, which means that the lateral chains are more or less randomly distributed among the aromatic cores (conventional SmA phase).

For the synthesized carboxylic acid derivatives, the influence of the length of the lateral polar chain on the formation of the liquid crystalline phase is obvious. Increasing the value of the volume fraction of the lateral polar chain gives rise to a transition from a smectic layer structure (SmA) to different columnar phases in the phase sequence $\text{Col}_{h(\Delta)}$ (triangular arranged aromatic cores) – $\text{Col}_{h(1)}$ – Col_{sq} ($p4gm$; triangular and square arranged aromatic cores) – $\text{Col}_{(h)}$.

5.3 Influence of the position of the lateral chain (Y-shaped amphiphiles)

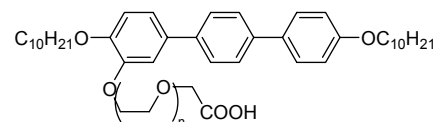
In the series of compounds **H*10/n**, the lateral hydrophilic chain is shifted from the middle of the aromatic core to the ortho-position beside one of the terminal alkoxy chains. Table 11 summarises the mesophase properties of the compounds **H*10/n**.

All three compounds exhibit exclusively conventional thermotropic SmA phases. The elongation of the lateral chain decreases the melting points and clearing temperatures. Compared to compounds **H10/n** with the polar chains in a central lateral position, the SmA mesophase in compounds **H*10/n** is stabilised by about 40°C, and no columnar phase is induced by elongation of the lateral polar chain.

In these Y-shaped amphiphiles, it seems that the polar group has a reduced disturbing effect upon the arrangement in layers. In other words, more bulky hydrophilic chains are needed to break the smectic layer structure (with formation of columnar phases) when the oligo(oxyethylene) chain is grafted to the ortho-position beside one of the terminal chains.

Table 11. Transition temperatures ($T/^{\circ}\text{C}$, as detected by DSC and cross checked by polarising microscopy), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics) and volume fraction values of terminal alkoxy chains (f_{R}), aromatic core (f_{Ar}) and lateral polar chain (f_{P}) of the series of compounds **H*10/*n***.

Comp.	<i>n</i>	Phase transitions ($T/^{\circ}\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	f_{R}	f_{Ar}	f_{P}
H*10/2	2	Cr 109 SmA 116 Iso <i>56.6</i> <i>4.48</i>	0.52	0.29	0.19
H*10/3	3	Cr 76 SmA 107 Iso <i>48.1</i> <i>4.66</i>	0.49	0.28	0.23
H*10/4	4	Cr 65 SmA 92 Iso <i>27.5</i> <i>3.32</i>	0.46	0.26	0.27



5.4 Compounds with two different terminal alkoxy chains

All compounds discussed previously have two identical terminal alkoxy chains, also asymmetric compounds with one terminal hexyloxy chain and one hexadecyloxy chain on the other end have been synthesized. Table 12 summarises the mesophase properties of the compounds **H16.6/*n*** and **H6.16/*n***.

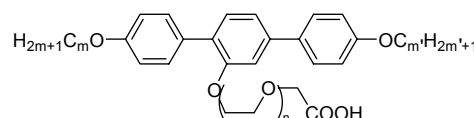
Compound **H16.6/4** has a hexagonal columnar structure according to the results of X-ray diffraction and the optical investigations. As the chemical structure of **H16.6/4** is similar to **H10/4** (nearly equal total length of the alkyl chains), it is most likely that they have the same supramolecular organisation ($\text{Col}_{\text{h}(\Delta)}$) phase, Figure 5.5a).

Compound **H16.6/3** with a shorter lateral chain has the similar texture (Figure 5.9a) as the $\text{Col}_{\text{h}(\Delta)}$ phase of **H10/4**. Additionally, the miscibility studies with compound **H16.6/4** indicate no phase boundary between these two mesophases (Figure 5.9b), so **H16.6/3** is assumed to have the same $\text{Col}_{\text{h}(\Delta)}$ phase too.

Table 12. Transition temperatures ($T/^{\circ}\text{C}$, as detected by DSC and cross checked by polarising microscopy), corresponding enthalpy values ($\Delta H/\text{kJ}\cdot\text{mol}^{-1}$, lower lines in italics), lattice parameters (nm) and volume fraction values of terminal alkoxy chains (f_{R}), aromatic core (f_{Ar}) and lateral polar chain (f_{P}) of the series of compounds **H16.6/*n*** and **H6.16/*n***.

Comp.	<i>m</i>	<i>m'</i>	<i>n</i>	Phase transitions ($T/^{\circ}\text{C}$) $\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	Lattice parameter (nm)	f_{Rt}	f_{Rm}	f_{Rl}
H6.16/3	6	16	3	Cr 68 ($\text{Col}_{\text{h}(\Delta)}$ 60) Iso <i>62.5</i> <i>2.12</i>		0.51	0.27	0.22
H6.16/4	6	16	4	Cr 66 ($\text{Col}_{\text{h}(\Delta)}$ 61) Iso <i>71.9</i> <i>2.16</i>		0.49	0.25	0.26
H6.16/6	6	16	6	Cr 52 [Col_{sq} (<i>p4gm</i>) 41.5 (M 42)] Iso <i>30.5</i> <i>1.27</i>	$a_{\text{sq}} = 8.0$	0.44	0.23	0.33
H16.6/3	16	6	3	Cr 48 $\text{Col}_{\text{h}(\Delta)}$ 63 Iso <i>48.1</i> <i>2.48</i>		0.51	0.27	0.22
H16.6/4	16	6	4	Cr ₁ 39 Cr ₂ 47 $\text{Col}_{\text{h}(\Delta)}$ 61 Iso <i>17.0</i> <i>28.8</i> <i>3.22</i>	$a_{\text{hex}} = 4.8$	0.49	0.25	0.26
H16.6/6	16	6	6	Cr 34 Col (uniaxial) 46 Iso		0.44	0.23	0.33

This Col_{sq} (*p4gm*) phase should have the same organisation as the Col_{sq} (*p4gm*) phase of **H8/4**.



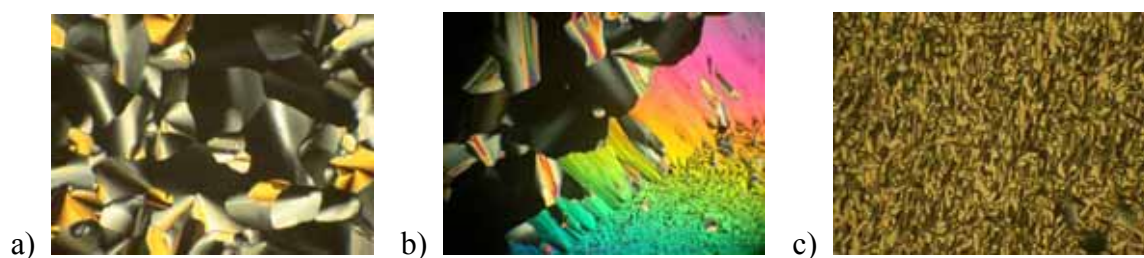


Figure 5.9. (a) Texture of the Col_h phase of compound **H16.6/3** at 60 °C; (b) contact region of compound **H16.6/4** (top left) and **H16.6/3** (bottom right) at 60 °C; (c) texture of compound **H16.6/6** at 46 °C.

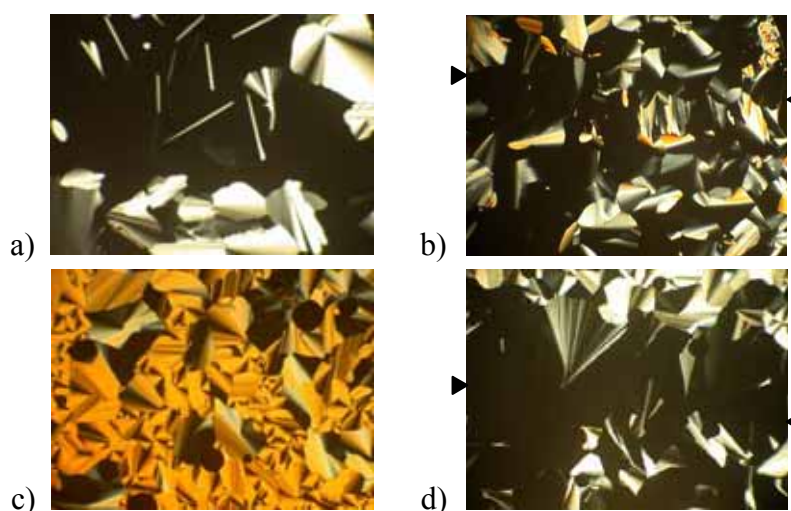


Figure 5.10. Representative textures of the: (a) Col_h phase of compound **H6.16/3** at 60 °C; (b) contact region of compound **H6.16/3** (bottom) and **H16.6/3** (top) at 60 °C; (c) Col_h phase of compound **H6.16/4** at 60 °C; (d) contact region of compounds **H6.16/4** (top) and **H6.16/3** (bottom) at 60 °C.

Compounds **H6.16/3** and **H16.6/3** with exchanged positions of the alkoxy chains have identical textures (Figure 5.10a). Compound **H6.16/4** has a similar texture (Figure 5.10c) as compound **H6.16/3**. Miscibility studies indicate no phase boundaries between each of these mesophases (Figure 5.10b, d). Hence, these three compounds seem to have hexagonal columnar mesophases.

For compound **H16.6/6**, a non-specific texture as shown in Figure 5.9c can be observed by cooling from the isotropic state. The behaviour of the isomeric compounds **H6.16/6** is different. Compound **H6.16/6** forms a sandy texture at first (Figure 5.11a), but as soon as this texture is formed, spherulitic regions start growing. Finally the whole area is filled by spherulites (Figure 5.11b and c). This behaviour is similar to the growing of textures of compound **H8/4** (see Chapter 5.2, Figure 5.7). The values of the volume ratio of the terminal chains to the lateral polar chain are nearly the same in these two compounds (compound **H8/4**, $V_R:V_P = 1.37$; compound **H6.16/6**, $V_R:V_P = 1.33$). It is reasonable to assume that compound **H6.16/6** has the same mesophase properties as compound **H8/4**. X-ray scattering investigation confirms this phase assignment and indicates a Col_{sq}(*p4gm*) with $a_{sq} = 8.0$ nm for the low temperature phase with spherulitic texture (organisation of the

polar cylinders surrounded by triangular and square shaped aromatic walls as shown in Figure 5.7 for **H8/4**).

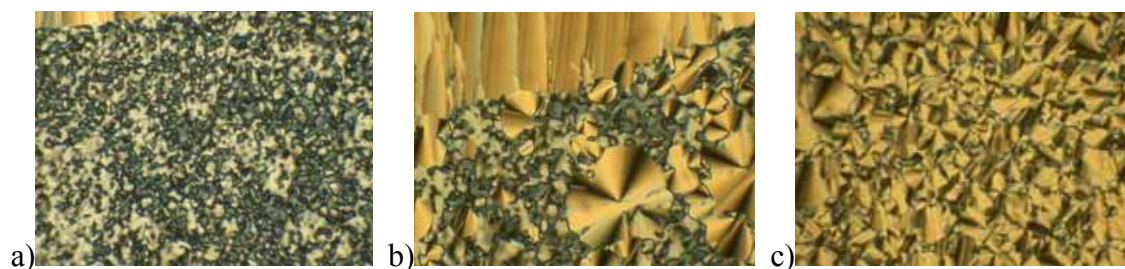


Figure 5.11. Textures of compound **H6.16/6** at 45 °C: (a) non-specific sandy texture; (b) growing of spherulitic texture; (c) spherulitic texture.

Interestingly, the three compounds **H6.16/*n***, in which the hexyloxy chains are closer to the lateral polar chain, show monotropic mesophases, whereas the compounds **H16.6/*n*** exhibit enantiotropic liquid crystalline phases.

5.5 Summary of the mesophase behaviour of the carboxylic acids

By increasing the volume fraction of the lateral polar chain, a phase sequence $\text{SmA} - \text{Col}_{h(\Delta)} - \text{Col}_{h(1)} - \text{Col}_{sq} (p4gm) - \text{Col}_{(h)}$ (“non-segregation”) has been found for the carboxylic acids (Figure 5.12). The Col_h and $\text{Col}_{sq} (p4gm)$ phases are different from those found in the carboxylates and the amides. The decreased incompatibility of the lateral polar chain in comparison with the corresponding carboxylates not only decreases the mesophase stabilities but also changes the mesophase types. In contrast to the smectic phase of carboxylates, where the polar chains always prefer to form segregated domains (SmA_{frm} phase, i.e., filled random mesh phase), the carboxylic acids seems to distribute the polar chains randomly among the calamitic parts of the molecules in their SmA phases. Thus, only a conventional SmA phase is observed. By increasing the volume fraction of the lateral polar chain (f_p), these lateral chains start to segregate into columns. However, the polar columns are framed only by three p-terphenyl cores ($\text{Col}_{h(\Delta)}$ phase), or by three and four p-terphenyl cores [$\text{Col}_{sq} (p4gm)$ phase]. With respect to the $\text{Col}_{sq} (p4gm)$ phases of the amides **Am/n**, the $\text{Col}_{sq} (p4gm)$ phase of carboxylic acids is reversed by the locations of polar and nonpolar columns. Compared to the Col_h and $\text{Col}_r (p2gg)$ phases of the bolaamphiphiles with nonpolar lateral chain, the $\text{Col}_{h(\Delta)}$ phase and the $\text{Col}_{sq} (p4gm)$ have the direction of the rigid rod-like cores changed by 90° as shown in Figure 5.5c and Figure 5.7e. Further increasing the volume fraction of the lateral polar group (f_p) by reduction of the length of the terminal alkyl chains leads to the loss of the segregation of the alkyl chains. The closest hexagonal packing of the polar columns seems to lead to the “non-segregation” Col_h phase.

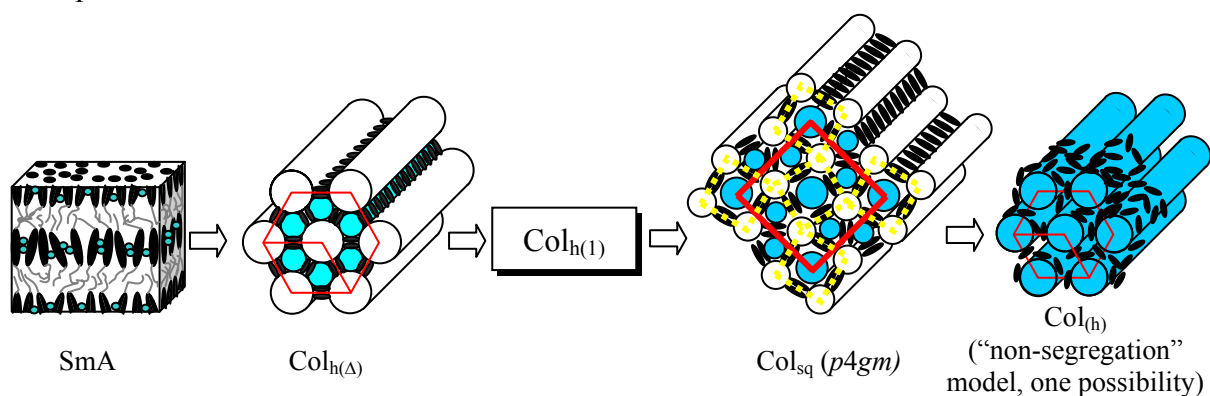


Figure 5.12. Schematic view of the phase sequence of the carboxylic acids. Along the arrows direction, the volume fraction of the later polar chain is increased.

6 Binary systems

In the systems reported in this work, complex sequences of different mesophases have been identified, and these mesophases occur depending on the volume fraction of the lateral polar chain, the degree of incompatibility of the lateral chains and the p-terphenyl units, the length of the terminal alkoxy chains, the position of the lateral group and the addition of solvents. For the investigated compounds, the following phase sequences were found.

1. Carboxylic acids (**Hm/n**): SmA – Col_{h(Δ)} (triangles around the polar regions) – Col_{h(⊥)} (hexagonal columnar phase with large lattice parameter) – Col_{sq} (*p4gm*, triangles and squares around the polar columns) – Col_h (“non-segregation”¹).
2. Metal carboxylates (**Mm/n**): SmA_{firm} – Rho – 3D-Hex – Col_{sq} (*p4mm*, squares around the polar columns).
3. Carbohydrates (amides, **Am/n**): 3D-Hex – Col_{sq} (*p4mm*, squares around the polar columns) – Col_{sq} (*p4gm*, pentagons around the polar columns) – Col_{h(⊥)} (“non-segregation”, aromatic cores perpendicular to the polar columns) – Col_{h(//)} (“non-segregation”, aromatic cores parallel to the polar columns) – Lam_N – Lam_{iso}.

In order to further clarify the mesophase morphologies, numerous binary systems of these molecules with each other and with solvents have been investigated by means of contact preparations.

Generally the carboxylates are incompatible with the other two classes of compounds, and therefore no convincing results could be obtained for these mixed systems.

The contact region between compound **H10/4** ($f_p = 0.27$) and **A6/6** ($f_p = 0.49$) is shown in Figure 6.1. These two compounds have two different hexagonal columnar phases. In the contact region, three different uniaxial columnar phases were induced, i.e. these mesophases should be either Col_h or Col_{sq} phases. According to the phase sequences found for the pure compounds, the phase sequence from the right to the left, seen in Figure 6.1, should be Col_{h(⊥)} (pure **A6/6** with “non-segregated” aromatic cores perpendicular to polar columns) – Col_{sq} (*p4gm*: pentagons around the polar columns) – Col_{sq} (*p4mm*: squares around the polar columns) – Col_{sq} (*p4gm*: triangles and squares around the polar columns) – Col_{h(Δ)} (pure **H10/4** with triangles around the polar columns). This phase sequence indicates that by increasing the volume fraction of the lateral polar chain, the shape of the frames around the polar columns changes from triangles, to triangles plus squares, to squares, to pentagons where the cross section of the columns of the lateral polar chains increases. This is followed by the loss of the segregation of the alkyl chains from the p-terphenyl cores (“non-segregation” Col_h phases).

¹ “non-segregation” means that there is no segregation of aromatic and aliphatic segments, the segregation of the polar units is still present.

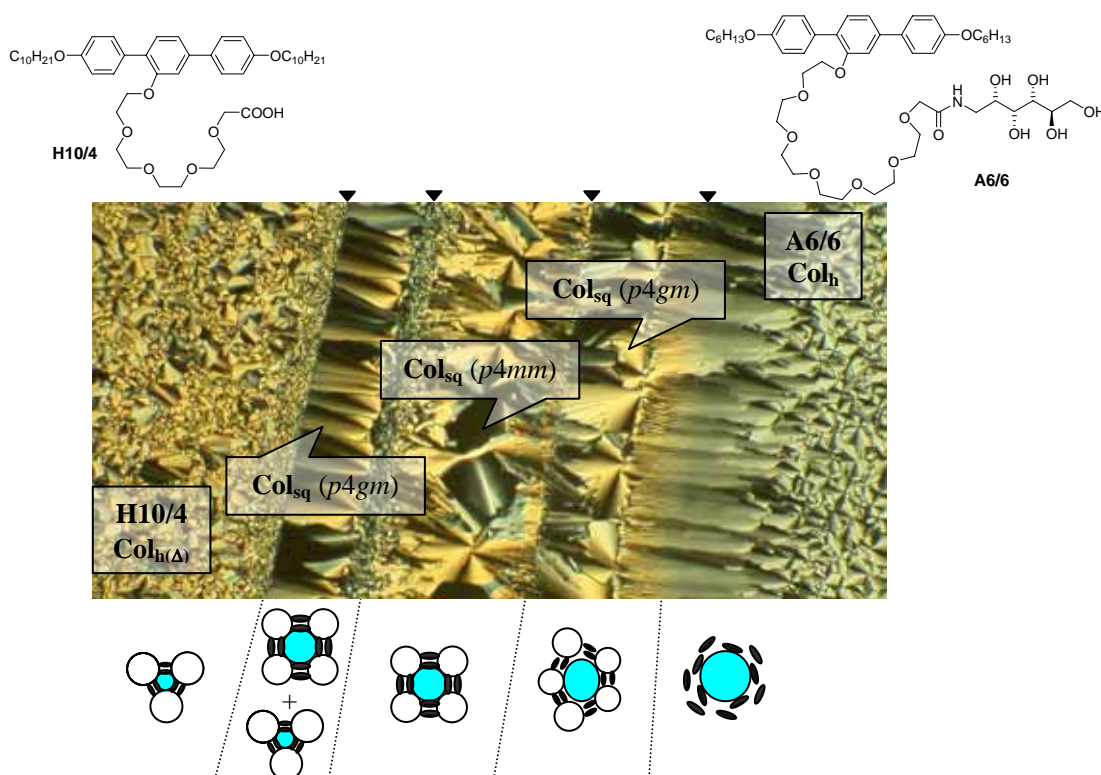


Figure 6.1. Contact region of compound **H10/4** and **A6/6** at 50 °C (crossed polarizers).

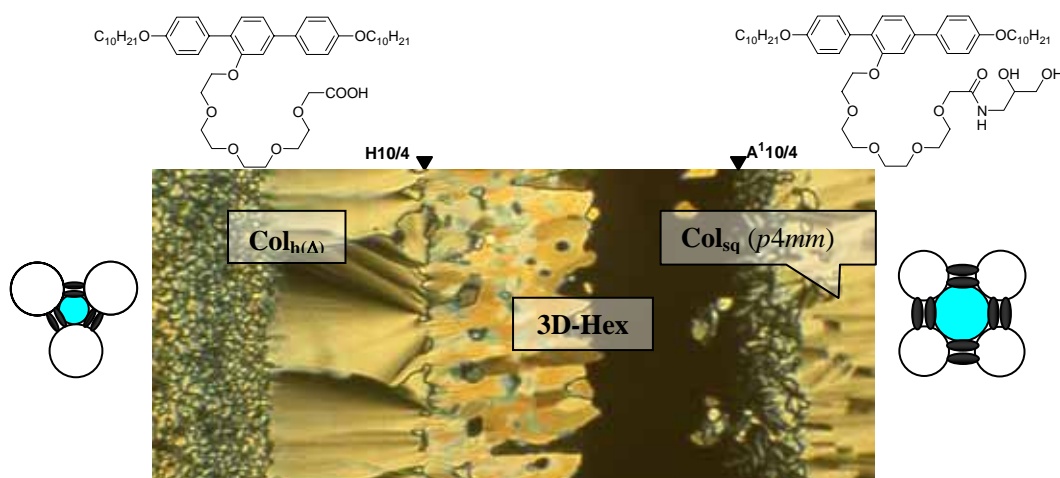


Figure 6.2. Contact region between **H10/4** and **A¹¹⁰/4** at 50 °C (there is a birefringent and an pseudoisotropic area of the 3D-Hex phase, which may be due to different alignment conditions).

In the contact region between **H10/4** (Col_h(Δ) with triangles around the polar columns) and **A¹¹⁰/4** [Col_{sq} (p4mm) with squares around the polar columns], only a 3D-Hex phase has been found (Figure 6.2). No columnar phases were observed. This observation is different to that expected on the basis of the results as shown above (Figure 6.1). A possible explanation can be derived from the comparison of compounds **H10/4** (Col_h, $f_P = 0.27$) with **Na10/4** (3D-Hex, $f_P = 0.28$). These two compounds have nearly the same volume fraction of the lateral polar chain. The only difference between these two compounds is, that the

carboxylic acid group in **H10/4** is changed to a sodium carboxylate group in **Na10/4**. This leads to a change of the mesophase type from Col_h to 3D-Hex. So the driving force for this change observed in the contact region between **H10/4** and **A¹10/4** is also believed to be due to the increased attractive interactions between the lateral groups and the enhanced incompatibility of these chains with the aromatic cores. In the contact region between **H10/4** and **A¹10/4**, the attractive intermolecular interactions and incompatibility increase from **H10/4** (left) to **A¹10/4** (right). Thus, the 3D-Hex phase is formed instead of the Col_{sq} ($p4gm$, triangles and squares around the polar columns) phase in the contact region between these two compounds.

The binary system **A¹10/3** (3D-Hex) and **A6/3** [Col_{sq} ($p4gm$)] was investigated quantitatively. Figure 6.3a shows the phase diagram of this binary system. In this diagram, the 3D-Hex phase occurs in a certain concentration range as low temperature mesophase below the Col_{sq} phase. This is the same phase sequence as observed for the carbohydrate derivative **A10/2** on reducing the temperature. This means that the low temperature 3D phase of **A10/2** should indeed be a 3D-Hex phase. This phase diagram also shows that no additional mesophase could be expected at the Col_{sq} ($p4mm$ with squares around the polar columns) to Col_{sq} ($p4gm$ with pentagons around the polar columns) transition.

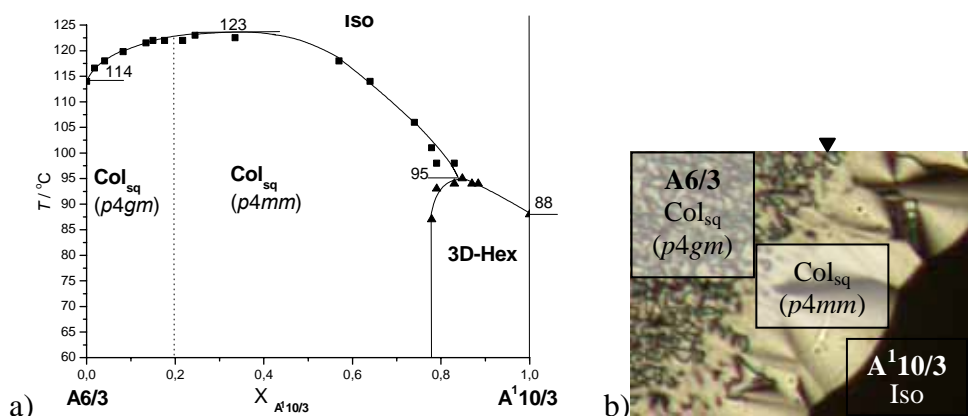


Figure 6.3. (a) Simplified phase diagram of the binary system between **A6/3** and **A¹10/3** (two-phase regions are not shown); (b) contact region between **A¹10/3** (left top) and **A6/3** (right bottom). [For all the mixtures, no phase transition between the Col_{sq} ($p4gm$) phase and the Col_{sq} ($p4mm$) phase was observed by optical investigation. For the mixtures with low concentration of **A¹10/3**, at the transition from the isotropic state to the liquid crystalline state, a low birefringent texture forms at first and changes to high birefringence as soon as it is formed, while for higher **A¹10/3** concentration mixtures, only high birefringent textures were found. This was thought to be the difference between the Col_{sq} ($p4gm$) and Col_{sq} ($p4mm$) phases. However, it is still not certain about the concentration boundary of these two phases. Thus a dotted line was drawn in the phase diagram to indicate the boundary of these two columnar phases. Nevertheless, in the contact preparation of these two compounds, see b, an additional mesophase was induced which should be Col_{sq} ($p4mm$) phase.]

7 Summary

Three series of novel T-shaped and Y-shaped facial amphiphiles have been synthesised *via* palladium catalysed C-C coupling reaction as the key step. These amphiphiles incorporate a p-terphenyl core, two terminal alkoxy chains and a lateral oligo(oxyethylene) chain. The oligo(oxyethylene) chains are terminated by three different types of polar groups: metal carboxylates (**Mm/n**), oligohydroxyalkyl amides (**Am/n**) and carboxylic acids (**Hm/n**). For each series, the influence of the length of the terminal alkyl chains and the length of the lateral polar oligo(oxyethylene) chain upon the mesophase properties has been investigated.

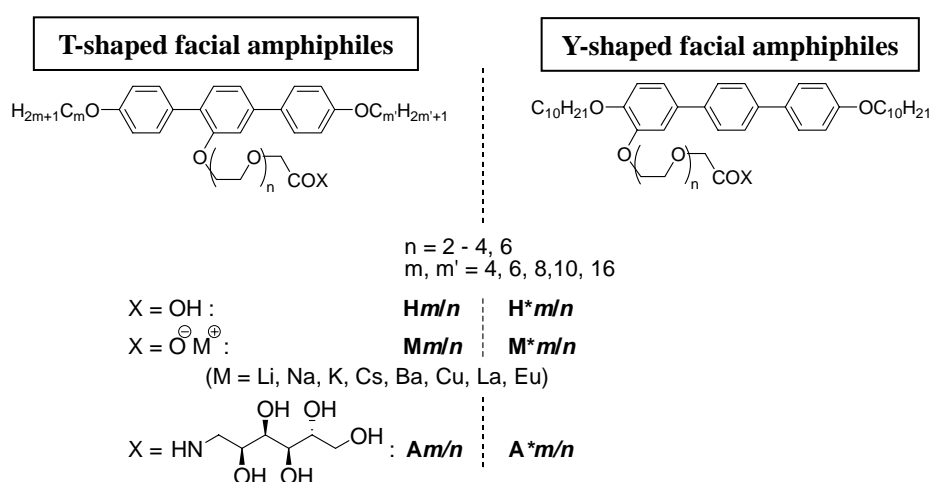


Figure 7.1. General formula of the synthesized molecules.

On the basis of the synthesized compounds, a wide variety of novel and quite different mesophases has been obtained. The formation of these mesophases is believed to be due to the segregation of the lateral polar chains, the terminal alkyl chains and the aromatic p-terphenyl cores into three distinct subspaces.

Metal carboxylates (Mm/n**).** A phase sequence SmA_{frm} (filled **random mesh**) – rhombohedral ($\text{R}3m$) – 3D hexagonal – Col_{sq} ($p4mm$) – Col_{sq} ($p4gm$) has been found by reduction of the length of the terminal alkoxy chains and/or by elongation of the lateral polar chain or with reducing the temperature (Figure 7.2). Generally, the mesophases are significantly stabilised with increasing the size of the cation.

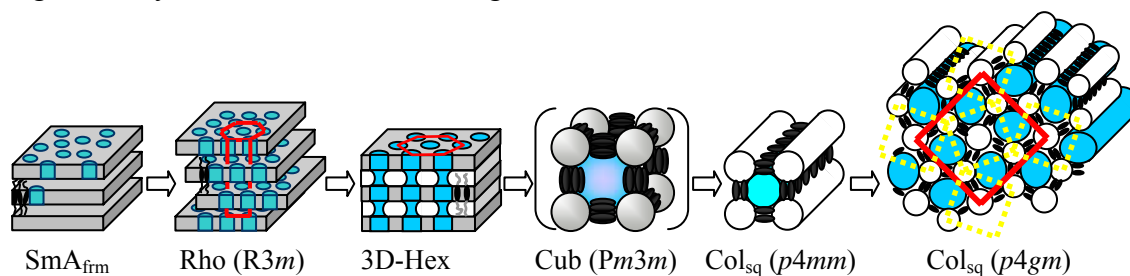


Figure 7.2. Schematic view of the phase sequence of the metal carboxylates (**Mm/n**).

Oligohydroxyalkyl amides (\mathbf{Am}/n). A phase sequence 3D hexagonal – $\text{Col}_{\text{sq}} (p4mm)$ – $\text{Col}_{\text{sq}} (p4gm)$ – $\text{Col}_{\text{h}(\perp)}$ (aromatic cores perpendicular to the polar columns) – $\text{Col}_{\text{h}(\parallel)}$ (aromatic cores parallel to the polar columns) has been found as shown in Figure 7.3.

Two lyotropic mesophases have been found for the binary system of **A4/4** with the polar protic solvent formamide. A laminated nematic phase (Lam_{N}) and a SmA (Lam_{iso}) phase are suggested for these phases (Figure 7.3).

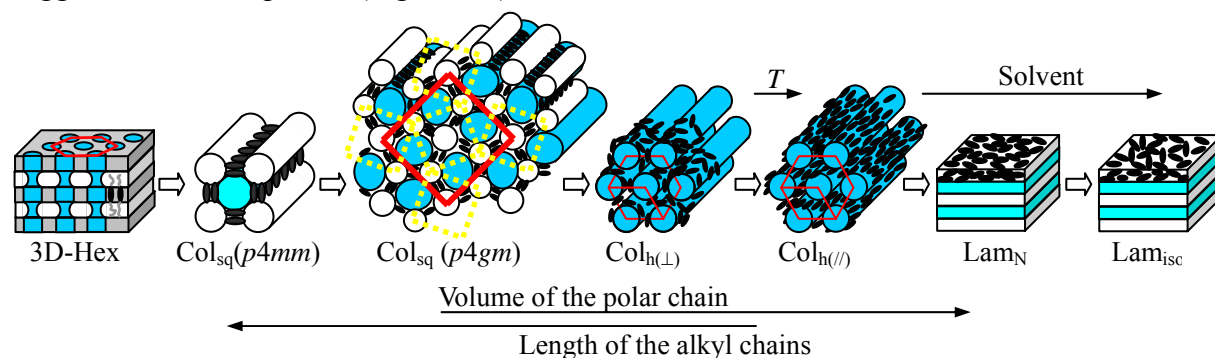


Figure 7.3. Schematic view of the phase sequence of the amides (\mathbf{Am}/n).

Carboxylic acids (\mathbf{Hm}/n). A phase sequence SmA – $\text{Col}_{\text{h}(\Delta)}$ – $\text{Col}_{\text{h}(1)}$ – $\text{Col}_{\text{sq}} (p4gm)$ – Col_{h} has been found (Figure 7.4).

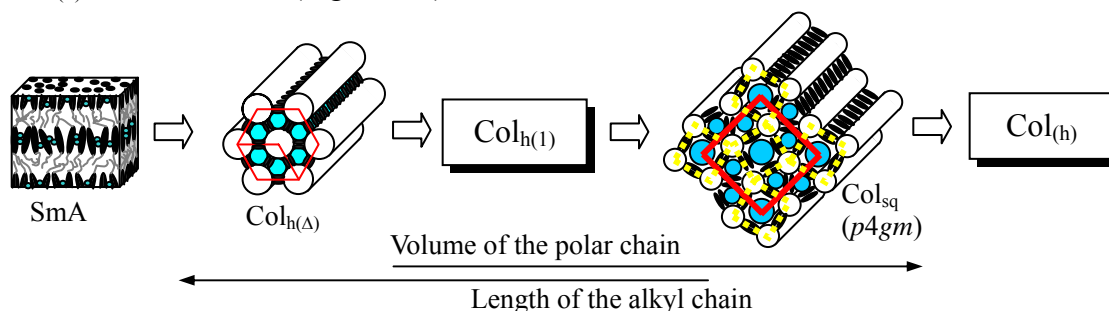


Figure 7.4. Schematic view of the phase sequence of carboxylic acids (\mathbf{Hm}/n), $\text{Col}_{\text{h}(1)}$ = hexagonal columnar phase with large lattice parameter, the Col_{h} phase has not been unambiguously confirmed by X-ray scattering yet.

At least three decisive factors determine the phase types: 1) volume of the polar lateral chains; 2) length of the terminal alkyl chains; 3) degree of the incompatibility of the lateral chain with the other segments.

Molecules with a small lateral polar chain form SmA phases which are quite often found in liquid crystalline phases of calamitic molecules. However, for the strongly incompatible metal carboxylates, polar domains are formed within the “aromatic” sub-layers. These polar domains are randomly distributed leading to the formation of a filled random mesh phase (SmA_{frm}). With decreasing the temperature, the polar domains become organised in a hexagonal 2D lattice which is accompanied by the correlation between adjacent layers in an ABC fashion leading to the Rho ($\text{R}3m$) phase (Figure 7.2). By increasing the volume fraction of the lateral polar chain (by increasing the number of oxyethylene units or by reduction of the length of the terminal chains), the polar domains of adjacent layers are enabled to fuse. Thus, a 3D-Hex phase with perforated aromatic and lipophilic layers which are penetrated perpendicularly by the hexagonal arranged polar columns is formed (Figure 7.2).

For the carboxylic acids (reduced incompatibility with the aromatic core in comparison with the carboxylates), increasing the volume fraction of the lateral polar chain directly brakes up the smectic layer structure with the formation of a $\text{Col}_{\text{h}(\Delta)}$ phase. In this $\text{Col}_{\text{h}(\Delta)}$ phase, the aromatic cores form triangular shells enclosing the polar columns, and the alkyl chains are segregated into rounded hexagonal columns at the corners of these triangles. Upon further increasing the volume fraction of the lateral polar chain, partial triangular aromatic shells are fused to form square organisation which gives rise to a $\text{Col}_{\text{sq}} (p4gm)$ mesophase. In this $\text{Col}_{\text{sq}} (p4gm)$ phase the lipophilic cylinders have a rounded pentagonal shape (Figure 7.4).

In the following step (after replacing the COOH group by a polyhydroxy group), exclusively square aromatic shells [$\text{Col}_{\text{sq}} (p4mm)$] and finally pentagonal aromatic shells [$\text{Col}_{\text{sq}} (p4gm)$] are formed around the polar columns (Figure 7.3). In the $\text{Col}_{\text{sq}} (p4mm)$ phase, the lipophilic columns interconnect four aromatic walls, whereas, four and three aromatic walls are interconnected by the lipophilic columns in the $\text{Col}_{\text{sq}} (p4gm)$ phase (Figure 7.3). This $\text{Col}_{\text{sq}} (p4gm)$ phase is the largest stable polygonal cylinder structure found for the synthesized facial amphiphiles. Upon reducing the length of the terminal alkyl chains, the segregation of these chains from the aromatic cores is lost and Col_{h} phases are formed as a result of the closest hexagonal packing of the polar columns within the continuum of the non-segregated aromatic and aliphatic segments. Honeycomb-like cylinder structures as reported for the bolaamphiphiles are, however, not found. In the continuum around the polar columns, the aromatic cores still have an orientational order and these cores are arranged either perpendicular or parallel to the column long axes. This leads to two different Col_{h} phases ($\text{Col}_{\text{h}(\perp)}$ and $\text{Col}_{\text{h}(\parallel)}$, see Figure 7.3).

Further increasing the size of the polar part by coordination of polar solvent (formamide) fuses the polar columns to layers and leads to the formation of laminated phases. In the Lam_{N} phase the aromatic cores should have an orientational long range order within the nonpolar layers. In the Lam_{iso} phase, the aromatic cores have no long range order (Figure 7.3).

Figure 7.5 summarises the mesophase morphologies found for all compounds. The $\text{Col}_{\text{sq}} (p4gm)$ phases are the most remarkable mesophases found for these facial amphiphiles, because they represent regular organisation of pentagons in a plane. Since a tiling of a plane is impossible with regular pentagons, these pentagons are slightly distorted, i.e., the length of the sides and the angles are slightly different. Such an organisation cannot be realised by well defined rigid building blocks as for example used in covalently bonded systems or coordination polymers.^[95, 96] Therefore no regular (flat) 2D organisation of pentagons has been reported until now. The liquid crystalline state, which combines order and mobility, seems to be a prerequisite for the formation of such an organisation. Up to now, four different types of such regular organisation of columns with a pentagonal cross section have been found for liquid crystalline phases of T-shaped ternary amphiphiles. Two of these mesophases have been reported for bolaamphiphiles with nonpolar lateral chains [$\text{Col}_{\text{r}} (p2gg)$ phases]^[70] and two new organisations are reported herein [$\text{Col}_{\text{sq}} (p4gm)$ phases]. This shows that pentagons represent a stable structure in these systems.

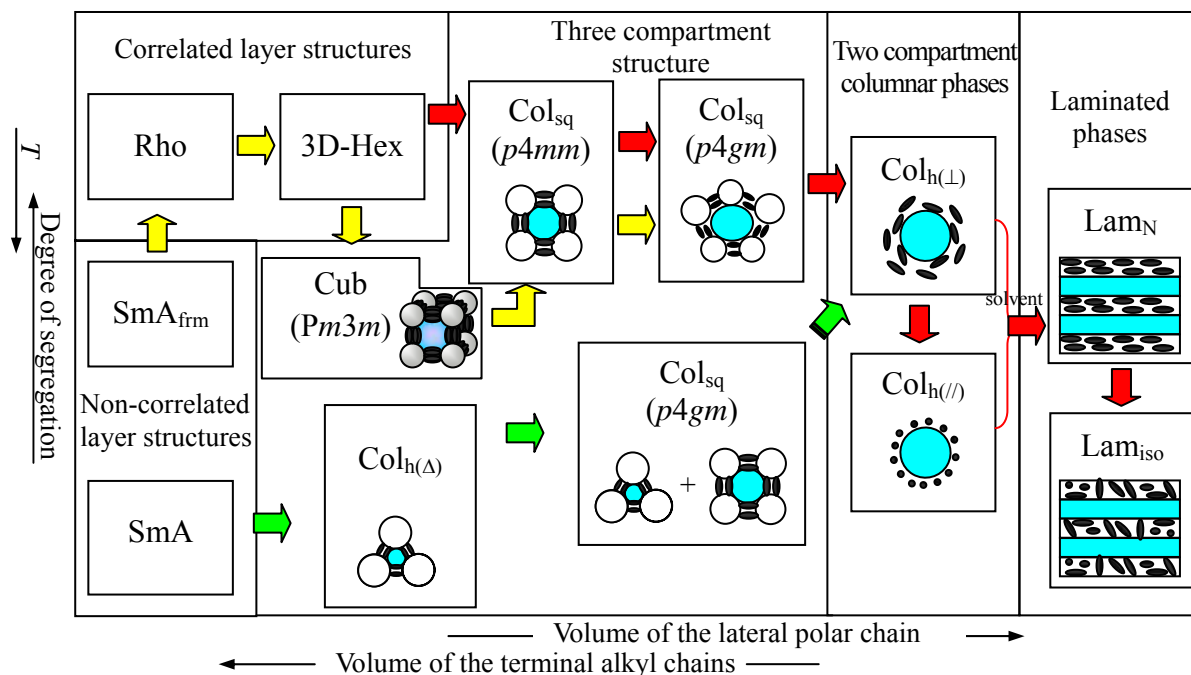


Figure 7.5. Schematic view of the phase sequence of all the compounds. (yellow arrow: metal carboxylates; red arrow: amides; green arrow: carboxylic acids)

With respect to the $\text{Col}_r(p2gg)$ phases of the bolaamphiphiles, the symmetry is enhanced in the mesophases of the facial amphiphiles [$\text{Col}_{sq}(p4gm)$ phases]. Furthermore, either the position of the polar and nonpolar columns with respect to the rod-like cores is exchanged (compounds **Am/n**) or the orientation of the rigid cores with respect to the polar and nonpolar domains is exchanged (compounds **Hm/n**) (Figure 7.6).

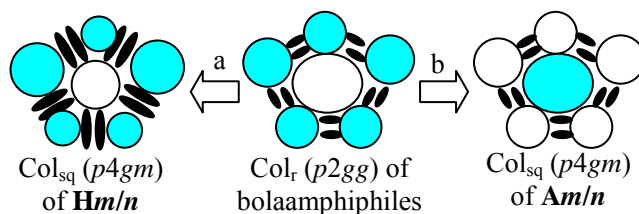


Figure 7.6. Schematic view of three different columnar phases with pentagonal cross sections (a: change of the orientation of the rigid cores; b: exchange the location of the polar and nonpolar columns).

Also the $\text{Col}_{h(\Delta)}$ phase of the acids **Hm/n** is remarkable, because they can be regarded as composed of polar columns with a triangular cross sectional area, which is found for the first time. The $\text{Col}_{sq}(p4gm)$ phase of **Hm/n** is even more complex, it is formed by two different types of polar columns, triangular and square shaped. Also this is a new organisation in liquid crystalline phases (Figure 7.7).

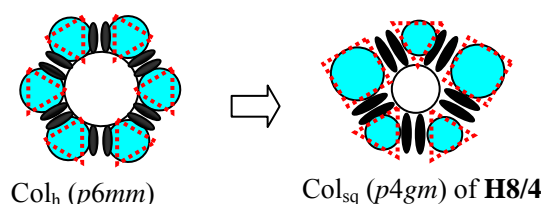


Figure 7.7. Schematic view of the Col_h phase and the $\text{Col}_{sq}(p4gm)$ phase, the Col_h phase has a triangular cross section and the $\text{Col}_{sq}(p4gm)$ phase has a triangular and squared cross section.

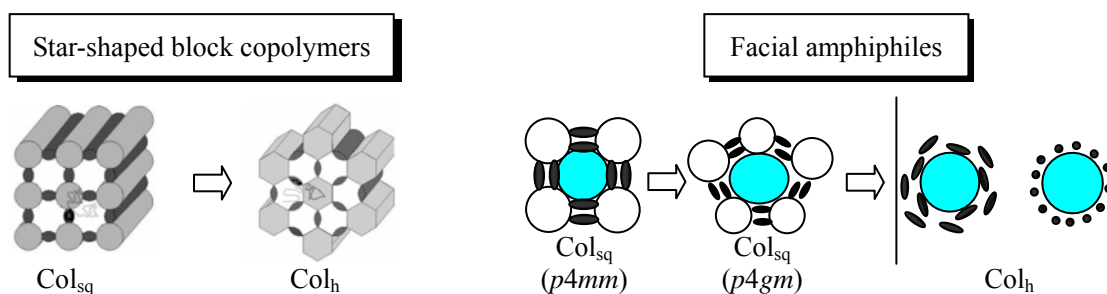


Figure 7.8. Comparison of the mesophases of star-shaped block copolymers and facial amphiphiles.

The molecules reported herein represent ternary amphiphilicities. Triblock copolymers^[44-57] represent another type of ternary amphiphiles. For example, ternary star-shaped block copolymers form the morphologies related to the Col_{sq} ($p4mm$) phases and the $\text{Col}_{\text{h}(\Delta)}$ phases but with a significantly larger length scale^[58] (3 - 10 nm for the low molecular weight molecules and 10 to > 100 nm for the polymer architectures). However, no organisation of pentagonal columns was reported for these flexible macromolecules at the transition from square to hexagonal organisation (Figure 7.8). It seems that the presence of a rigid rod-like segment is, besides the T-shaped ternary amphiphilic structure, another important prerequisite for the formation of this type of mesophase.

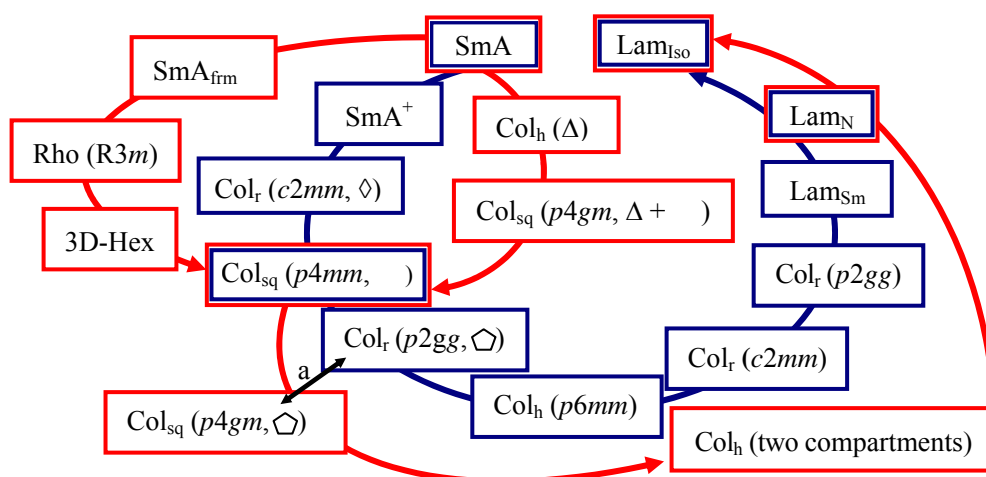


Figure 7.9. Comparison of the mesophases of the bolaamphiphiles and the facial amphiphiles (blue: the phase sequence of the bolaamphiphiles; red: the phase sequence of the facial amphiphiles; a similar pentagonal arrangement of the aromatic cores are found for both the Col_{r} ($c2mm$) phase of bolaamphiphiles and Col_{sq} ($p4gm$) phase of facial amphiphiles).

All the 3D phases (Rho, 3D-Hex) can be regarded as correlated layer structures resulting from the correlation of filled mesh layers. Though there have been reports of different types of mesh phases formed by AB diblock copolymers,^[87] conventional binary amphiphiles^[8-10] and coil-rod-coil molecules,^[22-26] the morphologies reported herein are different with respect to the three compartment structures. In the mesh phases reported herein, the meshes are filled by a third incompatible component, while the meshes formed by binary compounds are filled with the excess of the second component. The SmA_{fm} and Rho phases can also be regarded as “spheres-in-layers”, and the 3D-Hex phase can be regarded as

“columns-penetrating-layers” structures which are different to the “spheres-on-layers” and “columns-on-layers” structures reported in ABC linear triblock copolymers.^[51-57]

The Col_{sq} (*p4mm*) phase, one of the Col_{sq} (*p4gm*) phases (compounds **Am/n**) and the lyotropic laminated phases are similar to some of the mesophases found for bolaamphiphiles with lateral non-polar chains,^[65-70] however, with exchanged locations of the polar and nonpolar domains (Figure 7.9).

The two “two compartments” Col_h phases of compounds **Am/n** are related to the reversed Col_h phases of flexible amphiphiles. Except that the continuum is formed by the lipophilic chains incorporating the aromatic cores, and an additional orientational order of the aromatic cores is suggested.

The position of the lateral polar chain strongly influences the mesophase properties only in the case of the Y-shaped sodium carboxylates. Here a different mesophase with 3D lattice has been found for the 3-substituted compounds (**Na*10/n**) instead of the 3D-Hex phase of the 2'-substituted compounds. A 3D tetragonal structure is proposed for this mesophase.

All the experimental results indicate that competitive combination of different self-organisation forces in one molecule is a successful way to explore novel types of mesophases. More types of novel mesophases are expected by further investigations.

8 Experimental section

8.1 General considerations

Purification and drying of the solvents were performed according to the methods described in the literature.^[91] Silica Gel [0.040 – 0.036 mm, or 0.036 – 0.200 mm (*Merck*)] was used for column chromatography.

The confirmation of the structures of the intermediates and products was obtained by ¹H-NMR and ¹³C-NMR spectroscopy (Varian Unity 400, Varian Gemini 200 spectrometer). Microanalysis was performed by using a *Leco* CHNS-932 elemental analyzer. Due to the hygroscopic properties of some compounds¹, moisture was absorbed during the sample preparation. Therefore, before the investigations (transition temperature measurement, X-ray), the samples were heated to ca. 130 – 140 °C or kept in the melted liquid state (if the clearing temperature is higher than 140 °C) for about 10 seconds to remove traces of water and then sealed immediately.

Transition temperatures were measured by using a *Mettler* FP 82 HT hot stage and a control unit in conjunction with a *Nikon* Optiphot 2 polarization microscope and were confirmed by differential scanning calorimetry (*Perkin-Elmer* DSC-7, heating and cooling rate: 10 K min⁻¹).

X-Ray diffraction patterns were obtained on a Guinier-diffractometer (*Huber*) operating with a Cu-K α_1 beam. The diffraction patterns were recorded with a film camera. Aligned samples were measured with a two dimensional detector (HI-STAR, *Siemens*).

Measurements of the conductivity (AC, $f = 1$ kHz) were carried out by cooling the samples from the isotropic melt in a microcapacitor ($A = 2$ cm², $d = 0.02$ cm) without orientation.

¹ The hygroscopic property of compound **Li10/4** was checked. A sample of 3.838 mg was weighted, after heated to melt for 10 seconds to remove the traces of water, the sample weighted 3.807 mg, which indicates that 0.031 mg water was adsorbed in the original sample, it can be calculated that one **Li10/4** molecule contains 0.36 molecule of water. If the sample is kept in air, it weights 3.830 mg after 3 hours. If the humidity is high (rainy), the sample weights 3.866 mg, in this case, about 0.68 molecule of water is absorbed in one **Li10/4** molecule. This experiment indicates that in the case of the synthesized facial amphiphiles, the water content changes as the humidity of the air changes.

Commercial available substances:

Diethyleneglycol (ACROS)
Triethyleneglycol (ACROS)
Tetraethyleneglycol (ACROS)
2,5-Dichlorophenol (Fluka)
Sodium chloroacetate (Merck)
Palladium acetate (Lancaster)
Pearlman's catalyst (Merck)
Palladium on carbon (Merck)
DMAP (Merck)
Pentafluorophenol (ABCR)
3-Aminopropane-1,2-diol (Aldrich)
2-Aminopropane-1,3-diol (Aldrich)
Benzylchloride (Aldrich)
1-Bromooctane (Merck)
1-Bromohexadecane (Merck)
1-Amino-1-deoxy-D- sorbitol (Aldrich)
2-(Di-*tert*-butylphosphino)biphenyl (ABCR)

Substances which were synthesized before in our group:

4-Butoxybenzeneboronic acid
4-Hexoxybenzeneboronic acid
4-Octoxybenzeneboronic acid
4-Decyloxybenzeneboronic acid
4-Hexadecyloxybenzeneboronic acid
4-Benzyloxybenzeneboronic acid
1-Bromo-3,7-dimethyloctane
1-Benzyloxy-10-(4-methylbenzenesulfonyloxy)-1,4,7,10-tetraoxadecane

The numbering of the carbons in the chemical structures shown in this chapter are only used for the assignment of the NMR-signals and do not correspond to the IUPAC-Nomenclature. p-Terphenyl is always [1,1',4',1'']-terphenyl.

8.2 Synthesis and analytical data of the final compounds

8.2.1 Sodium salts (Na*m/n*, Na*10/*n*, Na6.16/*n* and Na16.6/*n*)

General procedure: The appropriate methyl ester **7/*m/n*** (or **17/10/*n***, **22/*m'/m/n***) (1 mmol) and NaOH (aq. 1 M, 50 mL) were heated 16 h under reflux. After cooling to r.t., the precipitated solid was filtered off and dried in air, the crude product was purified by column chromatography on silica gel with CHCl₃/CH₃OH as Eluent, and recrystallization from ethyl acetate or CHCl₃/n-hexane.

Sodium 8-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoate (**Na10/2**):

Reagents: **7/10/2** (1.9 g, 2.6 mmol)

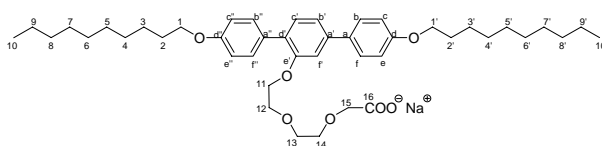
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 1.3 g (68.8 %), colorless waxy solid

Analytical data: C₄₄H₆₃O₇Na M_w = 726.96

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.45-7.27 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.24-7.20 (m, 1 H, Ar-H^{c'}), 7.18-7.08 (m, 1 H, Ar-H^{b'}), 7.07-6.98 (m, 1 H, Ar-H^{f'}), 6.93-6.86 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.10-3.95 (m, 2 H, CH₂¹¹), 3.94-3.82 (m, 6 H, CH₂^{1,1', 15}), 3.80-3.64 (m, 2 H, CH₂¹²), 3.56-3.33 (m, 4 H, CH₂^{13, 14}), 1.78-1.64 (m, 4 H, CH₂^{2,2'}), 1.45-1.22 (m, 28 H, CH₂^{3-9,3'-9'}), 0.89-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 158.9 (C^d), 158.2 (C^{d''}), 156.0 (C^{e'}), 140.9 (C^{a'}), 133.1 (C^{a''}), 130.9 (C^{c'}), 130.6 (C^{b, f, a''}), 129.0 (C^a), 128.0 (C^{b', f''}), 119.5 (C^{b'}), 114.9 (C^{c'', e''}), 114.0 (C^{c, e}), 111.3 (C^{f'}), 70.5, 68.2 (C¹¹⁻¹⁵), 68.1 (C^{1,1'}), 32.1 (C^{8,8'}), 29.8, 29.7, 29.6, 29.6, 29.5 (C^{2, 4-7, 2', 4'-7'}), 26.3, 26.3 (C^{3,3'}), 22.9 (C^{9,9'}), 14.3 (C^{10,10'}). EA: C₄₄H₆₃O₇Na·0.5H₂O (Cal.) C: 71.80 %, H: 8.76 %, (Found) C: 71.90 %, H: 8.66 %.



Sodium 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Na10/3**):

Reagents: **7/10/3** (0.45 g, 0.59 mmol)

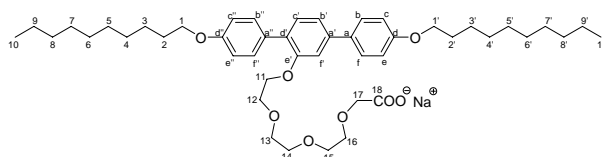
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 0.25 g (55.0 %), colorless waxy solid

Analytical data: C₄₆H₆₇O₈Na M_w = 771.01

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.47-7.43 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.26 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.12 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.06 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.90-6.83 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.06 (t, ³J(H,H) = 4.7, 2 H, CH₂¹¹), 3.93-3.89 (m, 4 H, CH₂^{1,1'}), 3.76 (s, 2 H, CH₂¹⁷), 3.69 (t, ³J(H,H) = 4.7, 2 H, CH₂¹²), 3.53-3.43 (m, 8 H, CH₂¹³⁻¹⁶), 1.78-1.71 (m, 4 H, CH₂^{2,2'}), 1.44-1.25 (m, 28 H, CH₂^{3-9,3'-9'}), 0.88-0.84 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 176.5 (C¹⁸), 159.3 (C^d), 158.6 (C^{d''}), 156.4 (C^{e'}), 141.3 (C^{a'}), 133.6 (C^{a''}), 131.2 (C^{c'}), 131.0 (C^{b, f}), 130.9 (C^{a''}), 129.4 (C^a), 128.4 (C^{b', f''}), 119.9 (C^{b'}), 115.2 (C^{c'', e''}), 114.4 (C^{c, e}), 111.8 (C^{f'}), 71.5, 71.0, 70.6, 70.2, 70.0 (C¹³⁻¹⁷), 69.4 (C¹²), 69.0 (C¹¹), 68.6, 68.5 (C^{1,1'}), 32.4 (C^{8,8'}), 30.1, 30.0, 30.0, 29.9, 29.9 (C^{2, 4-7, 2', 4'-7'}),



26.7, 26.6 ($C^{3,3'}$), 23.2 ($C^{9,9'}$), 14.6 ($C^{10,10'}$). EA: $C_{46}H_{67}O_8Na \cdot 0.5H_2O$ (Cal.) C: 70.83 %, H: 8.79 %, (Found) C: 70.70 %, H: 8.54 %.

Sodium 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (Na10/4):

Reagents: **7/10/4** (1.1 g, 1.4 mmol)

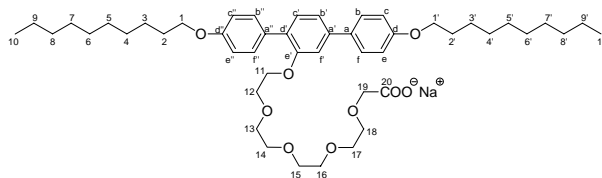
1 M NaOH (50 mL)

Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/MeOH = 10/1$ (V/V) and recrystallization from ethyl acetate

Yield: 0.74 g (64.9 %), colorless waxy solid

Analytical data: $C_{48}H_{71}O_9Na$ $M_w = 815.06$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.50-7.47$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.29 (d, $^3J(H,H) = 7.8$, 1 H, Ar- $H^{c'}$), 7.14 (dd, $^3J(H,H) = 7.8$, $^4J(H,H) = 1.6$, 1 H, Ar- $H^{b'}$), 7.09 (d, $^4J(H,H) = 1.6$, 1 H, Ar- $H^{f'}$), 6.93-6.86 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.10 (t, $^3J(H,H) = 4.5$, 2 H, CH_2^{11}), 3.96-3.91 (m, 4 H, $CH_2^{1,1'}$), 3.83 (s, 2 H, CH_2^{19}), 3.72-3.69 (m, 2 H, CH_2^{12}), 3.58-3.51 (m, 12 H, CH_2^{13-18}), 1.78-1.72 (m, 4 H, $CH_2^{2,2'}$), 1.43-1.26 (m, 28 H, $CH_2^{3-9,3'-9'}$), 0.89-0.85 (m, 6 H, $CH_3^{10,10'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 176.2$ (C^{20}), 159.3 (C^d), 158.6 ($C^{d''}$), 156.5 ($C^{e'}$), 141.3 ($C^{a'}$), 133.6 ($C^{a''}$), 131.3 ($C^{c'}$), 131.0 ($C^{b,f}$), 130.9 ($C^{a''}$), 129.5 ($C^{a'}$), 128.5 ($C^{b',f''}$), 120.0 ($C^{b'}$), 115.3 ($C^{c'',e''}$), 114.4 ($C^{c,e}$), 112.0 ($C^{f'}$), 71.5, 71.4, 71.0, 70.7, 70.6, 70.2, 70.1 (C^{13-19}), 69.6 (C^{12}), 68.8 (C^{11}), 68.6, 68.5 ($C^{1,1'}$), 32.4 ($C^{8,8'}$), 30.1, 30.0, 30.0, 29.9, 29.9 ($C^{2,4-7,2',4'-7'}$), 26.7, 26.6 ($C^{3,3'}$), 23.2 ($C^{9,9'}$), 14.7 ($C^{10,10'}$). EA: $C_{48}H_{71}O_9Na \cdot H_2O$ (Cal.) C: 69.20 %, H: 8.83 %, (Found) C: 69.12 %, H: 8.83 %.



Sodium 20-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoate (Na10/6):

Reagents: **7/10/6** (0.97 g, 1.1 mmol)

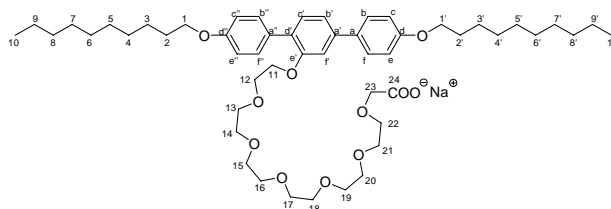
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/MeOH = 10/1$ (V/V) and recrystallization from ethyl acetate

Yield: 0.16 g (16.1 %), colorless waxy solid

Analytical data: $C_{52}H_{79}O_{11}Na$ $M_w = 903.17$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.53-7.46$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.32 (d, $^3J(H,H) = 7.5$, 1 H, Ar- $H^{c'}$), 7.20-7.14 (m, 1 H, Ar- $H^{b'}$), 7.12 (s, 1 H, Ar- $H^{f'}$), 6.98-6.86 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.18-4.12 (m, 2 H, CH_2^{11}), 4.02-3.82 (m, 6 H, $CH_2^{1,1',23}$), 3.81-3.70 (m, 2 H, CH_2^{12}), 3.67-3.46 (m, 20 H, CH_2^{13-22}), 1.83-1.69 (m, 4 H, $CH_2^{2,2'}$), 1.54-1.18 (m, 28 H, $CH_2^{3-9,3'-9'}$), 0.91-0.84 (m, 6 H, $CH_3^{10,10'}$). ^{13}C NMR ($CDCl_3$, 50 MHz) $\delta = 158.8$ (C^d), 158.2 ($C^{d''}$), 155.9 ($C^{e'}$), 140.9 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.3 ($C^{a''}$), 129.1 ($C^{a'}$), 127.9 ($C^{b',f''}$), 119.7 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.6 ($C^{f'}$), 70.5, 70.1, 69.9 (C^{13-23}), 69.7 (C^{12}), 68.3 (C^{11}), 68.0 ($C^{1,1'}$), 31.9 ($C^{8,8'}$), 29.5, 29.4, 29.3 ($C^{2,4-7,2',4'-7'}$), 26.0 ($C^{3,3'}$), 22.6 ($C^{9,9'}$), 14.1 ($C^{10,10'}$). EA: $C_{52}H_{79}O_{11}Na$ (Cal.) C: 69.15 %, H: 8.82 %, (Found) C: 69.03 %, H: 8.97 %.



Sodium 11-(4,4''-dibenzoyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**NaB/3**):Reagents: **7/B/3** (0.75 g, 1.1 mmol)

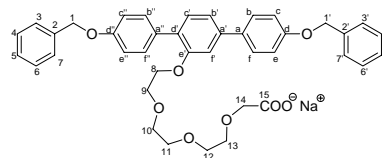
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 0.23 g (30.3 %), colorless solid

Analytical data: C₄₀H₃₉O₈Na M_w = 670.72

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.48-7.41 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.38-7.22 (m, 11 H, Ar-H^{3-7, 3'-7', c'}), 7.11-7.10 (m, 1 H, Ar-H^{b'}), 7.05-7.04 (m, 1 H, Ar-H^{f'}), 6.97-6.89 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.99, 4.98 (ds, 4 H, CH₂^{1, 1'}), 4.04 (s, 2 H, CH₂⁸), 3.81 (s, 2 H, CH₂¹⁴), 3.70 (s, 2 H, CH₂⁹), 3.48-3.40 (m, 8 H, CH₂¹⁰⁻¹³). ¹³C NMR (CDCl₃, 100 MHz) δ = 158.4 (C^d), 157.8 (C^{d''}), 155.9 (C^{e'}), 140.8 (C^{a'}), 137.1, 136.9 (C^{2, 2'}), 133.5 (C^{a''}), 130.9, 130.8, 130.6 (C^{b, f, a''}), 128.8 (C^a), 128.5, 128.5 (C^{4, 6, 4', 6'}), 128.0 (C^{b', f''}), 127.9 (C^{5, 5'}), 127.4 (C^{3, 7, 3', 7'}), 119.5 (C^{b'}), 115.1 (C^{c'', e''}), 114.2 (C^{c, e}), 111.2 (C^{f'}), 70.7, 70.1 (C¹⁰⁻¹⁴), 70.0 (C^{1, 1'}), 69.8 (C⁹), 68.5 (C⁸), EA: C₄₀H₃₉O₈Na·1.2H₂O (Cal.) C: 69.39 %, H: 6.03 %, (Found) C: 69.28 %, H: 5.96 %.

Sodium 8-(4,4''-dibutyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoate (**Na4/2**):Reagents: **7/4/2** (2.6 g, 4.7 mmol)

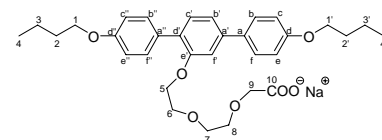
1 M NaOH aq. (100 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate/n-hexane

Yield: 1.7 g (64.5 %), colorless solid

Analytical data: C₃₂H₃₉O₇Na M_w = 558.64

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.46-7.33 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.26-7.22 (m, 1 H, Ar-H^{c'}), 7.17-7.07 (m, 1 H, Ar-H^{b'}), 7.06-7.00 (m, 1 H, Ar-H^{f'}), 6.94-6.76 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.10-3.36 (m, 14 H, CH₂^{1, 1', 5-9}), 1.81-1.67 (m, 4 H, CH₂^{2, 2'}), 1.46-1.38 (m, 4 H, CH₂^{3, 3'}), 1.00-0.84 (m, 6 H, CH₃^{4, 4'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 218.4 (C¹⁰), 158.7 (C^d), 158.0 (C^{d''}), 155.7 (C^{e'}), 140.8 (C^{a'}), 132.9 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b, f}), 130.3 (C^{a''}), 128.9 (C^a), 127.9 (C^{b', f''}), 119.5 (C^{b'}), 114.7 (C^{c'', e''}), 113.9 (C^{c, e}), 111.4 (C^{f'}), 70.4 (C⁵⁻⁹), 67.8, 67.7 (C^{1, 1'}), 31.5, 31.4 (C^{2, 2'}), 19.4, 19.4 (C^{3, 3'}), 14.0 (C^{4, 4'}). EA: C₃₂H₃₉O₇Na·0.5H₂O (Cal.) C: 67.71 %, H: 7.10 %, (Found) C: 67.79 %, H: 7.01 %.

Sodium 11-(4,4''-dibutyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Na4/3**):Reagents: **7/4/3** (3.1 g, 5.2 mmol)

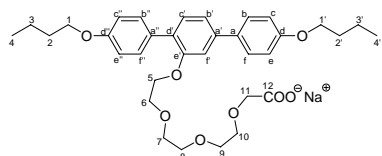
1 M NaOH aq. (100 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate/n-hexane

Yield: 2.2 g (69.9 %), colorless solid

Analytical data: C₃₄H₄₃O₈Na M_w = 602.69

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.50-7.45 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.28 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.14 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.5, 1 H, Ar-H^{b'}), 7.09 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{f'}), 6.93-6.85 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.09 (t, ³J(H,H) = 4.6, 2 H, CH₂⁵), 3.98-3.92 (m, 6 H, CH₂^{1, 1', 11}), 3.83-3.77 (m, 2 H, CH₂⁶), 3.59-3.41 (m, 8 H, CH₂⁷⁻¹⁰), 1.81-1.70 (m, 4 H, CH₂^{2, 2'}), 1.53-1.43 (m, 4 H, CH₂^{3, 3'}), 1.00-0.92 (m, 6 H, CH₃^{4, 4'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 174.4 (C¹⁴), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.8 (C^{a'}), 133.0 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b, f}), 130.4 (C^{a''}), 128.9 (C^a), 127.9 (C^{b', f''}),



119.5 ($C^{b'}$), 114.7 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.4 ($C^{f'}$), 70.6, 70.4, 70.0, 69.9 (C^{7-11}), 69.7 (C^6), 68.5 (C^5), 67.8, 67.7 ($C^{1,1'}$), 31.5, 31.4 ($C^{2,2'}$), 19.4, 19.4 ($C^{3,3'}$), 14.0, 14.0 ($C^{4,4'}$). EA: $C_{34}H_{43}O_8Na \cdot 0.2H_2O$ (Cal.) C: 67.35 %, H: 7.22 %, (Found) C: 67.29 %, H: 7.05 %.

Sodium 14-(4,4''-dibutyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Na4/4**):

Reagents: **7/4/4** (2.62 g, 4.11 mmol)

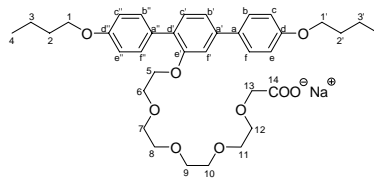
1 M NaOH (100 mL)

Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/MeOH = 10/1$ (V/V) and recrystallization from ethyl acetate/n-hexane

Yield: 1.78 g (67.0 %), colorless solid

Analytical data: $C_{36}H_{47}O_9Na$ $M_w = 646.74$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.52-7.48$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.30 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.16 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.11 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.94-6.87 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.13 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^5), 4.00-3.94 (m, 4 H, $CH_2^{1,1'}$), 3.92 (s, 2 H, CH_2^{13}), 3.74 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^6), 3.62-3.50 (m, 12 H, CH_2^{7-12}), 1.81-1.70 (m, 4 H, $CH_2^{2,2'}$), 1.53-1.43 (m, 4 H, $CH_2^{3,3'}$), 1.00-0.92 (m, 6 H, $CH_3^{4,4'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 174.3$ (C^{14}), 158.7 (C^d), 158.0 ($C^{d''}$), 155.8 ($C^{e'}$), 140.8 ($C^{a'}$), 133.1 ($C^{a''}$), 130.7 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.0 ($C^{a'}$), 127.9 ($C^{b',f''}$), 119.6 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.6 ($C^{f'}$), 70.8, 70.4, 70.2, 70.2, 69.9 (C^{7-13}), 69.7 (C^6), 68.4 (C^5), 67.8, 67.7 ($C^{1,1'}$), 31.5, 31.5 ($C^{2,2'}$), 19.4, 19.4 ($C^{3,3'}$), 14.0, 14.0 ($C^{4,4'}$). EA: $C_{36}H_{47}O_9Na \cdot 0.5H_2O$ (Cal.) C: 65.94 %, H: 7.38 %, (Found) C: 66.13 %, H: 7.23 %.



Sodium 11-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Na6/3**):

Reagents: **7/6/3** (3.2 g, 4.9 mmol)

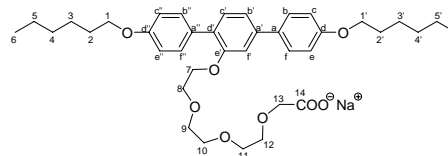
1 M NaOH aq. (100 mL)

Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/MeOH = 10/1$ (V/V) and recrystallization from ethyl acetate/n-hexane

Yield: 2.7 g (67.0 %), colorless solid

Analytical data: $C_{38}H_{51}O_8Na$ $M_w = 658.80$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.53-7.42$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.28 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.14 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{b'}$), 7.08 (s, 1 H, Ar- $H^{f'}$), 6.92-6.85 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.10-4.05 (m, 2 H, CH_2^7), 3.94-3.82 (m, 6 H, $CH_2^{1,1',13}$), 3.77-3.70 (m, 2 H, CH_2^8), 3.56-3.45 (m, 8 H, CH_2^{9-12}), 1.78-1.64 (m, 4 H, $CH_2^{2,2'}$), 1.45-1.40 (m, 4 H, $CH_2^{3,3'}$), 1.39-1.22 (m, 8 H, $CH_2^{4,5,4',5'}$), 0.89-0.85 (m, 6 H, $CH_3^{6,6'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 174.5$ (C^{14}), 158.7 (C^d), 158.0 ($C^{d''}$), 155.8 ($C^{e'}$), 140.8 ($C^{a'}$), 133.0 ($C^{a''}$), 130.7 ($C^{c'}$), 130.5, 130.4 ($C^{b,f,a''}$), 128.9 ($C^{a'}$), 127.9 ($C^{b',f''}$), 119.5 ($C^{b'}$), 114.7 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.4 ($C^{f'}$), 70.7, 70.4, 69.9 (C^{9-13}), 69.7 (C^8), 68.5 (C^7), 68.1, 68.0 ($C^{1,1'}$), 31.7 ($C^{4,4'}$), 29.4, 29.4 ($C^{2,2'}$), 25.9, 25.8 ($C^{3,3'}$), 22.7 ($C^{5,5'}$), 14.1 ($C^{6,6'}$). EA: $C_{38}H_{51}O_8Na \cdot 0.5H_2O$ (Cal.) C: 68.34 %, H: 7.85 %, (Found) C: 68.38 %, H: 8.00 %.

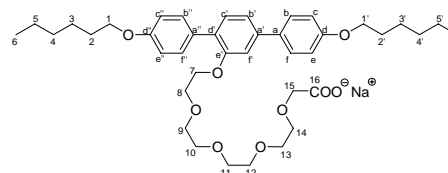


Sodium 14-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Na6/4**):

Reagents: **7/6/4** (3.5 g, 5.0 mmol)

1 M NaOH (50 mL)

Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/MeOH = 10/1$ (V/V) and recrystallization from ethyl acetate/n-hexane



Yield: 3.0 g (84.6 %), colorless solid

Analytical data: $C_{40}H_{55}O_9Na$ $M_w = 702.85$

1H NMR ($CDCl_3$, J/Hz , 500 MHz) $\delta = 7.53-7.48$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.32 (d, $^3J(H,H) = 7.7$, 1 H, Ar- H^c), 7.18 (dd, $^3J(H,H) = 7.7$, $^4J(H,H) = 1.5$, 1 H, Ar- $H^{b'}$), 7.12 (d, $^4J(H,H) = 1.5$, 1 H, Ar- H^f), 6.97-6.88 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.14 (t, $^3J(H,H) = 4.6$, 2 H, CH_2^7), 4.00-3.94 (m, 6 H, $CH_2^{1,1',15}$), 3.76 (t, $^3J(H,H) = 4.6$, 2 H, CH_2^8), 3.65-3.55 (m, 12 H, CH_2^{9-14}), 1.85-1.76 (m, 4 H, $CH_2^{2,2'}$), 1.50-1.43 (m, 4 H, $CH_2^{3,3''}$), 1.38-1.28 (m, 8 H, $CH_2^{4,5,4',5'}$), 0.94-0.87 (m, 6 H, $CH_3^{6,6'}$). ^{13}C NMR ($CDCl_3$, 125 MHz) $\delta = 173.8$ (C^{16}), 158.8 (C^d), 158.1 ($C^{d''}$), 155.9 (C^e), 140.9 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 (C^c), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.0 (C^a), 128.0 ($C^{b',f''}$), 119.6 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.5 (C^f), 70.8, 70.4, 70.3, 70.3, 70.2, 70.0 (C^{9-15}), 69.6 (C^8), 68.3 (C^7), 68.1, 68.0 ($C^{1,1'}$), 31.6, 31.6 ($C^{4,4'}$), 29.3, 29.2 ($C^{2,2'}$), 25.7, 25.7 ($C^{3,3'}$), 22.6 ($C^{5,5'}$), 14.0 ($C^{6,6'}$). EA: $C_{40}H_{55}O_9Na \cdot 0.3H_2O$ (Cal.) C: 67.83 %, H: 7.91 %, (Found) C: 67.82 %, H: 7.94 %

Sodium 20-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoate (**Na6/6**):

Reagents: **7/6/6** (1.1 g, 1.4 mmol)

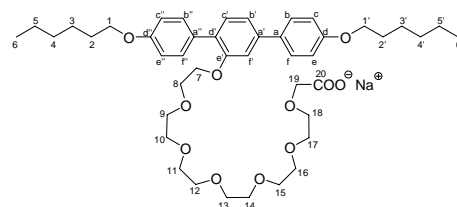
1 M NaOH aq. (40 mL)

Purification: Column chromatography with silica gel 60,
eluent: $CHCl_3/MeOH = 10/1$ (V/V) and
recrystallization from ethyl acetate/n-hexane

Yield: 0.8g (70.7 %), colorless solid

Analytical data: $C_{44}H_{63}O_{11}Na$ $M_w = 790.95$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.51-7.48$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.32 (d, $^3J(H,H) = 7.9$, 1 H, Ar- H^c), 7.18 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.11 (d, $^4J(H,H) = 1.7$, 1 H, Ar- H^f), 6.96-6.88 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.14 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^7), 3.99-3.94 (m, 4 H, $CH_2^{1,1'}$), 3.89 (s, 2 H, CH_2^{19}), 3.77 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^8), 3.61-3.56 (m, 20 H, CH_2^{9-18}), 1.82-1.74 (m, 4 H, $CH_2^{2,2'}$), 1.48-1.42 (m, 4 H, $CH_2^{3,3''}$), 1.38-1.31 (m, 8 H, $CH_2^{4,5,4',5'}$), 0.92-0.87 (m, 6 H, $CH_3^{6,6'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 174.6$ (C^{20}), 158.7 (C^d), 158.1 ($C^{d''}$), 155.8 (C^e), 140.8 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 (C^c), 130.5 ($C^{b,f}$), 130.3 ($C^{a''}$), 129.1 (C^a), 127.9 ($C^{b',f''}$), 119.6 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.6 (C^f), 70.8, 70.6, 70.1, 70.0, 69.7, 69.7, 69.6 (C^{9-19}), 69.2 (C^8), 68.4 (C^7), 68.2, 68.1 ($C^{1,1'}$), 31.7, 31.7 ($C^{4,4'}$), 29.4, 29.4 ($C^{2,2'}$), 25.9, 25.8 ($C^{3,3'}$), 22.7 ($C^{5,5'}$), 14.1, 14.1 ($C^{6,6'}$). EA: $C_{44}H_{63}O_{11}Na \cdot 1.8H_2O$ (Cal.) C: 64.18 %, H: 8.15 %, (Found) C: 64.22 %, H: 7.92 %



Sodium 11-[4,4''-bis(3,7-dimethyloctyloxy)-p-terphenyl-2'-yloxy]-3,6,9-trioxaundecanoate (**Na10*/3**):

Reagents: **7/10*/3** (0.7 g, 0.92 mmol)

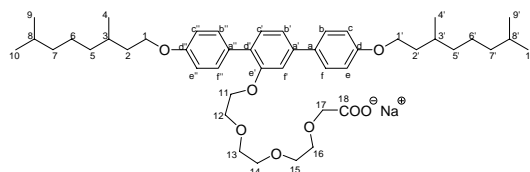
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel
60, eluent: $CHCl_3/MeOH = 10/1$ (V/V)
and recrystallization from ethyl
acetate/n-hexane

Yield: 0.35 g (49.4 %), colorless solid

Analytical data: $C_{46}H_{67}O_8Na$ $M_w = 771.01$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.50-7.42$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.27 (d, $^3J(H,H) = 7.9$, 1 H, Ar- H^c), 7.13 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.07 (d, $^4J(H,H) = 1.7$, 1 H, Ar- H^f), 6.92-6.84 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.09 (t, $^3J(H,H) = 4.8$, 2 H, CH_2^{11}), 3.99-3.91 (m, 4 H, $CH_2^{1,1'}$), 3.85 (s, 2 H, CH_2^{17}), 3.79-3.71 (m, 2 H, CH_2^{12}), 3.58-3.42 (m, 8 H, CH_2^{13-16}), 1.84-1.76 (m, 2 H, $CH^8, 8'$), 1.66-1.60 (m, 2 H, $CH^{3,3'}$), 1.59-1.42 (m, 4 H, $CH_2^{2,2'}$), 1.37-1.07 (m, 12 H, $CH_2^{5-7,5'-7'}$), 0.93-0.90 (m, 6



H, $\text{CH}_3^{4,4'}$), 0.89-0.70 (m, 12 H, $\text{CH}_3^{9,10,9',10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 158.7 (C^{d}), 158.0 ($\text{C}^{\text{d''}}$), 155.8 ($\text{C}^{\text{e'}}$), 140.8 ($\text{C}^{\text{a'}}$), 133.0 ($\text{C}^{\text{a''}}$), 130.7 ($\text{C}^{\text{c'}}$), 130.5 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a''}}$), 128.9 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.4 ($\text{C}^{\text{b'}}$), 114.7 ($\text{C}^{\text{c'',e''}}$), 113.9 ($\text{C}^{\text{c,e}}$), 111.2 ($\text{C}^{\text{f'}}$), 70.8, 70.6, 70.2, 69.8 (C^{13-17}), 69.4 (C^{12}), 68.6 (C^{11}), 66.5, 66.4 ($\text{C}^{1,1'}$), 39.3 ($\text{C}^{7,7'}$), 37.4 ($\text{C}^{5,5'}$), 36.4, 36.4 ($\text{C}^{2,2'}$), 30.0 ($\text{C}^{3,3'}$), 28.1 ($\text{C}^{8,8'}$), 24.8 ($\text{C}^{5,5'}$), 22.8, 22.7 ($\text{C}^{9,10,9',10'}$), 19.8 ($\text{C}^{4,4'}$). EA: $\text{C}_{46}\text{H}_{67}\text{O}_8\text{Na}\cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 70.83 %, H: 8.79 %, (Found) C: 70.80 %, H: 8.63 %.

Sodium 14-[4,4''-bis(3,7-dimethyloctyloxy)-p-terphenyl-2'-yloxy]-3,6,9,12-tetraoxatetradecanoate (Na10*/4):

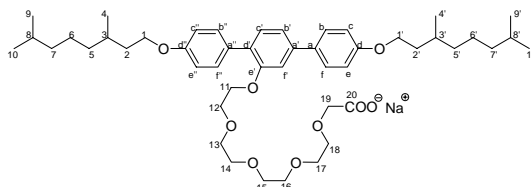
Reagents: **7/10*/4** (1.15 g, 1.43 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel
60, eluent: $\text{CHCl}_3/\text{MeOH}$ = 10/1 (V/V)
and recrystallization from n-hexane

Yield: 0.55 g (47.3 %), colorless solid

Analytical data: $\text{C}_{48}\text{H}_{71}\text{O}_9\text{Na}$ M_w = 815.06

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.51-7.47 (m, 4 H, Ar- $\text{H}^{\text{b,f,b'',f''}}$), 7.30 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{\text{c'}}$), 7.16 (dd, $^3J(\text{H,H})$ = 7.9, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- $\text{H}^{\text{b'}}$), 7.11 (d, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- $\text{H}^{\text{f'}}$), 6.95-6.87 (m, 4 H, Ar- $\text{H}^{\text{c,e,c'',e''}}$), 4.12 (t, $^3J(\text{H,H})$ = 5.0, 2 H, CH_2^{11}), 4.04-3.93 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.92 (s, 2 H, CH_2^{19}), 3.73 (t, $^3J(\text{H,H})$ = 5.0, 2 H, CH_2^{12}), 3.62-3.54 (m, 12 H, CH_2^{13-18}), 1.85-1.77 (m, 2 H, $\text{CH}^{8,8'}$), 1.67-1.61 (m, 2 H, $\text{CH}^{3,3'}$), 1.60-1.43 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.37-1.07 (m, 12 H, $\text{CH}_2^{5-7,5'-7'}$), 0.93-0.90 (m, 6 H, $\text{CH}_3^{4,4'}$), 0.89-0.70 (m, 12 H, $\text{CH}_3^{9,10,9',10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 175.0 (C^{20}), 158.7 (C^{d}), 158.0 ($\text{C}^{\text{d''}}$), 155.8 ($\text{C}^{\text{e'}}$), 140.8 ($\text{C}^{\text{a'}}$), 133.1 ($\text{C}^{\text{a''}}$), 130.7 ($\text{C}^{\text{c'}}$), 130.4 ($\text{C}^{\text{b,f}}$), 130.3 ($\text{C}^{\text{a''}}$), 128.9 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.5 ($\text{C}^{\text{b'}}$), 114.8 ($\text{C}^{\text{c'',e''}}$), 113.9 ($\text{C}^{\text{c,e}}$), 111.5 ($\text{C}^{\text{f'}}$), 70.8, 70.5, 70.4, 70.3, 70.2, 69.9, 69.7, (C^{13-19}), 69.7 (C^{12}), 68.3 (C^{11}), 66.5, 66.4 ($\text{C}^{1,1'}$), 39.3 ($\text{C}^{7,7'}$), 37.4, 37.4 ($\text{C}^{5,5'}$), 36.4, 36.3 ($\text{C}^{2,2'}$), 30.0, 30.0 ($\text{C}^{3,3'}$), 28.0 ($\text{C}^{8,8'}$), 24.7 ($\text{C}^{5,5'}$), 22.8, 22.7 ($\text{C}^{9,10,9',10'}$), 19.8 ($\text{C}^{4,4'}$). EA: $\text{C}_{48}\text{H}_{71}\text{O}_9\text{Na}\cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 69.96 %, H: 8.81 %, (Found) C: 69.80 %, H: 8.69 %.



Sodium 11-(4,4''-dioctyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (Na8/3):

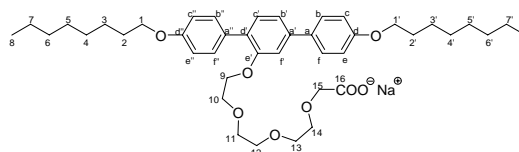
Reagents: **7/8/3** (0.71 g, 1.0 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel
60, eluent: $\text{CHCl}_3/\text{MeOH}$ = 10/1 (V/V)
and recrystallization from ethyl acetate

Yield: 0.32 g (44.5 %), colorless solid

Analytical data: $\text{C}_{42}\text{H}_{59}\text{O}_8\text{Na}$ M_w = 714.90

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.49-7.42 (m, 4 H, Ar- $\text{H}^{\text{b,f,b'',f''}}$), 7.26 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{\text{c'}}$), 7.13 (dd, $^3J(\text{H,H})$ = 7.9, $^4J(\text{H,H})$ = 1.5, 1 H, Ar- $\text{H}^{\text{b'}}$), 7.07 (d, $^4J(\text{H,H})$ = 1.5, 1 H, Ar- $\text{H}^{\text{f'}}$), 6.91-6.83 (m, 4 H, Ar- $\text{H}^{\text{c,e,c'',e''}}$), 4.08 (t, $^3J(\text{H,H})$ = 4.5, 2 H, CH_2^9), 3.94-3.89 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.84 (s, 2 H, CH_2^{15}), 3.77-3.70 (m, 2 H, CH_2^{10}), 3.58-3.43 (m, 8 H, CH_2^{11-14}), 1.81-1.70 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.49-1.40 (m, 4 H, $\text{CH}_2^{3,3'}$), 1.39-1.20 (m, 16 H, $\text{CH}_2^{4-7,4'-7'}$), 0.89-0.84 (m, 6 H, $\text{CH}_3^{8,8'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 176.6 (C^{16}), 158.8 (C^{d}), 158.0 ($\text{C}^{\text{d''}}$), 155.8 ($\text{C}^{\text{e'}}$), 140.8 ($\text{C}^{\text{a'}}$), 133.0 ($\text{C}^{\text{a''}}$), 130.7 ($\text{C}^{\text{c'}}$), 130.5 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a''}}$), 128.9 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.4 ($\text{C}^{\text{b'}}$), 114.7 ($\text{C}^{\text{c'',e''}}$), 113.8 ($\text{C}^{\text{c,e}}$), 111.2 ($\text{C}^{\text{f'}}$), 70.7, 70.2, 69.7 (C^{11-15}), 69.2 (C^{10}), 68.5 (C^9), 68.1, 68.0 ($\text{C}^{1,1'}$), 31.9, 31.9 ($\text{C}^{6,6'}$), 29.6, 29.4, 29.4, 29.3, 29.3 ($\text{C}^{2,4,5,2',4',5'}$), 26.1, 26.1 ($\text{C}^{3,3'}$), 22.7 ($\text{C}^{7,7'}$), 14.1 ($\text{C}^{8,8'}$). EA: $\text{C}_{42}\text{H}_{59}\text{O}_8\text{Na}\cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 69.68 %, H: 8.35 %, (Found) C: 69.69 %, H: 8.36 %.



Sodium 14-(4,4''-dioctyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Na8/4**):Reagents: **7/8/4** (0.71 g, 0.95 mmol)

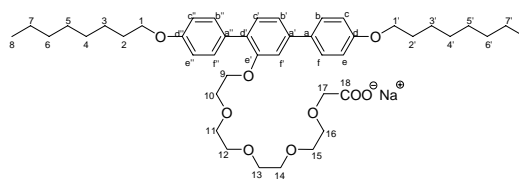
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate/n-hexane

Yield: 0.35 g (48.7 %), colorless solid

Analytical data: C₄₄H₆₃O₉Na M_w = 758.96

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.50-7.46 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.29 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.15 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.10 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.94-6.84 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.10 (t, ³J(H,H) = 5.0, 2 H, CH₂⁹), 3.96-3.91 (m, 4 H, CH₂^{1,1'}), 3.88 (s, 2 H, CH₂¹⁷), 3.71 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁰), 3.62-3.51 (m, 12 H, CH₂¹¹⁻¹⁶), 1.81-1.70 (m, 4 H, CH₂^{2, 2'}), 1.49-1.40 (m, 4 H, CH₂^{3, 3'}), 1.39-1.20 (m, 16 H, CH₂^{4-7, 4'-7'}), 0.89-0.84 (m, 6 H, CH₃^{8, 8'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.7 (C¹⁸), 158.8 (C^d), 158.1 (C^{d''}), 155.9 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b, f}), 130.4 (C^{a''}), 129.0 (C^a), 127.9 (C^{b', f''}), 119.5 (C^{b'}), 114.8 (C^{c'', e''}), 113.9 (C^{c, e}), 111.5 (C^{f'}), 70.8, 70.7, 70.5, 70.3, 70.1, 69.9, 69.6 (C¹¹⁻¹⁷), 69.4 (C¹⁰), 68.3 (C⁹), 68.1, 68.0 (C^{1,1'}), 31.9 (C^{6, 6'}), 29.4, 29.4, 29.4, 29.3 (C^{2, 4, 5, 2', 4', 5'}), 26.1, 26.1 (C^{3, 3'}), 22.7 (C^{7, 7'}), 14.1 (C^{8, 8'}). EA: C₄₄H₆₃O₉Na·0.5H₂O (Cal.) C: 68.81 %, H: 8.40 %, (Found) C: 68.64 %, H: 8.12 %.

Sodium 11-(4,4''-dihexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Na16/3**):Reagents: **7/17/3** (3.9 g, 4.2 mmol)

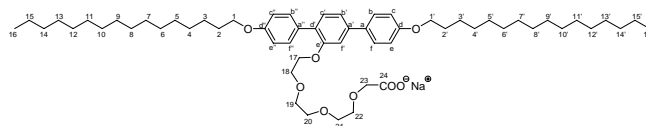
1 M NaOH aq. (100 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 3.3 g (83.8 %), colorless solid

Analytical data: C₅₈H₉₁O₈Na M_w = 939.33

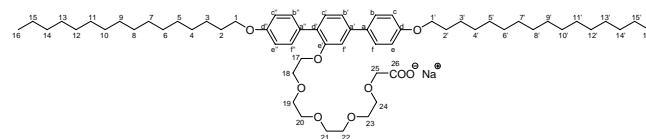
¹H NMR (CDCl₃, J/Hz, 500 MHz) δ = 7.53-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.29 (d, ³J(H,H) = 7.8, 1 H, Ar-H^{c'}), 7.16 (d, ³J(H,H) = 7.8, 1 H, Ar-H^{b'}), 7.11 (s, 1 H, Ar-H^{f'}), 6.94-6.87 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.14-4.07 (m, 2 H, CH₂¹⁷), 3.97-3.92 (m, 6 H, CH₂^{1,1', 23}), 3.79-3.73 (m, 2 H, CH₂¹⁸), 3.59-3.54 (m, 8 H, CH₂¹⁹⁻²²), 1.83-1.76 (m, 4 H, CH₂^{2, 2'}), 1.50-1.42 (m, 4 H, CH₂^{3, 3'}), 1.41-1.22 (m, 48 H, CH₂^{4-15, 4'-15'}), 0.94-0.87 (m, 6 H, CH₃^{16, 16'}). ¹³C NMR (CDCl₃, 125 MHz) δ = 175.7 (C²⁴), 158.8 (C^d), 158.1 (C^{d''}), 155.8 (C^{e'}), 140.8 (C^{a'}), 133.0 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b, f}), 130.3 (C^{a''}), 128.8 (C^a), 127.9 (C^{b', f''}), 119.4 (C^{b'}), 114.7 (C^{c'', e''}), 113.8 (C^{c, e}), 111.2 (C^{f'}), 70.6, 70.2, 70.1, 69.8 (C¹⁹⁻²³), 69.6 (C¹⁸), 68.3 (C¹⁷), 68.0, 67.9 (C^{1,1'}), 31.9 (C^{14, 14'}), 29.7, 29.6, 29.6, 29.6, 29.4, 29.4, 29.3 (C^{2, 4-13, 2', 4'-13'}), 26.1, 26.0 (C^{3, 3'}), 22.6 (C^{15, 15'}), 14.0 (C^{16, 16'}). EA: C₅₈H₉₁O₈Na (Cal.) C: 74.16 %, H: 9.76 %, (Found) C: 74.39 %, H: 9.72 %.

Sodium 14-(4,4''-dihexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Na16/4**):Reagents: **7/16/4** (1.3 g, 1.3 mmol)

1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 1.0 g (76.2 %), colorless solid

Analytical data: C₆₀H₉₅O₉Na M_w = 983.38

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.49-7.46 (m, 4 H, $\text{Ar-H}^{\text{b}, \text{f}, \text{b}'', \text{f}'}$), 7.28 (d, $^3J(\text{H}, \text{H}) = 7.9$, 1 H, $\text{Ar-H}^{\text{c}'}$), 7.14 (dd, $^3J(\text{H}, \text{H}) = 7.9$, $^4J(\text{H}, \text{H}) = 1.7$, 1 H, $\text{Ar-H}^{\text{b}'}$), 7.09 (d, $^4J(\text{H}, \text{H}) = 1.7$, 1 H, $\text{Ar-H}^{\text{f}'}$), 6.92-6.85 (m, 4 H, $\text{Ar-H}^{\text{c}, \text{e}, \text{c}'', \text{e}''}$), 4.09 (t, 2 H, $^3J(\text{H}, \text{H}) = 4.8$, CH_2^{17}), 3.96-3.87 (m, 6 H, $\text{CH}_2^{1, 1', 25}$), 3.70 (t, $^3J(\text{H}, \text{H}) = 4.8$, 2 H, CH_2^{18}), 3.63-3.43 (m, 12 H, CH_2^{19-24}), 1.78-1.73 (m, 4 H, $\text{CH}_2^{2, 2'}$), 1.43-1.38 (m, 4 H, $\text{CH}_2^{3, 3'}$), 1.37-1.23 (m, 48 H, $\text{CH}_2^{4-15, 4'-15'}$), 0.88-0.84 (m, 6 H, $\text{CH}_3^{16, 16'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 176.1 (C^{26}), 158.7 (C^{d}), 158.0 ($\text{C}^{\text{d}''}$), 155.8 ($\text{C}^{\text{e}'}$), 140.7 ($\text{C}^{\text{a}'}$), 133.0 ($\text{C}^{\text{a}''}$), 130.7 ($\text{C}^{\text{c}'}$), 130.4 ($\text{C}^{\text{b}, \text{f}}$), 130.3 ($\text{C}^{\text{a}''}$), 128.9 (C^{a}), 127.9 ($\text{C}^{\text{b}', \text{f}'}$), 119.5 ($\text{C}^{\text{b}'}$), 114.7 ($\text{C}^{\text{c}'', \text{e}''}$), 113.9 ($\text{C}^{\text{c}, \text{e}}$), 111.5 ($\text{C}^{\text{f}'}$), 70.9, 70.8, 70.5, 70.4, 70.2, 69.9, 69.6 (C^{19-25}), 69.4 (C^{18}), 68.2 (C^{17}), 68.1, 68.0 ($\text{C}^{1, 1'}$), 32.0 ($\text{C}^{14, 14'}$), 29.8, 29.7, 29.6, 29.5, 29.4 ($\text{C}^{2, 4-13, 2', 4'-13'}$), 26.2 ($\text{C}^{3, 3'}$), 22.8 ($\text{C}^{15, 15'}$), 14.2 ($\text{C}^{16, 16'}$). EA: $\text{C}_{60}\text{H}_{95}\text{O}_9\text{Na} \cdot 0.2\text{H}_2\text{O}$ (Cal.) C: 73.01 %, H: 9.74 %, (Found) C: 72.95 %, H: 9.64 %.

Sodium 11-(4,4''-didecyloxy-p-terphenyl-3-yloxy)-3,6,9-trioxaundecanoate (**Na*10/3**):

Reagents: **17/10/3** (0.70 g, 0.93 mmol)

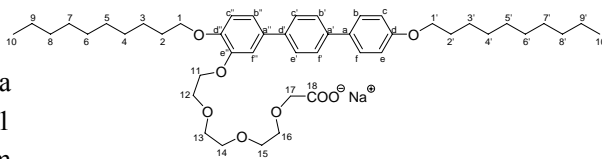
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH} = 10/1$ (V/V) and recrystallization from chloroform/n-hexane

Yield: 178 mg (25.1 %), colorless solid

Analytical data: $\text{C}_{46}\text{H}_{67}\text{O}_8\text{Na}$ $M_w = 771.01$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.53 (s, 4 H, $\text{Ar-H}^{\text{b}', \text{f}', \text{c}', \text{e}'}$), 7.48 (d, $^3J(\text{H}, \text{H}) = 8.7$, 2 H, $\text{Ar-H}^{\text{b}, \text{f}}$), 7.13 (d, $^4J(\text{H}, \text{H}) = 1.9$, 1 H, $\text{Ar-H}^{\text{f}'}$), 7.10 (dd, $^3J(\text{H}, \text{H}) = 7.5$, $^4J(\text{H}, \text{H}) = 1.9$, 1 H, $\text{Ar-H}^{\text{b}''}$), 6.91 (d, $^3J(\text{H}, \text{H}) = 8.7$, 2 H, $\text{Ar-H}^{\text{c}, \text{e}}$), 6.85 (d, $^3J(\text{H}, \text{H}) = 7.5$, 1 H, $\text{Ar-H}^{\text{c}''}$), 4.16 (t, $^3J(\text{H}, \text{H}) = 4.5$, 2 H, CH_2^{11}), 3.95-3.83 (m, 8 H, $\text{CH}_2^{1, 1', 12, 17}$), 3.80-3.45 (m, 8 H, CH_2^{13-16}), 1.90-1.75 (m, 4 H, $\text{CH}_2^{2, 2'}$), 1.52-1.18 (m, 28 H, $\text{CH}_2^{3-9, 3'-9'}$), 0.92-0.84 (m, 6 H, $\text{CH}_3^{10, 10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 175.8 (C^{18}), 158.6 (C^{d}), 148.7 ($\text{C}^{\text{d}', \text{e}''}$), 139.1, 138.9 ($\text{C}^{\text{a}', \text{d}'}$), 133.6, 132.8 ($\text{C}^{\text{a}, \text{a}''}$), 127.8 ($\text{C}^{\text{b}, \text{f}}$), 126.9, 126.8 ($\text{C}^{\text{b}', \text{c}', \text{e}', \text{f}'}$), 119.8 ($\text{C}^{\text{b}''}$), 114.7 ($\text{C}^{\text{c}, \text{e}}$), 113.8 ($\text{C}^{\text{c}''}$), 113.3 ($\text{C}^{\text{f}'}$), 70.8, 70.3, 69.9 (C^{13-17}), 69.3 (C^{12}), 69.1 (C^{11}), 68.1 ($\text{C}^{1, 1'}$), 32.0 ($\text{C}^{8, 8'}$), 29.7, 29.7, 29.7, 29.5, 29.5, 29.4 ($\text{C}^{2, 4-7, 2', 4'-7'}$), 26.2, 26.1 ($\text{C}^{3, 3'}$), 22.8 ($\text{C}^{9, 9'}$), 14.2 ($\text{C}^{10, 10'}$). EA: $\text{C}_{46}\text{H}_{67}\text{O}_8\text{Na}$ (Cal.) C: 71.66 %, H: 8.76 %, (Found) C: 71.56 %, H: 8.69 %.



Sodium 14-(4,4''-didecyloxy-p-terphenyl-3-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Na*10/4**):

Reagents: **17/10/4** (1.0 g, 1.2 mmol)

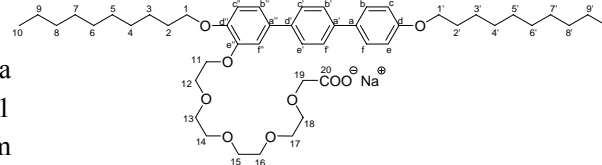
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH} = 10/1$ (V/V) and recrystallization from chloroform/n-hexane

Yield: 252 mg (24.9 %), colorless solid

Analytical data: $\text{C}_{48}\text{H}_{71}\text{O}_9\text{Na}$ $M_w = 815.06$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.55 (s, 4 H, $\text{Ar-H}^{\text{b}', \text{f}', \text{c}', \text{e}'}$), 7.52-7.49 (m, 2 H, $\text{Ar-H}^{\text{b}, \text{f}}$), 7.17 (d, $^4J(\text{H}, \text{H}) = 2.1$, 1 H, $\text{Ar-H}^{\text{f}'}$), 7.14 (dd, $^3J(\text{H}, \text{H}) = 8.3$, $^4J(\text{H}, \text{H}) = 2.1$, 1 H, $\text{Ar-H}^{\text{b}''}$), 6.95-6.92 (m, 2 H, $\text{Ar-H}^{\text{c}, \text{e}}$), 6.89 (d, $^3J(\text{H}, \text{H}) = 8.3$, 1 H, $\text{Ar-H}^{\text{c}''}$), 4.19 (t, $^3J(\text{H}, \text{H}) = 4.8$, 2 H, CH_2^{11}), 4.00-3.94 (m, 4 H, $\text{CH}_2^{1, 1'}$), 3.86-3.82 (m, 4 H, $\text{CH}_2^{12, 19}$), 3.72-3.55 (m, 12 H, CH_2^{13-18}), 1.81-1.75 (m, 4 H, $\text{CH}_2^{2, 2'}$), 1.46-1.18 (m, 28 H, $\text{CH}_2^{3-9, 3'-9'}$), 0.89-0.84 (m, 6 H, $\text{CH}_3^{10, 10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 174.7 (C^{20}), 158.6 (C^{d}), 148.8, 148.7 ($\text{C}^{\text{d}', \text{e}''}$), 139.1, 138.9 ($\text{C}^{\text{a}', \text{d}'}$), 133.7, 132.9 ($\text{C}^{\text{a}, \text{a}''}$), 127.8 ($\text{C}^{\text{b}, \text{f}}$), 126.9, 126.8 ($\text{C}^{\text{b}', \text{c}', \text{e}', \text{f}'}$), 120.0 ($\text{C}^{\text{b}''}$), 114.8 ($\text{C}^{\text{c}, \text{e}}$), 114.0 ($\text{C}^{\text{c}'', \text{f}'}$), 70.7, 70.4, 70.2, 70.0, 69.8 (C^{13-19}), 69.7 (C^{12}), 69.2 (C^{11}), 68.1 ($\text{C}^{1, 1'}$), 32.0 ($\text{C}^{8, 8'}$), 29.7, 29.7, 29.6, 29.5, 29.4, 29.4 ($\text{C}^{2, 4-7, 2', 4'-7'}$), 26.2, 26.1 ($\text{C}^{3, 3'}$), 22.8



(C^{9,9'}), 14.2 (C^{10,10'}). EA: C₄₈H₇₁O₉Na (Cal.) C: 70.73 %, H: 8.78 %, (Found) C: 70.60 %, H: 8.71 %.

Sodium 11-(4-hexyloxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (Na6.16/3):

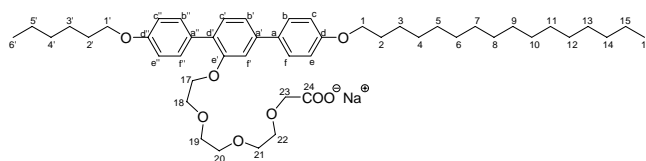
Reagents: **22/6/16/3** (0.48 g, 0.61 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 124 mg (25.5 %), colorless solid

Analytical data: C₄₈H₇₁O₈Na M_w = 799.06

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.52-7.46 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.29 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.15 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{b'}), 7.11 (s, 1 H, Ar-H^{f'}), 6.94-6.86 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.10 (bs, 2 H, CH₂¹⁷), 3.96-3.91 (m, 6 H, CH₂^{1,1',23}), 3.74 (bs, 2 H, CH₂¹⁸), 3.60-3.42 (m, 8 H, CH₂¹⁹⁻²²), 1.82-1.74 (m, 4 H, CH₂^{2,2'}), 1.48-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.22 (m, 28 H, CH₂^{4-15,4',5'}), 0.94-0.88 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 176.0 (C²⁴), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.7 (C^{a'}), 132.9 (C^{a''}), 130.7 (C^{c'}), 130.4 (C^{b,f}), 130.3 (C^{a''}), 128.8 (C^a), 127.8 (C^{b'', f''}), 119.4 (C^{b'}), 114.7 (C^{c'', e''}), 113.8 (C^{c,e}), 111.1 (C^{f'}), 70.6, 70.3, 70.1, 69.7, 69.6 (C¹⁹⁻²³), 69.4 (C¹⁸), 68.4 (C¹⁷), 68.0, 67.9 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.6, 29.6, 29.4, 29.3, 29.3 (C^{2, 4-13, 2'}), 26.1 (C³), 25.7 (C^{3'}), 22.6, 22.6 (C^{15, 5'}), 14.1 (C¹⁶), 14.0 (C^{6'}). EA: C₄₈H₇₁O₈Na·0.5H₂O (Cal.) C: 71.34 %, H: 8.98 %, (Found) C: 71.63 %, H: 8.87 %.



Sodium 14-(4-hexyloxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (Na6.16/4):

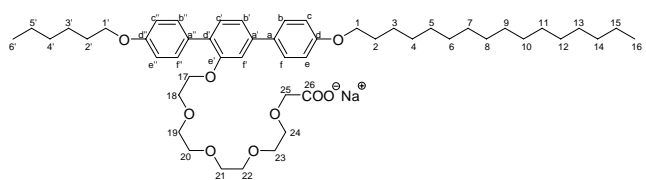
Reagents: **22/6/16/4** (1.1 g, 1.3 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 1.0 g (89.9 %), colorless solid

Analytical data: C₅₀H₇₅O₉Na M_w = 843.11

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.51-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.30 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.16 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.11 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.95-6.87 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.12 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 3.97-3.91 (m, 6 H, CH₂^{1,1',25}), 3.73 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁸), 3.75-3.50 (m, 12 H, CH₂¹⁹⁻²⁴), 1.81-1.73 (m, 4 H, CH₂^{2,2'}), 1.47-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.21 (m, 28 H, CH₂^{4-15,4',5'}), 0.91-0.85 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.2 (C²⁴), 158.8 (C^d), 158.1 (C^{d''}), 155.9 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.0 (C^a), 127.9 (C^{b'', f''}), 119.5 (C^{b'}), 114.8 (C^{c'', e''}), 113.9 (C^{c,e}), 111.5 (C^{f'}), 70.8, 70.4, 70.3, 70.2, 70.2, 69.9, 69.7 (C¹⁹⁻²⁵), 69.6 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4 (C^{2, 4-13, 2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7 (C¹⁵), 22.6 (C^{5'}), 14.1, 14.1 (C^{16, 6'}). EA: C₅₀H₇₅O₉Na (Cal.) C: 71.23 %, H: 8.97 %, (Found) C: 71.06 %, H: 8.80 %.



Sodium 20-(4-hexyloxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxa-eicosanoate (**Na6.16/6**):

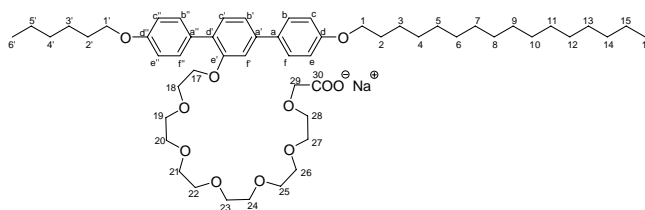
Reagents: **22/6/16/6** (1.1 g, 1.2 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 0.75 g (67.5 %), colorless solid

Analytical data: C₅₄H₈₃O₁₁Na M_w = 931.22

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.51-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.32 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.11 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.95-6.88 (m, 4 H, Ar-H^{c, c'', e'', e''}), 4.14 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 3.98-3.94 (m, 4 H, CH₂^{1,1'}), 3.88 (s, 2 H, CH₂²⁹), 3.77 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁸), 3.64-3.55 (m, 20 H, CH₂¹⁹⁻²⁸), 1.81-1.74 (m, 4 H, CH₂^{2,2'}), 1.47-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.22 (m, 28 H, CH₂^{4-15,4',5'}), 0.91-0.84 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.1 (C³⁰), 158.7 (C^d), 158.1 (C^{d''}), 155.8 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.7 (C^{c'}), 130.4 (C^{b,f}), 130.3 (C^{a''}), 129.0 (C^a), 127.9 (C^{b'',f''}), 119.6 (C^{b'}), 114.7 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^{f'}), 70.8, 70.6, 70.3, 70.1, 69.9, 69.8, 69.7, 69.6 (C¹⁹⁻²⁹), 69.3 (C¹⁸), 68.4 (C¹⁷), 68.2, 68.0 (C^{1,1'}), 32.0 (C¹⁴), 31.7 (C^{4'}), 29.8, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4 (C^{2,4-13,2'}), 26.2 (C³), 25.9 (C^{3'}), 22.8 (C¹⁵), 22.7 (C^{5'}), 14.2 (C¹⁶), 14.1 (C^{6'}). EA: C₅₄H₈₃O₁₁Na·1.5H₂O (Cal.) C: 67.68 %, H: 9.05 %, (Found) C: 67.52 %, H: 8.85 %.



Sodium 11-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Na16.6/3**):

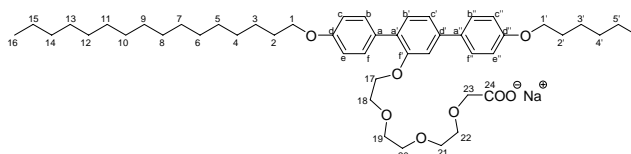
Reagents: **22/16/6/3** (0.75 g, 0.95 mmol)
1 M NaOH (50 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 (V/V) and recrystallization from ethyl acetate

Yield: 0.75 g (71.2 %), colorless solid

Analytical data: C₄₈H₇₁O₈Na M_w = 799.06

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.50-7.42 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.26 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.12 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.5, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{f'}), 6.91-6.83 (m, 4 H, Ar-H^{c, c'', e'', e''}), 4.08 (t, ³J(H,H) = 4.6, 2 H, CH₂¹⁷), 3.94-3.89 (m, 4 H, CH₂^{1,1'}), 3.85 (s, 2 H, CH₂²³), 3.75-3.71 (m, 2 H, CH₂¹⁸), 3.56-3.43 (m, 8 H, CH₂¹⁹⁻²²), 1.80-1.72 (m, 4 H, CH₂^{2,2'}), 1.46-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.91-0.85 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 176.7 (C²⁴), 158.7 (C^{d''}), 158.1 (C^d), 155.8 (C^{f'}), 140.8 (C^{d'}), 133.0 (C^a), 130.7 (C^{b'}), 130.5 (C^{b'',f''}), 130.4 (C^a), 128.9 (C^{a''}), 127.9 (C^{b,f}), 119.4 (C^{c'}), 114.7 (C^{c,e}), 113.8 (C^{c'',e''}), 111.2 (C^{c'}), 70.7, 70.2, 69.7 (C¹⁹⁻²³), 69.2 (C¹⁸), 68.5 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 29.3 (C^{2,4-13,2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7, 22.6 (C^{15,5'}), 14.1, 14.1 (C^{16,6'}). EA: C₄₈H₇₁O₈Na·0.5H₂O (Cal.) C: 71.34 %, H: 8.98 %, (Found) C: 71.36 %, H: 8.84 %.



Sodium 14-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetra-decanoate (**Na16.6/4**):

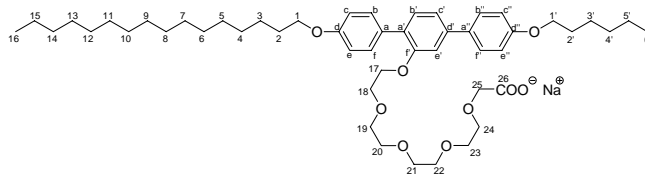
Reagents: **22/16/6/4** (1.0 g, 1.2 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography
with silica gel 60, eluent:
CHCl₃/MeOH = 10/1 (V/V)
and recrystallization from ethyl acetate

Yield: 0.65 g (77.1 %), colorless solid

Analytical data: C₅₀H₇₅O₉Na M_w = 843.11

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.51-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.30 (d, ³J(H,H) = 7.7, 1 H, Ar-H^{b'}), 7.16 (dd, ³J(H,H) = 7.7, ⁴J(H,H) = 1.5, 1 H, Ar-H^{c'}), 7.11 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{e'}), 6.94-6.86 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.11 (t, ³J(H,H) = 4.6, 2 H, CH₂¹⁷), 3.97-3.90 (m, 6 H, CH₂^{1,1',25}), 3.73 (t, ³J(H,H) = 4.6, 2 H, CH₂¹⁸), 3.63-3.50 (m, 12 H, CH₂¹⁹⁻²⁴), 1.81-1.75 (m, 4 H, CH₂^{2,2'}), 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.89-0.86 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.2 (C²⁶), 158.7 (C^{d''}), 158.0 (C^d), 155.8 (C^{f'}), 140.7 (C^{d'}), 133.0 (C^a), 130.7 (C^{b'}), 130.4 (C^{b'', f''}), 130.3 (C^a), 128.9 (C^{a''}), 127.8 (C^{b, f}), 119.5 (C^{c'}), 114.7 (C^{c, e}), 113.8 (C^{c'', e''}), 111.5 (C^{e'}), 70.8, 70.4, 70.2, 70.2, 69.9 (C¹⁹⁻²⁵), 69.6 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 32.0 (C¹⁴), 31.7 (C^{4'}), 29.8, 29.7, 29.7, 29.5, 29.4, 29.4, 29.3 (C^{2, 4-13, 2'}), 26.2 (C³), 25.8 (C^{3'}), 22.7, 22.7 (C^{15, 5'}), 14.2 (C¹⁶), 14.1 (C^{6'}). EA: C₅₀H₇₅O₉Na·0.5H₂O (Cal.) C: 70.47 %, H: 8.99 %, (Found) C: 70.74 %, H: 8.84 %.



Sodium 20-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxa-eicosanoate (**Na16.6/6**):

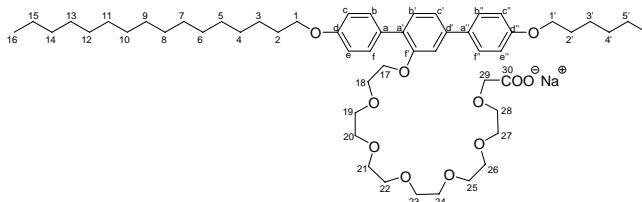
Reagents: **22/16/6/6** (1.05 g, 1.14 mmol)
1 M NaOH aq. (50 mL)

Purification: Column chromatography with
silica gel 60, eluent:
CHCl₃/MeOH = 10/1 (V/V)
and recrystallization from ethyl acetate

Yield: 0.640 g (60.3 %), colorless solid

Analytical data: C₅₄H₈₃O₁₁Na M_w = 931.22

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.51-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.32 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{b'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{c'}), 7.12 (d, ⁴J(H,H) = 1.6, 1 H, Ar-H^{e'}), 6.95-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.14 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 3.99-3.94 (m, 4 H, CH₂^{1,1'}), 3.88 (s, 2 H, CH₂²⁹), 3.76 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁸), 3.61-3.43 (m, 20 H, CH₂¹⁹⁻²⁸), 1.80-1.74 (m, 4 H, CH₂^{2,2'}), 1.48-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.91-0.84 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.4 (C³⁰), 158.7 (C^{d''}), 158.1 (C^d), 155.9 (C^{f'}), 140.8 (C^{d'}), 133.1 (C^a), 130.8 (C^{b'}), 130.5 (C^{b'', f''}), 130.3 (C^a), 129.0 (C^{a''}), 127.9 (C^{b, f}), 119.6 (C^{c'}), 114.8 (C^{c, e}), 113.9 (C^{c'', e''}), 111.6 (C^{e'}), 70.6, 70.3, 70.2, 70.1, 70.1, 69.9, 69.8, 69.7, 69.6 (C¹⁹⁻²⁹), 69.3 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 (C^{2, 4-13, 2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7, 22.6 (C^{15, 5'}), 14.1 (C¹⁶), 14.0 (C^{6'}). EA: C₅₄H₈₃O₁₁Na·H₂O (Cal.) C: 68.33 %, H: 9.03 %, (Found) C: 68.42 %, H: 8.85 %.



8.2.2 Carboxylic acids (**Hm/n**, **H*10/n**, **H6.16/n** and **H16.6/n**)

General procedure: The appropriate sodium carboxylate **Nam/n** (or **Na*m/n**, **Na6.16/n**, **Na16.6/n**) (1 mmol) was dissolved in the mixture of diethyl ether (50 mL) and aqueous HCl (10 %, 2 mL) with stirring. Stirring was continued ca. 4 h until the reaction mixture was clear and then the mixture was poured into a separatory funnel, the arogonic layer was separated and washed with distilled water until the water phase become neutral. The solvent was evaporated under vacuum and the crude product was purified by recrystallization from ethyl acetate/n-hexane.

8-(4,4''-Didecyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoic acid (**H10/2**):

Reagents: **Na10/2** (1.0 g, 1.4 mmol)

10 % HCl aq. (5 mL)

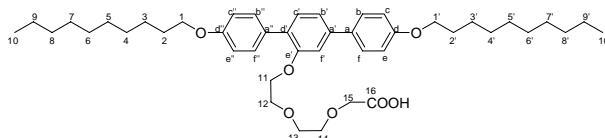
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.75 g (77.3 %), colorless solid

Analytical data: $C_{44}H_{64}O_7$ $M_w = 704.97$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) δ = 7.54-7.47 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-**H**^{c'}), 7.20 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-**H**^{b'}), 7.11 (d, $^4J(H,H) = 1.7$, 1 H, Ar-**H**^{f'}), 6.98-6.89 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.17 (t, $^3J(H,H) = 4.7$, 2 H, **CH**₂¹¹), 4.07 (s, 2 H, **CH**₂¹⁵), 4.00-3.96 (m, 4 H, **CH**₂^{1,1'}), 3.83 (t, $^3J(H,H) = 4.7$, 2 H, **CH**₂¹²), 3.66-3.61 (m, 4 H, **CH**₂^{13, 14}), 1.83-1.75 (m, 4 H, **CH**₂^{2,2'}), 1.50-1.27 (m, 24 H, **CH**₂^{3-9,3'-9'}), 0.89-0.86 (m, 6 H, **CH**₃^{10,10'}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.6 (**C**¹⁶), 158.9 (**C**^d), 158.2 (**C**^{d''}), 155.7 (**C**^{e'}), 141.1 (**C**^{a'}), 133.1 (**C**^{a''}), 130.9 (**C**^{c'}), 130.6 (**C**^{b, f}), 130.4 (**C**^{a''}), 129.3 (**C**^a), 128.0 (**C**^{b', f'}), 119.9 (**C**^{b'}), 114.8 (**C**^{c'', e''}), 113.9 (**C**^{c, e}), 111.7 (**C**^{f'}), 71.5, 70.4, 69.9 (**C**¹³⁻¹⁵), 68.7 (**C**¹²), 68.3 (**C**¹¹), 68.1, 68.1 (**C**^{1,1'}), 31.9 (**C**^{8,8'}), 29.6, 29.6, 29.6, 29.6, 29.4, 29.4, 29.3, 29.3, 29.3 (**C**^{2, 4-7, 2', 4'-7'}), 26.1, 26.1 (**C**^{3,3'}), 22.7 (**C**^{9,9'}), 14.1 (**C**^{10,10'}). EA: $C_{44}H_{64}O_7$ (Cal.) C: 74.96 %, H: 9.15 %, (Found) C: 75.04 %, H: 9.04 %.



11-(4,4''-Didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H10/3**):

Reagents: **Na10/3** (3.4 g, 4.4 mmol)

10 % HCl (10 mL)

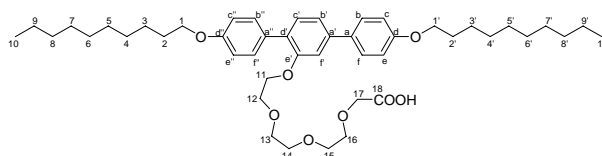
Diethyl ether (100 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 2.5 g (75.7 %), colorless solid

Analytical data: $C_{46}H_{68}O_8$ $M_w = 749.03$

1H NMR (Acetone- D_6 , J/Hz, 400 MHz) δ = 7.57-7.49 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.27 (d, $^3J(H,H) = 7.8$, 1 H, Ar-**H**^{c'}), 7.22 (d, $^4J(H,H) = 1.6$, 1 H, Ar-**H**^{f'}), 7.16 (dd, $^3J(H,H) = 7.8$, $^4J(H,H) = 1.6$, 1 H, Ar-**H**^{b'}), 6.95-6.87 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.17 (t, $^3J(H,H) = 4.7$, 2 H, **CH**₂¹¹), 4.01 (s, 2 H, **CH**₂¹⁷), 3.98-3.94 (m, 4 H, **CH**₂^{1,1'}), 3.73 (t, $^3J(H,H) = 4.7$, 2 H, **CH**₂¹²), 3.60-3.51 (m, 8 H, **CH**₂¹³⁻¹⁶), 1.75-1.68 (m, 4 H, **CH**₂^{2,2'}), 1.44-1.39 (m, 4 H, **CH**₂^{3,3'}), 1.28-1.21 (m, 24 H, **CH**₂^{4-9,4'-9'}), 0.82-0.78 (m, 6 H, **CH**₃^{10,10'}). EA: $C_{46}H_{68}NO_8$ (Cal.) C: 73.76 %, H: 9.15 %, (Found) C: 70.56 %, H: 8.99 %.



14-(4,4''-Didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid (**H10/4**):Reagents: **Na10/4** (3.0 g, 3.7 mmol)

10 % HCl (10 mL)

Diethyl ether (100 mL)

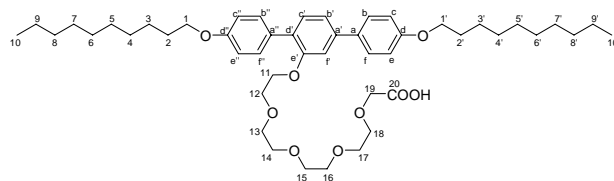
Purification: Recrystallization from ethyl

acetate/n-hexane

Yield: 2.3 g (78.8 %), colorless solid

Analytical data: $C_{48}H_{72}O_9$ $M_w = 793.08$

1H NMR (Acetone- D_6 , J /Hz, 400 MHz) $\delta = 10.8$ (bs, 1 H, OH), 7.64-7.57 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.35 (d, $^3J(H,H) = 8.0$, 1 H, Ar- $H^{c'}$), 7.29 (d, $^4J(H,H) = 1.8$, 1 H, Ar- $H^{f'}$), 7.23 (dd, $^3J(H,H) = 8.0$, $^4J(H,H) = 1.8$, 1 H, Ar- $H^{b'}$), 7.01-6.94 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.24 (t, $^3J(H,H) = 4.5$, 2 H, CH_2^{11}), 4.08 (s, 2 H, CH_2^{19}), 4.04-4.00 (m, 4 H, $CH_2^{1,1'}$), 3.81-3.78 (m, 2 H, CH_2^{12}), 3.67-3.56 (m, 12 H, CH_2^{13-18}), 1.81-1.75 (m, 4 H, $CH_2^{2,2'}$), 1.51-1.29 (m, 24 H, $CH_2^{3-9,3'-9'}$), 0.90-0.85 (m, 6 H, $CH_3^{10,10'}$). ^{13}C NMR (Acetone- D_6 , 100 MHz) $\delta = 171.5$ (C^{20}), 159.8 (C^d), 159.1 ($C^{d''}$), 157.1 ($C^{e'}$), 141.5 ($C^{a'}$), 133.8 ($C^{a''}$), 131.4 ($C^{c'}$), 131.3 ($C^{b,f}$), 129.6 (C^a), 128.7 ($C^{b'',f''}$), 119.7 ($C^{b'}$), 115.6 ($C^{c'',e''}$), 114.7 ($C^{c,e}$), 114.7 ($C^{d'}$), 111.9 ($C^{f'}$), 71.4, 71.3, 71.2, 71.1, 70.3 (C^{13-19}), 69.0 (C^{12}), 68.7 (C^{11}), 68.6, 68.5 ($C^{1,1'}$), 32.6 ($C^{8,8'}$), 29.8, 29.6, 29.4, 29.2, ($C^{2,4-7,2',4'-7'}$), 26.8 ($C^{3,3'}$), 23.3 ($C^{9,9'}$), 14.4 ($C^{10,10'}$). EA: $C_{48}H_{72}O_9 \cdot 0.5H_2O$ (Cal.) C: 71.87 %, H: 9.17 %, (Found) C: 71.88 %, H: 9.46 %.

11-(4,4''-Dibenzyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**HB/3**):Reagents: **NaB/3** (0.30 g, 0.44 mmol)

10 % HCl (3 mL)

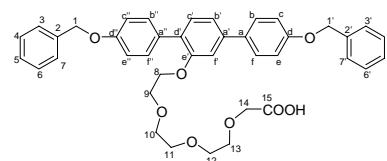
Diethyl ether (40 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.20 g (68.9 %), colorless solid

Analytical data: $C_{40}H_{40}O_8$ $M_w = 648.74$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.57$ -7.51 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.48-7.19 (m, 11 H, Ar- $H^{3-7,3'-7',c'}$), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.14 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 7.06-6.98 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 5.10, 5.09 (ds, 4 H, $CH_2^{1,1'}$), 4.16 (t, $^3J(H,H) = 4.5$, 2 H, CH_2^8), 4.07 (s, 2 H, CH_2^{14}), 3.78 (t, $^3J(H,H) = 4.5$, 2 H, CH_2^9), 3.68-3.58 (m, 8 H, CH_2^{10-13}). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 171.6$ (C^{15}), 158.4 (C^d), 157.7 ($C^{d''}$), 155.8 ($C^{e'}$), 140.8 ($C^{a'}$), 137.0, 136.9 ($C^{2,2'}$), 133.6 ($C^{a''}$), 130.8, 130.8, 130.5 ($C^{b,f,a''}$), 129.0 (C^a), 128.5, 128.5 ($C^{4,6,4',6'}$), 128.0 ($C^{b',f''}$), 127.9, 127.8 ($C^{5,5'}$), 127.4, 127.4 ($C^{3,7,3',7'}$), 119.7 ($C^{b'}$), 115.1 ($C^{c'',e''}$), 114.3 ($C^{c,e}$), 111.7 ($C^{f'}$), 71.5, 70.7, 70.6, 70.1, 69.8, 68.8, 68.5 (C^{8-14}), 70.1 ($C^{1,1'}$), EA: $C_{40}H_{40}O_8$ (Cal.) C: 74.05 %, H: 6.21 %, (Found) C: 73.83 %, H: 6.50 %.

8-(4,4''-Dibutyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoic acid (**H4/2**):Reagents: **Na4/2** (1.8 g, 3.2 mmol)

10 % HCl (30 mL)

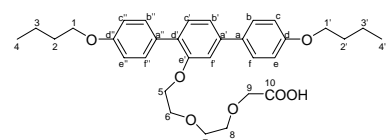
Diethyl ether (100 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 1.0 g (57.8 %), colorless solid

Analytical data: $C_{32}H_{40}O_7$ $M_w = 536.66$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.54$ -7.46 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.20 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.12 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.98-6.89 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.16 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^5), 4.08 (s, 2 H, CH_2^9), 4.03-3.97 (m, 4 H, $CH_2^{1,1'}$), 3.82 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^6), 3.66-3.60 (m, 4 H, $CH_2^{7,8}$), 1.82-1.74 (m, 4 H, $CH_2^{2,2'}$), 1.55-1.45 (m, 4 H, $CH_2^{3,3'}$), 1.00-0.96 (m, 6 H, $CH_3^{4,4'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 171.7$ (C^{10}),



158.8 (C^d), 158.1 ($C^{d''}$), 155.7 ($C^{e'}$), 141.0 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.3 ($C^{a''}$), 129.2 (C^a), 127.9 ($C^{b',f''}$), 119.8 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.7 ($C^{f'}$), 71.5, 70.4, 69.9 (C^{7-9}), 68.7 (C^6), 68.4 (C^5), 67.9, 67.8 ($C^{1,1'}$), 31.5, 31.4 ($C^{2,2'}$), 19.4, 19.4 ($C^{3,3'}$), 14.0, 14.0 ($C^{4,4'}$). EA: $C_{32}H_{40}O_7$ (Cal.) C: 71.62 %, H: 7.51 %, (Found) C: 71.99 %, H: 7.34 %.

11-(4,4''-Dibutyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H4/3**):

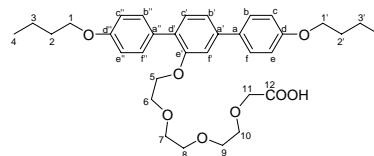
Reagents: **Na4/3** (1.7 g, 2.8 mmol)
10 % HCl (30 mL)
Diethyl ether (100 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 1.5 g (91.6 %), colorless solid

Analytical data: $C_{34}H_{44}O_8$ $M_w = 580.71$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.54$ -7.48 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.14 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.98-6.89 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 6.42 (bs, 1 H, OH), 4.16 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^5), 4.09 (s, 2 H, CH_2^{11}), 4.01-3.97 (m, 4 H, $CH_2^{1,1'}$), 3.78 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^6), 3.67-3.56 (m, 8 H, CH_2^{7-10}), 1.81-1.70 (m, 4 H, $CH_2^{2,2'}$), 1.56-1.44 (m, 4 H, $CH_2^{3,3'}$), 1.00-0.92 (m, 6 H, $CH_3^{4,4'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 172.4$ (C^{14}), 158.7 (C^d), 158.1 ($C^{d''}$), 155.8 ($C^{e'}$), 140.9 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.1 (C^a), 127.9 ($C^{b',f''}$), 119.7 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.7 ($C^{f'}$), 71.2, 70.6, 70.1, 69.7 (C^{7-11}), 68.7 (C^6), 68.5 (C^5), 67.8, 67.7 ($C^{1,1'}$), 31.4, 31.4 ($C^{2,2'}$), 19.3, 19.3 ($C^{3,3'}$), 13.9, 13.9 ($C^{4,4'}$). EA: $C_{34}H_{44}O_8 \cdot 0.5H_2O$ (Cal.) C: 69.25 %, H: 7.69 %, (Found) C: 69.32 %, H: 7.51 %.



14-(4,4''-Dibutyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid (**H4/4**):

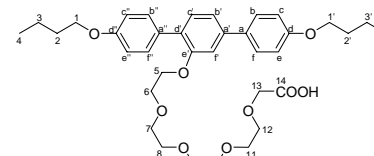
Reagents: **Na4/4** (1.56 g, 2.4 mmol)
10 % HCl (30 mL)
Diethyl ether (100 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 1.06 g (91.6 %), colorless solid

Analytical data: $C_{36}H_{48}O_9$ $M_w = 624.76$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.54$ -7.50 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.13 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.98-6.89 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 5.93 (bs, 1 H, OH), 4.17 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^5), 4.08 (s, 2 H, CH_2^{13}), 4.01-3.94 (m, 4 H, $CH_2^{1,1'}$), 3.78 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^6), 3.68-3.56 (m, 12 H, CH_2^{7-12}), 1.81-1.75 (m, 4 H, $CH_2^{2,2'}$), 1.53-1.43 (m, 4 H, $CH_2^{3,3'}$), 1.00-0.92 (m, 6 H, $CH_3^{4,4'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 171.8$ (C^{14}), 158.7 (C^d), 158.0 ($C^{d''}$), 155.8 ($C^{e'}$), 140.8 ($C^{a'}$), 133.1 ($C^{a''}$), 130.7 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.0 (C^a), 127.9 ($C^{b',f''}$), 119.6 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.6 ($C^{f'}$), 71.3, 70.9, 70.6, 70.5, 70.3, 70.2, 69.7 (C^{7-13}), 69.0 (C^6), 68.4 (C^5), 67.8, 67.7 ($C^{1,1'}$), 31.5, 31.4 ($C^{2,2'}$), 19.4, 19.3 ($C^{3,3'}$), 14.0, 13.9 ($C^{4,4'}$). EA: $C_{36}H_{48}O_9 \cdot 0.5H_2O$ (Cal.) C: 68.22 %, H: 7.79 %, (Found) C: 68.34 %, H: 7.63 %.



11-(4,4''-Dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H6/3**):

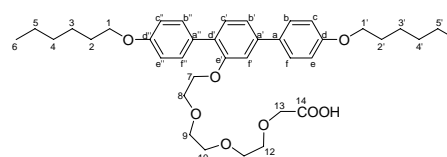
Reagents: **Na6/3** (2.9 g, 4.4 mmol)
10 % HCl (30 mL)
Diethyl ether (100 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 2.5 g (89.1 %), colorless solid

Analytical data: $C_{38}H_{52}O_8$ $M_w = 636.81$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.53$ -7.48 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$),



Ar-**H**^{c'}, 7.19 (dd, $^3J(\text{H},\text{H}) = 7.9$, $^4J(\text{H},\text{H}) = 1.7$, 1 H, Ar-**H**^{b'}), 7.13 (d, $^4J(\text{H},\text{H}) = 1.7$, 1 H, Ar-**H**^{f'}), 6.97-6.89 (m, 4 H, Ar-**H**^{c,e,c'',e''}), 4.16 (t, $^3J(\text{H},\text{H}) = 4.6$, 2 H, **CH**₂⁷), 4.08 (s, 2 H, **CH**₂¹³), 4.02-3.90 (m, 4 H, **CH**₂^{1,1'}), 3.78 (t, $^3J(\text{H},\text{H}) = 4.6$, 2 H, **CH**₂⁸), 3.69-3.59 (m, 8 H, **CH**₂⁹⁻¹²), 1.83-1.75 (m, 4 H, **CH**₂^{2,2'}), 1.50-1.41 (m, 4 H, **CH**₂^{3,3''}), 1.38-1.25 (m, 8 H, **CH**₂^{4,5,4',5'}), 0.92-0.84 (m, 6 H, **CH**₃^{6,6'}). ¹³C NMR (CDCl₃, 125 MHz) $\delta = 171.3$ (**C**¹⁶), 158.7 (**C**^d), 158.1 (**C**^{d''}), 155.8 (**C**^{e'}), 140.9 (**C**^{a'}), 133.1 (**C**^{a''}), 130.8 (**C**^{c'}), 130.5 (**C**^{b,f}), 130.4 (**C**^{a''}), 129.1 (**C**^a), 127.9 (**C**^{b',f''}), 119.7 (**C**^{b'}), 114.8 (**C**^{c'',e''}), 113.9 (**C**^{c,e}), 111.8 (**C**^{f'}), 71.6, 70.8, 70.7, 70.1, 69.8 (**C**⁹⁻¹³), 68.9 (**C**⁸), 68.6 (**C**⁷), 68.2, 68.1 (**C**^{1,1'}), 31.7, 31.7 (**C**^{4,4'}), 29.4 (**C**^{2,2'}), 25.9, 25.8 (**C**^{3,3'}), 22.7 (**C**^{5,5'}), 14.1 (**C**^{6,6'}). EA: C₃₈H₅₂O₈·0.7H₂O (Cal.) C: 70.27 %, H: 8.29 %, (Found) C: 70.10 %, H: 8.05 %.

14-(4,4''-Dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid (**H6/4**):

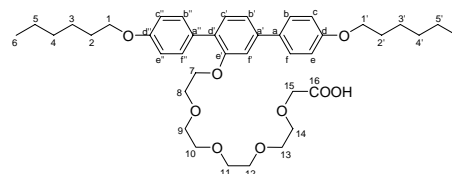
Reagents: **Na6/4** (3.0 g, 4.3 mmol)
10 % HCl (10 mL)
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 3.0 g (84.6 %), colorless liquid at r.t.

Analytical data: C₄₀H₅₆O₉ M_w = 680.97

¹H NMR (CDCl₃, J/Hz, 400 MHz) $\delta = 7.54$ -7.50 (m, 4 H, Ar-**H**^{b,f,b'',f''}), 7.33 (d, $^3J(\text{H},\text{H}) = 7.9$, 1 H, Ar-**H**^{c'}), 7.19 (dd, $^3J(\text{H},\text{H}) = 7.9$, $^4J(\text{H},\text{H}) = 1.7$, 1 H, Ar-**H**^{b'}), 7.13 (d, $^4J(\text{H},\text{H}) = 1.7$, 1 H, Ar-**H**^{f'}), 6.97-6.89 (m, 4 H, Ar-**H**^{c,e,c'',e''}), 4.17 (t, $^3J(\text{H},\text{H}) = 4.8$, 2 H, **CH**₂⁷), 4.08 (s, 2 H, **CH**₂¹⁵), 4.00-3.96 (m, 4 H, **CH**₂^{1,1'}), 3.80 (t, $^3J(\text{H},\text{H}) = 4.8$, 2 H, **CH**₂⁸), 3.70-3.57 (m, 12 H, **CH**₂⁹⁻¹⁴), 1.83-1.75 (m, 4 H, **CH**₂^{2,2'}), 1.50-1.41 (m, 4 H, **CH**₂^{3,3''}), 1.38-1.28 (m, 8 H, **CH**₂^{4,5,4',5'}), 0.95-0.87 (m, 6 H, **CH**₃^{6,6'}).



20-(4,4''-Dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoic acid (**H6/6**):

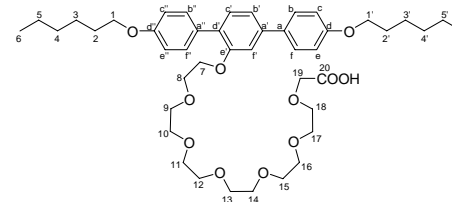
Reagents: **Na6/6** (0.65 g, 0.82 mmol)
10 % HCl (10 mL)
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.33 g (52.2 %), Colorless solid

Analytical data: C₄₄H₆₄O₁₁ M_w = 768.97

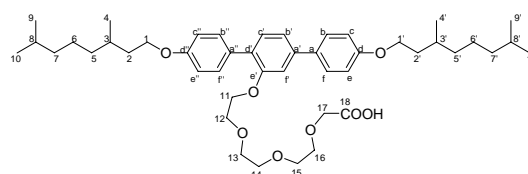
¹H NMR (CDCl₃, J/Hz, 400 MHz) $\delta = 7.53$ -7.49 (m, 4 H, Ar-**H**^{b,f,b'',f''}), 7.33 (d, $^3J(\text{H},\text{H}) = 7.9$, 1 H, Ar-**H**^{c'}), 7.18 (dd, $^3J(\text{H},\text{H}) = 7.9$, $^4J(\text{H},\text{H}) = 1.7$, 1 H, Ar-**H**^{b'}), 7.13 (d, $^4J(\text{H},\text{H}) = 1.7$, 1 H, Ar-**H**^{f'}), 6.97-6.89 (m, 4 H, Ar-**H**^{c,e,c'',e''}), 4.16 (t, $^3J(\text{H},\text{H}) = 4.8$, 2 H, **CH**₂⁷), 4.10 (s, 2 H, **CH**₂¹⁹), 4.00-3.95 (m, 4 H, **CH**₂^{1,1'}), 3.79 (t, $^3J(\text{H},\text{H}) = 4.8$, 2 H, **CH**₂⁸), 3.70-3.57 (m, 20 H, **CH**₂⁹⁻¹⁸), 1.83-1.75 (m, 4 H, **CH**₂^{2,2'}), 1.50-1.42 (m, 4 H, **CH**₂^{3,3''}), 1.38-1.31 (m, 8 H, **CH**₂^{4,5,4',5'}), 0.92-0.88 (m, 6 H, **CH**₃^{6,6'}). ¹³C NMR (CDCl₃, 100 MHz) $\delta = 171.1$ (**C**²⁰), 158.7 (**C**^d), 158.1 (**C**^{d''}), 155.9 (**C**^{e'}), 140.8 (**C**^{a'}), 133.2 (**C**^{a''}), 130.7 (**C**^{c'}), 130.5 (**C**^{b,f}), 130.4 (**C**^{a''}), 129.1 (**C**^a), 127.9 (**C**^{b',f''}), 119.6 (**C**^{b'}), 114.8 (**C**^{c'',e''}), 113.9 (**C**^{c,e}), 111.7 (**C**^{f'}), 71.3, 70.9, 70.6, 70.5, 70.4, 70.3, 70.3, 69.7 (**C**⁹⁻¹⁹), 69.2 (**C**⁸), 68.4 (**C**⁷), 68.2, 68.1 (**C**^{1,1'}), 31.7, 31.7 (**C**^{4,4'}), 29.4, 29.4 (**C**^{2,2'}), 25.9, 25.8 (**C**^{3,3'}), 22.7 (**C**^{5,5'}), 14.1 (**C**^{6,6'}). EA: C₄₄H₆₄O₁₁·H₂O (Cal.) C: 67.15 %, H: 8.45 %, (Found) C: 67.14 %, H: 8.14 %.



11-[4,4''-Bis(3,7-dimethyloctyloxy)-p-terphenyl-2'-yloxy]-3,6,9-trioxaundecanoic acid (**H10*/3**):

Reagents: **Na10*/3** (0.45 g, 0.58 mmol)
10 % HCl (5 mL)
Diethyl ether (20 mL)

Purification: Recrystallization from n-hexane



Yield: 0.25 g (63.6 %), colorless liquid (at r.t.)

Analytical data: $C_{46}H_{68}O_8$ $M_w = 749.03$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.54-7.49$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.20 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.15 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.98-6.90 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.17 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^{11}), 4.10 (s, 2 H, CH_2^{17}), 4.05-3.99 (m, 4 H, $CH_2^{1,1'}$), 3.79 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^{12}), 3.68-3.60 (m, 8 H, CH_2^{13-16}), 1.87-1.80 (m, 2 H, $CH^{8,8'}$), 1.72-1.64 (m, 2 H, $CH^{3,3'}$), 1.61-1.45 (m, 4 H, $CH_2^{2,2'}$), 1.39-1.07 (m, 12 H, $CH_2^{5-7,5'-7'}$), 0.97-0.92 (m, 6 H, $CH_3^{4,4'}$), 0.89-0.80 (m, 12 H, $CH_3^{9,10,9',10'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 172.3$ (C^{18}), 158.7 (C^d), 158.1 ($C^{d''}$), 155.8 ($C^{e'}$), 140.9 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.1 (C^a), 127.9 ($C^{b',f''}$), 119.7 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.8 ($C^{f'}$), 71.2, 70.6, 70.1, 69.7 (C^{13-17}), 68.7 (C^{12}), 68.5 (C^{11}), 66.5, 66.4 ($C^{1,1'}$), 39.3 ($C^{7,7'}$), 37.3 ($C^{5,5'}$), 36.3 ($C^{2,2'}$), 29.9 ($C^{3,3'}$), 28.0 ($C^{8,8'}$), 24.7 ($C^{5,5'}$), 22.7, 22.6 ($C^{9,10,9',10'}$), 19.7 ($C^{4,4'}$).

14-[4,4''-Bis(3,7-dimethyloctyloxy)-p-terphenyl-2'-yloxy]-3,6,9,12-tetraoxa-tetra-decanoic acid (**H10*/4**):

Reagents: **Na10*/4** (0.60 g, 0.74 mmol)

10 % HCl (5 mL)

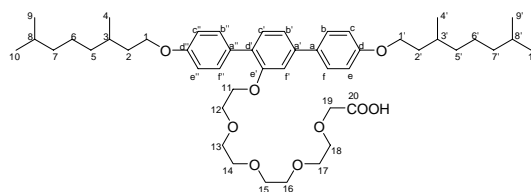
Diethyl ether (20 mL)

Purification: Recrystallization from n-hexane

Yield: 0.30 g (51.4 %), colorless liquid (at r.t.)

Analytical data: $C_{48}H_{72}O_9$ $M_w = 793.08$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.54-7.50$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.14 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.97-6.90 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.17 (t, $^3J(H,H) = 4.9$, 2 H, CH_2^{11}), 4.08 (s, 2 H, CH_2^{19}), 4.04-4.01 (m, 4 H, $CH_2^{1,1'}$), 3.80 (t, $^3J(H,H) = 4.9$, 2 H, CH_2^{12}), 3.67-3.56 (m, 12 H, CH_2^{13-18}), 1.90-1.79 (m, 2 H, $CH^{8,8'}$), 1.74-1.63 (m, 2 H, $CH^{3,3'}$), 1.62-1.47 (m, 4 H, $CH_2^{2,2'}$), 1.37-1.12 (m, 12 H, $CH_2^{5-7,5'-7'}$), 0.96-0.91 (m, 6 H, $CH_3^{4,4'}$), 0.89-0.82 (m, 12 H, $CH_3^{9,10,9',10'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 171.8$ (C^{20}), 158.7 (C^d), 158.0 ($C^{d''}$), 155.8 ($C^{e'}$), 140.8 ($C^{a'}$), 133.1 ($C^{a''}$), 130.7 ($C^{c'}$), 130.4 ($C^{b,f}$), 130.3 ($C^{a''}$), 129.0 (C^a), 127.9 ($C^{b',f''}$), 119.6 ($C^{b'}$), 114.7 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.6 ($C^{f'}$), 71.1, 70.9, 70.5, 70.4, 70.2, 69.7 (C^{13-19}), 69.0 (C^{12}), 68.3 (C^{11}), 66.5, 66.4 ($C^{1,1'}$), 39.3 ($C^{7,7'}$), 37.4, 37.3 ($C^{5,5'}$), 36.3 ($C^{2,2'}$), 30.0, 29.9 ($C^{3,3'}$), 28.0 ($C^{8,8'}$), 24.7 ($C^{5,5'}$), 22.8, 22.7 ($C^{9,10,9',10'}$), 19.7 ($C^{4,4'}$).



11-(4,4''-Dioctyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H8/3**):

Reagents: **Na8/3** (0.45 g, 0.63 mmol)

10 % HCl (3 mL)

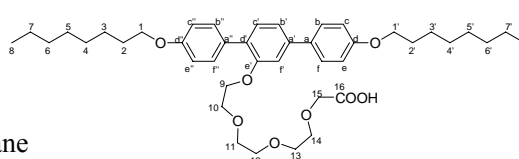
Diethyl ether (20 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.30 g (58.8 %), colorless solid

Analytical data: $C_{42}H_{60}O_8$ $M_w = 692.92$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.54-7.49$ (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.8$, 1 H, Ar- $H^{c'}$), 7.13 (dd, $^3J(H,H) = 7.8$, $^4J(H,H) = 1.5$, 1 H, Ar- $H^{b'}$), 7.14 (d, $^4J(H,H) = 1.5$, 1 H, Ar- $H^{f'}$), 6.97-6.90 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 6.10 (bs, 1 H, OH), 4.16 (t, $^3J(H,H) = 4.9$, 2 H, CH_2^9), 4.09 (s, 2 H, CH_2^{15}), 4.00-3.96 (m, 4 H, $CH_2^{1,1'}$), 3.77-3.70 (t, $^3J(H,H) = 4.9$, 2 H, CH_2^{10}), 3.67-3.60 (m, 8 H, CH_2^{11-14}), 1.83-1.75 (m, 4 H, $CH_2^{2,2'}$), 1.50-1.40 (m, 4 H, $CH_2^{3,3'}$), 1.39-1.20 (m, 16 H, $CH_2^{4-7,4'-7'}$), 0.90-0.85 (m, 6 H, $CH_3^{8,8'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 172.2$ (C^{16}), 158.7 (C^d), 158.0 ($C^{d''}$), 155.7 ($C^{e'}$), 140.8 ($C^{a'}$), 133.0 ($C^{a''}$), 130.7 ($C^{c'}$), 130.4 ($C^{b,f}$), 130.3 ($C^{a''}$), 129.1 (C^a), 127.9 ($C^{b',f''}$), 119.6 ($C^{b'}$), 114.7 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.7 ($C^{f'}$), 71.3, 70.6, 70.1, 69.7 (C^{11-15}), 68.7 (C^{10}), 68.5 (C^9), 68.1, 68.0 ($C^{1,1'}$),



31.9 ($C^{6,6'}$), 29.6, 29.6, 29.5, 29.5, 29.4, 29.3 ($C^{2,4,5,2',4',5'}$), 26.1, 26.1 ($C^{3,3'}$), 22.7 ($C^{7,7'}$), 14.2 ($C^{8,8'}$).
EA: $C_{42}H_{60}O_8$ (Cal.) C: 72.80 %, H: 8.73 %, (Found) C: 72.58 %, H: 8.65 %.

14-(4,4''-Dioctyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxa-tetradecanoic acid (**H8/4**):

Reagents: **Na8/4** (0.50 g, 0.66 mmol)

10 % HCl (5 mL)

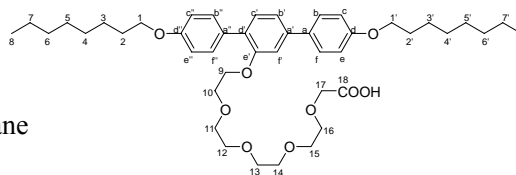
Diethyl ether (20 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.30 g (61.8 %), colorless solid

Analytical data: $C_{44}H_{64}O_9$ $M_w = 736.97$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) δ = 7.55-7.50 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.14 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.98-6.89 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 5.40 (bs, 1 H, OH), 4.17 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^9), 4.08 (s, 2 H, CH_2^{17}), 4.02-3.96 (m, 4 H, $CH_2^{1,1'}$), 3.79 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^{10}), 3.67-3.55 (m, 12 H, CH_2^{11-16}), 1.83-1.75 (m, 4 H, $CH_2^{2,2'}$), 1.50-1.40 (m, 4 H, $CH_2^{3,3'}$), 1.39-1.20 (m, 16 H, $CH_2^{4-7,4'-7'}$), 0.90-0.84 (m, 6 H, $CH_3^{8,8'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.8 (C^{18}), 158.7 (C^d), 158.1 ($C^{d''}$), 155.8 ($C^{e'}$), 140.9 ($C^{a'}$), 133.1 ($C^{a''}$), 130.7 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.1 (C^a), 127.9 ($C^{b',f''}$), 119.5 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.6 ($C^{f'}$), 71.1, 70.9, 70.5, 70.4, 70.3, 70.2, 69.7 (C^{11-17}), 69.0 (C^{10}), 68.4 (C^9), 68.1, 68.0 ($C^{1,1'}$), 31.8 ($C^{6,6'}$), 29.4, 29.4, 29.3, 29.3, 29.2 ($C^{2,4,5,2',4',5'}$), 26.1, 26.1 ($C^{3,3'}$), 22.7 ($C^{7,7'}$), 14.1 ($C^{8,8'}$). EA: $C_{44}H_{64}O_9 \cdot 0.5H_2O$ (Cal.) C: 70.84 %, H: 8.78 %, (Found) C: 70.79 %, H: 8.49 %.



11-(4,4''-Dihexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H16/3**):

Reagents: **Na16/3** (1.1 g, 1.2 mmol)

10 % HCl (5 mL)

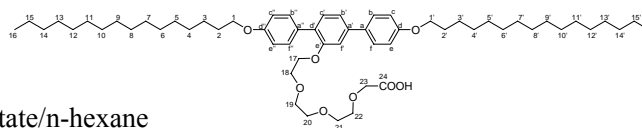
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.75 g (69.8 %), colorless solid

Analytical data: $C_{58}H_{92}O_8$ $M_w = 917.35$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) δ = 7.53-7.49 (m, 4 H, Ar- $H^{b,f,b'',f''}$), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar- $H^{c'}$), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{b'}$), 7.13 (d, $^4J(H,H) = 1.7$, 1 H, Ar- $H^{f'}$), 6.96-6.88 (m, 4 H, Ar- $H^{c,e,c'',e''}$), 4.16 (t, 2 H, $^3J(H,H) = 5.0$, CH_2^{17}), 4.08 (s, 2 H, CH_2^{23}), 3.99-3.95 (m, 4 H, $CH_2^{1,1'}$), 3.78 (t, $^3J(H,H) = 5.0$, 2 H, CH_2^{18}), 3.68-3.59 (m, 8 H, CH_2^{19-22}), 1.80-1.76 (m, 4 H, $CH_2^{2,2'}$), 1.47-1.42 (m, 4 H, $CH_2^{3,3'}$), 1.41-1.20 (m, 48 H, $CH_2^{4-15,4'-15'}$), 0.88-0.84 (m, 6 H, $CH_3^{16,16'}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 171.1 (C^{24}), 158.8 (C^d), 158.1 ($C^{d''}$), 155.8 ($C^{e'}$), 140.9 ($C^{a'}$), 133.1 ($C^{a''}$), 130.8 ($C^{c'}$), 130.5 ($C^{b,f}$), 130.4 ($C^{a''}$), 129.1 (C^a), 127.9 ($C^{b',f''}$), 119.7 ($C^{b'}$), 114.8 ($C^{c'',e''}$), 113.9 ($C^{c,e}$), 111.8 ($C^{f'}$), 71.6, 70.8, 70.7, 70.0, 69.8 (C^{19-23}), 69.8 (C^{18}), 68.6 (C^{17}), 68.2, 68.1 ($C^{1,1'}$), 32.0 ($C^{14,14'}$), 29.8, 29.7, 29.7, 29.7, 29.5, 29.5, 29.4, 29.4 ($C^{2,4-13,2',4'-13'}$), 26.2, 26.2 ($C^{3,3'}$), 22.8 ($C^{15,15'}$), 14.2 ($C^{16,16'}$). EA: $C_{58}H_{92}O_8 \cdot 0.3H_2O$ (Cal.) C: 75.49 %, H: 10.16 %, (Found) C: 75.47 %, H: 10.19 %.



14-(4,4''-Dihexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid (**H16/4**):

Reagents: **Na16/4** (1.2 g, 1.2 mmol)

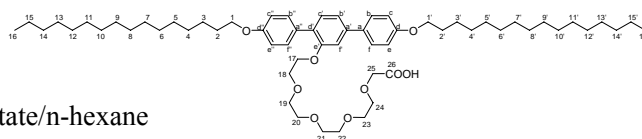
10 % HCl (5 mL)

Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 1.11 g (94.6 %), colorless solid

Analytical data: $C_{60}H_{96}O_9$ $M_w = 961.40$



^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.53-7.49 (m, 4 H, $\text{Ar-H}^{b,f,b'',f''}$), 7.33 (d, $^3J(\text{H,H}) = 7.9$, 1 H, $\text{Ar-H}^{c'}$), 7.18 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, $\text{Ar-H}^{b'}$), 7.13 (d, $^4J(\text{H,H}) = 1.7$, 1 H, $\text{Ar-H}^{f'}$), 6.96-6.89 (m, 4 H, $\text{Ar-H}^{c,e,c'',e''}$), 4.17 (t, 2 H, $^3J(\text{H,H}) = 5.0$, CH_2^{17}), 4.08 (s, 2 H, CH_2^{25}), 4.00-3.96 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.80 (t, $^3J(\text{H,H}) = 5.0$, 2 H, CH_2^{18}), 3.70-3.57 (m, 12 H, CH_2^{19-24}), 1.81-1.76 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.48-1.41 (m, 4 H, $\text{CH}_2^{3,3'}$), 1.40-1.21 (m, 48 H, $\text{CH}_2^{4-15,4'-15'}$), 0.88-0.84 (m, 6 H, $\text{CH}_3^{16,16'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.1 (C^{26}), 158.8 (C^d), 158.2 ($\text{C}^{d''}$), 155.9 ($\text{C}^{e'}$), 140.9 ($\text{C}^{a'}$), 133.2 ($\text{C}^{a''}$), 130.8 ($\text{C}^{c'}$), 130.6 ($\text{C}^{b,f}$), 130.5 ($\text{C}^{a''}$), 129.1 (C^a), 128.0 ($\text{C}^{b',f''}$), 119.7 ($\text{C}^{b'}$), 114.8 ($\text{C}^{c'',e''}$), 114.0 ($\text{C}^{c,e}$), 111.7 (C^f), 71.6, 71.0, 70.7, 70.6, 70.3, 70.2, 69.7 (C^{19-25}), 69.2 (C^{18}), 68.4 (C^{17}), 68.2, 68.1 ($\text{C}^{1,1'}$), 32.0 ($\text{C}^{14,14'}$), 29.7, 29.7, 29.7, 29.5, 29.5, 29.4, 29.4 ($\text{C}^{2,4-13,2',4'-13'}$), 26.2, 26.1 ($\text{C}^{3,3'}$), 22.7 ($\text{C}^{15,15'}$), 14.1 ($\text{C}^{16,16'}$). EA: $\text{C}_{60}\text{H}_{96}\text{O}_9 \cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 74.26 %, H: 10.07 %, (Found) C: 74.31 %, H: 9.75 %.

8-(4,4''-Didecyloxy-p-terphenyl-3-yloxy)-3,6-dioxaoctanoic acid (**H*10/2**):

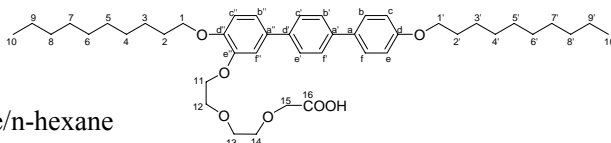
Reagents: **Na*10/2** (0.45 g, 0.63 mmol)
10 % HCl (5 mL)
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 55 m g (12.5 %), colorless solid

Analytical data: $\text{C}_{44}\text{H}_{64}\text{O}_7$ $M_w = 704.97$

^1H NMR (CDCl_3 , J/Hz , 200 MHz) δ = 7.58-7.50 (m, 6 H, $\text{Ar-H}^{b,f,b',f',c',e'}$), 7.22-7.12 (m, 2 H, $\text{Ar-H}^{b'',f''}$), 6.99-6.91 (m, 3 H, $\text{Ar-H}^{c,e,c''}$), 4.27-4.20 (m, 2 H, CH_2^{11}), 4.14 (s, 2 H, CH_2^{15}), 4.14-3.74 (m, 10 H, $\text{CH}_2^{1,1',12-14}$), 1.87-1.72 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.52-1.18 (m, 28 H, $\text{CH}_2^{3-9,3'-9'}$), 0.92-0.84 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 50 MHz) δ = 172.4 (C^{16}), 158.8 (C^d), 148.6, 148.5 ($\text{C}^{d'',e''}$), 139.3, 139.0 ($\text{C}^{a',d'}$), 133.9, 133.0 ($\text{C}^{a,a''}$), 127.9 ($\text{C}^{b,f}$), 127.0, 126.9 ($\text{C}^{b',c',e',f'}$), 120.2 ($\text{C}^{b''}$), 114.8 ($\text{C}^{c,e}$), 113.9 ($\text{C}^{c''}$), 113.4 ($\text{C}^{f''}$), 71.2, 70.6, 69.9 (C^{13-15}), 69.3 (C^{12}), 68.9 (C^1), 68.8 (C^{11}), 68.1 ($\text{C}^{1'}$), 31.9 ($\text{C}^{8,8'}$), 29.5, 29.4, 29.3, 29.2 ($\text{C}^{2,4-7,2',4'-7'}$), 26.0, 26.0 ($\text{C}^{3,3'}$), 22.6 ($\text{C}^{9,9'}$), 14.1 ($\text{C}^{10,10'}$). EA: $\text{C}_{44}\text{H}_{64}\text{O}_7$ (Cal.) C: 74.96 %, H: 9.15 %, (Found) C: 74.96 %, H: 8.98 %.



11-(4,4''-Didecyloxy-p-terphenyl-3-yloxy)-3,6,9-trioxaundecanoic acid (**H*10/3**):

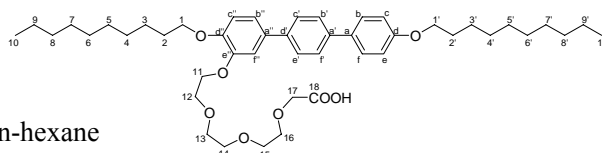
Reagents: **Na*10/3** (155 mg, 0.20 mmol)
10 % HCl (5 mL)
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 59 mg (39.2 %), colorless solid

Analytical data: $\text{C}_{46}\text{H}_{68}\text{O}_8$ $M_w = 749.03$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.60 (s, 4 H, $\text{Ar-H}^{b',f',c',e'}$), 7.55-7.52 (m, 2 H, $\text{Ar-H}^{b,f}$), 7.20-7.15 (m, 2 H, $\text{Ar-H}^{b'',f''}$), 6.97-6.92 (m, 3 H, $\text{Ar-H}^{c,e,c''}$), 4.25 (t, $^3J(\text{H,H}) = 4.7$, 2 H, CH_2^{11}), 4.11 (s, 2 H, CH_2^{17}), 4.04-3.96 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.89 (t, $^3J(\text{H,H}) = 4.7$, 2 H, CH_2^{12}), 3.80-3.63 (m, 8 H, CH_2^{13-16}), 1.90-1.75 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.52-1.41 (m, 4 H, $\text{CH}_2^{3,3'}$), 1.39-1.18 (m, 24 H, $\text{CH}_2^{4-9,4'-9'}$), 0.90-0.84 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.1 (C^{18}), 158.6 (C^d), 148.8, 148.7 ($\text{C}^{d'',e''}$), 139.2, 139.0 ($\text{C}^{a',d'}$), 133.7, 132.9 ($\text{C}^{a,a''}$), 127.8 ($\text{C}^{b,f}$), 127.0, 126.9 ($\text{C}^{b',c',e',f'}$), 120.1 ($\text{C}^{b''}$), 114.8 ($\text{C}^{c,e}$), 113.9 ($\text{C}^{c''}$), 110.0 ($\text{C}^{f''}$), 71.6, 70.9, 70.7, 70.2, 70.0 (C^{13-17}), 69.4 (C^{12}), 69.3 (C^1), 69.0 (C^{11}), 68.2 ($\text{C}^{1'}$), 32.0 ($\text{C}^{8,8'}$), 29.7, 29.7, 29.6, 29.5, 29.5, 29.4 ($\text{C}^{2,4-7,2',4'-7'}$), 26.2, 26.1 ($\text{C}^{3,3'}$), 22.8 ($\text{C}^{9,9'}$), 14.2 ($\text{C}^{10,10'}$). EA: $\text{C}_{46}\text{H}_{68}\text{O}_8 \cdot 0.4\text{H}_2\text{O}$ (Cal.) C: 73.06 %, H: 9.17 %, (Found) C: 73.06 %, H: 8.93 %.



14-(4,4''-Didecyloxy-p-terphenyl-3-yloxy)-3,6,9,12-tetraoxatetradecanoic acid (**H*10/4**):Reagents: **Na*10/4** (165 mg, 0.20 mmol)

10 % HCl (5 mL)

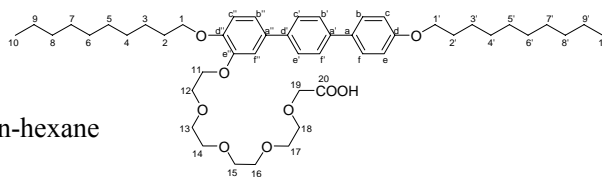
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 82 mg (50.9 %), colorless solid

Analytical data: $C_{48}H_{72}O_9$ $M_w = 793.08$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.57$ (s, 4 H, Ar-**H**^{b', f', c', e'}), 7.55-7.52 (m, 2 H, Ar-**H**^{b, f}), 7.20-7.15 (m, 2 H, Ar-**H**^{b'', f''}), 6.97-6.92 (m, 3 H, Ar-**H**^{c, e, c''}), 4.24 (t, $^3J(H,H) = 4.7$, 2 H, **CH**₂¹¹), 4.10 (s, 2 H, **CH**₂¹⁷), 4.04-3.96 (m, 4 H, **CH**₂^{1, 1'}), 3.89 (t, $^3J(H,H) = 4.7$, 2 H, **CH**₂¹²), 3.80-3.63 (m, 12 H, **CH**₂¹³⁻¹⁸), 1.90-1.75 (m, 4 H, **CH**₂^{2, 2'}), 1.52-1.41 (m, 4 H, **CH**₂^{3, 3'}), 1.39-1.18 (m, 24 H, **CH**₂^{4-9, 4'-9'}), 0.90-0.84 (m, 6 H, **CH**₃^{10, 10'}). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 171.3$ (**C**¹⁸), 158.6 (**C**^d), 148.9, 148.7 (**C**^{d'', e''}), 139.2, 139.0 (**C**^{a', d'}), 133.7, 132.9 (**C**^{a, a''}), 127.8 (**C**^{b, f}), 126.9, 126.8 (**C**^{b', c', e', f'}), 120.1 (**C**^{b''}), 114.8 (**C**^{c, e}), 114.0 (**C**^{c'', f''}), 71.6, 71.0, 70.7, 70.6, 70.4, 70.2, 69.9 (**C**¹³⁻¹⁹), 69.3 (**C**¹²), 69.3 (**C**¹), 69.1 (**C**¹¹), 68.1 (**C**^{1'}), 32.0 (**C**^{8, 8'}), 29.7, 29.7, 29.6, 29.5, 29.5, 29.4 (**C**^{2, 4-7, 2', 4'-7'}), 26.2, 26.1 (**C**^{3, 3'}), 22.8 (**C**^{9, 9'}), 14.2 (**C**^{10, 10'}). EA: $C_{48}H_{72}O_9 \cdot 0.5H_2O$ (Cal.) C: 71.87 %, H: 9.17 %, (Found) C: 71.98 %, H: 9.12 %.

11-(4-Hexoxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H6.16/3**):Reagents: **Na6.16/3** (250 mg, 0.31 mmol)

10 % HCl (5 mL)

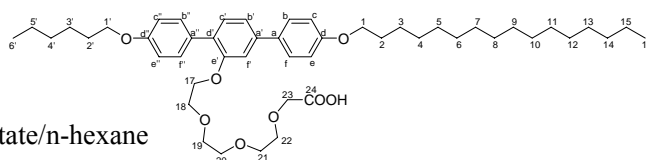
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 89 mg (36.6 %), colorless solid

Analytical data: $C_{48}H_{72}O_8$ $M_w = 777.08$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.54$ -7.49 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-**H**^{c'}), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-**H**^{b'}), 7.14 (d, $^4J(H,H) = 1.7$, 1 H, Ar-**H**^{f'}), 6.97-6.90 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.17 (t, $^3J(H,H) = 4.8$, 2 H, **CH**₂¹⁷), 4.10 (s, 2 H, **CH**₂²³), 4.00-3.96 (m, 4 H, **CH**₂^{1, 1'}), 3.79 (t, $^3J(H,H) = 4.8$, 2 H, **CH**₂¹⁸), 3.69-3.60 (m, 8 H, **CH**₂¹⁹⁻²²), 1.83-1.76 (m, 4 H, **CH**₂^{2, 2'}), 1.49-1.41 (m, 4 H, **CH**₂^{3, 3'}), 1.39-1.22 (m, 28 H, **CH**₂^{4-15, 4'-15'}), 0.93-0.85 (m, 6 H, **CH**₃^{16, 6'}). ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 172.2$ (**C**²⁴), 158.8 (**C**^d), 158.1 (**C**^{d''}), 155.9 (**C**^{e'}), 140.9 (**C**^{a'}), 133.1 (**C**^{a''}), 130.8 (**C**^{c'}), 130.5 (**C**^{b, f}), 130.4 (**C**^{a''}), 129.1 (**C**^a), 127.9 (**C**^{b', f'}), 119.7 (**C**^{b'}), 114.8 (**C**^{c'', e''}), 113.9 (**C**^{c, e}), 111.7 (**C**^{f'}), 71.4, 70.7, 70.7, 70.1, 69.8 (**C**¹⁹⁻²³), 68.7 (**C**¹⁸), 68.5 (**C**¹⁷), 68.1 (**C**^{1, 1'}), 31.9 (**C**¹⁴), 31.6 (**C**^{4'}), 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3 (**C**^{2, 4-13, 2'}), 26.1 (**C**³), 25.8 (**C**^{3'}), 22.7 (**C**¹⁵), 22.6 (**C**^{5'}), 14.1 (**C**¹⁶), 14.0 (**C**^{6'}). EA: $C_{48}H_{72}O_8$ (Cal.) C: 74.19 %, H: 9.34 %, (Found) C: 74.10 %, H: 9.31 %.

14-(4-Hexoxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoic acid (**H6.16/4**):Reagents: **Na6.16/4** (0.45 g, 0.53 mmol)

10 % HCl (5 mL)

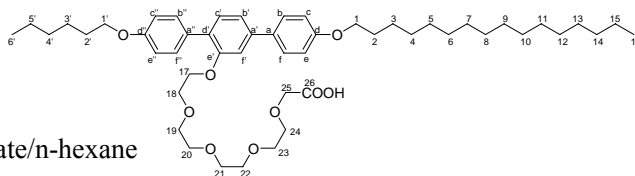
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.25 g (57.0 %), colorless solid

Analytical data: $C_{50}H_{76}O_9$ $M_w = 821.13$

1H NMR ($CDCl_3$, J /Hz, 400 MHz) $\delta = 7.53$ -7.49 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-**H**^{c'}), 7.19 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-**H**^{b'}), 7.13 (d, $^4J(H,H) = 1.7$, 1 H, Ar-**H**^{f'}), 6.97-6.89 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.17 (t, $^3J(H,H) = 5.0$, 2 H, **CH**₂¹⁷), 4.09 (s, 2 H, **CH**₂²⁵), 4.00-3.96 (m, 4 H, **CH**₂^{1, 1'}), 3.80 (t, $^3J(H,H) = 5.0$, 2 H, **CH**₂¹⁸), 3.69-3.56 (m, 12 H, **CH**₂¹⁹⁻²⁴), 1.83-1.75 (m, 4 H, **CH**₂^{2, 2'}).



^{2'}, 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.22 (m, 28 H, CH₂^{4-15,4',5'}), 0.93-0.85 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 172.0 (C²⁶), 158.8 (C^d), 158.1 (C^{d''}), 155.9 (C^{e'}), 140.9 (C^{a'}), 133.1 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.1 (C^a), 127.9 (C^{b'',f''}), 119.6 (C^{b'}), 114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^{f'}), 71.3, 70.9, 70.6, 70.5, 70.3, 70.2, 69.7 (C¹⁹⁻²⁵), 68.9 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3 (C^{2,4-13,2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7 (C¹⁵), 22.6 (C^{5'}), 14.1 (C¹⁶), 14.0 (C^{6'}). EA: C₅₀H₇₆O₉ (Cal.) C: 73.13 %, H: 9.33 %, (Found) C: 73.09 %, H: 9.25 %.

20-(4-Hexoxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoic acid (**H6.16/6**):

Reagents: **Na6.16/6** (0.55 g, 0.59 mmol)

10 % HCl (5 mL)

Diethyl ether (50 mL)

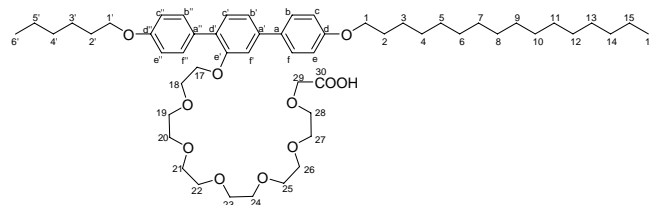
Purification: Recrystallization from ethyl

acetate/n-hexane

Yield: 0.30 g (55.9 %), colorless solid

Analytical data: C₅₄H₈₄O₁₁ M_w = 909.24

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.54-7.49 (m, 4 H, Ar-H^{b,f,b'',f''}), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.96-6.89 (m, 4 H, Ar-H^{c,e,c'',e''}), 6.10 (bs, 1 H, OH), 4.16 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 4.11 (s, 2 H, CH₂²⁹), 4.00-3.95 (m, 4 H, CH₂^{1,1'}), 3.79 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁸), 3.70-3.57 (m, 20 H, CH₂¹⁹⁻²⁸), 1.83-1.75 (m, 4 H, CH₂^{2,2'}), 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.22 (m, 28 H, CH₂^{4-15,4',5'}), 0.92-0.85 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.7 (C³⁰), 158.7 (C^d), 158.1 (C^{d''}), 155.9 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b,f}), 130.3 (C^{a''}), 129.1 (C^a), 127.9 (C^{b'',f''}), 119.5 (C^{b'}), 114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^{f'}), 71.1, 70.8, 70.6, 70.5, 70.4, 70.3, 69.7 (C¹⁹⁻²⁹), 69.0 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3 (C^{2,4-13,2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7 (C¹⁵), 22.6 (C^{5'}), 14.1, 14.1 (C^{16,6'}). EA: C₅₄H₈₄O₁₁·H₂O (Cal.) C: 69.95 %, H: 9.35 %, (Found) C: 70.25 %, H: 9.28 %.



11-(4-Hexadecyloxy-4''-hexoxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoic acid (**H16.6/3**):

Reagents: **Na16.6/3** (0.50 g, 0.63 mmol)

10 % HCl (5 mL)

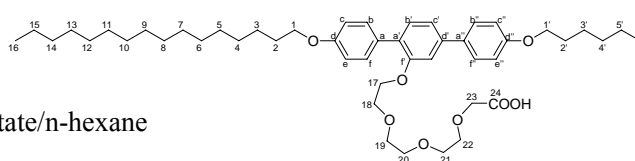
Diethyl ether (50 mL)

Purification: Recrystallization from ethyl acetate/n-hexane

Yield: 0.29 g (59.6 %), colorless solid

Analytical data: C₄₈H₇₂O₈ M_w = 777.08

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.54-7.50 (m, 4 H, Ar-H^{b,f,b'',f''}), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{b'}), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{c'}), 7.14 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.97-6.90 (m, 4 H, Ar-H^{c,e,c'',e''}), 6.0 (bs, 1 H, OH), 4.16 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 4.10 (s, 2 H, CH₂²³), 4.01-3.96 (m, 4 H, CH₂^{1,1'}), 3.79 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁸), 3.68-3.60 (m, 8 H, CH₂¹⁹⁻²²), 1.82-1.76 (m, 4 H, CH₂^{2,2'}), 1.49-1.42 (m, 4 H, CH₂^{3,3'}), 1.40-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.96-0.85 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.9 (C²⁶), 158.8 (C^{d''}), 158.1 (C^d), 155.9 (C^{f'}), 140.9 (C^{d'}), 133.1 (C^a), 130.8 (C^{b'}), 130.5 (C^{b'',f''}), 130.4 (C^a), 129.1 (C^{a''}), 127.9 (C^{b,f}), 119.7 (C^{c'}), 114.8 (C^{c,e}), 113.9 (C^{c'',e''}), 111.8 (C^{e'}), 71.5, 70.7, 70.7, 70.1, 69.8 (C¹⁹⁻²³), 68.8 (C¹⁸), 68.5 (C¹⁷), 68.2, 68.1 (C^{1,1'}), 32.0 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3 (C^{2,4-13,2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7, 22.6 (C^{15,5'}), 14.1, 14.1 (C^{16,6'}). EA: C₄₈H₇₂O₈·0.5H₂O (Cal.) C: 73.34 %, H: 9.36 %, (Found) C: 73.64 %, H: 9.31 %.



state/n-hexane

Yield: 0.33 g (67.8 %), colorless solid

¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 7.54-7.45 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.33 (d, ³*J*(H,H) = 7.9, 1 H, Ar-**H**^{b'}), 7.19 (dd, ³*J*(H,H) = 7.9, ⁴*J*(H,H) = 1.7, 1 H, Ar-**H**^c), 7.14 (d, ⁴*J*(H,H) = 1.7, 1 H, Ar-**H**^{c'}), 6.99-6.85 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 6.00 (bs, 1 H, OH), 4.17 (t, ³*J*(H,H) = 5.0, 2 H, CH₂¹⁷), 4.08 (s, 2 H, CH₂²⁵), 4.00-3.96 (m, 4 H, CH₂^{1,1'}), 3.80 (t, ³*J*(H,H) = 5.0, 2 H, CH₂¹⁸), 3.68-3.57 (m, 12 H, CH₂¹⁹⁻²⁴), 1.83-1.76 (m, 4 H, CH₂^{2, 2'}), 1.49-1.42 (m, 4 H, CH₂^{3, 3'}), 1.40-1.20 (m, 28 H, CH₂^{4-15, 4', 5'}), 0.96-0.85 (m, 6 H, CH₃^{16, 6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.8 (C²⁶), 158.8 (C^{d''}), 158.1 (C^d), 155.9 (C^f), 140.9 (C^{d'}), 133.1 (C^a), 130.7 (C^{b'}), 130.5 (C^{b'', f''}), 130.4 (C^a), 129.1 (C^{a''}), 127.9 (C^{b, f}), 119.6 (C^{c'}), 114.8 (C^{c, e}), 113.9 (C^{c'', e''}), 111.6 (C^{c'}), 71.2, 70.9, 70.6, 70.5, 70.3, 70.2, 69.7 (C¹⁹⁻²⁵), 69.0 (C¹⁸), 68.4 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 (C^{2, 4-13, 2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7, 22.6 (C^{15, 5'}), 14.1, 14.1 (C^{16, 6'}). EA: C₅₀H₇₆O₉·H₂O (Cal.) C: 71.56 %, H: 9.37 %, (Found) C: 71.81 %, H: 9.22 %.

Chemical structure of compound 1 is shown. It features a long-chain molecule with a hexamethylene chain (16 carbons) attached to a triphenyl ether core. The core consists of three phenyl rings linked by ether groups. The side chain is a polyether chain with a terminal carboxylic acid group (COOH) and a terminal hydroxyl group (OH). The structure is labeled with atom numbers 1 through 30.

Yield: 0.36 g (73.7 %), colorless solid

¹H NMR (CDCl₃, *J*/Hz, 500 MHz) δ = 7.53-7.50 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.33 (d, ³*J*(H,H) = 7.9, 1 H, Ar-**H**^{b'}), 7.18 (dd, ³*J*(H,H) = 7.9, ⁴*J*(H,H) = 1.5, 1 H, Ar-**H**^{c'}), 7.13 (d, ⁴*J*(H,H) = 1.5, 1 H, Ar-**H**^c), 6.96-6.89 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.16 (t, ³*J*(H,H) = 5.2, 2 H, CH₂¹⁷), 4.10 (s, 2 H, CH₂²³), 4.00-3.96 (m, 4 H, CH₂^{1, 1'}), 3.79 (t, ³*J*(H,H) = 5.2, 2 H, CH₂¹⁸), 3.69-3.57 (m, 20 H, CH₂¹⁹⁻²⁸), 1.82-1.75 (m, 4 H, CH₂^{2, 2'}), 1.49-1.42 (m, 4 H, CH₂^{3, 3'}), 1.40-1.20 (m, 28 H, CH₂^{4-15, 4', 5'}), 0.92-0.85 (m, 6 H, CH₃^{16, 6'}). ¹³C NMR (CDCl₃, 125 MHz) δ = 171.9 (C³⁰), 159.1 (C^{d''}), 158.4 (C^d), 156.2 (C^f), 141.1 (C^{d'}), 133.5 (C^a), 131.1 (C^{b'}), 130.8 (C^{b'', f''}), 130.6 (C^a), 129.3 (C^{a''}), 128.2 (C^{b, f}), 119.9 (C^c), 115.0 (C^{c, e}), 114.2 (C^{c'', e''}), 111.9 (C^{e'}), 71.5, 71.1, 70.8, 70.7, 70.6, 70.5, 69.9 (C¹⁹⁻²⁹), 69.4 (C¹⁸), 68.6 (C¹⁷), 68.4, 68.3 (C^{1, 1'}), 32.2 (C¹⁴), 31.8 (C^{4'}), 29.9, 29.9, 29.9, 29.9, 29.7, 29.6, 29.6, 29.5 (C^{2, 4, 13, 2'}), 26.4 (C³), 26.0 (C^{3'}), 22.9, 22.9 (C^{15, 5'}), 14.4 (C¹⁶), 14.3 (C^{6'}). EA: C₅₄H₈₄O₁₁·0.5H₂O (Cal.) C: 70.63 %, H: 9.33 %, (Found) C: 70.87 %, H: 9.32 %.

8.2.3 Amides (**Am/n**, **A*10/n**, **A6.16/n**, **A16.6/n**, **A¹10/n** and **A²10/n**)

General procedure: The appropriate carboxylic acid **Am/n** (or **A*10/n**, **A6.16/n**, **A16.6/n**) (2.33 mmol) was dissolved in dry THF (50 mL), to which, DCC (0.53 g, 2.56 mmol) was added at 0 °C. After 30 min, the reaction mixture was allowed to warm to r.t., then pentafluorophenol (0.50 g, 2.54 mmol) was added, and the reaction mixture was stirred at r.t. for 24h. The appropriate amino alcohol (3.6 mmol) was added and the resulting mixture was stirred for another 24 h. After that the reaction mixture was filtered and the residue was washed with chloroform (5 × 5 mL). The solvent of the combined organic solution was evaporated in vacuum, the residue was purified by column chromatography on silica gel with CHCl₃/MeOH as eluent and recrystallization from ethyl acetate/n-hexane.

N-(2,3-Dihydroxypropyl)-11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoylamide (**A¹10/3**):

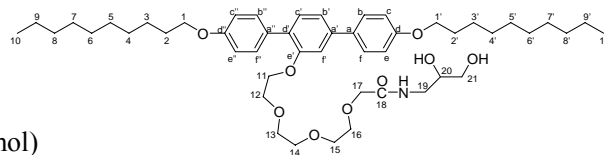
Reagents: **H10/3** (0.30 g, 0.40 mmol)

Dry THF (40 mL)

DCC (97 mg, 0.47 mmol)

Pentafluorophenol (96 mg, 0.52 mmol)

3-Aminopropane-1,2-diol (228 mg, 2.5 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/0.5 V/V, recrystallization from ethyl acetate/n-hexane

Yield: 0.11 g (33.4 %), colorless solid

Analytical data: C₄₉H₇₅O₉N

M_w = 822.12

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.54-7.48 (m, 5 H, Ar-**H^{b,f,b'',f''}**, **NH**), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-**H^{c'}**), 7.20 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H^{b'}**), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H^{f'}**), 6.97-6.89 (m, 4 H, Ar-**H^{c,e,c'',e''}**), 4.16 (t, ³J(H,H) = 4.7, 2 H, CH₂¹¹), 3.98-3.96 (m, 6 H, CH₂^{1,1',17}), 3.79 (t, ³J(H,H) = 4.7, 2 H, CH₂¹²), 3.70-3.57 (m, 9 H, CH₂¹³⁻¹⁶, CH₂²⁰), 3.47-3.41 (m, 2 H, OCH₂²¹), 3.38-3.34 (m, 2 H, CH₂¹⁹), 3.27 (d, ³J(H,H) = 6.0, 1 H, OH), 3.10 (t, ³J(H,H) = 6.0, 1 H, OH), 1.83-1.75 (m, 4 H, CH₂^{2,2'}), 1.51-1.40 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 24 H, CH₂^{4-9,4'-9'}), 0.89-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.8 (C¹⁸), 158.8 (C^d), 158.2 (C^{d''}), 155.8 (C^{e'}), 141.0 (C^{a'}), 133.1 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.2 (C^a), 127.9 (C^{b',f''}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.9 (C^f), 71.0, 70.7, 70.5, 70.1, 70.1 (C^{13-17,20}), 69.7 (C¹²), 68.6 (C¹¹), 68.2, 68.1 (C^{1,1'}), 63.5 (C²¹), 41.7 (C¹⁹), 31.9 (C^{8,8'}), 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 (C^{2,4-7,2',4'-7'}), 26.1, 26.1 (C^{3,3'}), 22.7 (C^{9,9'}), 14.1 (C^{10,10'}). EA: C₄₉H₇₅NO₉·0.5H₂O (Cal.) C: 70.81 %, H: 9.22 %, N:1.68 %, (Found) C: 70.73 %, H: 9.10 %, N:1.61 %.

N-(1,3-Dihydroxypropyl)-11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoylamide (**A²10/3**):

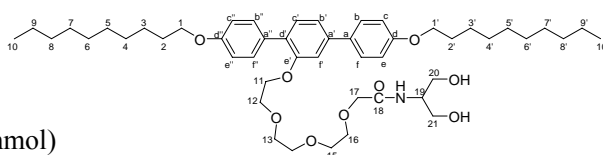
Reagents: **H10/3** (0.40 g, 0.54 mmol)

Dry THF (40 mL)

DCC (121 mg, 0.59 mmol)

Pentafluorophenol (108 mg, 0.59 mmol)

2-Aminopropane-1,3-diol (0.3 g, 3.3 mmol)



Purification: Column chromatography with silica gel 60, Eluent: CHCl₃/MeOH = 10/0.5 V/V, recrystallization from ethyl acetate/n-hexane

Yield: 42 mg (9.5 %), colorless solid

Analytical data: C₄₉H₇₅O₉NM_w = 822.12

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.52-7.48 (m, 5 H, Ar-H^{b, f, b'', f''}, NH), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.20 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.96-6.90 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.15 (t, ³J(H,H) = 4.7, 2 H, CH₂¹¹), 4.00-3.95 (m, 6 H, CH₂^{1,1',17}), 3.93-3.86 (m, 1 H, CH¹⁹), 3.78 (t, ³J(H,H) = 4.7, 2 H, CH₂¹²), 3.73-3.57 (m, 12 H, CH₂^{13-16, 20, 21}), 3.35 (bs, 2 H, OH), 1.83-1.76 (m, 4 H, CH₂^{2,2'}), 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 24 H, CH₂^{4-9,4'-9'}), 0.89-0.86 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 170.8 (C¹⁸), 158.9 (C^d), 158.2 (C^{d''}), 155.8 (C^{e'}), 141.0 (C^{a'}), 133.1 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.2 (C^a), 127.9 (C^{b',f''}), 119.9 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.9 (C^f), 70.9, 70.6, 70.5, 70.3, 70.1 (C¹³⁻¹⁷), 69.7 (C¹²), 68.6 (C¹¹), 68.2, 68.1 (C^{1,1'}), 63.3 (C^{20,21}), 52.9 (C¹⁹), 31.9 (C^{8,8'}), 29.6, 29.4, 29.4, 29.4, 29.3 (C^{2,4-7,2',4'-7'}), 26.1, 26.1 (C^{3,3'}), 22.7 (C^{9,9'}), 14.1 (C^{10,10'}). EA: C₄₉H₇₅NO₉·H₂O (Cal.) C: 70.05 %, H: 9.24 %, N:1.67 %, (Found) C: 70.12 %, H: 9.44 %, N:1.56 %.

N-(2,3-Dihydroxypropyl)-14-(4,4''-didecyloxy-*p*-terphenyl-2'-yloxy)-3,6,9,12-tetraoxa-tetradecanoylamide (**A^{10/4}**):

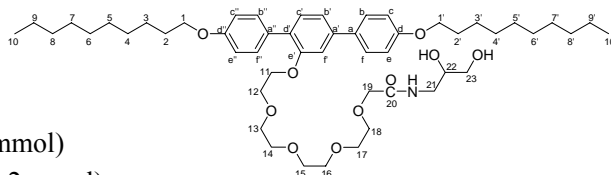
Reagents: **H10/4** (0.40 g, 0.50 mmol)

Dry THF (50 mL)

DCC (114 mg, 0.55 mmol)

Pentafluorophenol (102 mg, 0.55 mmol)

3-Aminopropane-1,2-diol (0.2 g, 2.2 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/0.5 V/V, recrystallization from ethyl acetate/n-hexane

Yield: 0.13 g (29.8 %), colorless solid

Analytical data: C₅₁H₇₉O₁₀NM_w = 866.17

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.64 (bs, 1 H, NH), 7.57-7.48 (m, 4H, Ar-H^{b, f, b'', f''}), 7.33 (d, ³J(H,H) = 7.7, 1 H, Ar-H^{c'}), 7.19 (d, ³J(H,H) = 7.7, 1 H, Ar-H^{b'}), 7.13 (s, 1 H, Ar-H^{f'}), 6.98-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.16 (t, ³J(H,H) = 5.0, 2 H, CH₂¹¹), 4.01-3.96 (m, 6 H, CH₂^{1,1',19}), 3.76 (t, ³J(H,H) = 5.0, 2 H, CH₂¹²), 3.70-3.37 (m, 9 H, CH₂^{13-18, 21, 23}, CH²²), 1.83-1.72 (m, 4 H, CH₂^{2,2'}), 1.51-1.20 (m, 28 H, CH₂^{3-9, 3'-9'}), 0.90-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.8 (C²⁰), 158.8 (C^d), 158.2 (C^{d''}), 155.9 (C^{e'}), 141.0 (C^{a'}), 133.1 (C^{a''}), 130.9 (C^{c'}), 130.6 (C^{b,f}), 130.4 (C^{a''}), 129.1 (C^a), 128.0 (C^{b',f''}), 119.7 (C^{b'}), 114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^f), 70.9, 70.8, 70.4, 70.3, 70.1, 70.0 (C^{13-19, 22}), 69.7 (C¹²), 68.4 (C¹¹), 68.1, 68.0 (C^{1,1'}), 63.5 (C²³), 41.6 (C²¹), 31.9 (C^{8,8'}), 29.5, 29.4, 29.3 (C^{2,4-7,2',4'-7'}), 26.0 (C^{3,3'}), 22.6 (C^{9,9'}), 14.1 (C^{10,10'}). EA: C₅₁H₇₉NO₁₀·1.2H₂O (Cal.) C: 68.99 %, H: 9.24 %, N:1.58 %, (Found) C: 68.95 %, H: 9.07 %, N:1.66 %.

N-(1,3-Dihydroxypropyl)-14-(4,4''-didecyloxy-*p*-terphenyl-2'-yloxy)-3,6,9,12-tetraoxa-tetradecanoylamide (**A^{210/4}**):

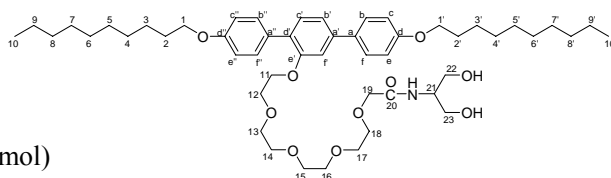
Reagents: **H10/4** (356 mg, 0.45 mmol)

Dry THF (50 mL)

DCC (102 mg, 0.49 mmol)

Pentafluorophenol (92 mg, 0.50 mmol)

2-Aminopropane-1,3-diol (0.45 g, 4.9 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/0.5 V/V, recrystallization from ethyl acetate/n-hexane

Yield: 42 mg (9.5 %), colorless solid

Analytical data: C₅₁H₇₉O₁₀NM_w = 866.17

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.49 (m, 5 H, Ar-H^{b, f, b'', f''}, NH), 7.33 (d, ³J(H,H) = 7.9, 1 H,

Ar-**H^{c'}**), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.5$, 1 H, Ar-**H^{b'}**), 7.13 (d, $^4J(\text{H,H}) = 1.5$, 1 H, Ar-**H^{f'}**), 6.96-6.89 (m, 4 H, Ar-**H^{c,e,c'',e''}**), 4.16 (t, $^3J(\text{H,H}) = 4.7$, 2 H, **CH₂¹¹**), 4.00-3.95 (m, 6 H, **CH₂^{1,1',19}**), 3.93-3.89 (m, 1 H, **CH²¹**), 3.78 (t, $^3J(\text{H,H}) = 4.7$, 2 H, **CH₂¹²**), 3.75-3.55 (m, 16 H, **CH₂^{13-18,22,23}**), 1.82-1.76 (m, 4 H, **CH₂^{2,2'}**), 1.49-1.41 (m, 4 H, **CH₂^{3,3'}**), 1.39-1.20 (m, 24 H, **CH₂^{4-9,4'-9'}**), 0.89-0.86 (m, 6 H, **CH₃^{10,10'}**). ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 170.8$ (**C¹⁸**), 158.8 (**C^d**), 158.1 (**C^{d''}**), 155.8 (**C^{e'}**), 140.9 (**C^{a'}**), 133.1 (**C^{a''}**), 130.8 (**C^{c'}**), 130.5 (**C^{b,f}**), 130.4 (**C^{a''}**), 129.1 (**C^a**), 127.9 (**C^{b',f''}**), 119.7 (**C^{b'}**), 114.8 (**C^{c'',e''}**), 113.9 (**C^{c,e}**), 111.7 (**C^f**), 70.9, 70.8, 70.5, 70.5, 70.3, 70.1 (**C¹³⁻¹⁹**), 69.8 (**C¹²**), 68.5 (**C¹¹**), 68.2, 68.1 (**C^{1,1'}**), 63.2 (**C^{22,23}**), 52.9 (**C²¹**), 31.9 (**C^{8,8'}**), 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 (**C^{2,4-7,2',4'-7'}**), 26.2, 26.1 (**C^{3,3'}**), 22.7 (**C^{9,9'}**), 14.1 (**C^{10,10'}**). EA: $\text{C}_{51}\text{H}_{79}\text{NO}_{10} \cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 69.99 %, H: 9.21 %, N: 1.60 %, (Found) C: 69.75 %, H: 9.23 %, N: 1.53 %.

***N*-[*(2S,3R,4R,5R)*-2,3,4,5,6-Pentahydroxyhexyl]-8-(4,4''-didecyloxy-*p*-terphenyl-2'-yl-oxy)-3,6-dioxaocetanoylamide (**A10/2**):**

Reagents: **H10/2** (0.30 g, 0.43 mmol)

Dry THF (50 mL)

DCC (97 mg, 0.47 mmol)

Pentafluorophenol (95 mg, 0.52 mmol)

1-Amino-1-deoxy-D-sorbitol (0.40 g, 2.2 mmol)

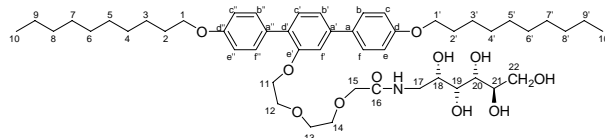
Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH} = 10/1$ V/V, recrystallization from ethyl acetate

Yield: 0.19 g (51.4 %), colorless solid

Analytical data: $\text{C}_{50}\text{H}_{77}\text{O}_{11}\text{N}$

$M_w = 868.15$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) $\delta = 7.52$ -7.43 (m, 5 H, Ar-**H^{b,f,b'',f''}**, **NH**), 7.32 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-**H^{c'}**), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.5$, 1 H, Ar-**H^{b'}**), 7.12 (d, $^4J(\text{H,H}) = 1.5$, 1 H, Ar-**H^{f'}**), 6.95-6.87 (m, 4 H, Ar-**H^{c,e,c'',e''}**), 4.15 (t, $^3J(\text{H,H}) = 4.7$, 2 H, **CH₂¹¹**), 3.97-3.93 (m, 4 H, **CH₂^{1,1'}**), 3.90 (s, 2 H, **CH₂¹⁵**), 3.77 (t, $^3J(\text{H,H}) = 4.7$, 2 H, **CH₂¹²**), 3.75-3.55 (m, 12 H, **CH₂^{13,14,17,22}**, **CH¹⁸⁻²¹**), 3.40-3.21 (m, 2 H, **OH**), 1.83-1.73 (m, 4 H, **CH₂^{2,2'}**), 1.46-1.41 (m, 4 H, **CH₂^{3,3'}**), 1.39-1.20 (m, 24 H, **CH₂^{4-9,4'-9'}**), 0.89-0.85 (m, 6 H, **CH₃^{10,10'}**). ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 172.0$ (**C¹⁶**), 158.9 (**C^d**), 158.2 (**C^{d''}**), 155.7 (**C^{e'}**), 141.0 (**C^{a'}**), 132.9 (**C^{a''}**), 130.9 (**C^{c'}**), 130.5 (**C^{b,f}**), 130.2 (**C^{a''}**), 129.1 (**C^a**), 127.9 (**C^{b',f''}**), 119.9 (**C^{b'}**), 114.9 (**C^{c'',e''}**), 114.0 (**C^{c,e}**), 111.7 (**C^{f'}**), 73.1, 73.0, 72.0, 70.0 (**C²⁶⁻²⁹**), 71.0, 70.5, 70.1 (**C¹³⁻¹⁵**), 69.9 (**C¹²**), 68.5 (**C¹¹**), 68.2, 68.1 (**C^{1,1'}**), 63.9 (**C²²**), 42.3 (**C¹⁷**), 31.9 (**C^{8,8'}**), 29.6, 29.6, 29.5, 29.5, 29.4, 29.4 (**C^{2,4-7,2',4'-7'}**), 26.1, 26.1 (**C^{3,3'}**), 22.7, (**C^{9,9'}**), 14.1 (**C^{10,10'}**). EA: $\text{C}_{50}\text{H}_{77}\text{NO}_{11} \cdot \text{H}_2\text{O}$ (Cal.) C: 67.76 %, H: 8.99 %, N: 1.58 %, (Found) C: 67.58 %, H: 8.81 %, N: 1.47 %.



***N*-[*(2S,3R,4R,5R)*-2,3,4,5,6-Pentahydroxyhexyl]-11-(4,4''-didecyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9-trioxaundecanoylamide (**A10/3**):**

Reagents: **H10/3** (0.52 g, 0.69 mmol)

Dry THF (50 mL)

DCC (157 mg, 0.76 mmol)

Pentafluorophenol (141 mg, 0.77 mmol)

1-Amino-1-deoxy-D-sorbitol (0.63 g, 3.5 mmol)

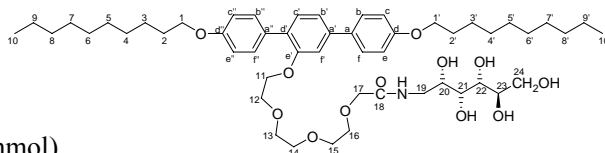
Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH} = 10/1$ V/V, recrystallization from ethyl acetate

Yield: 0.10 g (15.9 %), colorless solid

Analytical data: $\text{C}_{52}\text{H}_{81}\text{O}_{12}\text{N}$

$M_w = 912.20$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) $\delta = 7.57$ (bs, 1 H, **NH**), 7.51-7.46 (m, 4 H, Ar-**H^{b,f,b'',f''}**), 7.30 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-**H^{c'}**), 7.17 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.5$, 1 H, Ar-**H^{b'}**), 7.11 (s, 1 H, Ar-**H^{f'}**),



6.94-6.87 (m, 4 H, Ar- $\text{H}^{c, e, c'', e''}$), 4.14-4.10 (m, 2 H, CH_2^{11}), 3.96-3.87 (m, 6 H, $\text{CH}_2^{1,1',17}$), 3.83-3.28 (m, 18 H, $\text{CH}_2^{12-16, 19, 24}$, CH^{20-23}), 1.83-1.77 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.49-1.41 (m, 4 H, $\text{CH}_2^{3,3'}$), 1.39-1.20 (m, 24 H, $\text{CH}_2^{4-9,4'-9'}$), 0.89-0.85 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.8 (C^{18}), 158.8 (C^d), 158.1 ($\text{C}^{d''}$), 155.9 ($\text{C}^{e'}$), 140.9 ($\text{C}^{a'}$), 133.1 ($\text{C}^{a''}$), 130.8 ($\text{C}^{c'}$), 130.5 ($\text{C}^{b,f}$), 130.4 ($\text{C}^{a''}$), 129.1 (C^a), 127.9 ($\text{C}^{b',f''}$), 119.7 ($\text{C}^{b'}$), 114.8 ($\text{C}^{c'',e''}$), 114.0 ($\text{C}^{c,e}$), 111.6 ($\text{C}^{f'}$), 73.0, 72.5, 71.9, 70.2 (C^{20-23}), 71.0, 70.7, 70.5, 70.1 (C^{13-17}), 69.7 (C^{12}), 68.6 (C^{11}), 68.2, 68.1 ($\text{C}^{1,1'}$), 63.9 (C^{24}), 42.1 (C^{21}), 31.9 ($\text{C}^{8,8'}$), 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3 ($\text{C}^{2,4-7,2',4'-7'}$), 26.1, 26.1 ($\text{C}^{3,3'}$), 22.7, ($\text{C}^{9,9'}$), 14.1 ($\text{C}^{10,10'}$). EA: $\text{C}_{52}\text{H}_{81}\text{NO}_{12}\cdot\text{H}_2\text{O}$ (Cal.) C: 67.14 %, H: 8.99 %, N:1.50 %, (Found) C: 67.04 %, H: 9.06 %, N:1.42 %.

***N*-[*(2S,3R,4R,5R)*-2,3,4,5,6-Pentahydroxyhexyl]-14-(4,4''-didecyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9,12-tetraoxatetradecanoylamide (**A10/4**):**

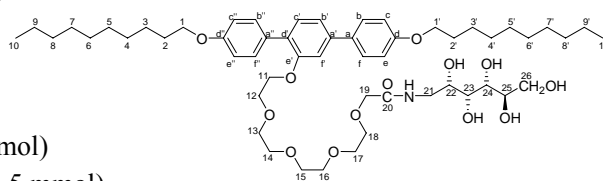
Reagents: **H10/4** (0.49 g, 0.62 mmol)

Dry THF (50 mL)

DCC (140 mg, 0.68 mmol)

Pentafluorophenol (126 mg, 0.68 mmol)

1-Amino-1-deoxy-D-sorbitol (1 g, 5.5 mmol)



Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH}$ = 10/1 V/V, recrystallization from ethyl acetate

Yield: 70 mg (9.5 %), colorless solid

Analytical data: $\text{C}_{54}\text{H}_{85}\text{O}_{13}\text{N}$ M_w = 956.25

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.61 (t, $^3J(\text{H,H})$ = 5.6, 1 H, NH), 7.51-7.48 (m, 4 H, Ar- $\text{H}^{b, f, b'', f''}$), 7.31 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{c'}$), 7.17 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{b'}$), 7.11 (s, 1 H, Ar- $\text{H}^{f'}$), 6.95-6.88 (m, 4 H, Ar- $\text{H}^{c, e, c'', e''}$), 4.46 (bs, 1 H, OH), 4.14 (t, $^3J(\text{H,H})$ = 4.5, 2 H, CH_2^{11}), 3.96-3.90 (m, 6 H, $\text{CH}_2^{1,1',19}$), 3.83 (bs, 1 H, OH), 3.76 (t, $^3J(\text{H,H})$ = 4.5, 2 H, CH_2^{12}), 3.74-3.28 (m, 20 H, $\text{CH}_2^{13-18, 21, 26}$, CH^{22-25}), 1.81-1.74 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.46-1.41 (m, 4 H, $\text{CH}_2^{3,3'}$), 1.39-1.20 (m, 24 H, $\text{CH}_2^{4-9,4'-9'}$), 0.89-0.85 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.7 (C^{20}), 158.8 (C^d), 158.1 ($\text{C}^{d''}$), 155.9 ($\text{C}^{e'}$), 140.9 ($\text{C}^{a'}$), 133.1 ($\text{C}^{a''}$), 130.8 ($\text{C}^{c'}$), 130.5 ($\text{C}^{b,f}$), 130.4 ($\text{C}^{a''}$), 129.1 (C^a), 127.9 ($\text{C}^{b',f''}$), 119.7 ($\text{C}^{b'}$), 114.8 ($\text{C}^{c'',e''}$), 114.0 ($\text{C}^{c,e}$), 111.6 ($\text{C}^{f'}$), 73.0, 72.5, 71.9, 70.2 (C^{22-25}), 70.9, 70.8, 70.4, 70.4, 70.3, 70.1 (C^{13-19}), 69.7 (C^{12}), 68.5 (C^{11}), 68.2, 68.1 ($\text{C}^{1,1'}$), 63.9 (C^{26}), 42.1 (C^{21}), 31.9 ($\text{C}^{8,8'}$), 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 ($\text{C}^{2,4-7,2',4'-7'}$), 26.1, 26.1 ($\text{C}^{3,3'}$), 22.7, ($\text{C}^{9,9'}$), 14.1 ($\text{C}^{10,10'}$). EA: $\text{C}_{54}\text{H}_{85}\text{NO}_{13}\cdot\text{H}_2\text{O}$ (Cal.) C: 66.57 %, H: 9.00 %, N:1.44 %, (Found) C: 66.74 %, H: 9.03 %, N:1.31 %.

***N*-[*(2S,3R,4R,5R)*-2,3,4,5,6-Pentahydroxyhexyl]-20-(4,4''-didecyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9,12,15,18-hexaoxaicosanoylamide (**A10/6**):**

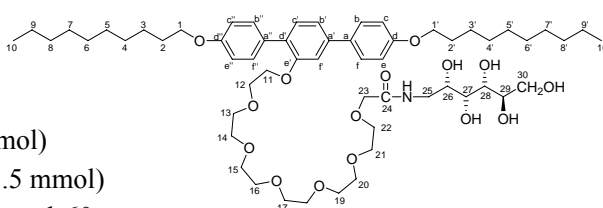
Reagents: **H10/6** (0.60 g, 0.66 mmol)

Dry THF (50 mL)

DCC (130 mg, 0.63 mmol)

Pentafluorophenol (116 mg, 0.63 mmol)

1-Amino-1-deoxy-D-sorbitol (1 g, 5.5 mmol)



Purification: Column chromatography with silica gel 60, Eluent: $\text{CHCl}_3/\text{MeOH}$ = 10/1 V/V, recrystallization from ethyl acetate

Yield: 280 mg (39.4 %), colorless solid

Analytical data: $\text{C}_{58}\text{H}_{93}\text{O}_{15}\text{N}$ M_w = 1044.36

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.68 (t, $^3J(\text{H,H})$ = 6.0, 1 H, NH), 7.52-7.48 (m, 4 H, Ar- $\text{H}^{b, f, b'', f''}$), 7.32 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{c'}$), 7.18 (dd, $^3J(\text{H,H})$ = 7.9, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- $\text{H}^{b'}$), 7.12 (d, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- $\text{H}^{f'}$), 6.96-6.88 (m, 4 H, Ar- $\text{H}^{c, e, c'', e''}$), 4.42 (d, $^3J(\text{H,H})$ = 4.6, 1 H, OH), 4.15 (t, $^3J(\text{H,H})$ = 4.7, 2 H, CH_2^{11}), 4.00-3.90 (m, 6 H, $\text{CH}_2^{1,1',23}$), 3.86 (bs, 2 H, OH), 3.80-3.28 (m, 30 H, $\text{CH}_2^{12-22, 25, 30}$),

CH^{26-29}), 1.83-1.77 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.49-1.41 (m, 4 H, $\text{CH}_2^{3,3'}$), 1.39-1.20 (m, 24 H, $\text{CH}_2^{4-9,4'-9'}$), 0.89-0.85 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.7 (C^{24}), 158.8 (C^{d}), 158.1 ($\text{C}^{\text{d}''}$), 155.9 ($\text{C}^{\text{e'}}$), 140.9 ($\text{C}^{\text{a'}}$), 133.1 ($\text{C}^{\text{a}''}$), 130.8 ($\text{C}^{\text{c'}}$), 130.5 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a}''}$), 129.1 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.6 ($\text{C}^{\text{b'}}$), 114.8 ($\text{C}^{\text{c'',e''}}$), 114.0 ($\text{C}^{\text{c,e}}$), 111.7 (C^{f}), 73.0, 72.6, 72.0, 70.2 (C^{26-29}), 71.0, 70.8, 70.5, 70.5, 70.4, 70.4, 70.3, 70.1 (C^{13-23}), 69.7 (C^{12}), 68.4 (C^{11}), 68.2, 68.1 ($\text{C}^{1,1'}$), 63.9 (C^{30}), 42.2 (C^{25}), 31.9 ($\text{C}^{8,8'}$), 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 ($\text{C}^{2,4-7,2',4'-7'}$), 26.1, 26.1 ($\text{C}^{3,3'}$), 22.7, ($\text{C}^{9,9'}$), 14.1 ($\text{C}^{10,10'}$). EA: $\text{C}_{58}\text{H}_{93}\text{NO}_{15}\cdot\text{H}_2\text{O}$ (Cal.) C: 65.57 %, H: 9.01 %, N:1.32 %, (Found) C: 65.41 %, H: 9.02 %, N:1.22 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-8-(4,4''-dibutyloxy-*p*-terphenyl-2'-yl-oxy)-3,6-dioxaoctanoylamide (**A4/2**):

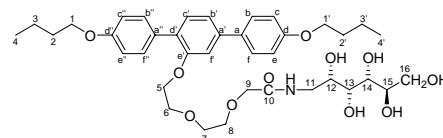
Reagents: **H4/2** (0.40 g, 0.75 mmol)

Dry THF (50 mL)

DCC (170 mg, 0.83 mmol)

Pentafluorophenol (170 mg, 0.91 mmol)

1-Amino-1-deoxy-D-sorbitol (0.69 g, 3.8 mmol)



Purification: Column chromatography with silica gel 60, Eluent: $\text{CHCl}_3/\text{MeOH}$ = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.18 g (34.5 %), colorless solid

Analytical data: $\text{C}_{38}\text{H}_{53}\text{O}_{11}\text{N}$

M_w = 699.83

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.49-7.43 (m, 5 H, Ar- $\text{H}^{\text{b,f,b'',f''}}$, NH), 7.27 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{\text{c'}}$), 7.14 (dd, $^3J(\text{H,H})$ = 7.9, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- $\text{H}^{\text{b'}}$), 7.08 (d, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- H^{f}), 6.91-6.84 (m, 4 H, Ar- $\text{H}^{\text{c,e,c'',e''}}$), 4.09 (t, $^3J(\text{H,H})$ = 5.0, 2 H, CH_2^5), 3.95-3.90 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.87 (s, 2 H, CH_2^9), 3.80-3.40 (m, 12 H, $\text{CH}_2^{7,8,11,16}$, CH^{12-14}), 3.39-3.20 (m, 2 H, OH), 1.79-1.69 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.50-1.40 (m, 4 H, $\text{CH}_2^{3,3'}$), 0.96-0.90 (m, 6 H, $\text{CH}_3^{4,4'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.6 (C^{10}), 158.7 (C^{d}), 158.1 ($\text{C}^{\text{d}''}$), 155.7 ($\text{C}^{\text{e'}}$), 140.8 ($\text{C}^{\text{a'}}$), 132.9 ($\text{C}^{\text{a}''}$), 130.8 ($\text{C}^{\text{c'}}$), 130.4 ($\text{C}^{\text{b,f}}$), 130.2 ($\text{C}^{\text{a}''}$), 129.0 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.7 ($\text{C}^{\text{b'}}$), 114.8 ($\text{C}^{\text{c'',e''}}$), 113.9 ($\text{C}^{\text{c,e}}$), 111.5 (C^{f}), 72.8, 72.4, 71.9, 70.2 (C^{12-15}), 70.9, 70.4, 70.2 (C^{7-9}), 69.8 (C^6), 68.5 (C^5), 67.8, 67.8 ($\text{C}^{1,1'}$), 63.8 (C^{16}), 42.2 (C^{11}), 31.5, 31.4 ($\text{C}^{2,2'}$), 19.4, 19.4 ($\text{C}^{3,3'}$), 14.0 ($\text{C}^{4,4'}$). EA: $\text{C}_{38}\text{H}_{53}\text{O}_{11}\text{N}\cdot\text{H}_2\text{O}$ (Cal.) C: 63.58 %, H: 7.77 %, N:1.95 %, (Found) C: 63.44 %, H: 7.45 %, N:1.99 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-11-(4,4''-dibutyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9-trioxaundecanoylamide (**A4/3**):

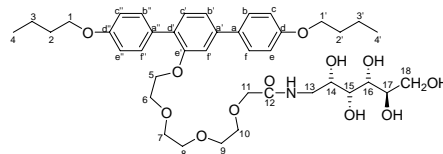
Reagents: **H4/3** (0.45 g, 0.78 mmol)

Dry THF (50 mL)

DCC (180 mg, 0.86 mmol)

Pentafluorophenol (180 mg, 0.95 mmol)

1-Amino-1-deoxy-D-sorbitol (0.71 g, 3.9 mmol)



Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH}$ = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.23 g (39.9 %), colorless solid

Analytical data: $\text{C}_{40}\text{H}_{57}\text{O}_{12}\text{N}$

M_w = 743.88

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.57 (t, $^3J(\text{H,H})$ = 6.0, 1 H, NH), 7.51-7.46 (m, 4 H, Ar- $\text{H}^{\text{b,f,b'',f''}}$), 7.29 (d, $^3J(\text{H,H})$ = 7.9, 1 H, Ar- $\text{H}^{\text{c'}}$), 7.15 (dd, $^3J(\text{H,H})$ = 7.9, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- $\text{H}^{\text{b'}}$), 7.10 (d, $^4J(\text{H,H})$ = 1.7, 1 H, Ar- H^{f}), 6.94-6.86 (m, 4 H, Ar- $\text{H}^{\text{c,e,c'',e''}}$), 4.11 (t, $^3J(\text{H,H})$ = 4.9, 2 H, CH_2^5), 3.97-3.93 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.92 (s, 2 H, CH_2^{11}), 3.82-3.18 (m, 18 H, $\text{CH}_2^{6-10,13,18}$, CH^{14-17}), 1.79-1.70 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.52-1.42 (m, 4 H, $\text{CH}_2^{3,3'}$), 0.97-0.93 (m, 6 H, $\text{CH}_3^{4,4'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 171.7 (C^{12}), 158.7 (C^{d}), 158.1 ($\text{C}^{\text{d}''}$), 155.7 ($\text{C}^{\text{e'}}$), 140.9 ($\text{C}^{\text{a'}}$), 133.0 ($\text{C}^{\text{a}''}$), 130.8 ($\text{C}^{\text{c'}}$), 130.5 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a}''}$), 129.0 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.7 ($\text{C}^{\text{b'}}$),

114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^f), 72.9, 72.5, 71.9 (C¹⁴⁻¹⁷), 70.9, 70.7, 70.5, 70.2, 70.1 (C⁷⁻¹¹), 69.7 (C⁶), 68.5 (C⁵), 67.8, 67.8 (C^{1,1'}), 63.9 (C¹⁸), 42.2 (C¹³), 31.5, 31.4 (C^{2,2'}), 19.4, 19.4 (C^{3,3'}), 14.0, 14.0 (C^{4,4'}). EA: C₄₀H₅₇O₁₂·1.5H₂O (Cal.) C: 62.32 %, H: 7.85 %, N:1.82 %, (Found) C: 62.59 %, H: 7.64 %, N:1.91 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-(4,4''-dibutyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9,12-tetraoxatetradecanoylamide (**A4/4**):

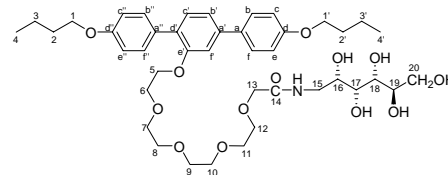
Reagents: **H4/4** (0.56 g, 0.90 mmol)

Dry THF (50 mL)

DCC (200 mg, 0.99 mmol)

Pentafluorophenol (200 mg, 1.09 mmol)

1-Amino-1-deoxy-D-sorbitol (0.81 g, 4.5 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.29 g (41.0 %), colorless solid

Analytical data: C₄₂H₆₁O₁₃N M_w = 787.93

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.61 (t, ³J(H,H) = 6.0, 1 H, NH), 7.51-7.47 (m, 4 H, Ar-H^{b,f,b'',f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.11 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.96-6.87 (m, 4 H, Ar-H^{c,e,c'',e''}), 4.13 (t, ³J(H,H) = 5.0, 2 H, CH₂⁵), 3.99-3.94 (m, 4 H, CH₂^{1,1'}), 3.93 (s, 2 H, CH₂¹³), 3.82-3.40 (m, 22 H, CH₂^{6-12,15,20}, CH¹⁶⁻¹⁹), 3.39-3.30 (m, 1 H, OH), 1.80-1.70 (m, 4 H, CH₂^{2,2'}), 1.53-1.42 (m, 4 H, CH₂^{3,3'}), 0.98-0.94 (m, 6 H, CH₃^{4,4'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.6 (C¹²), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.8 (C^{a'}), 133.0 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b,f}), 130.3 (C^{a''}), 129.0 (C^a), 127.9 (C^{b',f''}), 119.6 (C^{b'}), 114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^f), 72.9, 72.5, 71.9 (C¹⁶⁻¹⁹), 70.9, 70.8, 70.4, 70.4, 70.3, 70.2, 70.1 (C⁷⁻¹³), 69.7 (C⁶), 68.5 (C⁵), 67.8, 67.7 (C^{1,1'}), 63.9 (C²⁰), 42.2 (C¹⁵), 31.5, 31.4 (C^{2,2'}), 19.4, 19.4 (C^{3,3'}), 14.0, 14.0 (C^{4,4'}). EA: C₄₂H₆₁O₁₃·2H₂O (Cal.) C: 61.22 %, H: 7.95 %, N:1.70 %, (Found) C: 61.16 %, H: 7.89 %, N:1.70 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-8-(4,4''-dibutyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9-trioxaundecanoylamide (**A6/3**):

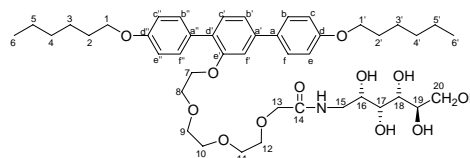
Reagents: **H6/3** (0.80 g, 1.26 mmol)

Dry THF (50 mL)

DCC (286 mg, 1.39 mmol)

Pentafluorophenol (278 mg, 1.51 mmol)

1-Amino-1-deoxy-D-sorbitol (2.3 g, 12.6 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

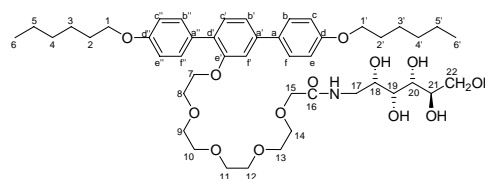
Yield: 0.43 g (42.7 %), colorless solid

Analytical data: C₄₄H₆₅O₁₂N M_w = 799.99

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.57 (t, ³J(H,H) = 6.0, 1 H, NH), 7.51-7.46 (m, 4 H, Ar-H^{b,f,b'',f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.5, 1 H, Ar-H^{b'}), 7.11 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{f'}), 6.94-6.87 (m, 4 H, Ar-H^{c,e,c'',e''}), 4.12 (t, ³J(H,H) = 5.0, 2 H, CH₂⁷), 3.98-3.91 (m, 6 H, CH₂^{1,1',13}), 3.74 (t, ³J(H,H) = 5.0, 2 H, CH₂⁸), 3.72-3.28 (m, 16 H, CH₂^{9-12,15,20}, CH¹⁶⁻¹⁹), 1.82-1.73 (m, 4 H, CH₂^{2,2'}), 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 8 H, CH₂^{4,5,4',5'}), 0.91-0.87 (m, 6 H, CH₃^{6,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.8 (C¹⁴), 158.8 (C^d), 158.1 (C^{d''}), 155.8 (C^{e'}), 141.0 (C^{a'}), 133.0 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 128.9 (C^a), 128.0 (C^{b',f''}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.7 (C^f), 73.0, 72.7, 71.9, 70.1 (C¹⁶⁻¹⁹), 70.9, 70.7, 70.5 (C⁹⁻¹³), 69.7 (C⁸), 68.5 (C⁷), 68.2, 68.1 (C^{1,1'}), 63.9 (C²⁰), 42.2 (C¹⁵), 31.6 (C^{4,4'}), 29.3, 29.3 (C^{2,2'}), 25.8, 25.8 (C^{3,3'}), 22.6 (C^{5,5'}), 14.1 (C^{6,6'}). EA: C₄₄H₆₅NO₁₂·1.5H₂O (Cal.) C: 63.90 %, H: 8.29 %, N:1.69 %, (Found) C: 63.94 %, H: 8.29 %, N:1.54 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-(4,4''-dihexyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9,12-tetraoxatetradecanoxamide (**A6/4**):

Reagents: **H6/4** (0.85 g, 1.76 mmol)
 Dry THF (50 mL)
 DCC (234 mg, 1.14 mmol)
 Pentafluorophenol (229 mg, 1.14 mmol)
 1-Amino-1-deoxy-D-sorbitol (1 g, 5.5 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

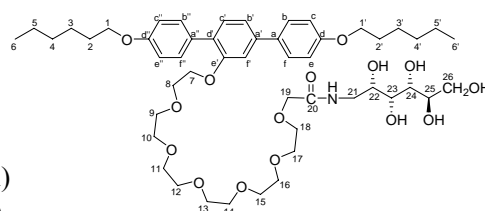
Yield: 0.43 g (28.9 %), colorless solid

Analytical data: C₄₆H₆₉O₁₃N M_w = 844.04

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.66 (t, ³J(H,H) = 6.0, 1 H, NH), 7.53-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.32 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.97-6.87 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.15 (t, ³J(H,H) = 5.0, 2 H, CH₂⁷), 3.99-3.83 (m, 6 H, CH₂^{1,1', 15}), 3.77 (t, ³J(H,H) = 5.0, 2 H, CH₂⁸), 3.74-3.32 (m, 16 H, CH₂^{9-14, 17, 22}, CH¹⁸⁻²¹), 1.82-1.73 (m, 4 H, CH₂^{2,2'}), 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.27 (m, 8 H, CH₂^{4,5,4',5'}), 0.92-0.87 (m, 6 H, CH₃^{6,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.8 (C¹⁶), 158.8 (C^d), 158.2 (C^{d''}), 155.9 (C^{e'}), 141.0 (C^{a'}), 133.1 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.1 (C^a), 128.0 (C^{b',f'}), 119.7 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.7 (C^{f'}), 73.0, 72.7, 72.0, 70.0 (C¹⁸⁻²¹), 70.9, 70.8, 70.4, 70.4, 70.3, 70.2, 70.1 (C⁹⁻¹⁵), 69.7 (C⁸), 68.5 (C⁷), 68.2, 68.1 (C^{1,1'}), 63.9 (C²²), 42.2 (C¹⁷), 31.6 (C^{4,4'}), 29.4, 29.3 (C^{2,2'}), 25.8, 25.8 (C^{3,3'}), 22.6 (C^{5,5'}), 14.1 (C^{6,6'}). EA: C₄₆H₆₉NO₁₃·1.8H₂O (Cal.) C: 63.03 %, H: 8.35 %, N:1.60 %, (Found) C: 62.78 %, H: 8.13 %, N:1.46 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-20-(4,4''-dihexyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9,12,15,18-hexaoxaeicosanoylamide (**A6/6**):

Reagents: **H6/6** (0.40 g, 0.52 mmol)
 Dry THF (50 mL)
 DCC (118 mg, 0.57 mmol)
 Pentafluorophenol (115 mg, 0.62 mmol)
 1-Amino-1-deoxy-D-sorbitol (1.0 g, 5.5 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.18 g (37.1 %), colorless solid

Analytical data: C₅₅H₇₇O₁₅N M_w = 932.14

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.70 (t, ³J(H,H) = 6.0, 1 H, NH), 7.52-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.96-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.14 (t, ³J(H,H) = 5.0, 2 H, CH₂⁷), 3.99-3.95 (m, 6 H, CH₂^{1,1', 19}), 3.80-3.20 (m, 30 H, CH₂^{8-18, 21, 26}, CH²²⁻²⁵), 1.82-1.73 (m, 4 H, CH₂^{2,2'}), 1.48-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.30 (m, 8 H, CH₂^{4,5,4',5'}), 0.91-0.87 (m, 6 H, CH₃^{6,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.6 (C²⁰), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.7 (C^{c'}), 130.5 (C^{b,f}), 130.3 (C^{a''}), 129.0 (C^a), 127.9 (C^{b',f'}), 119.6 (C^{b'}), 114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^{f'}), 73.0, 72.5, 71.9, 70.2 (C²²⁻²⁵), 70.9, 70.8, 70.5, 70.4, 70.4, 70.3, 70.3, 70.1 (C⁹⁻¹⁹), 69.7 (C⁸), 68.4 (C⁷), 68.2, 68.1 (C^{1,1'}), 63.9 (C²⁶), 42.2 (C²¹), 31.7, 31.7 (C^{4,4'}), 29.4, 29.4 (C^{2,2'}), 25.9, 25.8 (C^{3,3'}), 22.7 (C^{5,5'}), 14.1 (C^{6,6'}). EA: C₅₀H₇₇NO₅₂·2H₂O (Cal.) C: 62.03 %, H: 8.43 %, N:1.45 %, (Found) C: 62.01 %, H: 8.32 %, N:1.32 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-11-[4,4''-bis(3,7-dimethyloctyloxy)-*p*-terphenyl-2'-yloxy]-3,6,9-trioxaundecanoylamide (**A10*/3**):

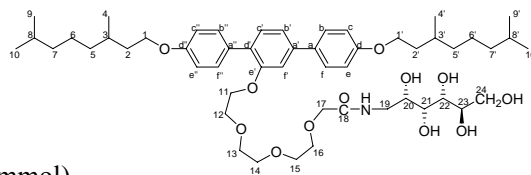
Reagents: **H10*/3** (0.31 g, 0.41 mmol)

Dry THF (50 mL)

DCC (94 mg, 0.45 mmol)

Pentafluorophenol (92 mg, 0.50 mmol)

1-Amino-1-deoxy-D-sorbitol (0.40 g, 2.2 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate/n-hexane

Yield: 0.10 g (26.5 %), colorless solid

Analytical data: C₅₂H₈₁O₁₂N M_w = 912.20

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.58 (t, ³J(H,H) = 6.0, 1 H, NH), 7.51-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.5, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{f'}), 6.95-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.14 (t, ³J(H,H) = 4.7, 2 H, CH₂¹¹), 4.02-3.97 (m, 4 H, CH₂^{1,1'}), 3.93 (s, 2 H, CH₂¹⁷), 3.77 (t, ³J(H,H) = 4.7, 2 H, CH₂¹²), 3.74-3.30 (m, 16 H, CH₂^{13-16, 19, 24}, CH²⁰⁻²³), 1.85-1.78 (m, 2 H, CH^{8,8'}), 1.73-1.64 (m, 2 H, CH^{3,3'}), 1.62-1.45 (m, 4 H, CH₂^{2,2'}), 1.37-1.07 (m, 12 H, CH₂^{5-7, 5'-7'}), 0.93-0.90 (m, 6 H, CH₃^{4,4'}), 0.89-0.82 (m, 12 H, CH₃^{9,10,9',10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.9 (C¹⁸), 158.8 (C^d), 158.2 (C^{d''}), 155.8 (C^{e'}), 141.0 (C^{a'}), 133.1 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.1 (C^a), 128.0 (C^{b',f''}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.7 (C^{f'}), 73.0, 72.8, 72.0, 70.0 (C²⁰⁻²³), 71.0, 70.7, 70.5, 70.2, 70.1 (C¹³⁻¹⁷), 69.7 (C¹²), 68.5 (C¹¹), 66.5, 66.4 (C^{1,1'}), 63.9 (C²⁴), 42.2 (C¹⁹), 39.3 (C^{7,7'}), 37.4 (C^{5,5'}), 36.3, 36.3 (C^{2,2'}), 29.9 (C^{3,3'}), 28.0 (C^{8,8'}), 24.7 (C^{5,5'}), 22.7, 22.6 (C^{9,10,9',10'}), 19.7 (C^{4,4'}). EA: C₅₂H₈₁O₁₂N·1.5H₂O (Cal.) C: 66.50 %, H: 9.01 %, N:1.49 %, (Found) C: 66.46 %, H: 8.94 %, N:1.42 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-[4,4''-bis(3,7-dimethyloctyloxy)-*p*-terphenyl-2'-yloxy]-3,6,9,12-tetraoxatetradecanoylamide (**A10*/4**):

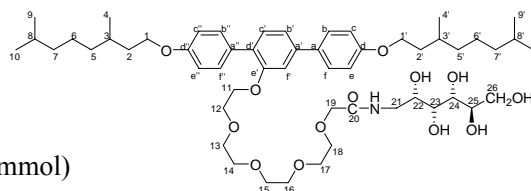
Reagents: **H10*/4** (0.50 g, 0.63 mmol)

Dry THF (50 mL)

DCC (144 mg, 0.70 mmol)

Pentafluorophenol (142 mg, 0.77 mmol)

1-Amino-1-deoxy-D-sorbitol (0.58 g, 3.2 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate/n-hexane

Yield: 0.20 g (33.0 %), colorless solid

Analytical data: C₅₄H₈₅O₁₃N M_w = 956.25

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.62 (t, ³J(H,H) = 6.0, 1 H, NH), 7.52-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.32 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{f'}), 6.96-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.15 (t, ³J(H,H) = 5.2, 2 H, CH₂¹¹), 4.02-3.98 (m, 4 H, CH₂^{1,1'}), 3.94 (s, 2 H, CH₂¹⁹), 3.77 (t, ³J(H,H) = 5.2, 2 H, CH₂¹²), 3.78-3.30 (m, 20 H, CH₂^{13-18, 21, 26}, CH²²⁻²⁵), 1.87-1.78 (m, 2 H, CH^{8,8'}), 1.73-1.64 (m, 2 H, CH^{3,3'}), 1.62-1.45 (m, 4 H, CH₂^{2,2'}), 1.37-1.07 (m, 12 H, CH₂^{5-7, 5'-7'}), 0.93-0.90 (m, 6 H, CH₃^{4,4'}), 0.89-0.82 (m, 12 H, CH₃^{9,10,9',10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.7 (C²⁰), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.9 (C^{a'}), 133.0 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.0 (C^a), 127.9 (C^{b',f''}), 119.7 (C^{b'}), 114.8 (C^{c'',e''}), 113.9 (C^{c,e}), 111.6 (C^{f'}), 73.0, 72.7, 72.0, 70.0 (C²²⁻²⁵), 71.0, 70.8, 70.5, 70.4, 70.3, 70.2, 70.1 (C¹³⁻¹⁹), 69.7 (C¹²), 68.5 (C¹¹), 66.5, 66.4 (C^{1,1'}), 63.9 (C²⁶), 42.2 (C²¹), 39.3 (C^{7,7'}), 37.4, 37.4 (C^{5,5'}), 36.4, 36.3 (C^{2,2'}), 30.0 (C^{3,3'}), 28.1 (C^{8,8'}), 24.8 (C^{5,5'}), 22.8, 22.7 (C^{9,10,9',10'}), 19.8 (C^{4,4'}). EA: C₅₄H₈₅O₁₃N·H₂O (Cal.) C: 66.57 %, H: 9.00 %, N:1.44 %, (Found) C: 66.38 %, H: 8.69 %, N:1.52 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-11-(4,4''-dioctyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9-trioxaundecanoylamide (**A8/3**):

Reagents: **H8/3** (0.24 g, 0.35 mmol)

Dry THF (50 mL)

DCC (80 mg, 0.39 mmol)

Pentafluorophenol (79 mg, 0.43 mmol)

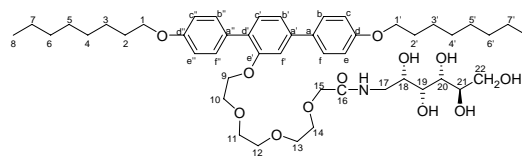
1-Amino-1-deoxy-D-sorbitol (0.33 g, 1.8 mmol)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.15 g (50.5 %), colorless solid

Analytical data: C₄₈H₇₃O₁₂N M_w = 856.09

¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 7.58 (bs, 1 H, NH), 7.51-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³*J*(H,H) = 7.7, 1 H, Ar-H^{c'}), 7.18 (dd, ³*J*(H,H) = 7.7, ⁴*J*(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.12 (d, ⁴*J*(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.95-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.14 (t, ³*J*(H,H) = 4.5, 2 H, CH₂⁹), 3.98-3.93 (m, 6 H, CH₂^{1,1',15}), 3.82-3.30 (m, 2 H, CH₂^{10-14, 17, 22}, CH¹⁸⁻²¹), 1.79-1.73 (m, 4 H, CH₂^{2,2'}), 1.49-1.40 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 16 H, CH₂^{4-7, 4'-7'}), 0.89-0.84 (m, 6 H, CH₃^{8,8'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.9 (C¹⁶), 158.8 (C^d), 158.1 (C^{d''}), 155.7 (C^{e'}), 140.9 (C^{a'}), 133.0 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.1 (C^a), 127.9 (C^{b',f'}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.7 (C^{f'}), 73.1, 72.9, 72.0, 70.0 (C¹⁸⁻²¹), 71.0, 70.7, 70.5, 70.1 (C¹¹⁻¹⁵), 69.7 (C¹⁰), 68.6 (C⁹), 68.2, 68.1 (C^{1,1'}), 63.9 (C²²), 42.4 (C¹⁷), 32.0, 31.9 (C^{6,6'}), 31.0, 29.6, 29.5, 29.4, 29.4, 29.4 (C^{2,4,5,2',4',5'}), 26.2, 26.2 (C^{3,3'}), 22.8 (C^{7,7'}), 14.2 (C^{8,8'}). EA: C₄₈H₇₃O₁₂N·0.5H₂O (Cal.) C: 66.64 %, H: 8.62 %, N:1.62 %, (Found) C: 66.68 %, H: 8.69 %, N:1.64 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-11-(4,4''-dihexadecyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9-trioxaundecanoylamide (**A16/3**):

Reagents: **H16/3** (0.40 g, 0.44 mmol)

Dry THF (50 mL)

DCC (99 mg, 0.48 mmol)

Pentafluorophenol (97 mg, 0.53 mmol)

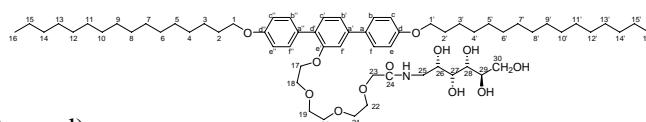
1-Amino-1-deoxy-D-sorbitol (0.40 g, 2.2 mmol)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.18 g (38.2 %), colorless solid

Analytical data: C₆₄H₁₀₅O₁₂N M_w = 1080.52

¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 7.59 (t, ³*J*(H,H) = 6.0, 1 H, NH), 7.53-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.33 (d, ³*J*(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.20 (dd, ³*J*(H,H) = 7.9, ⁴*J*(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.13 (d, ⁴*J*(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.96-6.89 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.17 (t, 2 H, ³*J*(H,H) = 4.5, CH₂¹⁷), 4.00-3.94 (m, 6 H, CH₂^{1,1',23}), 3.80 (t, ³*J*(H,H) = 4.5, 2 H, CH₂¹⁸), 3.70-3.53 (m, 16 H, CH₂^{19-22, 25, 30, 26-29}), 3.50-3.35 (m, 2 H, OH), 1.82-1.75 (m, 4 H, CH₂^{2,2'}), 1.47-1.42 (m, 4 H, CH₂^{3,3''}), 1.41-1.20 (m, 48 H, CH₂^{4-15, 4'-15'}), 0.88-0.84 (m, 6 H, CH₃^{16,16'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 182.5 (C²⁴), 158.8 (C^d), 158.1 (C^{d''}), 155.7 (C^{e'}), 141.0 (C^{a'}), 133.0 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 129.1 (C^a), 127.9 (C^{b',f'}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.0 (C^{c,e}), 111.7 (C^{f'}), 73.2, 72.1, 70.0 (C²⁶⁻²⁹), 71.1, 70.7, 70.5, 70.1 (C¹⁹⁻²³), 69.8 (C¹⁸), 68.6 (C¹⁷), 68.2, 68.2 (C^{1,1'}), 64.0 (C³⁰), 42.5 (C²⁵), 32.0 (C^{14,14'}), 29.8, 29.7, 29.7, 29.5, 29.5, 29.4 (C^{2,4-13,2',4'-13'}), 26.2, 26.2 (C^{3,3'}), 22.8 (C^{15,15'}), 14.2 (C^{16,16'}). EA: C₆₄H₁₀₅NO₁₂·0.5H₂O (Cal.) C: 70.55 %, H: 9.81 %, N:1.29 %, (Found) C: 70.38 %, H: 9.57 %, N:1.42 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-(4,4''-dihexadecyloxy-*p*-terphenyl-2'-yl-oxy)-3,6,9,12-tetraoxatetradecanoylamide (**A16/4**):

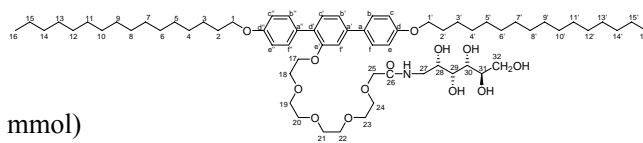
Reagents: **H16/4** (0.40 g, 0.42 mmol)

Dry THF (50 mL)

DCC (0.10 g, 0.48 mmol)

Pentafluorophenol (0.10 g, 0.54 mmol)

1-Amino-1-deoxy-D-sorbitol (0.5 g, 2.8 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.13 g (27.7 %), colorless solid

Analytical data: C₆₆H₁₀₉O₁₃N

M_w = 1124.57

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.70 (t, ³J(H,H) = 6.0, 1 H, NH), 7.53-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.33 (d, ³J(H,H) = 8.1, 1 H, Ar-H^{c'}), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{f'}), 6.96-6.89 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.16 (t, 2 H, ³J(H,H) = 4.5, CH₂¹⁷), 4.00-3.95 (m, 6 H, CH₂^{1, 1', 25}), 3.78 (t, ³J(H,H) = 4.5, 2 H, CH₂¹⁸), 3.75-3.35 (m, 16 H, CH₂^{19-24, 27, 32, 28-21}), 1.82-1.75 (m, 4 H, CH₂^{2, 2'}), 1.47-1.42 (m, 4 H, CH₂^{3, 3'}), 1.41-1.20 (m, 48 H, CH₂^{4-15, 4'-15'}), 0.88-0.84 (m, 6 H, CH₃^{16, 16'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 172.0 (C²⁶), 158.8 (C^d), 158.1 (C^{d''}), 155.8 (C^{e'}), 140.9 (C^{a'}), 133.0 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b, f}), 130.4 (C^{a''}), 129.0 (C^a), 127.9 (C^{b, f''}), 119.7 (C^{b'}), 114.8 (C^{c'', e''}), 114.0 (C^{c, e}), 111.6 (C^{f'}), 73.1, 73.0, 72.1, 70.0 (C²⁸⁻³¹), 71.0, 70.8, 70.5, 70.4, 70.3, 70.2, 70.1 (C¹⁹⁻²⁵), 69.8 (C¹⁸), 68.5 (C¹⁷), 68.2, 68.2 (C^{1, 1'}), 42.3 (C²⁷), 32.0 (C^{14, 14'}), 29.8, 29.7, 29.7, 29.5, 29.5, 29.4 (C^{2, 4-13, 2', 4'-13'}), 26.2, 26.2 (C^{3, 3'}), 22.8 (C^{15, 15'}), 14.2 (C^{16, 16'}). EA: C₆₆H₁₀₉NO₁₃·H₂O (Cal.) C: 69.38 %, H: 9.79 %, N:1.23 %, (Found) C: 69.51 %, H: 9.52 %, N:1.30 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-11-(4,4''-didecyloxy-*p*-terphenyl-3-yl-oxy)-3,6,9-trioxaundecanoylamide (**A*10/3**):

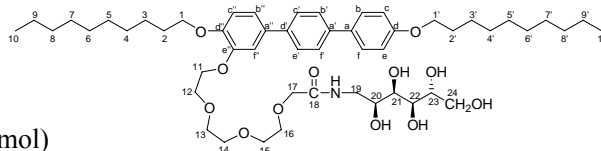
Reagents: **H*10/3** (0.40 g, 0.53 mmol)

Dry THF (50 mL)

DCC (132 mg, 0.64 mmol)

Pentafluorophenol (118 mg, 0.64 mmol)

1-Amino-1-deoxy-D-sorbitol (0.5 g, 2.8 mmol)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.11 g (22.5 %), colorless solid

Analytical data: C₅₂H₈₁O₁₂N

M_w = 912.20

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.66 (t, ³J(H,H) = 6.0, 1 H, NH), 7.57 (s, 4 H, Ar-H^{b, f, c', e'}), 7.55-7.51 (m, 2 H, Ar-H^{b, f}), 7.20-7.15 (m, 2 H, Ar-H^{b'', f''}), 6.97-6.92 (m, 3 H, Ar-H^{c, e, c''}), 4.23 (t, ³J(H,H) = 4.7, 2 H, CH₂¹¹), 4.08-3.95 (m, 6 H, CH₂^{1, 1', 17}), 3.88 (t, ³J(H,H) = 4.7, 2 H, CH₂¹²), 3.80-3.28 (m, 16 H, CH₂^{13-16, 19, 24, CH₂²¹⁻²³), 1.83-1.77 (m, 4 H, CH₂^{2, 2'}), 1.49-1.41 (m, 4 H, CH₂^{3, 3'}), 1.39-1.20 (m, 24 H, CH₂^{4-9, 4'-9'}), 0.89-0.85 (m, 6 H, CH₃^{10, 10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 172.0 (C¹⁸), 158.7 (C^d), 148.9, 148.5 (C^{d'', e''}), 139.3, 138.9 (C^{a', d'}), 133.8, 132.9 (C^{a, a''}), 127.8 (C^{b, f}), 127.0, 126.9 (C^{b', c', e', f'}), 120.4 (C^{b''}), 114.8 (C^{c, e}), 114.3, 114.0 (C^{c'', f''}), 73.1, 73.0, 72.1, 70.0 (C²⁰⁻²³), 71.1, 70.7, 70.6, 70.2, 69.9 (C¹³⁻¹⁷), 69.5 (C¹²), 69.3 (C¹¹), 68.2 (C^{1, 1'}), 64.0 (C²⁴), 42.4 (C¹⁹), 32.0 (C^{8, 8'}), 29.7, 29.7, 29.7, 29.5, 29.4 (C^{2, 4-7, 2', 4'-7'}), 26.2, 26.1 (C^{3, 3'}), 22.8, (C^{9, 9'}), 14.2 (C^{10, 10'}). EA: C₅₂H₈₁NO₁₂·0.5H₂O (Cal.) C: 67.79 %, H: 8.97 %, N:1.52 %, (Found) C: 67.48 %, H: 8.97 %, N:1.40 %.}

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-(4,4''-dihexadecyloxy-*p*-terphenyl-3-yloxy)]-3,6,9,12-tetraoxatetradecanoylamide (**A*10/4**):

Reagents: **H*10/4** (0.45 g, 0.57 mmol)

Dry THF (50 mL)

DCC (140 mg, 0.68 mmol)

Pentafluorophenol (126 mg, 0.68 mmol)

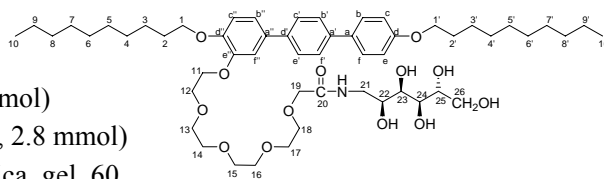
1-Amino-1-deoxy-D-sorbitol (0.5 g, 2.8 mmol)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.11 g (22.5 %), colorless solid

Analytical data: C₅₄H₈₅O₁₃N M_w = 956.25

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.66 (t, ³J(H,H) = 6.0, 1 H, NH), 7.57 (s, 4 H, Ar-H^{b', f', c', e'}), 7.55-7.51 (m, 2 H, Ar-H^{b, f}), 7.20-7.15 (m, 2 H, Ar-H^{b'', f''}), 6.97-6.92 (m, 3 H, Ar-H^{c, e, c''}), 4.23 (t, ³J(H,H) = 4.7, 2 H, CH₂¹¹), 4.02-3.95 (m, 6 H, CH₂^{1,1',19}), 3.88 (t, ³J(H,H) = 4.7, 2 H, CH₂¹²), 3.80-3.28 (m, 20 H, CH₂^{13-18, 21, 26}, CH²³⁻²⁵), 1.83-1.77 (m, 4 H, CH₂^{2,2'}), 1.49-1.41 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 24 H, CH₂^{4-9,4'-9'}), 0.89-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.9 (C²⁰), 158.7 (C^d), 148.9, 148.6 (C^{d'', e''}), 139.2, 138.9 (C^{a', d'}), 133.8, 132.9 (C^{a, a''}), 127.8 (C^{b, f}), 126.9, 126.8 (C^{b', c', e', f'}), 120.2 (C^{b''}), 114.8 (C^{c, e}), 114.2, 114.1 (C^{c'', f''}), 73.1, 72.9, 72.1, 70.0 (C²²⁻²⁵), 71.0, 70.8, 70.5, 70.4, 70.5, 70.1, 69.9 (C¹³⁻¹⁹), 69.5 (C¹²), 69.3 (C¹¹), 68.2 (C^{1,1'}), 64.0 (C²⁶), 42.4 (C²¹), 32.0 (C^{8, 8'}), 29.7, 29.7, 29.6, 29.5, 29.5, 29.4 (C^{2, 4-7, 2', 4'-7'}), 26.2, 26.1 (C^{3, 3'}), 22.8, (C^{9, 9'}), 14.2 (C^{10, 10'}). EA: C₅₄H₈₅NO₁₃ (Cal.) C: 67.82 %, H: 8.96 %, N:1.46 %, (Found) C: 67.57 %, H: 8.67 %, N:1.29 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-pentahydroxyhexyl]-11-(4-hexyloxy-4''-hexadecyloxy-*p*-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoylamide (**A6.16/3**):

Prepared according to the general procedure 8.2.12

Reagents: **H6.16/3** (0.15 g, 0.19 mmol)

Dry THF (50 mL)

DCC (43 mg, 0.21 mmol)

Pentafluorophenol (42 mg, 0.23 mmol)

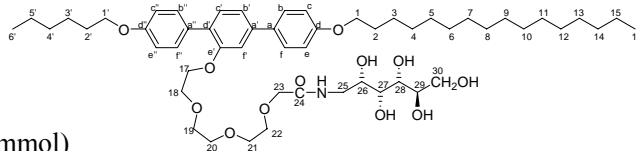
1-Amino-1-deoxy-D-sorbitol (0.24 g, 1.3 mmol)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.09 g (49.5 %), colorless solid

Analytical data: C₅₄H₈₅O₁₂N M_w = 940.25

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.57 (bs, 1 H, NH), 7.50-7.47 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.29 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.16 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.5, 1 H, Ar-H^{b'}), 7.10 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{f'}), 6.93-6.87 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.43 (bs, 3 H, OH), 4.11 (t, ³J(H,H) = 4.5, 2 H, CH₂¹⁷), 3.96-3.90 (m, 6 H, CH₂^{1,1',23}), 3.74 (t, ³J(H,H) = 4.5, 2 H, CH₂¹⁸), 3.72-3.28 (m, 16 H, CH₂^{19-22, 25, 30}, CH²⁶⁻²⁹), 1.82-1.76 (m, 4 H, CH₂^{2, 2'}), 1.49-1.41 (m, 4 H, CH₂^{3, 3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15,4'-5'}), 0.89-0.86 (m, 6 H, CH₃^{16, 6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.7 (C²⁴), 158.8 (C^d), 158.1 (C^{d''}), 155.8 (C^{c'}), 140.8 (C^{a'}), 133.0 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b, f}), 130.4 (C^{a''}), 129.0 (C^a), 127.9 (C^{b'', f''}), 119.6 (C^{b'}), 114.8 (C^{c'', e''}), 113.9 (C^{c, e}), 111.7 (C^{f'}), 72.8, 72.3, 71.8, 70.1 (C²⁶⁻²⁹), 70.8, 70.6, 70.4, 70.0, (C¹⁹⁻²³), 69.6 (C¹⁸), 68.4 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 63.8 (C³⁰), 42.0 (C²⁵), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.6, 29.6, 29.5, 29.3 29.3 (C^{2, 4-13, 2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7 (C¹⁵), 22.6 (C^{5'}), 14.1 (C¹⁶), 14.0 (C^{6'}). EA: C₅₄H₈₅NO₁₂·0.7H₂O (Cal.) C: 68.07 %, H: 9.14 %, N:1.47 %, (Found) C: 68.06 %, H: 9.22 %, N:1.54 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-(4-hexyloxy-4''-hexadecyloxy-*p*-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoylamide (**A6.16/4**):

Reagents: **H6.16/4** (0.25 g, 0.30 mmol)

Dry THF (50 mL)

DCC (68 mg, 0.33 mmol)

Pentafluorophenol (66 mg, 0.36 mmol)

1-Amino-1-deoxy-D-sorbitol (0.27 g, 1.5 mmol)

Purification: column chromatography with silica gel 60,

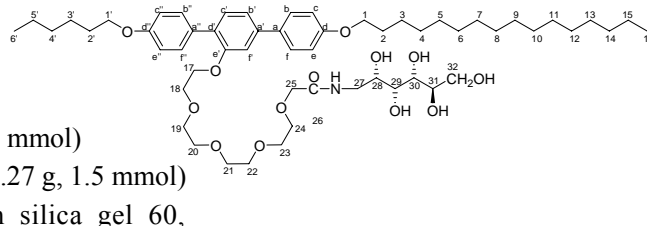
eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.15 g (49.5 %), colorless solid

Analytical data: C₅₆H₈₉O₁₃N

M_w = 984.30

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.63 (bs, 1 H, NH), 7.52-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.3, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.3, 1 H, Ar-H^{f'}), 6.95-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.58 (bs, 3 H, OH), 4.13 (t, ³J(H,H) = 4.6, 2 H, CH₂¹⁷), 3.98-3.90 (m, 6 H, CH₂^{1, 1', 25}), 3.80-3.28 (m, 22 H, CH₂^{18-24, 27, 32}, CH²⁸⁻³¹), 1.82-1.74 (m, 4 H, CH₂^{2, 2'}), 1.48-1.41 (m, 4 H, CH₂^{3, 3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15, 4', 5'}), 0.93-0.86 (m, 6 H, CH₃^{16, 6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.6 (C²⁶), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.7 (C^{a'}), 133.0 (C^{a''}), 130.7 (C^{c'}), 130.4 (C^{b, f}), 130.3 (C^{a''}), 128.9 (C^a), 127.8 (C^{b'', f''}), 119.5 (C^{b'}), 114.7 (C^{c'', e''}), 113.8 (C^{c, e}), 111.4 (C^{f'}), 72.7, 72.1, 71.7, 70.2 (C²⁸⁻³¹), 70.8, 70.7, 70.3, 70.2, 70.2, 70.1, 70.0 (C¹⁹⁻²⁵), 69.6 (C¹⁸), 68.3 (C¹⁷), 68.0, 67.9 (C^{1, 1'}), 63.7 (C³²), 42.0 (C²⁷), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3 (C^{2, 4-13, 2'}), 26.0 (C³), 25.7 (C^{3'}), 22.6 (C¹⁵), 22.5 (C^{5'}), 14.0, 14.0 (C^{16, 6'}). EA: C₅₆H₈₉NO₁₃·0.5H₂O (Cal.) C: 67.71 %, H: 9.13 %, N:1.41 %, (Found) C: 67.72 %, H: 8.88 %, N:1.45 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-pentahydroxyhexyl]-20-(4-hexyloxy-4''-hexadecyloxy-*p*-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaecicosanoylamide (**A6.16/6**):

Reagents: **H6.16/6** (0.25 g, 0.28 mmol)

Dry THF (50 mL)

DCC (64 mg, 0.31 mmol)

Pentafluorophenol (63 mg, 0.34 mmol)

1-Amino-1-deoxy-D-sorbitol (0.25 g, 1.4 mmol)

Purification: Column chromatography with silica gel 60,

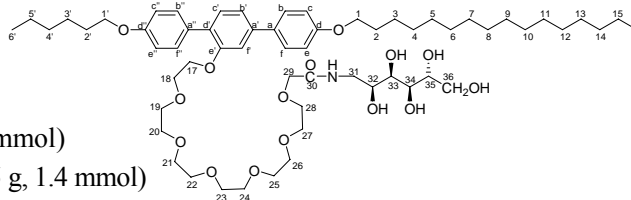
eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.13 g (44.0 %), colorless solid

Analytical data: C₆₀H₉₇O₁₅N

M_w = 1072.41

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.69 (bs, 1 H, NH), 7.52-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{c'}), 7.16 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.3, 1 H, Ar-H^{b'}), 7.12 (d, ⁴J(H,H) = 1.3, 1 H, Ar-H^{f'}), 6.92-6.88 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.71 (bs, 3 H, OH), 4.13 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 3.97-3.87 (m, 6 H, CH₂^{1, 1', 29}), 3.77-3.43 (m, 30 H, CH₂^{18-28, 31, 36}, CH³²⁻³⁵), 1.82-1.74 (m, 4 H, CH₂^{2, 2'}), 1.48-1.41 (m, 4 H, CH₂^{3, 3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15, 4', 5'}), 0.93-0.83 (m, 6 H, CH₃^{16, 6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.4 (C³⁰), 158.6 (C^d), 157.9 (C^{d''}), 155.7 (C^{e'}), 140.6 (C^{a'}), 132.9 (C^{a''}), 130.6 (C^{c'}), 130.3 (C^{b, f}), 130.2 (C^{a''}), 128.8 (C^a), 127.7 (C^{b'', f''}), 119.4 (C^{b'}), 114.6 (C^{c'', e''}), 113.7 (C^{c, e}), 111.3 (C^{f'}), 72.4, 71.8, 71.6 (C³²⁻³⁵), 70.6, 70.6, 70.3, 70.3, 70.2, 70.2, 70.1, 69.9 (C¹⁹⁻²⁹), 69.5 (C¹⁸), 68.1 (C¹⁷), 67.9, 67.8 (C^{1, 1'}), 63.6 (C³⁶), 41.9 (C³¹), 31.8 (C¹⁴), 31.5 (C^{4'}), 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2 (C^{2, 4-13, 2'}), 25.9 (C³), 25.6 (C^{3'}), 22.5, 22.5 (C^{15, 5'}), 14.0 (C¹⁶), 13.9 (C^{6'}). EA: C₆₀H₉₇NO₁₅·H₂O (Cal.) C: 66.09 %, H: 9.15 %, N:1.28 %, (Found) C: 66.18 %, H: 8.55 %, N:1.18 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-11-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoylamide (**A16.6/3**):

Reagents: **H16.6/3** (0.15 g, 0.19 mmol)

Dry THF (50 mL)

DCC (43 mg, 0.21 mmol)

Pentafluorophenol (42 mg, 0.23 mmol)

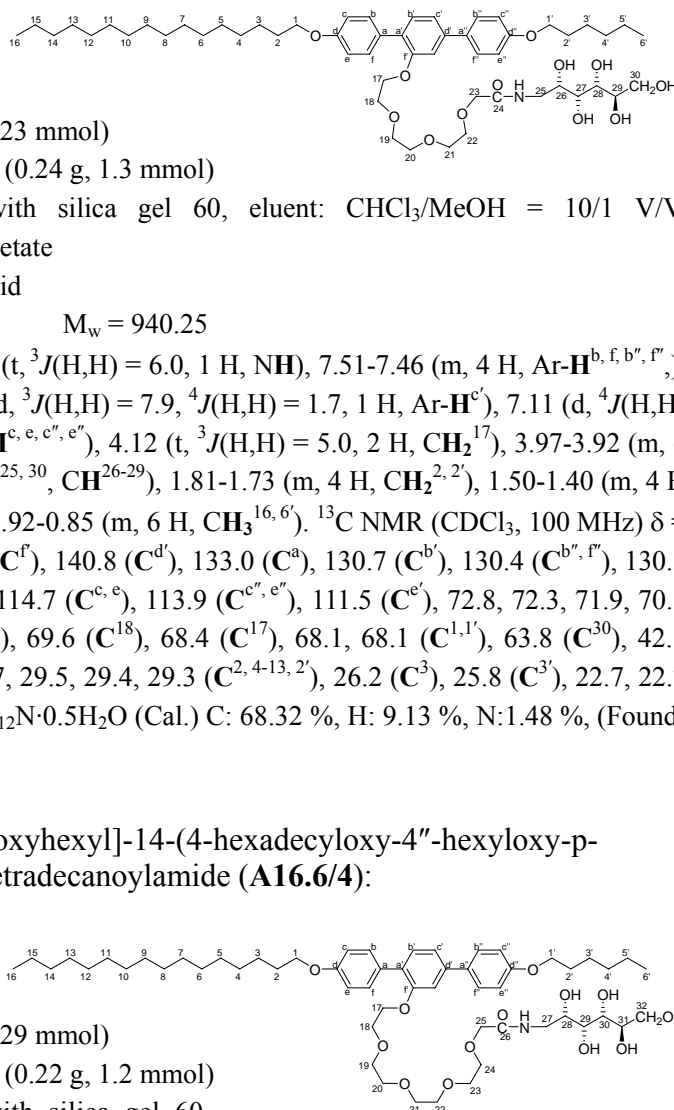
1-Amino-1-deoxy-D-sorbitol (0.24 g, 1.3 mmol)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 89 mg (49.0 %), colorless solid

Analytical data: C₅₄H₈₅O₁₂N M_w = 940.25

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.58 (t, ³J(H,H) = 6.0, 1 H, NH), 7.51-7.46 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.30 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{b'}), 7.16 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H^{c'}), 7.11 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H^{e'}), 6.93-6.86 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.12 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 3.97-3.92 (m, 6 H, CH₂^{1,1',23}), 3.82-3.34 (m, 18 H, CH₂^{18-22,25,30}, CH²⁶⁻²⁹), 1.81-1.73 (m, 4 H, CH₂^{2,2'}), 1.50-1.40 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.92-0.85 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.6 (C²⁶), 158.7 (C^{d''}), 158.0 (C^d), 155.7 (C^{f'}), 140.8 (C^{d'}), 133.0 (C^a), 130.7 (C^{b'}), 130.4 (C^{b'',f''}), 130.3 (C^a), 129.0 (C^{a''}), 127.8 (C^{b,f}), 119.6 (C^{c'}), 114.7 (C^{c,e}), 113.9 (C^{c'',e''}), 111.5 (C^{e'}), 72.8, 72.3, 71.9, 70.1 (C²⁶⁻²⁹), 70.9, 70.7, 70.4, 70.2, 70.1 (C¹⁹⁻²³), 69.6 (C¹⁸), 68.4 (C¹⁷), 68.1, 68.1 (C^{1,1'}), 63.8 (C³⁰), 42.1 (C²⁵), 32.0 (C¹⁴), 31.7 (C^{4'}), 29.8, 29.7, 29.7, 29.5, 29.4, 29.3 (C^{2,4-13,2'}), 26.2 (C³), 25.8 (C^{3'}), 22.7, 22.7 (C^{15,5'}), 14.2 (C¹⁶), 14.1 (C^{6'}). EA: C₅₄H₈₅O₁₂N·0.5H₂O (Cal.) C: 68.32 %, H: 9.13 %, N:1.48 %, (Found) C: 68.41 %, H: 9.20 %, N:1.40 %.



N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-14-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoylamide (**A16.6/4**):

Reagents: **H16.6/4** (0.20 g, 0.24 mmol)

Dry THF (50 mL)

DCC (54 mg, 0.26 mmol)

Pentafluorophenol (54 mg, 0.29 mmol)

1-Amino-1-deoxy-D-sorbitol (0.22 g, 1.2 mmol)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.10 g (41.7 %), colorless solid

Analytical data: C₅₆H₈₉O₁₃N M_w = 984.30

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.62 (t, ³J(H,H) = 6.0, 1 H, NH), 7.51-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³J(H,H) = 7.9, 1 H, Ar-H^{b'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.5, 1 H, Ar-H^{c'}), 7.12 (d, ⁴J(H,H) = 1.5, 1 H, Ar-H^{e'}), 6.95-6.87 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.45 (bs, 3 H, OH), 4.13 (t, ³J(H,H) = 5.0, 2 H, CH₂¹⁷), 3.98-3.93 (m, 6 H, CH₂^{1,1',25}), 3.80-3.45 (m, 22 H, CH₂^{18-24,27,32}, CH²⁸⁻³¹), 1.82-1.74 (m, 4 H, CH₂^{2,2'}), 1.50-1.42 (m, 4 H, CH₂^{3,3'}), 1.40-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.92-0.83 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.6 (C²⁶), 158.7 (C^{d''}), 158.1 (C^d), 155.8 (C^{f'}), 140.8 (C^{d'}), 133.0 (C^a), 130.7 (C^{b'}), 130.5 (C^{b'',f''}), 130.3 (C^a), 128.9 (C^{a''}), 127.9 (C^{b,f}), 119.6 (C^{c'}), 114.7 (C^{c,e}), 113.9 (C^{c'',e''}), 111.5 (C^{e'}), 72.7, 72.2, 71.8, 70.0 (C²⁸⁻³¹), 70.8, 70.7, 70.4, 70.3, 70.0 (C¹⁹⁻²⁵), 69.6 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 63.9 (C³²), 42.0 (C²⁷), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.6, 29.6, 29.4, 29.3, 29.3 (C^{2,4-13,2'}), 26.1 (C³), 25.7 (C^{3'}), 22.7, 22.6 (C^{15,5'}), 14.1 (C¹⁶), 14.0 (C^{6'}). EA: C₅₆H₈₉O₁₃N·H₂O (Cal.) C: 67.10 %, H: 9.15 %, N:1.40 %, (Found) C: 67.34 %, H: 9.28 %, N:1.36 %.

N-[(2*S*,3*R*,4*R*,5*R*)-2,3,4,5,6-Pentahydroxyhexyl]-20-(4-hexadecyloxy-4''-hexyloxy-*p*-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoylamide (**A16.6/6**):

Reagents: **H16.6/6** (0.30 g, 0.33 mmol)

Dry THF (50 mL)

DCC (74 mg, 0.36 mmol)

Pentafluorophenol (74 mg, 0.40 mmol)

1-Amino-1-deoxy-D-sorbitol (0.31 g, 1.7 mmol)

Purification: Column chromatography with silica gel 60,

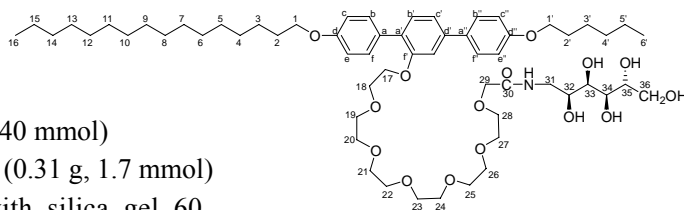
eluent: CHCl₃/MeOH = 10/1 V/V, recrystallization from ethyl acetate

Yield: 0.16 g (45.2 %), colorless solid

Analytical data: C₆₀H₉₇O₁₅N

M_w = 1072.41

¹H NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 7.62 (t, ³*J*(H,H) = 6.0, 1 H, NH), 7.52-7.48 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.31 (d, ³*J*(H,H) = 7.8, 1 H, Ar-H^{b'}), 7.17 (dd, ³*J*(H,H) = 7.8, ⁴*J*(H,H) = 1.7, 1 H, Ar-H^{c'}), 7.12 (d, ⁴*J*(H,H) = 1.7, 1 H, Ar-H^{c''}), 6.95-6.87 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.14 (t, ³*J*(H,H) = 4.9, 2 H, CH₂¹⁷), 4.00-3.94 (m, 6 H, CH₂^{1,1',29}), 3.83-3.34 (m, 30 H, CH₂^{18-28,31,36}, CH³²⁻³⁵), 1.81-1.73 (m, 4 H, CH₂^{2,2'}), 1.48-1.40 (m, 4 H, CH₂^{3,3'}), 1.39-1.20 (m, 28 H, CH₂^{4-15,4',5'}), 0.92-0.83 (m, 6 H, CH₃^{16,6'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 171.4 (C²⁶), 158.6 (C^{d''}), 158.0 (C^d), 155.8 (C^f), 140.7 (C^{d'}), 133.0 (C^a), 130.7 (C^{b'}), 130.4 (C^{b'',f''}), 130.3 (C^a), 128.9 (C^{a''}), 127.8 (C^{b,f}), 119.5 (C^{c'}), 114.7 (C^{c,e}), 113.8 (C^{c'',e''}), 111.5 (C^{e'}), 72.8, 72.2, 71.8, 70.1 (C³²⁻³⁵), 70.9, 70.7, 70.5, 70.4, 70.4, 70.3, 70.2, 70.1 (C¹⁹⁻²⁹), 69.6 (C¹⁸), 68.3 (C¹⁷), 68.1, 68.0 (C^{1,1'}), 63.8 (C³⁶), 42.0 (C³¹), 31.9 (C¹⁴), 31.6 (C^{4'}), 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 (C^{2,4-13,2'}), 26.1 (C³), 25.8 (C^{3'}), 22.7, 22.6 (C^{15,5'}), 14.1, 14.1 (C^{16,6'}). EA: C₆₀H₉₇O₁₅N·1.5H₂O (Cal.) C: 65.55 %, H: 9.17 %, N:1.27 %, (Found) C: 65.64 %, H: 8.94 %, N:1.31 %.



8.2.4 Alkali metal and alkali earth metal carboxylates (Li10/n, K10/n, Csm/n and Ba10/n)

General procedure: The appropriate carboxylic acid **Hm/n** (2 mmol) was dissolved in diethyl ether (50 mL), then the metal hydroxide [LiOH: 2 mmol, KOH: 2 mmol, Ba(OH)₂: 1 mmol] or cesium carbonate (1 mmol) which was dissolved in water (2 mL) was added, the salt was precipitated as soon as the base was added (in most cases, stirring was avoided, because after stirring the solid becomes too finely distributed to be filtered), the reaction mixture was, then, kept at r.t. over night to complete the reaction. After that, the solid was filtered off and washed with water and dried in air, the crude product was purified by recrystallization from ethyl acetate.

Cesium 14-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Cs6/4**):

Reagents: **H6/4** (0.26 g, 0.38 mmol)

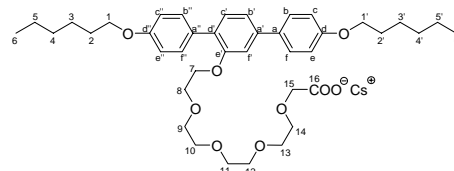
CS₂CO₃ (66 mg, 0.19 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.13 g (41.7 %), colorless waxy solid

Analytical data: C₄₀H₅₅O₉Cs M_w = 812.76

¹H NMR (CDCl₃, J/Hz, 500 MHz) δ = 7.51-7.43 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.27 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{c'}), 7.14 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H**^{b'}), 7.11 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H**^{f'}), 6.93-6.85 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.13 (t, ³J(H,H) = 4.8, 2 H, CH₂⁷), 4.00-3.91 (m, 2 H, CH₂^{1,1'}), 3.76 (s, 2 H, CH₂¹⁵), 3.73 (t, ³J(H,H) = 4.8, 2 H, CH₂⁸), 3.54-3.43 (m, 12 H, CH₂⁹⁻¹⁴), 1.80-1.71 (m, 4 H, CH₂^{2,2'}), 1.47-1.40 (m, 4 H, CH₂^{3,3'}), 1.38-1.28 (m, 8 H, CH₂^{4,5,4',5'}), 0.91-0.87 (m, 6 H, CH₃^{6,6'}). ¹³C NMR (CDCl₃, 125 MHz) δ = 174.5 (C¹⁶), 158.7 (C^d), 158.1 (C^{d''}), 155.7 (C^{e'}), 140.8 (C^{a'}), 132.9 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b,f}), 130.4 (C^{a''}), 128.8 (C^a), 127.9 (C^{b',f'}), 119.5 (C^{b'}), 114.7 (C^{c'',e''}), 113.9 (C^{c,e}), 111.5 (C^{f'}), 71.7, 70.5, 70.3, 70.1, 70.0, 69.8, 69.3 (C⁹⁻¹⁵), 69.1 (C⁸), 68.5 (C⁷), 68.1, 68.0 (C^{1,1'}), 31.6, 31.6 (C^{4,4'}), 29.3, 29.2 (C^{2,2'}), 25.7 (C^{3,3'}), 22.6 (C^{5,5'}), 14.0 (C^{6,6'}). EA: C₄₀H₅₅O₉Cs·2H₂O (Cal.) C: 56.60 %, H: 7.01 %, (Found) C: 56.63 %, H: 6.92 %.



Cesium 8-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoate (**Cs10/2**):

Reagents: **H10/2** (0.40 g, 0.57 mmol)

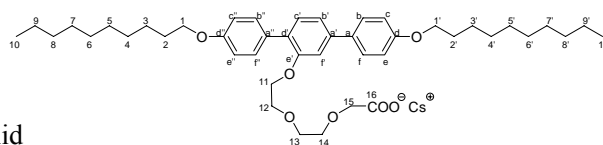
CS₂CO₃ (93 mg, 0.28 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.15 g (31.6 %), colorless waxy solid

Analytical data: C₄₄H₆₃O₇Cs M_w = 836.87

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.46-7.33 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.22 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{c'}), 7.11 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{b'}), 7.04 (s, 1 H, Ar-**H**^{f'}), 6.89-6.82 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.05-3.98 (m, 2 H, CH₂¹¹), 3.92-3.85 (m, 6 H, CH₂^{1,1'}), 3.71 (s, 2 H, CH₂¹⁵), 3.65-3.58 (m, 2 H, CH₂¹²), 3.46-3.34 (m, 4 H, CH₂^{13,14}), 1.76-1.66 (m, 4 H, CH₂^{2,2'}), 1.45-1.28 (m, 28 H, CH₂^{3-9,3'-9'}), 0.89-0.83 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.0 (C¹⁶), 158.8 (C^d), 158.2 (C^{d''}), 155.5 (C^{e'}), 140.9 (C^{a'}), 132.8 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b,f}), 130.2 (C^{a''}), 128.7 (C^a), 127.9 (C^{b',f'}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.2 (C^{c,e}), 111.5 (C^{f'}), 71.4, 70.6 (C¹³⁻¹⁵), 69.3 (C¹²), 68.3 (C¹¹), 68.1 (C^{1,1'}), 32.0 (C^{8,8'}), 29.7, 29.6, 29.6, 29.4 (C^{2,4-7,2',4'-7'}), 26.2 (C^{3,3'}), 22.8 (C^{9,9'}), 14.2 (C^{10,10'}). EA: C₄₄H₆₃O₇Cs·3.5H₂O (Cal.) C: 58.72 %, H: 7.84 %, (Found) C: 58.72 %, H: 7.70 %.



Lithium 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Li10/3**):Reagents: **H10/3** (0.47 g, 0.63 mmol)

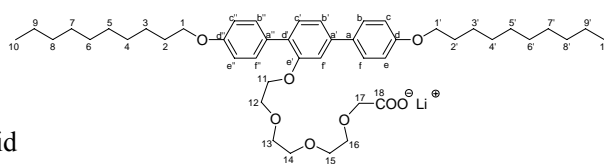
LiOH (15 mg, 0.63 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.23 g (48.6 %), colorless waxy solid

Analytical data: C₄₆H₆₇O₈Li M_w = 754.96

¹H NMR (CDCl₃, J/Hz, 500 MHz) δ = 7.48-7.44 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.27 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{c'}), 7.13 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{b'}), 7.08 (s, 1 H, Ar-**H**^{f'}), 6.91-6.84 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.07 (t, ³J(H,H) = 4.5, 2 H, CH₂¹¹), 3.94-3.90 (m, 4 H, CH₂^{1,1'}), 3.82 (s, 2 H, CH₂¹⁷), 3.73-3.64 (m, 2 H, CH₂¹²), 3.55-3.43 (m, 8 H, CH₂¹³⁻¹⁶), 1.78-1.70 (m, 4 H, CH₂^{2,2'}), 1.42-1.22 (m, 28 H, CH₂^{3-9,3'-9'}), 0.88-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 125 MHz) δ = 175.9 (C¹⁸), 158.8 (C^d), 158.1 (C^{d''}), 155.9 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.8 (C^{c'}), 130.5 (C^{b, f}), 130.4 (C^{a''}), 128.9 (C^a), 127.9 (C^{b', f'}), 119.5 (C^{b'}), 114.8 (C^{c'', e''}), 113.9 (C^{c, e}), 111.3 (C^{f'}), 70.9, 70.5, 69.9, 69.6 (C¹³⁻¹⁷), 68.9 (C¹²), 68.4 (C¹¹), 68.1, 68.0 (C^{1,1'}), 31.9 (C^{8,8'}), 29.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, (C^{2, 4-7, 2', 4'-7'}), 26.1, 26.1 (C^{3,3'}), 22.7 (C^{9,9'}), 14.1 (C^{10,10'}). EA: C₄₆H₆₇O₈Li·0.5H₂O (Cal.) C: 72.32 %, H: 8.97 %, (Found) C: 72.33 %, H: 9.08 %.

Potassium 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**K10/3**):Reagents: **H10/3** (0.47 g, 0.63 mmol)

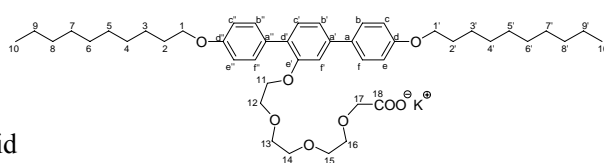
KOH (35 mg, 0.63 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.20 g (40.5 %), colorless waxy solid

Analytical data: C₄₆H₆₇O₈K M_w = 787.12

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.47-7.39 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.24 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{c'}), 7.11 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.6, 1 H, Ar-**H**^{b'}), 7.06 (d, ⁴J(H,H) = 1.6, 1 H, Ar-**H**^{f'}), 6.89-6.81 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.06 (t, ³J(H,H) = 4.5, 2 H, CH₂¹¹), 3.92-3.88 (m, 4 H, CH₂^{1,1'}), 3.72 (s, 2 H, CH₂¹⁷), 3.69 (t, ³J(H,H) = 4.5, 2 H, CH₂¹²), 3.46-3.36 (m, 8 H, CH₂¹³⁻¹⁶), 1.78-1.70 (m, 4 H, CH₂^{2,2'}), 1.42-1.22 (m, 28 H, CH₂^{3-9,3'-9'}), 0.88-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.7 (C¹⁸), 159.3 (C^d), 158.6 (C^{d''}), 156.3 (C^{e'}), 141.3 (C^{a'}), 133.5 (C^{a''}), 131.3 (C^{c'}), 131.0 (C^{b, f}), 130.9 (C^{a''}), 129.4 (C^a), 128.4 (C^{b', f'}), 120.0 (C^{b'}), 115.2 (C^{c'', e''}), 114.4 (C^{c, e}), 111.9 (C^{f'}), 71.8, 70.9, 70.5, 70.4, 69.9 (C¹³⁻¹⁷), 69.5 (C¹²), 69.2 (C¹¹), 68.6, 68.5 (C^{1,1'}), 32.4 (C^{8,8'}), 30.2, 30.1, 30.0, 30.0, 29.9, 29.9, 29.9 (C^{2, 4-7, 2', 4'-7'}), 26.7, 26.6 (C^{3,3'}), 23.2 (C^{9,9'}), 14.6 (C^{10,10'}). EA: C₄₆H₆₇O₈K·2H₂O (Cal.) C: 67.12 %, H: 8.69 %, (Found) C: 67.39 %, H: 8.66 %.

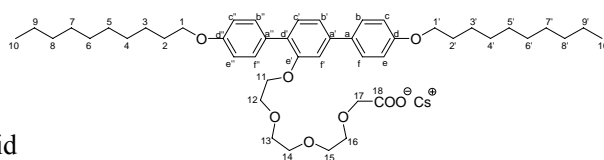
Cesium 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Cs10/3**):Reagents: **H10/3** (0.25 g, 0.33 mmol)Cs₂CO₃ (54 mg, 0.17 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.14 g (47.6 %), colorless waxy solid

Analytical data: C₄₆H₆₇O₈Cs M_w = 880.92

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.52-7.43 (m, 4 H, Ar-**H**^{b, f, b'', f''}), 7.28 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**^{c'}), 7.17 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.6, 1 H, Ar-**H**^{b'}), 7.11 (d, ⁴J(H,H) = 1.6, 1 H, Ar-**H**^{f'}), 6.95-6.90 (m, 4 H, Ar-**H**^{c, e, c'', e''}), 4.16 (t, ³J(H,H) = 4.3, 2 H, CH₂¹¹), 3.97-3.94 (m, 4 H, CH₂^{1,1'}), 3.76 (s, 2 H, CH₂¹⁷), 3.73 (t, ³J(H,H) = 4.3, 2 H, CH₂¹²), 3.54-3.43 (m, 8 H, CH₂¹³⁻¹⁶), 1.79-1.73 (m, 4 H, CH₂^{2,2'}), 1.45-1.26 (m, 28 H, CH₂^{3-9,3'-9'}), 0.88-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 174.4 (C¹⁸), 158.8 (C^d), 158.2 (C^{d''}), 155.6 (C^{e'}), 141.0 (C^{a'}), 132.9 (C^{a''}), 130.9 (C^{c'}), 130.5 (C^{b, f}), 130.3 (C^{a''}),



128.9 (C^a), 127.9 (C^{b',f''}), 119.8 (C^{b'}), 114.8 (C^{c'',e''}), 114.1 (C^{c,e}), 111.6 (C^{f'}), 71.8, 71.5, 70.3, 70.0, 69.3 (C¹³⁻¹⁷), 69.1 (C¹²), 68.5 (C¹¹), 68.1, 68.0 (C^{1,1'}), 31.9 (C^{8,8'}), 29.6, 29.5, 29.4, 29.4, 29.3 (C^{2, 4-7, 2', 4'-7'}), 26.1, 26.1 (C^{3,3'}), 22.7 (C^{9,9'}), 14.1 (C^{10,10'}). EA: C₄₆H₆₇O₈Cs·H₂O (Cal.) C: 61.46 %, H: 7.74 %, (Found) C: 61.67 %, H: 7.41 %.

Barium 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Ba10/3**):

Reagents: **H10/3** (0.69 g, 0.92 mmol)

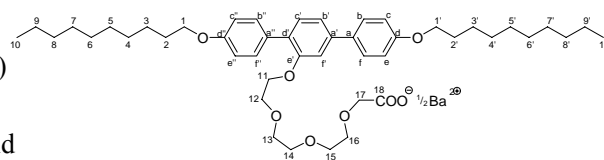
Ba(OH)₂·8H₂O (145 mg, 0.46 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.49 g (65.1 %), colorless waxy solid

Analytical data: C₉₂H₁₃₄O₁₆Ba M_w = 1633.32

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.46-7.39 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.23 (d, ³J(H,H) = 8.0, 1 H, Ar-H^{c'}), 7.09 (d, ³J(H,H) = 8.0, 1 H, Ar-H^{b'}), 7.04 (s, 1 H, Ar-H^{f'}), 6.89-6.80 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.03 (bs, 2 H, CH₂¹¹), 3.91-3.85 (m, 4 H, CH₂^{1,1'}), 3.80 (s, 2 H, CH₂¹⁷), 3.69 (bs, 2 H, CH₂¹²), 3.53-3.40 (m, 8 H, CH₂¹³⁻¹⁶), 1.77-1.69 (m, 4 H, CH₂^{2,2'}), 1.42-1.20 (m, 28 H, CH₂^{3-9, 3'-9'}), 0.88-0.84 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 177.1 (C¹⁸), 158.7 (C^d), 158.0 (C^{d''}), 155.8 (C^{e'}), 140.7 (C^{a'}), 133.0 (C^{a''}), 130.7 (C^{c'}), 130.4 (C^{b,f}), 130.3 (C^{a''}), 128.8 (C^a), 127.9 (C^{b',f''}), 119.4 (C^{b'}), 114.7 (C^{c'',e''}), 113.8 (C^{c,e}), 111.2 (C^{f'}), 71.8, 70.6, 70.0, 69.4, 69.2 (C¹³⁻¹⁷), 68.5 (C¹²), 68.8 (C¹¹), 68.1, 68.0 (C^{1,1'}), 32.0 (C^{8,8'}), 29.7, 29.5, 29.4, 29.4, 29.4 (C^{2, 4-7, 2', 4'-7'}), 26.2, 26.2 (C^{3,3'}), 22.7 (C^{9,9'}), 14.2 (C^{10,10'}). EA: C₉₂H₁₃₄O₁₆Ba·0.5H₂O (Cal.) C: 67.28 %, H: 8.28 %, (Found) C: 67.27 %, H: 8.30 %.



Lithium 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Li10/4**):

Reagents: **H10/4** (0.50 g, 0.63 mmol)

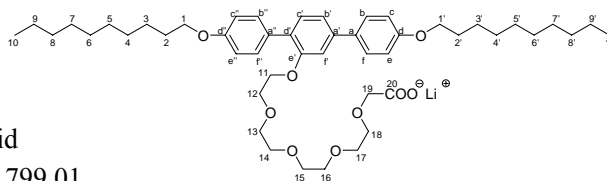
LiOH (15 mg, 0.63 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.23 g (45.7 %), colorless waxy solid

Analytical data: C₄₈H₇₁O₉Li M_w = 799.01

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.50-7.46 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.30 (d, ³J(H,H) = 7.8, 1 H, Ar-H^{c'}), 7.16 (dd, ³J(H,H) = 7.8, ⁴J(H,H) = 1.6, 1 H, Ar-H^{b'}), 7.10 (d, ⁴J(H,H) = 1.6, 1 H, Ar-H^{f'}), 7.94-6.85 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.11 (t, ³J(H,H) = 4.5, 2 H, CH₂¹¹), 3.97-3.93 (m, 4 H, CH₂^{1,1'}), 3.87 (s, 2 H, CH₂¹⁹), 3.74-3.72 (m, 2 H, CH₂¹²), 3.56-3.50 (m, 12 H, CH₂¹³⁻¹⁸), 1.81-1.73 (m, 4 H, CH₂^{2,2'}), 1.46-1.26 (m, 28 H, CH₂^{3-9, 3'-9'}), 0.89-0.85 (m, 6 H, CH₃^{10,10'}). ¹³C NMR (CDCl₃, 100 MHz) δ = 175.4 (C²⁰), 158.7 (C^d), 158.1 (C^{d''}), 155.9 (C^{e'}), 140.8 (C^{a'}), 133.1 (C^{a''}), 130.7 (C^{c'}), 130.5, (C^{b,f}), 130.3 (C^{a''}), 128.9 (C^a), 127.9 (C^{b',f''}), 119.5 (C^{b'}), 114.7 (C^{c'',e''}), 113.9 (C^{c,e}), 111.5 (C^{f'}), 70.8, 70.6, 70.4, 70.3, 70.1, 69.7, 69.6 (C¹³⁻¹⁹), 69.4 (C¹²), 68.3 (C¹¹), 68.1, 68.0 (C^{1,1'}), 31.9 (C^{8,8'}), 29.6, 29.6, 29.5, 29.5, 29.4, 29.4 (C^{2, 4-7, 2', 4'-7'}), 26.2, 26.1 (C^{3,3'}), 22.7 (C^{9,9'}), 14.2 (C^{10,10'}). EA: C₄₈H₇₁O₉Li·0.5H₂O (Cal.) C: 71.35 %, H: 8.98 %, (Found) C: 71.21 %, H: 8.81 %.



Potassium 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**K10/4**):

Reagents: **H10/4** (0.50 g, 0.63 mmol)

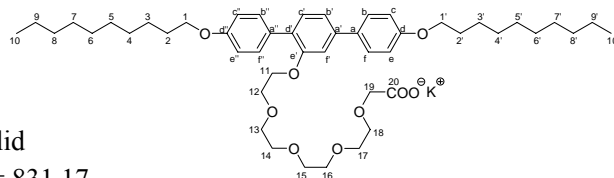
KOH (35 mg, 0.63 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.24 g (45.8 %), colorless waxy solid

Analytical data: C₄₈H₇₁O₉K M_w = 831.17

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.50-7.44 (m, 4 H, Ar-H^{b, f, b'', f''}), 7.27 (d, ³J(H,H) = 7.8, 1 H, Ar-H^{c'}), 7.16-7.13 (m, 1 H, Ar-H^{b'}), 7.11 (s, 1 H, Ar-H^{f'}), 6.92-6.85 (m, 4 H, Ar-H^{c, e, c'', e''}), 4.13 (t, ³J(H,H) = 4.5, 2 H, CH₂¹¹), 3.96-3.91 (m, 4 H, CH₂^{1,1'}), 3.78 (s, 2 H, CH₂¹⁹), 3.77-3.74 (m, 2 H, CH₂¹²),



3.55-3.40 (m, 12 H, CH_2^{13-18}), 1.80-1.73 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.45-1.22 (m, 28 H, $\text{CH}_2^{3-9,3'-9'}$), 0.88-0.85 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 125 MHz) δ = 174.8 (C^{20}), 158.7 (C^{d}), 158.1 ($\text{C}^{\text{d''}}$), 155.8 ($\text{C}^{\text{e'}}$), 140.9 ($\text{C}^{\text{a'}}$), 133.0 ($\text{C}^{\text{a''}}$), 130.7 ($\text{C}^{\text{c'}}$), 130.5 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a''}}$), 128.9 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.5 ($\text{C}^{\text{b'}}$), 114.7 ($\text{C}^{\text{c'',e''}}$), 113.9 ($\text{C}^{\text{c,e}}$), 111.6 (C^{f}), 71.3, 70.4, 70.0, 70.0, 69.6, 69.4 (C^{13-19}), 68.9 (C^{12}), 68.7 (C^{11}), 68.1, 68.0 ($\text{C}^{1,1'}$), 31.9 ($\text{C}^{8,8'}$), 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, ($\text{C}^{2,4-7,2',4'-7'}$), 26.2, 26.1 ($\text{C}^{3,3'}$), 22.7 ($\text{C}^{9,9'}$), 14.2 ($\text{C}^{10,10'}$). EA: $\text{C}_{48}\text{H}_{71}\text{O}_9\text{K}\cdot\text{H}_2\text{O}$ (Cal.) C: 67.89 %, H: 8.66 %, (Found) C: 67.78 %, H: 8.74 %.

Cesium 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Cs10/4**):

Reagents: **H10/4** (0.50 g, 0.63 mmol)

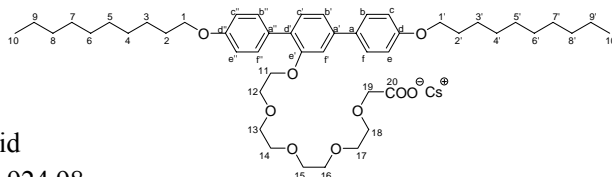
Cs_2CO_3 (102 mg, 0.31 mmol)

Purification: recrystallization from ethyl acetate

Yield: 0.30 g (51.4 %), colorless waxy solid

Analytical data: $\text{C}_{48}\text{H}_{71}\text{O}_9\text{Cs}$ $M_w = 924.98$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.52-7.45 (m, 4 H, Ar- $\text{H}^{\text{b,f,b'',f''}}$), 7.29 (d, $^3J(\text{H,H}) = 7.8$, 1 H, Ar- $\text{H}^{\text{c'}}$), 7.16 (dd, $^3J(\text{H,H}) = 7.8$, $^4J(\text{H,H}) = 1.6$, 1 H, Ar- $\text{H}^{\text{b'}}$), 7.12 (d, $^4J(\text{H,H}) = 1.6$, 1 H, Ar- H^{f}), 6.94-6.88 (m, 4 H, Ar- $\text{H}^{\text{c,e,c'',e''}}$), 4.17 (t, $^3J(\text{H,H}) = 4.5$, 2 H, CH_2^{11}), 3.97-3.93 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.79 (s, 2 H, CH_2^{19}), 3.77-3.75 (m, 2 H, CH_2^{12}), 3.56-3.40 (m, 12 H, CH_2^{13-18}), 1.78-1.73 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.48-1.22 (m, 28 H, $\text{CH}_2^{3-9,3'-9'}$), 0.88-0.85 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 125 MHz) δ = 174.2 (C^{20}), 158.8 (C^{d}), 158.2 ($\text{C}^{\text{d''}}$), 155.6 ($\text{C}^{\text{e'}}$), 141.0 ($\text{C}^{\text{a'}}$), 133.0 ($\text{C}^{\text{a''}}$), 130.9 ($\text{C}^{\text{c'}}$), 130.6 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a''}}$), 128.8 (C^{a}), 128.0 ($\text{C}^{\text{b',f''}}$), 119.7 ($\text{C}^{\text{b'}}$), 114.8 ($\text{C}^{\text{c'',e''}}$), 114.0 ($\text{C}^{\text{c,e}}$), 111.6 (C^{f}), 71.9, 70.5, 70.1, 70.0, 69.9, 69.4 (C^{13-19}), 69.1 (C^{12}), 68.5 (C^{11}), 68.1, 68.0 ($\text{C}^{1,1'}$), 31.9 ($\text{C}^{8,8'}$), 29.6, 29.6, 29.5, 29.4, 29.4, 29.3 ($\text{C}^{2,4-7,2',4'-7'}$), 26.1, 26.1 ($\text{C}^{3,3'}$), 22.7 ($\text{C}^{9,9'}$), 14.1 ($\text{C}^{10,10'}$). EA: $\text{C}_{48}\text{H}_{71}\text{O}_9\text{Cs}\cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 61.13 %, H: 7.80 %, (Found) C: 61.01 %, H: 7.99 %.



Barium 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Ba10/4**):

Reagents: **H10/4** (0.54 g, 0.68 mmol)

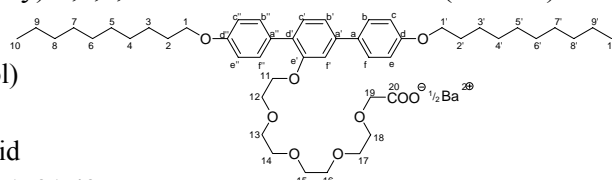
$\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$ (107 mg, 0.34 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.34 g (51.4 %), colorless waxy solid

Analytical data: $\text{C}_{96}\text{H}_{142}\text{O}_{18}\text{Ba}$ $M_w = 1721.43$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.49-7.43 (m, 4 H, Ar- $\text{H}^{\text{b,f,b'',f''}}$), 7.27 (d, $^3J(\text{H,H}) = 7.8$, 1 H, Ar- $\text{H}^{\text{c'}}$), 7.13 (dd, $^3J(\text{H,H}) = 7.8$, $^4J(\text{H,H}) = 1.6$, 1 H, Ar- $\text{H}^{\text{b'}}$), 7.07 (d, $^4J(\text{H,H}) = 1.6$, 1 H, Ar- H^{f}), 6.92-6.84 (m, 4 H, Ar- $\text{H}^{\text{c,e,c'',e''}}$), 4.09 (t, $^3J(\text{H,H}) = 4.5$, 2 H, CH_2^{11}), 3.95-3.90 (m, 4 H, $\text{CH}_2^{1,1'}$), 3.84 (s, 2 H, CH_2^{19}), 3.74 (t, $^3J(\text{H,H}) = 4.5$, 2 H, CH_2^{12}), 3.59-3.42 (m, 12 H, CH_2^{13-18}), 1.79-1.71 (m, 4 H, $\text{CH}_2^{2,2'}$), 1.44-1.22 (m, 28 H, $\text{CH}_2^{3-9,3'-9'}$), 0.87-0.85 (m, 6 H, $\text{CH}_3^{10,10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 177.0 (C^{20}), 158.8 (C^{d}), 158.1 ($\text{C}^{\text{d''}}$), 155.9 ($\text{C}^{\text{e'}}$), 140.8 ($\text{C}^{\text{a'}}$), 133.0 ($\text{C}^{\text{a''}}$), 130.8 ($\text{C}^{\text{c'}}$), 130.5 ($\text{C}^{\text{b,f}}$), 130.4 ($\text{C}^{\text{a''}}$), 128.9 (C^{a}), 127.9 ($\text{C}^{\text{b',f''}}$), 119.4 ($\text{C}^{\text{b'}}$), 114.7 ($\text{C}^{\text{c'',e''}}$), 113.9 ($\text{C}^{\text{c,e}}$), 111.2 (C^{f}), 71.7, 70.7, 70.3, 70.1, 69.9, 69.6 (C^{13-19}), 69.3 (C^{12}), 68.5 (C^{11}), 68.1, 68.0 ($\text{C}^{1,1'}$), 31.9 ($\text{C}^{8,8'}$), 29.6, 29.5, 29.5, 29.4, 29.3 ($\text{C}^{2,4-7,2',4'-7'}$), 26.1, 26.1 ($\text{C}^{3,3'}$), 22.7 ($\text{C}^{9,9'}$), 14.1 ($\text{C}^{10,10'}$). EA: $\text{C}_{96}\text{H}_{142}\text{O}_{18}\text{Ba}\cdot 0.5\text{H}_2\text{O}$ (Cal.) C: 66.63 %, H: 8.33 %, (Found) C: 66.68 %, H: 8.36 %.



Cesium 11-(4,4''-dihexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Cs16/3**):

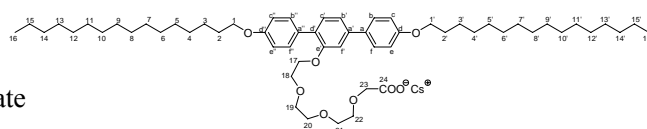
Reagents: **H16/3** (0.50 g, 0.54 mmol)

Cs_2CO_3 (88 mg, 0.27 mmol)

Purification: recrystallization from ethyl acetate

Yield: 0.23 g (40.4 %), colorless solid

Analytical data: $\text{C}_{58}\text{H}_{91}\text{O}_8\text{Cs}$ $M_w = 1049.24$



^1H NMR (CDCl_3 , J/Hz , 400 MHz) δ = 7.51-7.42 (m, 4 H, Ar- $\text{H}^{b, f, b'', f''}$), 7.28 (d, $^3J(\text{H}, \text{H})$ = 7.9, 1 H, Ar- $\text{H}^{c'}$), 7.17 (dd, $^3J(\text{H}, \text{H})$ = 7.9, $^4J(\text{H}, \text{H})$ = 1.2, 1 H, Ar- $\text{H}^{b'}$), 7.11 (d, $^4J(\text{H}, \text{H})$ = 1.2, 1 H, Ar- $\text{H}^{f'}$), 6.94-6.89 (m, 4 H, Ar- $\text{H}^{c, c', c'', e''}$), 4.16 (t, 2 H, $^3J(\text{H}, \text{H})$ = 4.8, CH_2^{17}), 3.97-3.83 (m, 4 H, $\text{CH}_2^{1, 1'}$), 3.77 (s, 2 H, CH_2^{23}), 3.74 (t, $^3J(\text{H}, \text{H})$ = 4.8, 2 H, CH_2^{18}), 3.56-3.41 (m, 10 H, CH_2^{19-22}), 1.81-1.73 (m, 4 H, $\text{CH}_2^{2, 2'}$), 1.44-1.23 (m, 52 H, $\text{CH}_2^{3-15, 3'-15'}$), 0.88-0.84 (m, 6 H, $\text{CH}_3^{16, 16'}$). ^{13}C NMR (CDCl_3 , 100 MHz) δ = 206.5 (C^{24}), 158.8 (C^d), 158.3 ($\text{C}^{d''}$), 155.3 ($\text{C}^{e'}$), 141.1 ($\text{C}^{a'}$), 132.8 ($\text{C}^{a''}$), 130.9 ($\text{C}^{c'}$), 130.6 ($\text{C}^{b, f}$), 130.2 ($\text{C}^{a''}$), 128.7 (C^a), 127.9 ($\text{C}^{b', f''}$), 120.0 ($\text{C}^{b'}$), 114.8 ($\text{C}^{c'', e''}$), 114.2 ($\text{C}^{c, e}$), 111.6 ($\text{C}^{f'}$), 71.6, 70.5, 70.5, 70.0 (C^{19-23}), 69.5 (C^{18}), 68.4 (C^{17}), 68.12 ($\text{C}^{1, 1'}$), 32.0 ($\text{C}^{14, 14'}$), 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4 ($\text{C}^{2, 4-13, 2', 4'-13'}$), 26.2, 26.2 ($\text{C}^{3, 3'}$), 22.8 ($\text{C}^{15, 15'}$), 14.2 ($\text{C}^{16, 16'}$). EA: $\text{C}_{58}\text{H}_{91}\text{O}_8\text{Cu} \cdot 1.5\text{H}_2\text{O}$ (Cal.) C: 64.73 %, H: 8.80 %, (Found) C: 64.80 %, H: 8.59 %.

8.2.5 Copper carboxylates (**Cu10/n**)

General procedure: In a 50 mL round bottom flask was filled by THF (30 mL), the appropriate barium carboxylate **Ba10/n** (1 mmol) and copper(II) sulphate pentahydrate (0.26 g, 1.05 mmol). The resulting suspension was stirring at r.t. for several days to complete the ion exchange process (the reaction time decisively depending on the size of the particles of CuSO_4 . Generally, the reaction was finished when the suspension became white and the solution became blue). The solid was filtered off and the solvent was removed in vacuum, the crude product was purified by recrystallization from ethyl acetate.

Copper(II) 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Cu10/3**):

Reagents: **Ba10/3** (0.50 g, 0.31 mmol)

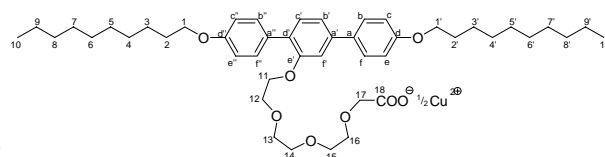
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (77 mg, 0.31 mmol)

Purification: recrystallization from ethyl acetate

Yield: 0.14 g (29.3 %), green wax like solid

Analytical data: $\text{C}_{92}\text{H}_{134}\text{O}_{16}\text{Cu}$ M_w = 1559.54

EA: $\text{C}_{92}\text{H}_{134}\text{O}_{16}\text{Cu} \cdot \text{H}_2\text{O}$ (Cal.) C: 70.04 %, H: 8.69 %, (Found) C: 70.25 %, H: 8.52 %.



Copper(II) 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**Cu10/4**):

Reagents: **Ba10/4** (0.54 g, 0.31 mmol)

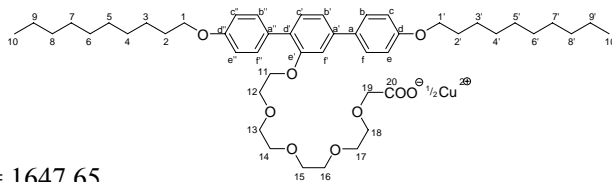
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (78 mg, 0.31 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.21 g (41.0 %), green waxy solid

Analytical data: $\text{C}_{96}\text{H}_{142}\text{O}_{18}\text{Cu}$ M_w = 1647.65

EA: $\text{C}_{96}\text{H}_{142}\text{O}_{18}\text{Cu} \cdot \text{H}_2\text{O}$ (Cal.) C: 69.22 %, H: 8.71 %, (Found) C: 69.26 %, H: 8.53 %.



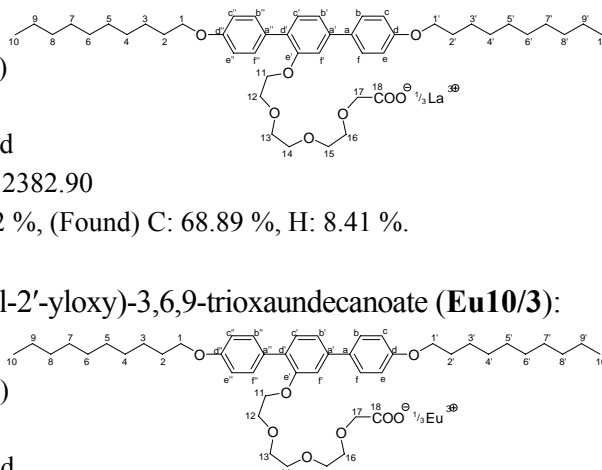
8.2.6 Rear earth metal carboxylates (**La10/n** and **Eu10/3**)

General procedure: The sodium carboxylate **Na10/n** (3 mmol) and the appropriate nitrate (1 mmol) were dissolved in THF (25 mL), the mixture was stirred for 30 min, then the solvent was removed in vacuum, the residue was washed with hot ethanol (3×10 mL), after that, the residual solid was dissolved in chloroform (70 mL) and washed with water (3×30 mL), the solvent was removed and the crude product was purified by recrystallization from ethyl acetate.

Lanthanum (III) 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**La10/3**):Reagents: **Na10/3** (0.31 g, 0.40 mmol) $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (58 mg, 0.40 mmol)

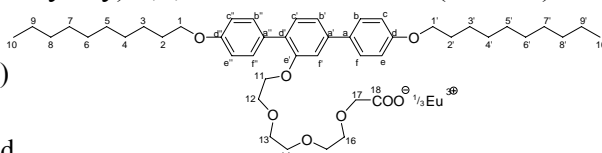
Purification: Recrystallization from ethyl acetate

Yield: 0.11 g (11.5 %), colorless waxy solid

Analytical data: $\text{C}_{138}\text{H}_{201}\text{O}_{24}\text{La}$ $M_w = 2382.90$ EA: $\text{C}_{138}\text{H}_{201}\text{O}_{24}\text{La} \cdot \text{H}_2\text{O}$ (Cal.) C: 69.03 %, H: 8.52 %, (Found) C: 68.89 %, H: 8.41 %.Europium (III) 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**Eu10/3**):Reagents: **Na10/3** (0.51 g, 0.66 mmol) $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (94 mg, 0.22 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.16 g (11.5 %), colorless waxy solid

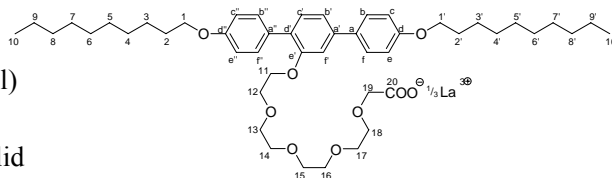
Analytical data: $\text{C}_{138}\text{H}_{201}\text{O}_{24}\text{Eu}$ $M_w = 2395.96$ EA: $\text{C}_{138}\text{H}_{201}\text{O}_{24}\text{Eu} \cdot 5\text{H}_2\text{O}$ (Cal.) C: 66.67 %, H: 8.56 %, (Found) C: 66.63 %, H: 8.56 %.Lanthanum (III) 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**La10/4**):Reagents: **Na10/4** (0.35 g, 0.42 mmol) $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (61 mg, 0.14 mmol)

Purification: Recrystallization from ethyl acetate

Yield: 0.12 g (11.3 %), colorless waxy solid

Analytical data: $\text{C}_{144}\text{H}_{213}\text{O}_{27}\text{La}$ $M_w = 2515.12$

^1H NMR (CDCl_3 , J/Hz , 400 MHz) $\delta = 7.4\text{--}7.46$ (m, 4 H, $\text{Ar-H}^{b, f, b'', f''}$), $7.29\text{--}7.27$ (m, 1 H, $\text{Ar-H}^{c'}$), $7.14\text{--}7.09$ (m, 2 H, $\text{Ar-H}^{b', f'}$), $6.91\text{--}6.85$ (m, 4 H, $\text{Ar-H}^{c, e, c'', e''}$), $4.17\text{--}4.02$ (m, 2 H, CH_2^{11}), $3.98\text{--}3.84$ (m, 4 H, $\text{CH}_2^{1, 1'}$), $3.78\text{--}3.44$ (m, 16 H, $\text{CH}_2^{12\text{--}19}$), $1.80\text{--}1.69$ (bs, 4 H, $\text{CH}_2^{2, 2'}$), $1.49\text{--}1.18$ (m, 28 H, $\text{CH}_2^{3\text{--}9, 3'\text{--}9'}$), $0.90\text{--}0.82$ (m, 6 H, $\text{CH}_3^{10, 10'}$). ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 159.3$ (C^d), 158.6 ($\text{C}^{d''}$), 156.4 ($\text{C}^{e'}$), 141.3 ($\text{C}^{a'}$), 133.6 ($\text{C}^{a''}$), 131.3 ($\text{C}^{c'}$), 131.0 ($\text{C}^{b, f}$), 130.9 ($\text{C}^{a''}$), 129.5 (C^a), 128.4 ($\text{C}^{b', f''}$), 120.1 ($\text{C}^{b'}$), 115.3 ($\text{C}^{c'', e''}$), 114.4 ($\text{C}^{c, e}$), 111.9 (C^f), 71.1 , 70.1 ($\text{C}^{13\text{--}19}$), 68.6 (C^{12}), 68.5 (C^{11} , $\text{C}^{1, 1'}$), 32.4 ($\text{C}^{8, 8'}$), 30.1 , 30.0 , 29.9 ($\text{C}^{2, 4\text{--}7, 2', 4'\text{--}7'}$), 26.7 ($\text{C}^{3, 3'}$), 23.2 ($\text{C}^{9, 9'}$), 14.7 ($\text{C}^{10, 10'}$). EA: $\text{C}_{144}\text{H}_{213}\text{O}_{27}\text{La} \cdot \text{H}_2\text{O}$ (Cal.) C: 68.27 %, H: 8.56 %, (Found) C: 68.19 %, H: 8.56 %.



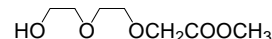
9 Synthesis and analytical data of intermediates

9.1 Synthesis of methyl ω -hydroxy[oligo(oxyethylene)yl]acetates (1/n)

General procedure: Metallic Na (15.4 g) was dissolved in the oligoethyleneglycol (2.7 mol) under an argon atmosphere, sodium chloroacetate (78 g, 0.67 mol) was added to the resulting solution at 100 °C, the mixture was then stirred at 100 °C for 10h. The excess oligoethyleneglycol was removed in vacuum. Water (100 mL), and 35 % hydrochloric acid (35 mL) were added to the residue, then the NaCl was removed by filtration. After evaporation of the water, methanol (600 mL) and sulphuric acid (10 mL) were added to the residue and the resulting mixture was refluxed for 10h. The solution was neutralized with saturated aqueous sodium carbonate solution and then the solvent was evaporated under reduced pressure. Water (400 mL) was added to the residue and the mixture was extracted with dichloromethane, the extraction procedure was repeated several times until the last extraction contains no product as proven by TLC analysis. The combined organic phase was dried over Na₂SO₄, after filtration the solvent was evaporated in vacuum, the product was purified by column chromatography on silica gel with CHCl₃/CH₃OH as eluent or by flash distillation below 150 °C.

Methyl 8-hydroxy-3,6-dioxaoctanoate (1/2):

Reagents: Diethylene glycol (239 g, 2.25mol)
Na (13 g, 0.57mol)
Sodium chloroacetate (66 g, 0.57mol)
36 % HCl (100 g, 0.99mol)
Dry methanol (500 mL)
96 % H₂SO₄ (20 g, 0.20mol)



Purification: Vacuum distillation, b.p. = 120 °C (8 Pa)

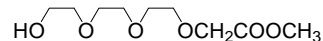
Yield: 24.9 g (24.5 %), colorless liquid

Analytical data: C₇H₁₄O₅ M_w = 178.18

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 4.12 (s, 2 H, OCH₂), 3.75-3.55 (m, 11 H, OCH₂, OCH₃).

Methyl 11-hydroxy-3,6,9-trioxaundecanoate (1/3):

Reagents: Triethylene glycol (312 g, 2.08mol)
Na (12 g, 0.52mol)
Sodium chloroacetate (61 g, 0.52mol)
36 % HCl (80 g, 0.79mol)
Dry methanol (450 mL)
96 % H₂SO₄ (17 g, 0.17mol)



Purification: Vacuum distillation, b.p. = 135 °C (3 Pa)

Yield: 14.1 g (12.2 %), colorless liquid

Analytical data: C₉H₁₈O₆ M_w = 222.24

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 4.06 (s, 2 H, OCH₂), 3.64-3.47 (m, 15 H, OCH₂, OCH₃).

Methyl 14-hydroxy-3,6,9,12-tetraoxatetradecanoate (1/4):

Reagents: Tetraethylene glycol (334 g, 1.72 mol)

Na (9.9 g)

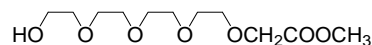
Sodium chloroacetate (50 g, 0.42 mol)

36 % HCl (80 g, 0.79 mol)

Dry methanol (450 mL)

96 % H₂SO₄ (20 g, 0.20 mol)Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/1 (V/V)

Yield: 22.0 g (19.2 %), yellow liquid

Analytical data: C₁₁H₂₂O₇ M_w = 266.29¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 4.13 (s, 2 H, OCH₂), 3.71-3.53 (m, 19 H, OCH₂, OCH₃).**9.2 Synthesis of methyl 20-hydroxy-3,6,9,12,15,18-hexaoxaeicosanoate (1/6)**

Procedure:

Hexaethyleneglycol monobenzyl ether: Under an argon atmosphere, metallic Na (5.0 g) was dissolved in the triethyleneglycol (130 g, 0.87 mol). To the resulting solution, 8-[4-toluenesulfonyloxy]-3,6-dioxaoctylbenzyl ether (78 g, 0.20 mol) was added dropwise. The resulting mixture was heated at 100 °C for 8 h, after that the reaction mixture was poured into 200 mL water and extracted with CH₂Cl₂ (3 × 150 mL), the combined organic phase was washed with water (2 × 100 mL) and brine (100 mL), dried over Na₂SO₄ and filtered. The solvent was removed in vacuum, the crude product was purified by column chromatography over silica gel with CHCl₃/CH₃OH = 10/1.5 (V/V) as eluent, which afforded a colorless liquid, 52 g (0.14 mol), yield 70 %.

20-Benzyloxy-3,6,9,12,15,18-hexaoxaeicosanoic acid: In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, hexaethyleneglycol monobenzyl ether (52 g, 0.14 mol) was dissolved in dry THF (400 mL) under an argon atmosphere. After the addition of NaH (80 %, 4.5 g, 0.15 mol), the mixture was stirred at reflux for 2h. After cooling, sodium chloroacetate (27 g, 0.23 mol) was added and the reaction mixture was heated at reflux again for 10 h. Afterward, the solvent was evaporated in vacuum, and the residue was dissolved in water (100 mL), acidified with HCl (10 %) and extracted with diethyl ether (3 × 150 mL). The combined organic phase was washed with water (2 × 100 mL), and with brine (100 mL). After drying over Na₂SO₄ and filtration, the solvent was removed in vacuum, which afforded a yellow liquid, 25 g (58 mmol), yield 41 %. The crude product was used for the next step without further purification.

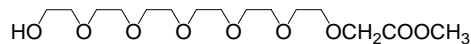
Methyl 20-benzyloxy-3,6,9,12,15,18-hexaoxaeicosanoate: Dry methanol (250 mL), sulphuric acid (96 %, 5 mL, 0.10 mol) and the 20-benzyloxy-3,6,9,12,15,18-hexaoxaeicosanoic acid (25 g, 58 mmol), were carefully mixed and heated to reflux for 10 h. The solution was neutralized with saturated aqueous Na₂CO₃ solution, then the solvent was removed in vacuum and the residue was dissolved in CH₂Cl₂ (350 mL) and washed with water (3 × 100 mL). After drying over Na₂SO₄ and filtration, the crude product was purified by column chromatography over silica gel with CHCl₃/CH₃OH as eluent which afforded a yellow liquid, 12.5 g (28 mmol), yield 48 %.

Methyl 20-hydroxy-3,6,9,12,15,18-hexaoxaecosanoate (1/6): The methyl 20-benzyloxy-3,6,9,12,15,18-hexaoxaecosanoate (12.5 g, 28 mmol) was dissolved in ethyl acetate (30 mL), the resulting solution was treated with palladium (10 % on carbon) catalyst (0.2 g, 5 % by mol) and was hydrogenated (1.05×10^5 Pa) at 40 °C until the starting benzyl ether had been completely consumed as judged by TLC analysis. The catalyst was filtered off and all volatiles were removed in vacuum, which afforded a colorless liquid, 9.3 g (26 mmol), yield 94 %. The crude product was used for the next step without further purifications.

Analytical data: $C_{15}H_{30}O_9$ $M_w = 354.39$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 4.14$ (s, 2 H, OCH_2),

3.72 (s, 3 H, OCH_3), 3.71-3.55 (m, 24 H, OCH_2).



9.3 Synthesis of methyl ω -tosyloxy[oligo(oxyethylene)yl]acetates (2/n)

General procedure: Under an Argon atmosphere, the appropriate alcohol **1/n** (0.1mol) was dissolved in dry pyridine (32 mL) at 0 °C, after the addition of *p*-tosylchloride (38.1 g, 0.2mol) the reaction mixture was stirred for another 2h at 0 °C, and then was put into the refrigerator overnight. Afterwards the reaction mixture was poured into ice water mixture and extracted with diethyl ether (3×100 mL). The combined organic phases was washed with hydrochloric acid (aq. 10 %, 2×30 mL), water (2×50 mL) and brine (50 mL), and was dried over Na_2SO_4 . After filtration, evaporation of the solvent, in most cases, the crude product was used for the next step without further purification. Purification can also be done by column chromatography on silica gel with $CHCl_3/CH_3OH$ as eluent.

Methyl 8-(4-toluenesulfonyloxy)-3,6-dioxaoctanoate (2/2):

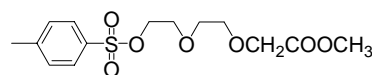
Reagents: **1/2** (8.83 g, 49.6 mmol)
p-Tosyl chloride (19.0 g, 99.7mol)
 Pyridine (15.8 g, 199.4 mmol)

Purification: Used for next step without purification

Yield: 16.4 g (99.5 %), yellow oil

Analytical data: $C_{14}H_{20}O_7S$ $M_w = 332.37$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.79$ (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 7.33 (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 4.17-4.05 (m, 4 H, OCH_2), 3.76-3.62 (m, 6 H, OCH_2), 3.57 (s, 3 H, OCH_3), 2.43 (s, 3 H, CH_3).



Methyl 11-[*p*-toluenesulfonyloxy]-3,6,9-trioxaundecanoate (2/2):

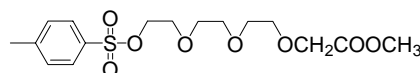
Reagents: **1/3** (5.4 g, 24 mmol)
p-Tosyl chloride (9.2 g, 48mmol)
 Pyridine (7.6 g, 96 mmol)

Purification: Used to next step without purification

Yield: 9.1 g (100 %), yellow oil

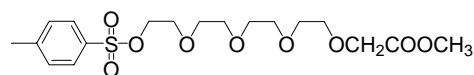
Analytical data: $C_{16}H_{24}O_8S$ $M_w = 376.42$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.79$ (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 7.32 (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 4.18-4.05 (m, 4 H, OCH_2), 3.77-3.63 (m, 10 H, OCH_2), 3.57 (s, 3 H, OCH_3), 2.43 (s, 3 H, CH_3).



Methyl 14-[p-toluenesulfonyloxy]-3,6,9,12-tetraoxatetradecanoate (2/4):

Reagents: **2/4** (15.5 g, 58.2 mmol)
 p-Tosyl chloride (22.2 g, 117 mol)
 Pyridine (18.5 g, 234 mmol)



Purification: Used to next step without purification

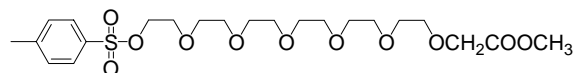
Yield: 21.5 g (88.6 %), yellow oil

Analytical data: $C_{18}H_{28}O_9S$ $M_w = 420.47$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.77$ (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 7.31 (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 4.16-4.09 (m, 4 H, OCH_2), 3.74-3.51 (m, 17 H, OCH_2 , OCH_3), 2.42 (s, 3 H, Ar- CH_3).

Methyl 20-[p-toluenesulfonyloxy]-3,6,9,12,15,18-hexaoxa-eicosanoate (2/6):

Reagents: **2/6** (9.0 g, 25.4 mmol)
 p-Tosyl chloride (9.7 g, 50.8 mol)
 Pyridine (8.1 g, 102 mmol)



Purification: Used to next step without purification

Yield: 12.0 g (93 %), yellow oil

Analytical data: $C_{22}H_{36}O_{11}S$ $M_w = 508.58$

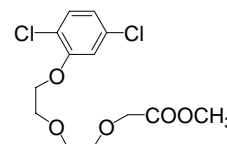
1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.78$ (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 7.32 (d, $^3J(H,H) = 8.3$, 2 H, Ar-H), 4.16-4.11 (m, 4 H, OCH_2), 3.72-3.56 (m, 25 H, OCH_2 , OCH_3), 2.43 (s, 3 H, CH_3).

9.4 Synthesis of methyl ω -(2,5-dichlorophenyloxy)[oligo(oxyethylene)yl]acetates (3/n)

General producer: Under an Argon atmosphere, the 2,5-dichlorophenol (17.9 g, 0.11 mol) was dissolved in dry acetonitrile (150 mL), K_2CO_3 (34.5 g, 0.25 mol), the appropriate tosylate (0.1 mol), and Bu_4NI (50 mg) were added, and the mixture was stirred under reflux for 4-8 h. Afterwards, the solvent was evaporated in vacuum, the residue was dissolved in water and diethyl ether and the water phase was extracted by diethyl ether (3×100 mL). The combined organic phase was washed with water and brine. After drying over Na_2SO_4 and filtration, the solvent was removed. The crude product was purified by column chromatography on silica gel with $CHCl_3/CH_3OH$ (or ethyl acetate/PE) as eluent.

Methyl 8-(2,5-dichlorophenyloxy)-3,6-dioxaoctanoate (3/2):

Reagents: **2/2** (16.4 g, 49.3 mmol)
 2,5-Dichlorophenol (8.4 g, 51.5 mmol)
 K_2CO_3 (17.0 g, 123 mmol)
 Dry acetonitrile (100 mL)
 $(n-Bu)_4NI$ (50 mg)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/PE = 1/2 (V/V)

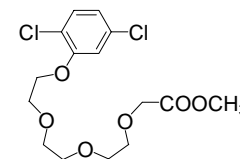
Yield: 12.9 g (80.9 %), yellow oil

Analytical data: $C_{13}H_{16}Cl_2O_5$ $M_w = 323.17$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.24$ (d, $^3J(H,H) = 8.3$, 1 H, Ar-H), 6.93 (d, $^4J(H,H) = 2.3$, 1 H, Ar-H), 6.86 (dd, $^3J(H,H) = 8.3$, $^4J(H,H) = 2.3$, 1 H, Ar-H), 4.15-4.09 (m, 4 H, OCH_2), 3.89 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.80-3.77 (m, 2 H, OCH_2), 3.73-3.54 (m, 5 H, OCH_2 , OCH_3)

Methyl 11-(2,5-dichlorophenyloxy)-3,6,9-trioxaundecanoate (3/3):

Reagents: **2/3** (9.1 g, 24 mmol)
 2,5-Dichlorophenol (4.3 g, 26 mmol)
 K_2CO_3 (8.3 g, 60 mmol)
 Dry acetonitrile (100 mL)
 $(n-Bu)_4NI$ (10 mg)



Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/CH_3OH = 10/1$ (V/V)

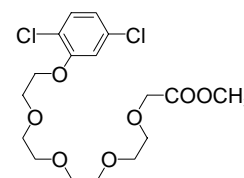
Yield: 5.6 g (63.5 %), yellow oil

Analytical data: $C_{15}H_{20}Cl_2O_6$ $M_w = 367.22$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.24$ (d, $^3J(H,H) = 8.3$, 1 H, Ar-H), 6.93 (d, $^4J(H,H) = 2.3$, 1 H, Ar-H), 6.86 (dd, $^3J(H,H) = 8.3$, $^4J(H,H) = 2.3$, 1 H, Ar-H), 4.18-4.13 (m, 4 H, OCH_2), 3.88 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.77-3.63 (m, 11 H, OCH_2 , OCH_3)

Methyl 14-(2,5-dichlorophenyloxy)-3,6,9,12-tetraoxatetradecanoate (3/4):

Reagents: **2/4** (21.5 g, 51.2 mmol)
 2,5-Dichlorophenol (8.6 g, 52.7 mmol)
 K_2CO_3 (25.0 g, 181 mmol)
 Dry acetonitrile (150 mL)
 $(n-Bu)_4NI$ (50 mg)



Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/CH_3OH = 10/1$ (V/V)

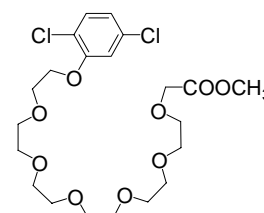
Yield: 15.0 g (71.2 %), yellow oil

Analytical data: $C_{17}H_{24}Cl_2O_7$ $M_w = 411.27$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.23$ (d, $^3J(H,H) = 8.4$, 1 H, Ar-H), 6.92 (d, $^4J(H,H) = 2.2$, 1 H, Ar-H), 6.84 (dd, $^3J(H,H) = 8.4$, $^4J(H,H) = 2.2$, 1 H, Ar-H), 4.17-4.12 (m, 4 H, OCH_2), 3.86 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.75-3.63 (m, 15 H, OCH_2 , OCH_3).

Methyl 20-(2,5-dichlorophenyloxy)-3,6,9,12,15,18-hexaoxaeicosanoate (3/6):

Reagents: **2/6** (3.5 g, 6.9 mmol)
 2,5-Dichlorophenol (1.3 g, 8.0 mmol)
 K_2CO_3 (2.4 g, 17.3 mmol)
 Dry acetonitrile (100 mL)
 $(n-Bu)_4NI$ (10 mg)



Purification: Column chromatography with silica gel 60, eluent: $CHCl_3/MeOH = 10/1.5$ (V/V)

Yield: 2.52 g (73.2 %), yellow oil

Analytical data: $C_{21}H_{32}Cl_2O_9$ $M_w = 499.38$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.24$ (d, $^3J(H,H) = 8.5$, 1 H, Ar-H), 6.93 (d, $^4J(H,H) = 2.3$, 1 H, Ar-H), 6.85 (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 2.3$, 1 H, Ar-H), 4.16-4.12 (m, 4 H, OCH_2), 3.88 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.75-3.62 (m, 23 H, OCH_2 , OCH_3).

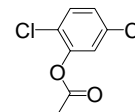
9.5 Synthesis of 2,5-dichlorophenylacetate (4)

Procedure: 2,5-Dichlorophenol (16.3 g, 0.10 mol) was dissolved in toluene (200 mL). Acetic acid anhydride (12.2 g, 0.12 mol), triethylamine (13.1 g, 0.13 mol) and DMAP (0.12 g, 1 mmol) were added and the mixture was heated to reflux for 8 h. After cooling down, the reaction mixture was extracted with diethyl ether. The organic phase was washed with

water, dried over Na_2SO_4 and filtered. The solvent was removed in vacuum and the crude product was purified by vacuum distillation (b.p. = 59 °C, 60 Pa) to afford a colorless oil, 17.5 g (85 mmol), yield 85.3 %.

Analytical data: $\text{C}_8\text{H}_6\text{Cl}_2\text{O}_2$ $M_w = 205.04$

^1H NMR (CDCl_3 , J/Hz, 200 MHz) $\delta = 7.33$ (d, $^3J(\text{H,H}) = 9.3$, 1 H, Ar-H), 7.23-7.10 (m, 2 H, Ar-H), 2.32 (s, 3 H, CH_3).



9.6 Synthesis of methyl ω -(4,4''-dialkoxy-p-terphenyl-2'-yloxy)[oligo(oxyethylene)-yl]acetates (7/*m*/*n*)

9.6.1 Procedure (I)

General procedure: An oven-dried Schlenk flask was evacuated and backfilled with argon and charged with $\text{Pd}(\text{OAc})_2$ (20 mg, 3.0 % by mol), 2-(di-*tert*-butylphosphino)biphenyl (53 mg, 6.0 mol %), the appropriate boronic acid **5/*m*** or **5/B** (3.0 mmol), and dry KF (0.35 g, 6.0 mmol). The flask was evacuated and backfilled with argon, dry THF (3 mL) and the appropriate 1,4-dichlorobenzene derivatives **3/*n*** or **4** (1 mmol) were added by syringe through a rubber septum. The reaction mixture was stirred at room temperature until the starting dichloro compound had been completely consumed as judged by TLC analysis (ca. 24 h). The reaction mixture was diluted with diethyl ether and poured into a separatory funnel. The mixture was washed with aqueous NaOH (aq. 1 M), and the aqueous phase was extracted with diethyl ether, and the combined organic phase was washed with brine, dried over Na_2SO_4 , filtered, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel. The $\text{CHCl}_3/\text{CH}_3\text{OH}$ (or ethyl acetate/PE) was used as eluent.

Methyl 8-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoate (7/10/2):

Reagents: **3/2** (0.917 g, 2.84 mmol)

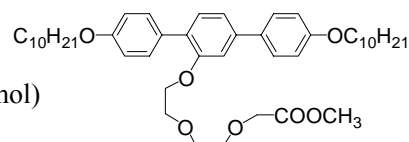
$\text{Pd}(\text{OAc})_2$ (20 mg, 0.089 mmol)

2-(Di-*tert*-butylphosphino)biphenyl (53 mg, 0.18 mmol)

4-Decyloxybenzeneboronic acid (2.37 g, 8.5 mmol)

KF (1.55 g, 26.7 mmol)

Dry THF (10 mL)



Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{MeOH} = 10/0.1$ (V/V)

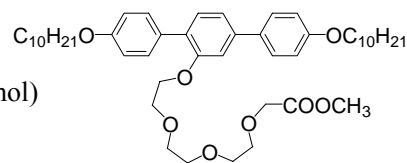
Yield: 1.9 g (71.2 %), colorless waxy solid

Analytical data: $\text{C}_{45}\text{H}_{66}\text{O}_7$ $M_w = 719.00$

^1H NMR (CDCl_3 , J/Hz, 200 MHz) $\delta = 7.54$ -7.47 (m, 4 H, Ar-H), 7.34 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.8$, 1 H, Ar-H), 7.14 (d, $^4J(\text{H,H}) = 1.8$, 1 H, Ar-H), 6.98-6.89 (m, 4 H, Ar-H), 4.17 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 4.11 (s, 2 H, OCH_2), 3.99 (t, $^3J(\text{H,H}) = 6.6$, 2 H, OCH_2), 3.99 (t, $^3J(\text{H,H}) = 6.6$, 2 H, OCH_2), 3.79 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 3.73-3.61 (m, 7 H, OCH_2 , OCH_3), 1.88-1.73 (m, 4 H, CH_2), 1.53-1.18 (m, 28 H, CH_2), 0.90-0.84 (m, 6 H, CH_3).

Methyl 11-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (7/10/3):

Reagents: **3/3** (1.16 g, 3.2 mmol)
 Pd(OAc)₂ (15 mg, 0.067 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (45 mg, 0.15 mmol)
 4-Decyloxybenzeneboronic acid (2.6 g, 9.4 mmol)
 KF (2.02 g, 35 mmol)
 Dry THF (7 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/0.1 (V/V)

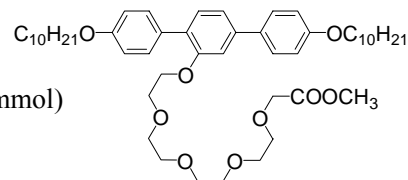
Yield: 2.1 g (86.0 %), colorless waxy solid

Analytical data: C₄₇H₇₀O₈ M_w = 763.05

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.54-7.47 (m, 4 H, Ar-**H**), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.8, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.8, 1 H, Ar-**H**), 6.97-6.89 (m, 4 H, Ar-**H**), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.11 (s, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 4 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.69-3.56 (m, 11 H, OCH₂, OCH₃), 1.88-1.73 (m, 4 H, CH₂), 1.53-1.18 (m, 28 H, CH₂), 0.90-0.84 (m, 6 H, CH₃).

Methyl 14-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (7/10/4):

Reagents: **3/4** (1.18 g, 2.9 mmol)
 Pd(OAc)₂ (18.5 mg, 0.083 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (60.5 mg, 0.20 mmol)
 4-Decyloxybenzeneboronic acid (2.7 g, 9.7 mmol)
 KF (4.0 g, 69 mmol)
 Dry THF (6 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/0.1 (V/V)

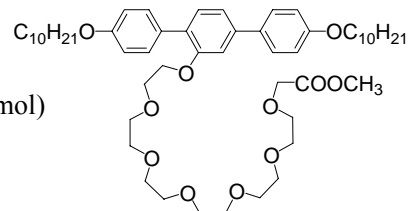
Yield: 1.1 g (47.8 %), yellow oil

Analytical data: C₄₉H₇₄O₉ M_w = 807.11

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.49 (m, 4 H, Ar-**H**), 7.33 (d, ³J(H,H) = 7.8, 1 H, Ar-**H**), 7.18 (dd, ³J(H,H) = 7.8, ⁴J(H,H) = 1.8, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.8, 1 H, Ar-**H**), 6.97-6.89 (m, 4 H, Ar-**H**), 4.16 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.78 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.71-3.56 (m, 15 H, OCH₂, OCH₃), 1.82-1.75 (m, 4 H, CH₂), 1.57-1.31 (m, 4 H, CH₂), 1.27-1.10 (m, 24 H, CH₂), 0.89-0.82 (m, 6 H, CH₃).

Methyl 20-(4,4''-didecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoate (7/10/6):

Reagents: **3/6** (0.60 g, 1.2 mmol)
 Pd(OAc)₂ (15 mg, 0.067 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (45 mg, 0.15 mmol)
 4-Decyloxybenzeneboronic acid (1.01 g, 3.6 mmol)
 KF (2.0 g, 34 mmol)
 Dry THF (4 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/MeOH = 10/0.3 (V/V)

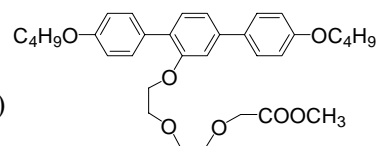
Yield: 0.97 g (90.3 %), yellow oil

Analytical data: C₅₃H₈₂O₁₁ M_w = 895.21

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.46 (m, 4 H, Ar-**H**), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 6.97-6.73 (m, 4 H, Ar-**H**), 4.16 (t, ³J(H,H) = 5.1, 2 H, OCH₂), 4.14 (s, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.78 (t, ³J(H,H) = 5.1, 2 H, OCH₂), 3.72 (s, 3 H, OCH₃), 3.71-3.53 (m, 20 H, OCH₂), 1.82-1.75 (m, 4 H, CH₂), 1.50-1.42 (m, 4 H, CH₂), 1.37-1.22 (m, 24 H, CH₂), 0.89-0.85 (m, 6 H, CH₃).

Methyl 8-(4,4''-dibutyloxy-p-terphenyl-2'-yloxy)-3,6-dioxaoctanoate (7/4/2):

Reagents: **3/2** (1.38 g, 4.3 mmol)
 Pd(OAc)₂ (34 mg, 0.15 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (91 mg, 0.30 mmol)
 4-Butyloxybenzeneboronic acid (2.5 g, 13 mmol)
 KF (2.6 g, 45 mmol)
 Dry THF (7 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/0.1 (V/V)

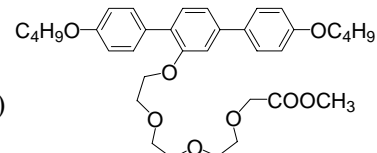
Yield: 2.4 g (100 %), colorless solid

Analytical data: C₃₃H₄₂O₇ M_w = 550.68

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.53-7.50 (m, 4 H, Ar-**H**), 7.34 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 6.98-6.89 (m, 4 H, Ar-**H**), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.11 (s, 2 H, OCH₂), 4.00 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.78-3.65 (m, 7 H, OCH₂, OCH₃), 1.81-1.74 (m, 4 H, CH₂), 1.55-1.47 (m, 4 H, CH₂), 1.00-0.95 (m, 6 H, CH₃).

Methyl 11-(4,4''-dibutyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (7/4/3):

Reagents: **3/3** (1.89 g, 5.1 mmol)
 Pd(OAc)₂ (29 mg, 0.13 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (77 mg, 0.26 mmol)
 4-Butyloxybenzeneboronic acid (3.0 g, 15 mmol)
 KF (2.3 g, 40 mmol)
 Dry THF (7 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/0.1 (V/V)

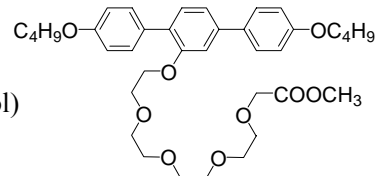
Yield: 3.1 g (100 %), colorless solid

Analytical data: C₃₅H₄₆O₈ M_w = 594.73

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.54-7.49 (m, 4 H, Ar-**H**), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 6.97-6.89 (m, 4 H, Ar-**H**), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 4.00 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.71-3.56 (m, 11 H, OCH₂, OCH₃), 1.82-1.73 (m, 4 H, CH₂), 1.57-1.45 (m, 4 H, CH₂), 1.00-0.95 (m, 6 H, CH₃).

Methyl 14-(4,4''-dibutyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxa-tetradecanoate (7/4/4):

Reagents: **3/4** (1.96 g, 4.8 mmol)
 Pd(OAc)₂ (21 mg, 0.094 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (57 mg, 0.19 mmol)
 4-Butyloxybenzeneboronic acid (2.8 g, 14 mmol)
 KF (1.6 g, 28 mmol)
 Dry THF (6 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/0.3 (V/V)

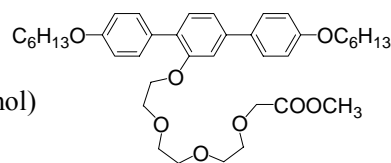
Yield: 2.6 g (84.8 %), yellow oil

Analytical data: C₃₇H₅₀O₉ M_w = 638.79

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.49 (m, 4 H, Ar-**H**), 7.33 (d, ³J(H,H) = 7.8, 1 H, Ar-**H**), 7.18 (dd, ³J(H,H) = 7.8, ⁴J(H,H) = 1.5, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.5, 1 H, Ar-**H**), 6.97-6.89 (m, 4 H, Ar-**H**), 4.16 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 4.00 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.78 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.77-3.58 (m, 15 H, OCH₂, OCH₃), 1.80-1.75 (m, 4 H, CH₂), 1.53-1.42 (m, 4 H, CH₂), 1.00-0.95 (m, 6 H, CH₃).

Methyl 11-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (7/6/3):

Reagents: **3/3** (1.98 g, 5.4 mmol)
 Pd(OAc)₂ (38 mg, 0.17 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (102 mg, 0.34 mmol)
 4-Hexyloxybenzeneboronic acid (3.0 g, 14 mmol)
 KF (3.0 g, 52 mmol)
 Dry THF (10 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/0.1 (V/V)

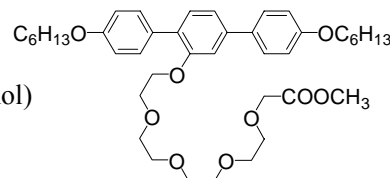
Yield: 3.2 g (100 %), yellow oil

Analytical data: C₃₉H₅₄O₈ M_w = 650.84

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.54-7.50 (m, 4 H, Ar-**H**), 7.34 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 6.92 (m, 4 H, Ar-**H**), 4.16 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.7 (s, 3 H, OCH₃), 3.64 (m, 8 H, OCH₂), 1.78 (m, 4 H, CH₂), 1.41 (m, 12 H, CH₂), 0.91 (m, 6 H, CH₃).

Methyl 14-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxa-tetradecanoate (7/6/4):

Reagents: **3/4** (2.22 g, 5.4 mmol)
 Pd(OAc)₂ (26 mg, 0.12 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (69 mg, 0.23 mmol)
 4-Hexyloxybenzeneboronic acid (3.0 g, 14 mmol)
 KF (2.1 g, 36 mmol)
 Dry THF (6 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/0.3 (V/V)

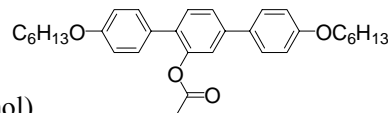
Yield: 3.5 g (93.3 %), yellow oil

Analytical data: C₄₁H₅₈O₉ M_w = 694.89

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.54-7.50 (m, 4 H, Ar-**H**), 7.34 (d, ³J(H,H) = 7.9, 1 H, Ar-**H**), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-**H**), 6.97-6.88 (m, 4 H, Ar-**H**), 4.16 (t, ³J(H,H) = 5.4, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.78 (t, ³J(H,H) = 5.4, 2 H, OCH₂), 3.70 (s, 3 H, OCH₃), 3.67-3.59 (m, 12 H, OCH₂), 1.84-1.72 (m, 4 H, CH₂), 1.50-1.29 (m, 12 H, CH₂), 0.94-0.87 (m, 6 H, CH₃).

4,4''-Dihexyloxy-p-terphenyl-2'-ylacetate (8):

Reagents: **4** (1.15 g, 5.6 mmol)
 Pd(OAc)₂ (39 mg, 0.17 mmol)
 2-(Di-*tert*-butylphosphino)biphenyl (104 mg, 0.35 mmol)
 4-Hexyloxybenzeneboronic acid (3.0 g, 14 mmol)
 KF (3.0 g, 52 mmol)
 Dry THF (6 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃

Yield: 2.5 g (91.4 %), colorless solid

Analytical data: C₃₂H₄₀O₄ M_w = 488.66

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.55-7.29 (m, 6 H, Ar-**H**), 7.27 (d, ⁴J(H,H) = 1.5, 1 H, Ar-**H**), 6.98-6.90 (m, 4 H, Ar-**H**), 3.99 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 2.11 (s, 3 H, CH₃), 1.86-1.72 (m, 4 H, CH₂), 1.52-1.25 (m, 12 H, CH₂), 0.94-0.87 (m, 6 H, CH₃).

Methyl 11-(4,4''-dibenzyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (7/B/3):Reagents: **3/3** (2.69 g, 7.34 mmol)Pd(OAc)₂ (43.6 mg, 0.19 mmol)2-(Di-*tert*-butylphosphino)biphenyl (128 mg, 0.43 mmol)

4-Benzyloxybenzeneboronic acid (5.02 g, 22.0 mmol)

KF (3.3 g, 57.0 mmol)

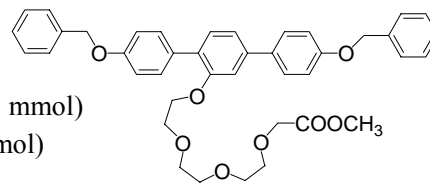
Dry THF (10 mL)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/PE = 1/1 (V/V)

Yield: 4.7 g (96.6 %), colorless solid

Analytical data: C₄₁H₄₂O₈ M_w = 662.77

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.55-7.28 (m, 15 H, Ar-H), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.08-6.96 (m, 4 H, Ar-H), 5.11 (s, 2 H, OCH₂), 5.10 (s, 2 H, OCH₂), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.11 (s, 2 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.70-3.57 (m, 11 H, OCH₂, OCH₃).

**Methyl 14-(4,4''-dibenzyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (7/B/4):**Reagents: **3/4** (3.24 g, 7.88 mmol)Pd(OAc)₂ (50.5 mg, 0.22 mmol)2-(Di-*tert*-butylphosphino)biphenyl (148 mg, 0.50 mmol)

4-Benzyloxybenzeneboronic acid (5.39 g, 23.7 mmol)

KF (3.8 g, 66.0 mmol)

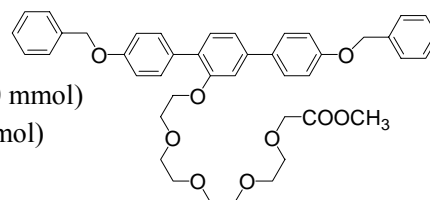
Dry THF (10 mL)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/PE = 2/1 (V/V)

Yield: 5.0 g (89.8 %), colorless solid

Analytical data: C₄₃H₄₆O₉ M_w = 706.82

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.55-7.52 (m, 4 H, Ar-H), 7.45 (d, ³J(H,H) = 7.7, 4 H, Ar-H), 7.40-7.43 (m, 7 H, Ar-H), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.06-6.99 (m, 4 H, Ar-H), 5.11 (s, 2 H, OCH₂), 5.09 (s, 2 H, OCH₂), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.11 (s, 2 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.70 (s, 3 H, OCH₃), 3.68-3.59 (m, 12 H, OCH₂).

**Methyl 11-(4,4''-dioctyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (7/8/3):**Reagents: **3/3** (0.587 g, 1.6 mmol)Pd(OAc)₂ (14.5 mg, 0.065 mmol)2-(Di-*tert*-butylphosphino)biphenyl (38.6 mg, 0.129 mmol)

4-Octyloxybenzeneboronic acid (1.0 g, 4.0 mmol)

KF (1.1 g, 19 mmol)

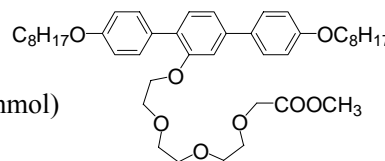
Dry THF (7 mL)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/2 (V/V)

Yield: 0.71 g (100 %), colorless solid

Analytical data: C₄₂H₆₂O₈ M_w = 706.95

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.49 (m, 4 H, Ar-H), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H), 7.19 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H), 6.97-6.89 (m, 4 H, Ar-H), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.71-3.58 (m, 11 H, OCH₂, OCH₃), 1.83-1.73 (m, 4 H, CH₂), 1.57-1.24 (m, 20 H, CH₂), 0.89-0.86 (m, 6 H, CH₃).



9.6.2 Procedure (II)

Methyl ω -(4,4''-dihydroxy-p-terphenyl-2'-yloxy)[oligo(oxy-ethylene)yl] acetates (**10/n**):

General procedure: The appropriate benzyl ether **7/B/n** (1 mmol) dissolved in methanol (15 mL) was treated with cyclohexene (12 mL) and Pearlman's catalyst (0.74 g, 20 %) under reflux until the starting benzyl ether had been completely consumed as judged by TLC analysis. The catalyst was filtered off and all volatiles were removed in vacuum, the crude product was purified by column chromatography over silica gel with $\text{CHCl}_3/\text{CH}_3\text{OH}$ as eluent.

Methyl 11-(4,4''-dihydroxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**10/3**):

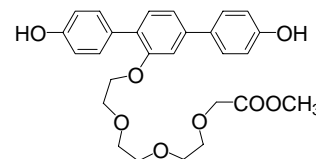
Reagents: **7/B/3** (4.5 g, 6.8 mmol)
 Pearlman's catalyst (0.9 g)
 Methanol (70 mL)
 Cyclohexene (60 mL)

Purification: Column chromatography with silica gel 60,
 eluent: $\text{CHCl}_3/\text{CH}_3\text{OH} = 10/0.5$ (V/V)

Yield: 3.1 g (94.5 %), yellow oil

Analytical data: $\text{C}_{27}\text{H}_{30}\text{O}_8$ $M_w = 482.52$

^1H NMR (CDCl_3 , J/Hz, 200 MHz) $\delta = 7.50\text{--}7.43$ (m, 4 H, Ar-H), 7.33 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.16 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.09 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.93-6.86 (m, 4 H, Ar-H), 4.18-4.05 (m, 4 H, OCH_2), 3.79-3.53 (m, 13 H, OCH_2 , OCH_3).



Methyl 14-(4,4''-dihydroxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (**10/4**):

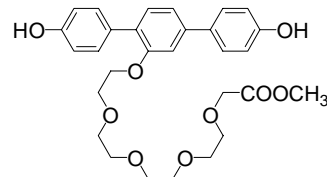
Reagents: **7/B/4** (3.5 g, 5.0 mmol)
 Pearlman's catalyst (0.7 g)
 Methanol (70 mL)
 Cyclohexene (60 mL)

Purification: Column chromatography with silica gel 60,
 eluent: $\text{CHCl}_3/\text{CH}_3\text{OH} = 10/0.5$ (V/V)

Yield: 2.3 g (88.2 %), yellow oil

Analytical data: $\text{C}_{29}\text{H}_{34}\text{O}_9$ $M_w = 526.57$

^1H NMR (CDCl_3 , J/Hz, 200 MHz) $\delta = 7.49\text{--}7.40$ (m, 4 H, Ar-H), 7.32 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.15 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.08 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.93-6.84 (m, 4 H, Ar-H), 4.17 (s, 2 H, OCH_2), 4.13 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 3.78-3.57 (m, 17 H, OCH_2 , OCH_3).



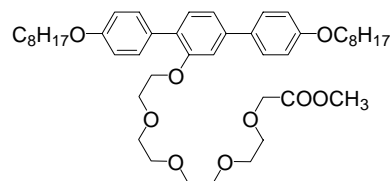
Methyl ω -(4,4''-dialkoxy-p-terphenyl-2'-yloxy)[oligo(oxyethylene)yl] acetates (**7/m/n**):

General procedure: Under an Argon atmosphere, the diphenol **10/n** (55 mmol) was dissolved in dry acetonitrile (150 mL), K_2CO_3 (34.5 g, 0.25 mol), the alkyl bromide (0.1 mol), and Bu_4NI (50 mg) were added, and the mixture was stirred under reflux for 4-8 h. Afterwards, the solvent was evaporated in vacuum, and the residue was dissolved in water and diethyl ether, the water phase was extracted by diethyl ether (3×100 mL). The combined organic phase was washed with water and brine. After drying over Na_2SO_4 and

filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with $\text{CHCl}_3/\text{CH}_3\text{OH}$ (or ethyl acetate/PE) as eluent.

Methyl 14-(4,4''-dioctyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (7/8/4):

Reagents: **10/4** (0.66 g, 1.3 mmol)
 Dry acetonitrile (50 mL)
 K_2CO_3 (0.87 g, 6.3 mmol)
 1-Bromooctane (1.2 g, 6.3 mmol)
 $(n\text{-Bu})_4\text{NI}$ (20 mg)



Purification: Column chromatography with silica gel 60, Eluent: ethyl acetate/n-hexane = 1/2 (V/V)

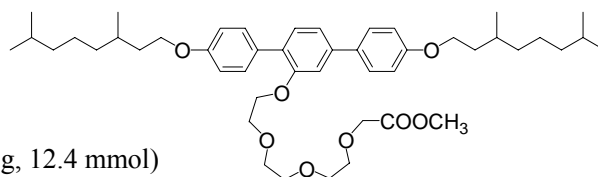
Yield: 0.71 g (75.3 %), yellow oil

Analytical data: $\text{C}_{45}\text{H}_{66}\text{O}_9$ $M_w = 751.00$

^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.53\text{--}7.49$ (m, 4 H, Ar-H), 7.33 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.97-6.89 (m, 4 H, Ar-H), 4.16 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 4.12 (s, 2 H, OCH_2), 3.99 (t, $^3J(\text{H,H}) = 6.6$, 2 H, OCH_2), 3.98 (t, $^3J(\text{H,H}) = 6.6$, 2 H, OCH_2), 3.79 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 3.71-3.55 (m, 15 H, OCH_2 , OCH_3), 1.83-1.73 (m, 4 H, CH_2), 1.57-1.22 (m, 20 H, CH_2), 0.89-0.84 (m, 6 H, CH_3).

Methyl 11-[4,4''-bis(3,7-dimethyloctyloxy)-p-terphenyl-2'-yloxy]-3,6,9-trioxaundecanoate (7/10*/3):

Reagents: **10/3** (0.6 g, 1.2 mmol)
 Dry acetonitrile (50 mL)
 K_2CO_3 (0.86 g, 6.2 mmol)
 1-Bromo-3,7-dimethyloctane (2.74 g, 12.4 mmol)
 $(n\text{-Bu})_4\text{NI}$ (20 mg)



Purification: Column chromatography with silica gel 60, eluent: $\text{CHCl}_3/\text{CH}_3\text{OH} = 10/0.1$ (V/V)

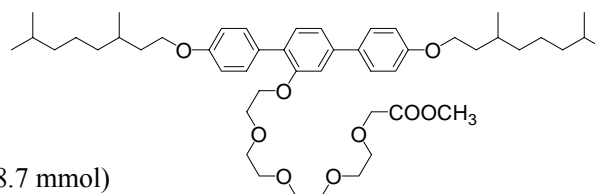
Yield: 0.7 g (73.7 %), yellow oil

Analytical data: $\text{C}_{47}\text{H}_{70}\text{O}_8$ $M_w = 763.05$

^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.53\text{--}7.49$ (m, 4 H, Ar-H), 7.34 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.97-6.90 (m, 4 H, Ar-H), 4.17 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 4.13 (s, 2 H, OCH_2), 4.04-3.96 (m, 4 H, OCH_2), 3.79 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH_2), 3.70-3.58 (m, 11 H, CH_2 , OCH_3), 1.85-1.77 (m, 2 H, CH), 1.67-1.61 (m, 2 H, CH), 1.60-1.43 (m, 4 H, CH_2), 1.37-1.07 (m, 12 H, CH_2), 0.93-0.90 (m, 6 H, CH_3), 0.89-0.70 (m, 12 H, CH_3).

Methyl 14-[4,4''-bis(3,7-dimethyloctyloxy)-p-terphenyl-2'-yloxy]-3,6,9,12-tetraoxatetradecanoate (7/10*/4):

Reagents: **10/4** (0.9 g, 1.7 mmol)
 Dry acetonitrile (50 mL)
 K_2CO_3 (1.2 g, 8.7 mmol)
 1-Bromo-3,7-dimethyloctane (1.9 g, 8.7 mmol)
 $(n\text{-Bu})_4\text{NI}$ (20 mg)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/2 (V/V)

Yield: 1.15 g (82.4 %), yellow oil

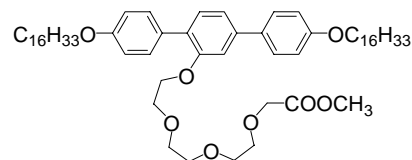
Analytical data: $\text{C}_{49}\text{H}_{74}\text{O}_9$ $M_w = 807.11$

^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.54\text{--}7.49$ (m, 4 H, Ar-H), 7.34 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.19

(dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.97-6.90 (m, 4 H, Ar-H), 4.16 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 4.08-3.94 (m, 4 H, OCH₂), 3.79 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH₂), 3.71-3.55 (m, 15 H, OCH₂, OCH₃), 1.88-1.79 (m, 2 H, CH), 1.69-1.61 (m, 2 H, CH), 1.60-1.43 (m, 4 H, CH₂), 1.37-1.07 (m, 12 H, CH₂), 0.96-0.90 (m, 6 H, CH₃), 0.89-0.70 (m, 12 H, CH₃).

Methyl 11-(4,4''-dihexadecyloxy-p-terphenyl-2'-yloxy)3,6,9-trioxaundecanoate (7/16/3):

Reagents: **10/3** (2.2 g, 4.6 mmol)
 Dry acetonitrile (100 mL)
 K₂CO₃ (3.1 g, 23 mmol)
 1-Bromohexadecane (4.2 g, 14 mmol)
 (n-Bu)₄NI (20 mg)



Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/0.1 (V/V)

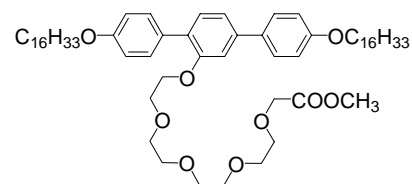
Yield: 3.9 g (91.7 %), colorless solid

Analytical data: C₅₉H₉₄O₈ M_w = 931.37

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.53-7.49 (m, 4 H, Ar-H), 7.34 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.97-6.88 (m, 4 H, Ar-H), 4.16 (t, $^3J(\text{H,H}) = 5.4$, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 4.00 (t, $^3J(\text{H,H}) = 6.5$, 2 H, OCH₂), 3.98 (t, $^3J(\text{H,H}) = 6.5$, 2 H, OCH₂), 3.78 (t, $^3J(\text{H,H}) = 5.4$, 2 H, OCH₂), 3.70 (s, 3 H, OCH₃), 3.66-3.61 (m, 8 H, OCH₂), 1.88-1.72 (m, 4 H, CH₂), 1.52-1.20 (m, 52 H, CH₂), 0.90-0.83 (m, 6 H, CH₃).

Methyl 14-(4,4''-dihexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetradecanoate (7/16/4):

Reagents: **10/4** (2.3 g, 4.4 mmol)
 Dry acetonitrile (100 mL)
 K₂CO₃ (3.0 g, 22 mmol)
 1-Bromohexadecane (5.3 g, 17 mmol)
 (n-Bu)₄NI (20 mg)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 2/5 (V/V)

Yield: 1.3 g (75.3 %), yellow oil

Analytical data: C₆₁H₉₈O₉ M_w = 975.43

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.54-7.49 (m, 4 H, Ar-H), 7.33 (d, $^3J(\text{H,H}) = 7.9$, 1 H, Ar-H), 7.19 (dd, $^3J(\text{H,H}) = 7.9$, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(\text{H,H}) = 1.7$, 1 H, Ar-H), 6.97-6.88 (m, 4 H, Ar-H), 4.16 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 3.99 (t, $^3J(\text{H,H}) = 6.6$, 2 H, OCH₂), 3.98 (t, $^3J(\text{H,H}) = 6.6$, 2 H, OCH₂), 3.79 (t, $^3J(\text{H,H}) = 5.0$, 2 H, OCH₂), 3.76-3.55 (m, 15 H, OCH₂, OCH₃), 1.83-1.73 (m, 4 H, CH₂), 1.57-1.16 (m, 52 H, CH₂), 0.89-0.82 (m, 6 H, CH₃).

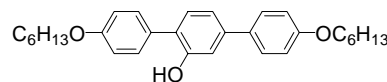
9.6.3 Procedure (III)

4,4''-Dihexyloxy-p-terphenyl-2'-ol (9): 4,4''-Dihexyl- oxy-p-terphenyl-2'-ylacetate (**8**) (2.5 g, 5.1 mmol) and NaOH (aq. 1M, 50 mL) were heated 16h under reflux. After cooling to r.t., the reaction mixture was acidified by aqueous HCl (10 %, 30 mL), then the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic phase was washed with water (2 × 50 mL) and brine (50 mL). After drying over Na₂SO₄ and filtration, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel with CHCl₃ as eluent to afford 1.8 g (4.0 mmol) colorless

solid, yield 79.0 %.

Analytical data: $C_{30}H_{38}O_3$ $M_w = 446.62$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.55-7.49$ (m, 2 H, Ar-H), 7.41-7.36 (m, 2 H, Ar-H), 7.26-7.22 (m, 1 H, Ar-H), 7.19-7.13 (m, 2 H, Ar-H), 7.04-6.91 (m, 4 H, Ar-H), 5.22 (s, 1 H, OH), 3.99 (t, $^3J(H,H) = 6.5$, 2 H, OCH_2), 3.98 (t, $^3J(H,H) = 6.5$, 2 H, OCH_2), 1.86-1.72 (m, 4 H, CH_2), 1.46-1.24 (m, 12 H, CH_2), 0.94-0.87 (m, 6 H, CH_3).

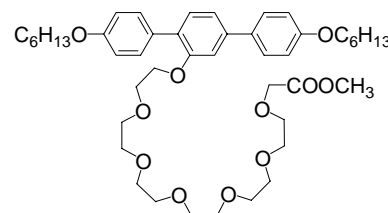


9.6.4 Procedure (IV)

Methyl-20-(4,4''-dihexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxaicosanoate (7/6/6): Under an argon atmosphere, the 4,4''-Dihexyloxy-p-terphenyl-2'-ol (**9**) (1.0 g, 2.2 mmol) was dissolved in dry acetonitrile (60 mL), K_2CO_3 (1.2 g, 8.7 mmol), the tosylate **2/6** (1.7 g, 3.3 mmol), and Bu_4NI (20 mg) were added, and the mixture was stirred under reflux for 4-8h. Afterwards, the solvent was evaporated in vacuum, and the residue was dissolved in water and diethyl ether, the water phase was extracted by diethyl ether (3×100 mL). The combined organic phase was washed with water and brine. After drying over Na_2SO_4 and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with ethyl acetate/n-hexane as eluent.

Analytical data: $C_{45}H_{66}O_{11}$ $M_w = 783.00$

1H NMR ($CDCl_3$, J/Hz, 400 MHz) $\delta = 7.53-7.50$ (m, 4 H, Ar-H), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-H), 7.18 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-H), 7.12 (d, $^4J(H,H) = 1.7$, 1 H, Ar-H), 6.97-6.89 (m, 4 H, Ar-H), 4.16 (t, $^3J(H,H) = 5.1$, 2 H, OCH_2), 4.13 (s, 2 H, OCH_2), 3.99 (t, $^3J(H,H) = 6.5$, 2 H, OCH_2), 3.98 (t, $^3J(H,H) = 6.5$, 2 H, OCH_2), 3.78 (t, $^3J(H,H) = 5.1$, 2 H, OCH_2), 3.72 (s, 3 H, OCH_3), 3.71-3.35 (m, 20 H, OCH_2), 1.81-1.75 (m, 4 H, CH_2), 1.50-1.43 (m, 4 H, CH_2), 1.39-1.22 (m, 8 H, CH_2), 0.92-0.87 (m, 6 H, CH_3).

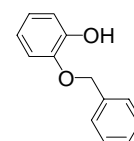


9.7 Synthesis of 3-substituted p-terphenyl derivatives 17/10/n

2-Benzyloxyphenol (11): Catechol (33 g, 0.30 mol) was dissolved in dry methanol (300 mL), NaOH (12 g, 0.30 mol) dissolved in dry methanol (100 mL) was added dropwise at 0-3 °C, after that, benzyl chloride (38 g, 0.30 mol) dissolved in dry methanol (100 mL) was added dropwise, the reaction mixture was heated to reflux for 2 H, cooled, acidified with concentrated HCl (ca. 10 mL), extracted with diethyl ether (3×150 mL) and washed with water (3×150 mL) and brine (100 mL). After drying over Na_2SO_4 and filtration, the solvent was removed in vacuum and the crude product was purified with column chromatography on silica gel with $CHCl_3$ as eluent and vacuum distillation (b.p. = 108-120 °C at 5Pa) which afforded a colorless oil, 19.3 g (96.4 mmol), yield 32.1 %.

Analytical data: $C_{13}H_{12}O_2$ $M_w = 200.23$

1H NMR ($CDCl_3$, J/Hz, 200 MHz) $\delta = 7.45-7.32$ (m, 5 H, Ar-H), 6.98-6.80 (m, 4 H, Ar-H), 5.68 (s, 1 H, OH), 5.07 (s, 2 H, Ar- CH_2).

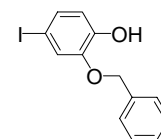


2-Benzyloxy-4-iodophenol (12): 2-Benzyloxyphenol (**11**) (19 g, 95 mmol) was dissolved

in methanol (500 mL), NaI 14.3 g, 95 mmol) and NaOH (3.8 g, 95 mmol) was added, and the solution was cooled to 0 °C. Aqueous sodium hypochlorite (4 %, 0.1mol) was added dropwise over 75min at 0-3 °C, as each drop hit the solution, a red colour appeared and faded instantly. The resulting mixture was stirred for 1h at 0-2 °C, and then aqueous sodium thiosulfate solution (10 %, 20 mL) was added, the mixture was adjusted to pH = 7 by using 5 % aqueous HCl and the product was extracted by diethyl ether (3 × 100 mL). The combined organic phases were washed with water (3 × 100 mL) and brine (100 mL). After drying over Na₂SO₄ and filtration, the solvent was removed in vacuum and the residue was purified by column chromatography (CHCl₃ as eluent) and recrystallization (diethyl ether/n-hexane) which afforded a colorless crystal, 10.9 g (33.4 mmol), yield 35.2 %.

Analytical data: C₁₃H₁₁IO₂ M_w = 326.13

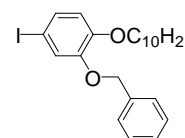
¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.43-7.36 (m, 5 H, Ar-H), 7.20 (d, ⁴J(H,H) = 2.1, 1 H, Ar-H), 7.19 (dd, ³J(H,H) = 8.1, ⁴J(H,H) = 2.1 1 H, Ar-H), 6.69 (d, ³J(H,H) = 8.1, 1 H, Ar-H), 5.60 (s, 1 H, OH), 5.05 (s, 2 H, Ar-CH₂).



1-Benzyloxy-2-decyloxy-5-iodobenzene (13): Under an Argon atmosphere, 2-benzyloxy-4-iodophenol (**12**) (8.0 g, 25 mmol) was dissolved in dry acetonitrile (100 mL), K₂CO₃ (8.7 g, 63 mmol), the 1-bromodecane (5.7 g, 26 mmol), and Bu₄NI (20 mg) were added, and the mixture was stirred under reflux for 4-8h. Afterwards, the solvent was evaporated in vacuum, and the residue was dissolved in water (50 mL) and diethyl ether (50 mL), the water phase was extracted by diethyl ether (3 × 50 mL). The combined organic phase was washed with water (2 × 50 mL) and brine (50 mL). After drying over Na₂SO₄ and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with ethyl acetate/PE (1/100 V/V) as eluent which afforded a colorless oil, 10.4 g (22.3 mmol), yield 89.6 %.

Analytical data: C₂₃H₃₁IO₂ M_w = 466.40

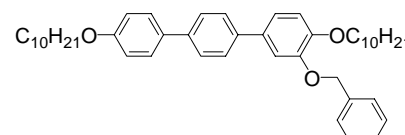
¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.43-7.18 (m, 7 H, Ar-H), 6.63 (d, ³J(H,H) = 8.7, 1 H, Ar-H), 5.06 (s, 2 H, OCH₂), 3.96 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 1.82-1.71 (m, 2 H, CH₂), 1.51-1.25 (m, 14 H, CH₂), 0.86 (t, ³J(H,H) = 6.6, 3 H, CH₃).



3-Benzyloxy-4,4''-didecyloxy-p-terphenyl (15): In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, Pd(PPh₃)₄ (0.1 g, 0.09 mmol) was added under an argon atmosphere to a mixture consisting of the 1-benzyloxy-2-decyloxy-5-iodo-benzene (**13**) (0.80 g, 1.7 mmol), 4'-decyloxybiphenyl-4-boronic acid (0.67 g, 1.9 mmol), dimethoxyethane (30 mL), and saturated NaHCO₃/H₂O solution (30 mL). The resulting mixture was stirred at reflux temperature for 5h. After cooling, the solvent was evaporated and the residue was dissolved in diethyl ether. The organic phase was separated, and was washed with water. After drying over Na₂SO₄ and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with CHCl₃ as eluent.

Analytical data: C₄₅H₆₀O₃ M_w = 648.96

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.65-7.25 (m, 11 H, Ar-H), 7.22-7.16 (m, 2 H, Ar-H), 6.98-6.95 (m, 3 H, Ar-H), 5.19 (s, 2 H, Ar-CH₂), 4.06 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.99 (t, ³J(H,H) =

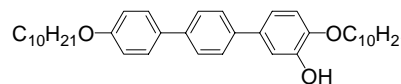


6.6, 2 H, OCH₂), 1.88-1.76 (m, 4 H, CH₂), 1.58-1.27 (m, 28 H, CH₂), 0.89-0.86 (m, 6 H, CH₃).

4,4''-Didecyloxy-p-terphenyl-3-ol (16): The 4,4''-didecyloxy-p-terphenyl-3-benzyloxy (15) (1.0 g, 1.5 mmol), dissolved in methanol (35 mL) was treated with cyclohexene (30 mL) and Pearlman's catalyst (30 mg, 20 %) under reflux until the starting benzyl ether had been completely consumed as judged by TLC analysis. The catalyst was filtered off and all volatiles were removed in vacuum, the crude product was purified by column chromatography over silica gel with CHCl₃ as eluent.

Analytical data: C₃₈H₅₄O₃ M_w = 558.83

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.58-7.52 (m, 6 H, Ar-H), 7.22 (d, ⁴J(H,H) = 2.3, 1 H, Ar-H), 7.09 (dd, ³J(H,H) = 8.5, ⁴J(H,H) = 2.3, 1 H, Ar-H), 6.98-6.89 (m, 2 H, Ar-H), 6.89 (d, ³J(H,H) = 8.5, 1 H, Ar-H), 5.68 (s, 1 H, OH), 4.07 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 3.99 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 1.86-1.76 (m, 4 H, CH₂), 1.50-1.43 (m, 4 H, CH₂), 1.42-1.20 (m, 24 H, CH₂), 0.89-0.86 (m, 6 H, CH₃).



Methyl ω-(4,4''-didecyloxy-p-terphenyl-3-yloxy)[oligo-(oxyethylene)]acetate (17/10/n):

General procedure: Under an Argon atmosphere, the 4,4''-Dihexyloxy-p-terphenyl-3-ol (16) (2.2 mmol) was dissolved in dry acetonitrile (60 mL), K₂CO₃ (1.2 g, 8.7 mmol), the tosylate 2/n (3.3 mmol), and Bu₄NI (20 mg) were added, and the mixture was stirred under reflux for 4-8h. Afterwards, the solvent was evaporated in vacuum, and the residue was dissolved in water and diethyl ether, the water phase was extracted by diethyl ether (3 × 100 mL). The combined organic phase was washed with water and brine. After drying over Na₂SO₄ and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with CHCl₃/CH₃OH (or ethyl acetate/n-hexane) as eluent.

Methyl 8-(4,4''-didecyloxy-p-terphenyl-3-yloxy)-3,6-dioxaoctanoate (17/10/2):

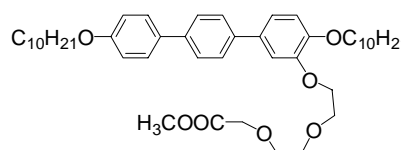
Reagents: 16 (0.4 g, 0.72 mmol)
2/2 (0.34 g, 1.1 mmol)
Dry acetonitrile (30 mL)
K₂CO₃ (0.3 g, 2.2 mmol)
(n-Bu)₄NI (20 mg)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃/CH₃OH = 10/1.5 (V/V)

Yield: 0.45 g (87.3 %), colorless solid

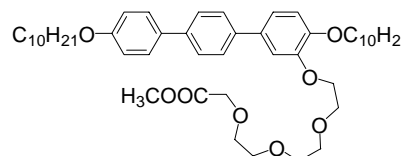
Analytical data: C₄₅H₆₆O₇ M_w = 719.00

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.58-7.51 (m, 6 H, Ar-H), 7.20-7.15 (m, 2 H, Ar-H), 6.98-6.91 (m, 3 H, Ar-H), 4.24 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.15 (s, 2 H, OCH₂), 4.08-3.62 (m, 13 H, OCH₂, OCH₃), 1.85-1.76 (m, 4 H, CH₂), 1.50-1.15 (m, 28 H, CH₂), 0.90-0.84 (m, 6 H, CH₃).



Methyl 11-(4,4''-didecyloxy-p-terphenyl-3-yloxy)-3,6,9-trioxaundecanoate (17/10/3):

Reagents: 16 (0.6 g, 1.1 mmol)
2/3 (0.8 g, 2.2 mmol)
Dry acetonitrile (50 mL)
K₂CO₃ (0.9 g, 6.5 mmol)



(n-Bu)₄NI (20 mg)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 2/5 (V/V)

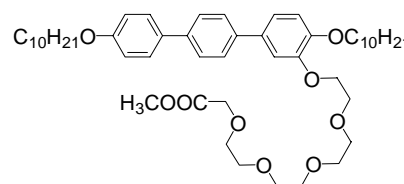
Yield: 0.7 g (85.3 %), colorless solid

Analytical data: C₄₇H₇₀O₈ M_w = 763.05

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.57-7.51 (m, 6 H, Ar-H), 7.24-7.14 (m, 2 H, Ar-H), 6.98-6.91 (m, 3 H, Ar-H), 4.24 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.13 (s, 2 H, OCH₂), 4.05-3.95 (m, 4 H, OCH₂), 3.89 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.78-3.64 (m, 11 H, OCH₂, OCH₃), 1.85-1.72 (m, 4 H, CH₂), 1.45-1.26 (m, 28 H, CH₂), 0.90-0.84 (m, 6 H, CH₃).

Methyl 14-(4,4''-didecyloxy-p-terphenyl-3-yloxy)-3,6,9,12-tetraoxa-tetradecanoate (17/10/4):

Reagents: **16** (0.6 g, 1.1 mmol)
2/4 (0.9 g, 2.2 mmol)
 Dry acetonitrile (50 mL)
 K₂CO₃ (0.9 g, 6.5 mmol)
 (n-Bu)₄NI (20 mg)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 2/5 (V/V)

Yield: 0.7 g (80.7 %), colorless solid

Analytical data: C₄₉H₇₄O₉ M_w = 807.11

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.57-7.51 (m, 6 H, Ar-H), 7.24-7.14 (m, 2 H, Ar-H), 6.98-6.91 (m, 3 H, Ar-H), 4.24 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.13 (s, 2 H, OCH₂), 4.05-3.88 (m, 4 H, OCH₂), 3.83 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.80-3.63 (m, 15 H, OCH₂, OCH₃), 1.85-1.71 (m, 4 H, CH₂), 1.45-1.15 (m, 28 H, CH₂), 0.90-0.84 (m, 6 H, CH₃).

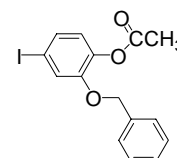
9.8 Synthesis of 2'-substituted 4-hexadecyloxy-4''-hexyloxy-p-terphenyl derivatives and 2'-substituted 4''-hexadecyloxy-4-hexyloxy-p-terphenyl derivatives (22/m'/m/n)

9.8.1 Synthesis of intermediates

2-Benzyloxy-4-iodophenyl acetate (14): The 2-benzyloxy-4-iodo-phenol (**12**) (19.5 g, 59.8 mmol) was dissolved in toluene (400 mL), acetic anhydride (9.15 g, 89.7 mmol), triethylamine (9.66 g, 95.7 mmol) and DMAP (0.12 g, 1 mmol) were added and the mixture was heated to reflux for 8 h. After cooling down, the reaction mixture was extracted with diethyl ether (3 × 100 mL) and the combined organic phase was washed with water (2 × 100 mL). After drying over Na₂SO₄ and filtration, the solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel with CHCl₃ as eluent which afforded a colorless oil, 18.4 g (68.6 mmol), yield 83.6 %.

Analytical data: C₁₅H₁₃IO₃ M_w = 368.17

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.37-7.26 (m, 7 H, Ar-H), 6.77 (d, ³J(H,H) = 8.3, 1 H, Ar-H), 5.03 (s, 2 H, OCH₂), 2.23 (s, 3 H, CH₃).



3-Benzyloxy-4'-alkoxybiphenyl-4-ols (18/n):

General procedure: In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, Pd(PPh₃)₄ (0.2 g, 5 mol %) was added under an argon atmosphere to a mixture consisting 2-benzyl-4-iodophenyl acetate (**14**) (1.25 g, 3.4 mmol), the boronic acid

(3.5 mmol), dimethoxyethane (30 mL), and saturated NaHCO₃/H₂O solution (20 mL). The mixture was stirred at reflux temperature for 5 h. After cooling, the solvent was evaporated and the residue was dissolved in diethyl ether (150 mL). The organic phase was separated, and was washed with water (3 × 50 mL). After drying over Na₂SO₄ and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel (CHCl₃ as eluent) and recrystallization (in most cases, the acetate group was removed after the coupling reaction, if not the case, hydrolysis was carried out by using NaOH in ethanol).

3-Benzyloxy-4'-hexyloxybiphenyl-4-ol (**18/6**)

Reagents: **14** (11.0 g, 30 mmol)

4-Hexyloxybenzeneboronic acid (7.33, 33 mmol)

Pd(PPh₃)₄ (1.73g, 1.5 mmol)

DME (85 mL)

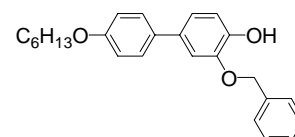
Saturated NaHCO₃/H₂O (85 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃ and recrystallization from diethyl ether

Yield: 8.2 g (72.7 %), colorless solid

Analytical data: C₂₅H₂₈O₃ M_w = 376.49

¹H NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.44-7.38 (m, 7 H, Ar-H), 7.11-6.90 (m, 5 H, Ar-H), 5.61 (s, 1 H, OH), 5.15 (s, 2 H, OCH₂), 3.98 (t, ³J(H,H) = 6.5, 2 H, OCH₂), 1.83-1.72 (m, 2 H, CH₂), 1.53-1.25 (m, 6 H, CH₂), 0.91 (t, ³J(H,H) = 6.5, 3 H, CH₃).



3-Benzyloxy-4'-hexadecyloxybiphenyl-4-ol (**18/16**)

Reagents: **14** (4.5 g, 12.2 mmol)

4-Hexadecyloxybenzeneboronic acid (4.9, 13.5 mmol)

Pd(PPh₃)₄ (0.7 g, 0.61 mmol)

DME (60 mL)

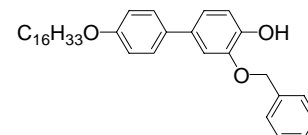
Saturated NaHCO₃/H₂O (60 mL)

Purification: Column chromatography with silica gel 60, eluent: CHCl₃ and recrystallization from acetone

Yield: 3.75 g (59.5 %), colorless solid

Analytical data: C₃₅H₄₈O₃ M_w = 516.75

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.45-7.33 (m, 7 H, Ar-H), 7.10 (d, ⁴J(H,H) = 1.9, 1 H, Ar-H), 7.05 (dd, ³J(H,H) = 8.3, ⁴J(H,H) = 1.9, 1 H, Ar-H), 6.96 (d, ³J(H,H) = 8.3, 1 H, Ar-H), 5.60 (s, 1 H, OH), 5.15 (s, 2 H, OCH₂), 3.97 (t, ³J(H,H) = 6.6, 2 H, OCH₂), 1.81-1.74 (m, 2 H, CH₂), 1.53-1.41 (m, 2 H, CH₂), 1.33-1.20 (m, 24 H, CH₂), 0.87 (t, ³J(H,H) = 6.6, 3 H, CH₃).



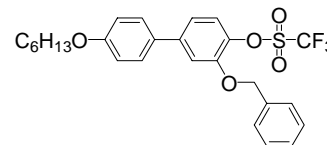
3-Benzyloxy-4'-alkoxybiphenyl-4-yltrifluoromethanesulfonates (**19/n**):

General procedure: To a solution of the phenol **18/n** (5.0 mmol) in dry pyridine (3 mL) at 0 °C, trifluoromethanesulfonic anhydride (1.6 g, 5.5 mmol) was slowly added. The resulting mixture was stirred at 0 °C for 5min, then allowed to warm to r.t. and stirred at this temperature for 25h. The resulting mixture was poured into water and extracted with diethyl ether (3 × 50 mL). The diethyl ether extract was washed sequentially with water (2 × 50 mL), 10 % aq HCl (30 mL), water (2 × 50 mL) and brine (30 mL), after dried over Na₂SO₄

and concentrated. The crude product was purified by flash column chromatography on silica gel with CHCl_3 as eluent.

3-benzyloxy-4'-hexyloxybiphenyl-4-yltrifluoromethanesulfonate (**19/6**)

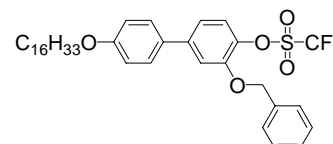
Reagents: **18/6** (7.1 g, 18.9 mmol)
 Dry pyridine (10 mL)
 Trifluoromethanesulfonic anhydride (5.9 g, 21.0 mmol)
 Purification: Column chromatography with silica gel 60, eluent: CHCl_3
 Yield: 9.5 g (98.8 %), yellow oil
 Analytical data: $\text{C}_{26}\text{H}_{27}\text{F}_3\text{O}_5\text{S}$ $M_w = 508.55$



^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.47\text{--}7.45$ (m, 2 H, Ar-H), $7.40\text{--}7.37$ (m, 4 H, Ar-H), $7.35\text{--}7.30$ (m, 1 H, Ar-H), 7.24 (d, $^3J(\text{H,H}) = 8.3$, 1 H, Ar-H), 7.19 (d, $^4J(\text{H,H}) = 2.1$, 1 H, Ar-H), 7.10 (dd, $^3J(\text{H,H}) = 8.3$, $^4J(\text{H,H}) = 2.1$, 1 H, Ar-H), $6.96\text{--}6.92$ (m, 2 H, Ar-H), 5.21 (s, 2 H, OCH_2), 3.98 (t, $^3J(\text{H,H}) = 6.5$, 2 H, OCH_2), $1.82\text{--}1.75$ (m, 2 H, CH_2), $1.50\text{--}1.43$ (m, 2 H, CH_2), $1.38\text{--}1.24$ (m, 4 H, CH_2), 0.90 (t, $^3J(\text{H,H}) = 6.5$, 3 H, CH_3). ^{19}F NMR (CDCl_3 , 188 MHz) $\delta = -74.44$ (s, 3 F, CF_3).

3-benzyloxy-4'-hexadecyloxybiphenyl-4-yltrifluoromethanesulfonate (**19/16**)

Reagents: **18/16** (4.6 g, 8.9 mmol)
 Dry pyridine (10 mL)
 Trifluoromethanesulfonic anhydride (2.8 g, 9.8 mmol)
 Purification: Column chromatography with silica gel 60, eluent: CHCl_3
 Yield: 5.7 g (98.7 %), yellow oil
 Analytical data: $\text{C}_{36}\text{H}_{47}\text{F}_3\text{O}_5\text{S}$ $M_w = 648.82$



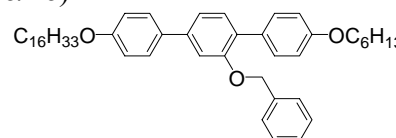
^1H NMR (CDCl_3 , J/Hz, 200 MHz) $\delta = 7.48\text{--}7.34$ (m, 7 H, Ar-H), 7.24 (d, $^3J(\text{H,H}) = 8.3$, 1 H, Ar-H), 7.19 (d, $^4J(\text{H,H}) = 1.9$, 1 H, Ar-H), 7.10 (dd, $^3J(\text{H,H}) = 8.3$, $^4J(\text{H,H}) = 1.9$, 1 H, Ar-H), $6.96\text{--}6.91$ (m, 2 H, Ar-H), 5.21 (s, 2 H, OCH_2), 3.97 (t, $^3J(\text{H,H}) = 6.4$, 2 H, OCH_2), $1.79\text{--}1.74$ (m, 2 H, CH_2), $1.53\text{--}1.24$ (m, 26 H, CH_2), 0.86 (t, $^3J(\text{H,H}) = 6.5$, 3 H, CH_3). ^{19}F NMR (CDCl_3 , 188 MHz) $\delta = -74.44$ (s, 3 F, CF_3).

2'-Benzyloxy-4-hexadecyloxy-4''-hexyloxy-p-terphenyl (**20/16/6**) and 2'-benzyloxy-4''-hexadecyloxy-4-hexyloxy-p-terphenyl (**20/6/16**):

General procedure: In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, $\text{Pd}(\text{PPh}_3)_4$ (0.37 g, 0.32 mmol) was added under an argon atmosphere to a mixture consisting the appropriate trifluoromethanesulfonate **19/n** (6.40 mmol), the boronic acid (12.8 mmol), dry toluene (45 mL), and Na_2CO_3 (dry solid, 1.33 g, 12.5 mmol). The mixture was stirred at reflux temperature for 5 h. After cooling, the solvent was evaporated and the residue was dissolved in diethyl ether (300 mL) and water (50 mL). The organic phase was separated, and was washed with water (3×50 mL). After drying over Na_2SO_4 and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with ethyl acetate/n-hexane as eluent.

2'-benzyloxy-4-hexyloxy-4''-hexadecyloxy-p-terphenyl (**20/6/16**)

Reagents: **19/16** (1.08 g, 1.67 mmol)
 Dry toluene (10 mL)
 4-Hexyloxybenzeneboronic acid (0.74 g, 3.33 mmol)
 $\text{Pd}(\text{PPh}_3)_4$ (96 mg, 0.08 mmol)



Na_2CO_3 (0.35 g, 3.30 mmol)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/20 V/V

Yield: 0.74 g (65.7 %), colorless solid

Analytical data: $\text{C}_{47}\text{H}_{64}\text{O}_3$ $M_w = 677.01$

^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.56\text{--}7.48$ (m, 4 H, Ar-H), 7.40-7.18 (m, 8 H, Ar-H), 6.97-6.89 (m, 4 H, Ar-H), 5.12 (s, 2 H, CH_2), 4.00-3.95 (m, 4 H, CH_2), 1.83-1.75 (m, 4 H, CH_2), 1.49-1.41 (m, 4 H, CH_2), 1.39-1.22 (m, 28 H, CH_2), 0.92-0.82 (m, 6 H, CH_3)

2'-Benzyloxy 4-hexadecyloxy-4''-hexyloxy-p-terphenyl (**20/16/6**)

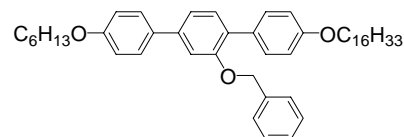
Reagents: **19/6** (3.25 g, 6.40 mmol)

Dry toluene (45 mL)

4-Hexyloxybenzeneboronic acid (4.63 g, 12.8 mmol)

$\text{Pd}(\text{PPh}_3)_4$ (0.37 g, 0.32 mmol)

Na_2CO_3 (1.33 g, 12.5 mmol)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/20 V/V

Yield: 2.56 g (59.1 %), colorless solid

Analytical data: $\text{C}_{47}\text{H}_{64}\text{O}_3$ $M_w = 677.01$

^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.56\text{--}7.46$ (m, 4 H, Ar-H), 7.40-7.18 (m, 8 H, Ar-H), 6.97-6.89 (m, 4 H, Ar-H), 5.12 (s, 2 H, CH_2), 4.00-3.93 (m, 4 H, CH_2), 1.83-1.75 (m, 4 H, CH_2), 1.49-1.41 (m, 4 H, CH_2), 1.39-1.22 (m, 28 H, CH_2), 0.92-0.82 (m, 6 H, CH_3)

4''-Hexadecyloxy-4-hexyloxy-p-terphenyl-2'-ol (**21/6/16**) and 4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-ol (**21/16/6**):

General procedure: The benzyl ether **20/6/16** or **20/16/6** (3.79 mmol) dissolved in methanol (60 mL) was treated with cyclohexene (60 mL) and Pearlman's catalyst (0.5 g, 20 %) under reflux until the starting benzyl ether had been completely consumed as judged by TLC analysis. The catalyst was filtered off and all volatiles were removed in vacuum, the crude product was purified by column chromatography over silica gel with CHCl_3 as eluent.

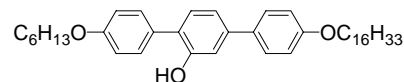
4''-Hexadecyloxy-4-hexyloxy-p-terphenyl-2'-ol (**21/6/16**)

Reagents: **20/6/16** (2.99 g, 4.42 mmol)

Pearlman's catalyst (500 mg)

Methanol (50 mL)

Cyclohexene (50 mL)



Purification: Column chromatography with silica gel 60, eluent: CHCl_3

Yield: 1.77 g (68.2 %), colorless solid

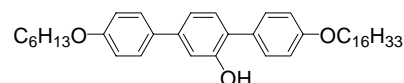
Analytical data: $\text{C}_{40}\text{H}_{58}\text{O}_3$ $M_w = 586.89$

^1H NMR (CDCl_3 , J/Hz, 400 MHz) $\delta = 7.55\text{--}7.51$ (m, 2 H, Ar-H), 7.41-7.37 (m, 2 H, Ar-H), 7.24 (d, $^3J(\text{H,H}) = 8.5$, 1 H, Ar-H), 7.17-7.15 (m, 2 H, Ar-H), 7.03-6.92 (m, 4 H, Ar-H), 5.24 (s, 1 H, OH), 4.01-3.97 (m, 4 H, CH_2), 1.84-1.75 (m, 4 H, CH_2), 1.49-1.41 (m, 4 H, CH_2), 1.39-1.22 (m, 28 H, CH_2), 0.92-0.82 (m, 6 H, CH_3)

4-Hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-ol (**21/16/6**)

Reagents: **20/16/6** (2.56 g, 3.79 mmol)

Pearlman's catalyst (500 mg)



Dry methanol (60 mL)
 Cyclohexene (60 mL)
 Purification: Column chromatography with silica gel 60, eluent: CHCl₃
 Yield: 1.00 g (45.0 %), colorless solid
 Analytical data: C₄₀H₅₈O₃ M_w = 586.89

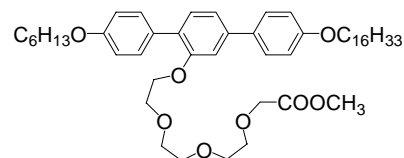
¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.54-7.51 (m, 2 H, Ar-H), 7.40-7.37 (m, 2 H, Ar-H), 7.24 (d, ³J(H,H) = 8.3, 1 H, Ar-H), 7.17-7.13 (m, 2 H, Ar-H), 7.02-6.91 (m, 4 H, Ar-H), 5.22 (s, 1 H, OH), 4.01-3.97 (m, 4 H, CH₂), 1.83-1.75 (m, 4 H, CH₂), 1.49-1.41 (m, 4 H, CH₂), 1.39-1.22 (m, 28 H, CH₂), 0.92-0.82 (m, 6 H, CH₃).

9.8.2 Synthesis of 2'-substituted 4-hexadecyloxy-4''-hexyloxy-p-terphenyl derivatives and 2'-substituted 4''-hexadecyloxy-4-hexyloxy-p-terphenyl derivatives (22/m'/m/n)

General procedure: Under an Argon atmosphere, the 4,4''-dialkoxy-p-terphenyl-2'-ol **21/6/16** or **21/16/6** (2.2 mmol) was dissolved in dry acetonitrile (60 mL), K₂CO₃ (1.2 g, 8.7 mmol), the tosylate **2/n** (3.3 mmol), and Bu₄NI (20 mg) were added, and the mixture was stirred under reflux for 4-8 h. Afterwards, the solvent was evaporated in vacuum, and the residue was dissolved in water and diethyl ether, the aqueous phase was extracted by diethyl ether (3 × 100 mL). The combined organic phase was washed with water and brine. After drying over Na₂SO₄ and filtration, the solvent was removed, the crude product was purified by column chromatography on silica gel with ethyl acetate/n-hexane as eluent.

Methyl 11-(4-hexyloxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**22/6/16/3**):

Reagents: **21/6/16** (0.86 g, 1.47 mmol)
2/3 (1.11 g, 2.94 mmol)
 Dry acetonitrile (50 mL)
 K₂CO₃ (0.51 g, 3.68 mmol)
 (n-Bu)₄NI (20 mg)

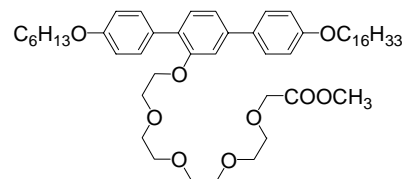


Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/2 (V/V)
 Yield: 0.48 g (41.3 %), colorless solid

Analytical data: C₄₉H₇₄O₈ M_w = 791.11 Cr 56 iso
¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.50 (m, 4 H, Ar-H), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.11 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H), 6.96-6.89 (m, 4 H, Ar-H), 4.17 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 4.00-3.96 (m, 4 H, CH₂), 3.79 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.71-3.54 (m, 11 H, OCH₂, OCH₃), 1.83-1.75 (m, 4 H, CH₂), 1.51-1.41 (m, 4 H, CH₂), 1.39-1.22 (m, 28 H, CH₂), 0.92-0.82 (m, 6 H, CH₃).

Methyl 14-(4-hexyloxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetra-decanoate (**22/6/16/4**):

Prepared according to the general procedure 8.2.1
 Reagents: **21/6/16** (0.89 g, 1.52 mmol)
2/4 (1.28 g, 3.04 mmol)
 Dry acetonitrile (50 mL)
 Potassium carbonate (0.53 g, 3.80 mmol)
 Tetra-n-butylammoniumiodide (20 mg)



Purification: Column chromatography with silica gel 60, Eluent: ethyl acetate/n-hexane = 1/2 (V/V)

Yield: 1.10 g (86.7 %), colorless solid

Analytical data: $C_{51}H_{78}O_9$ $M_w = 835.16$ Cr 51 Iso

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.53$ -7.50 (m, 4 H, Ar-H), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-H), 7.18 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(H,H) = 1.7$, 1 H, Ar-H), 6.96-6.89 (m, 4 H, Ar-H), 4.16 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 4.12 (s, 2 H, OCH_2), 4.00-3.96 (m, 4 H, CH_2), 3.78 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.71-3.58 (m, 15 H, OCH_2 , OCH_3), 1.83-1.75 (m, 4 H, CH_2), 1.51-1.41 (m, 4 H, CH_2), 1.39-1.22 (m, 28 H, CH_2), 0.92-0.84 (m, 6 H, CH_3).

Methyl 20-(4-hexyloxy-4''-hexadecyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxa-eicosanoate (**22/6/16/6**):

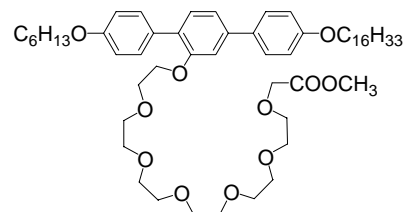
Reagents: **21/6/16** (0.80 g, 1.36 mmol)

2/6 (1.39 g, 2.73 mmol)

Dry acetonitrile (50 mL)

K_2CO_3 (0.47 g, 3.40 mmol)

(n-Bu) $_4$ NI (20 mg)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate

Yield: 1.10 g (87.3 %), colorless solid

Analytical data: $C_{55}H_{86}O_{11}$ $M_w = 923.26$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.53$ -7.50 (m, 4 H, Ar-H), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-H), 7.18 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-H), 7.12 (d, $^4J(H,H) = 1.7$, 1 H, Ar-H), 6.96-6.89 (m, 4 H, Ar-H), 4.16 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 4.13 (s, 2 H, OCH_2), 4.00-3.96 (m, 4 H, CH_2), 3.78 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.72-3.58 (m, 23 H, OCH_2 , OCH_3), 1.81-1.75 (m, 4 H, CH_2), 1.51-1.41 (m, 4 H, CH_2), 1.39-1.22 (m, 28 H, CH_2), 0.92-0.84 (m, 6 H, CH_3).

Methyl 11-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9-trioxaundecanoate (**22/16/6/3**):

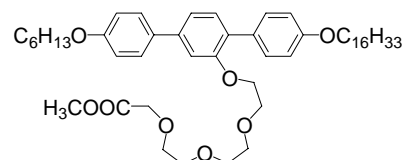
Reagents: **21/16/6** (0.71 g, 1.21 mmol)

2/3 (0.91 g, 2.42 mmol)

Dry acetonitrile (50 mL)

K_2CO_3 (0.42 g, 3.03 mmol)

(n-Bu) $_4$ NI (20 mg)



Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/1 (V/V)

Yield: 0.75 g (78.2 %), colorless solid

Analytical data: $C_{49}H_{74}O_8$ $M_w = 791.11$

1H NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 7.55$ -7.50 (m, 4 H, Ar-H), 7.33 (d, $^3J(H,H) = 7.9$, 1 H, Ar-H), 7.18 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 1.7$, 1 H, Ar-H), 7.13 (d, $^4J(H,H) = 1.7$, 1 H, Ar-H), 6.96-6.89 (m, 4 H, Ar-H), 4.16 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 4.12 (s, 2 H, OCH_2), 4.00-3.95 (m, 4 H, CH_2), 3.79 (t, $^3J(H,H) = 5.0$, 2 H, OCH_2), 3.75-3.58 (m, 11 H, OCH_2 , OCH_3), 1.83-1.75 (m, 4 H, CH_2), 1.53-1.41 (m, 4 H, CH_2), 1.39-1.22 (m, 28 H, CH_2), 0.92-0.84 (m, 6 H, CH_3).

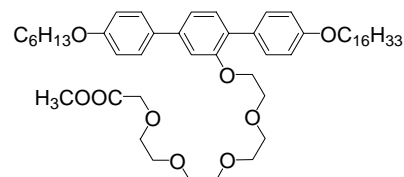
Methyl 14-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12-tetraoxatetra-decanoate (**22/16/6/4**):

Reagents: **21/16/6** (0.86 g, 1.47 mmol)

2/4 (1.23 g, 2.94 mmol)

Dry acetonitrile (50 mL)

K_2CO_3 (0.51 g, 3.68 mmol)



(n-Bu)₄NI (20 mg)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 1/2 (V/V)

Yield: 1.00 g (81.6 %), colorless solid

Analytical data: C₅₁H₇₈O₉ M_w = 835.16 Cr 35 Iso

¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.49 (m, 4 H, Ar-H), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H), 6.97-6.88 (m, 4 H, Ar-H), 4.16 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.12 (s, 2 H, OCH₂), 4.01-3.95 (m, 4 H, CH₂), 3.78 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.71-3.55 (m, 15 H, OCH₂, OCH₃), 1.83-1.75 (m, 4 H, CH₂), 1.51-1.41 (m, 4 H, CH₂), 1.39-1.22 (m, 28 H, CH₂), 0.92-0.84 (m, 6 H, CH₃).

Methyl 20-(4-hexadecyloxy-4''-hexyloxy-p-terphenyl-2'-yloxy)-3,6,9,12,15,18-hexaoxa-eicosanoate (**22/16/6/6**):

Reagents: **21/16/6** (0.69 g, 1.18 mmol)**2/6** (1.20 g, 2.36 mmol)

Dry acetonitrile (50 mL)

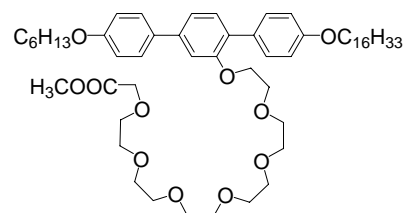
K₂CO₃ (0.41 g, 2.95 mmol)(n-Bu)₄NI (20 mg)

Purification: Column chromatography with silica gel 60, eluent: ethyl acetate/n-hexane = 2/1 V/V

Yield: 1.05 g (96.6 %), colorless solid

Analytical data: C₅₅H₈₆O₁₁ M_w = 923.26

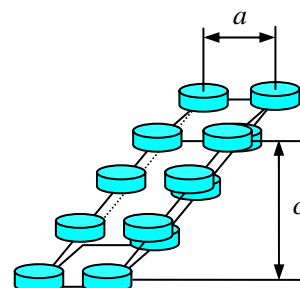
¹H NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.53-7.49 (m, 4 H, Ar-H), 7.33 (d, ³J(H,H) = 7.9, 1 H, Ar-H), 7.18 (dd, ³J(H,H) = 7.9, ⁴J(H,H) = 1.7, 1 H, Ar-H), 7.13 (d, ⁴J(H,H) = 1.7, 1 H, Ar-H), 6.97-6.89 (m, 4 H, Ar-H), 4.16 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 4.13 (s, 2 H, OCH₂), 4.00-3.95 (m, 4 H, CH₂), 3.78 (t, ³J(H,H) = 5.0, 2 H, OCH₂), 3.72-3.55 (m, 23 H, OCH₂, OCH₃), 1.83-1.75 (m, 4 H, CH₂), 1.51-1.41 (m, 4 H, CH₂), 1.39-1.22 (m, 28 H, CH₂), 0.92-0.84 (m, 6 H, CH₃).



10 Appendix

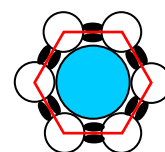
1 Calculation of the number of polar chains in one polar domain of the Rho phase of Na16/3

According to the lattice parameters ($a = 2.98$ nm, $c = 12.5$ nm), it can be calculated that the volume of the unit cell is $V_{\text{cell}} = \sqrt{3}/2 \cdot a^2 \cdot c = 96.1$ nm³. The volume of one **Na16/3** molecule is $V_{\text{molecule}} = 1.39$ nm³ [89]. So, the number of molecules in one unit cell is $N_{\text{molecule}} = V_{\text{cell}}/V_{\text{molecule}} = 96.1/1.39 = 69$. Because there are three polar domains in one unit cell, the number of polar chains in one polar domain can be calculated as $N_p = N_{\text{molecule}}/3 = 23$.



2 calculations of col_h phase of A6/4, A6/6, A4/4 and A4/3 based on the segregated model

Comp.	A6/6	A6/4	A4/4	A4/3
Lattice parameter a_{hex} (nm)	4.85	4.34	4.3	4.1
$V_{\text{cell}} = 0.45^a \times (\sqrt{3} \times a_{\text{hex}}^2 / 2)$ (nm ³)	9.17	7.37	7.21	6.55
V_{molecule} (nm ³)	1.25	1.13	1.03	0.97
Number of molecules in one cell = $V_{\text{cell}}/V_{\text{molecule}}$	7.33	6.50	7.00	6.75
Width of the lipophilic column: $d = \sqrt{3} / 3 \times a_{\text{hex}} - 1.25^b$ (nm)	1.55	1.26	1.23	1.12
Volume of the lipophilic column in one cell $V = 0.45 \times \pi d^2 / 4$ (nm ³) (circular shape of lipophilic column)	0.85	0.56	0.54	0.44
$V = 0.45 \times \sqrt{3} / 2 \times d^2$ (nm ³) (hexagonal shape of lipophilic column)	0.94	0.61	0.59	0.49
Volume of one terminal alkyl chain (V_R , nm ³)	0.156	0.156	0.106	0.106
Number of alkyl chains in one cell = V/V_R				
N with circular shape of lipophilic column	5.44	3.57	5.06	4.16
N with hexagonal shape of lipophilic column	6.00	3.94	5.58	4.59

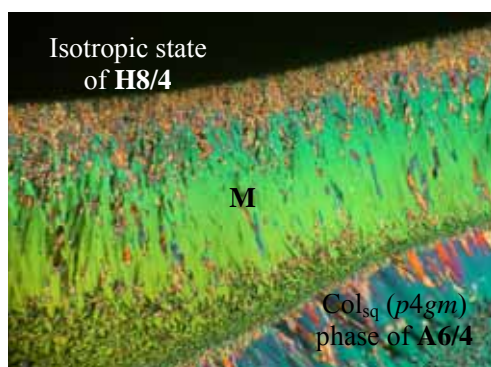


^a the height of the molecule is assumed as 0.45nm, ^b the length of the p-terphenyl cores is assumed as 1.25nm.

3 Solvent-penetration technique

The pure compound was surrounded by the solvent between two cover glasses. These samples were then placed on a heating stage and the contact region was observed by means of optical microscopy between crossed polarizer. The penetration of the solvent into the sample gives rise to a successive concentration gradient at the amphiphile/solvent boundary and the lyomesophases formed develop as bands and can be monitored as a function of temperature.

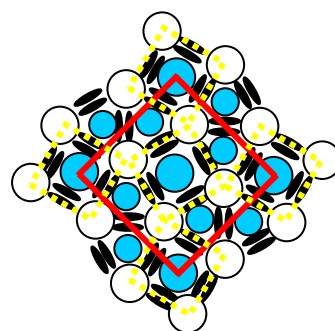
4 Texture of the contact region of H8/4 and A6/4 at 54 °C



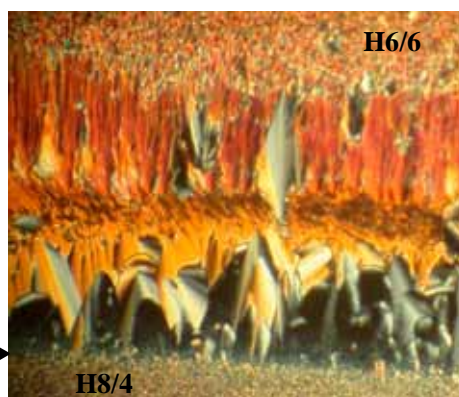
5 Calculation on the basis of the model of the Col_{sq} (*p4gm*) phase for H8/4

Comp.	H8/4
Lattice parameter a_{hex} (nm)	7.9
$V_{\text{cell}} = 0.45^a \times a_{\text{sq}}^2$ (nm ³)	28.1
V_{molecule} (nm ³) ^d	1.04
Number of molecules in one cell = $V_{\text{cell}}/V_{\text{molecule}}$	27.0
Width of the lipophilic column (nm)	2.84
Volume of the lipophilic column in one cell ^c	4×2.84
Volume of one terminal alkyl chain (V_R , nm ³) ^d	0.206
Number of alkyl chains in one cell = V/V_R	55.3

^a the height of the molecule is assumed as 0.45 nm, ^b the length of the p-terphenyl cores is 1.25 nm, ^c circular shape is assumed for the lipophilic columns, ^d the volume values of the molecules and the alkoxy chains were calculated using the crystal volume increments of Immirzi.^[89]



6 Textures of the contact region of H8/4 with H6/6 at 13 °C



11

References

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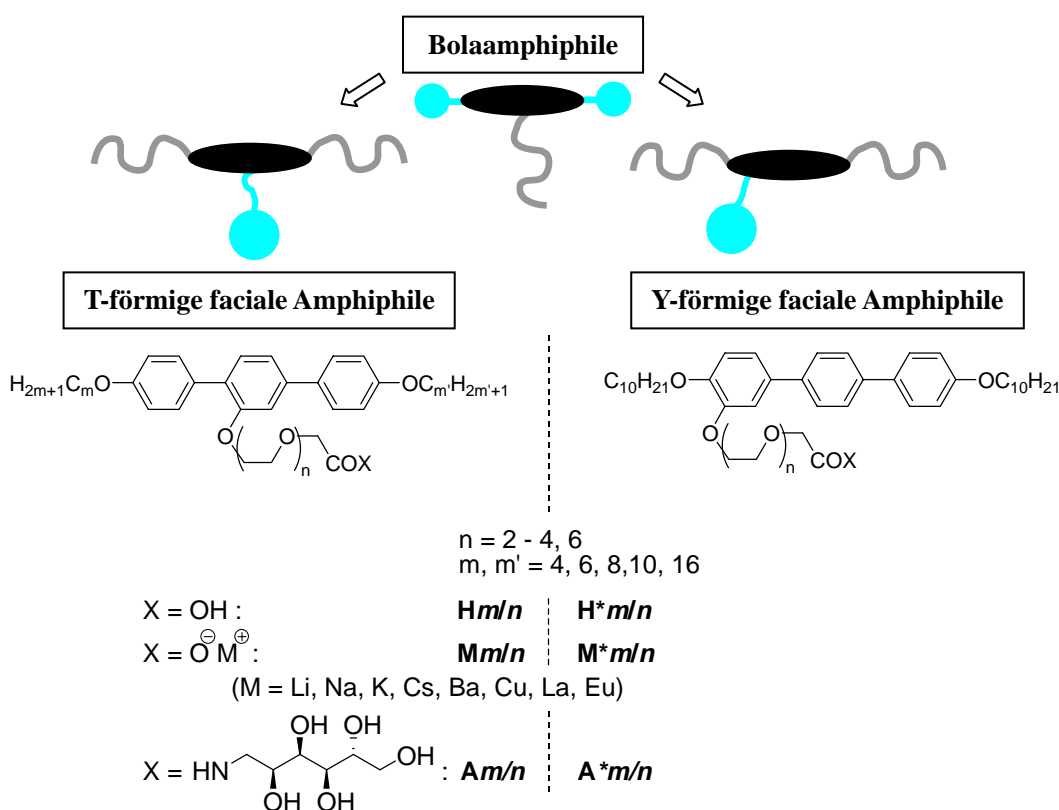
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Die Kenntnis der Triebkräfte der molekularen Selbstorganisation ist von fundamentaler Bedeutung für das Verständnis biologischer Prozesse und für das Design neuer funktioneller Materialien. Flüssigkristalline Phasen sind gute Modelle selbstorganisierender Systeme, in denen die Prinzipien der Selbstorganisation systematisch studiert werden können. Allerdings sind die meisten der bekannten flüssigkristallinen Phasen relativ einfach aufgebaut (Schichtstrukturen oder Organisationen von Kolumnen).



Wie jüngste Untersuchungen zeigen, bilden bolaamphiphile Moleküle bestehend aus Biphenyleinheiten mit terminalen Diolgruppen und unpolaren lateralen Substituenten verschiedene neuartige Mesophasenstrukturen aus. Durch Vergrößerung der unpolaren lateralen Kette ändert sich die Mesophasenstruktur von einer konventionellen SmA-Phase über dreifach segregierte wabenartige kolumnare Phasen (Col) zu neuartigen lamellaren Strukturen (Lam), in denen die Biphenyleinheiten parallel zu den Schichtebenen angeordnet sind.^[65-70] Es stellte sich die Frage, ob durch den Austausch der Positionen der polaren und unpolaren Gruppen andere Mesophasenstrukturen erzeugt werden können. Aus diesem Grunde wurden 3 Typen neuartiger T- und Y-förmiger facialer Amphiphile über Palladium-katalysierte Kreuzkupplungsreaktionen als Schlüsselschritt synthetisiert. Diese Amphiphile sind aufgebaut aus einem starren p-Terphenylkern, zwei flexiblen terminalen Alkoxyketten sowie einer lateralen Oligo(oxyethylen)kette. Die Oligo(oxyethylen)ketten

sind mit 3 verschiedenen Typen endständiger polarer Gruppen verknüpft: Metallcarboxylate (**Mm/n**), Oligohydroxyalkylamide (**Am/n**) und Carbonsäuren (**Hm/n**). Die erhaltenen Substanzen wurden mittels Polarisationsmikroskopie, DSC, Röntgenbeugungs- und Mischungsexperimenten untersucht. Für jede Serie wurde dabei der Einfluß der Länge der terminalen Alkoxyketten sowie der Länge der lateralen polaren Oligo(oxyethylen)kette auf das Mesophasenverhalten studiert.

Auf der Grundlage der synthetisierten Verbindungen wurden eine große Anzahl neuartiger Mesophasen beobachtet. Neben verschiedenen kolumnaren Mesophasen (Col) wurde ein neuer Typ von Mesh-Phasen und zwei Mesophasen mit 3D-Gitter gefunden. Die Ausbildung dieser Mesophasen erfolgt, gemäß dem Konzept der Mikrophasenseparation, unter der Segregation der lateralen polaren Kette, der lipophilen Alkylketten und der rigiden p-Terphenylkerne in drei verschiedene Regionen.

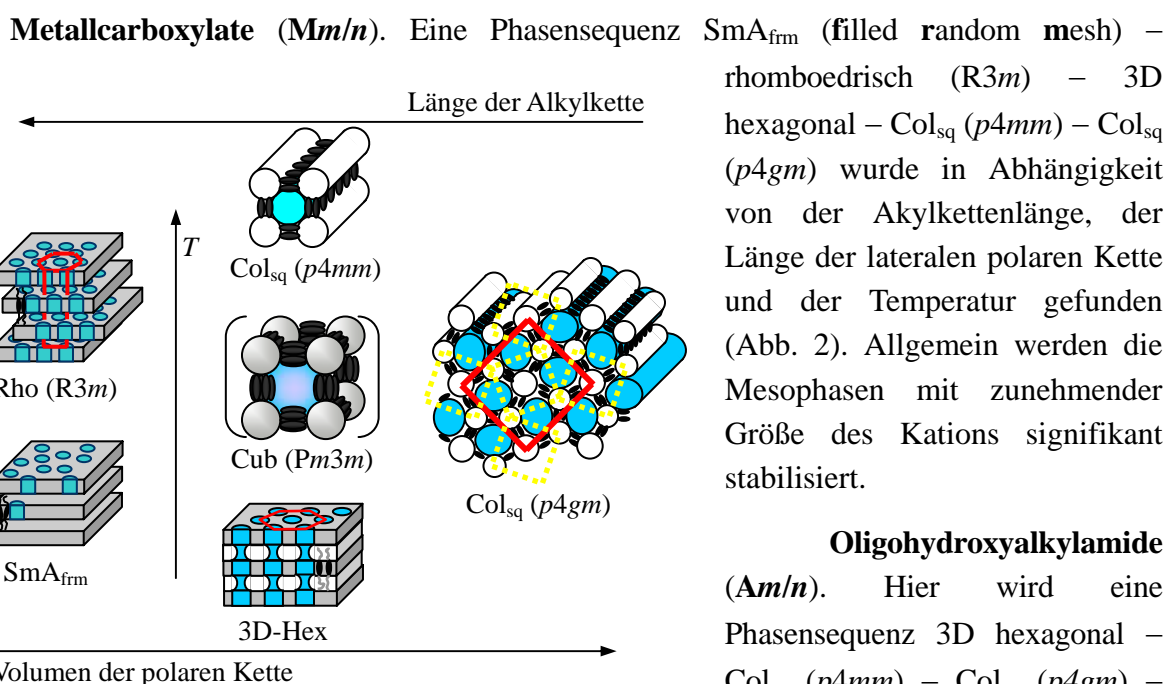


Abb. 2. Schematische Darstellung der Phasensequenz der Metallcarboxylate (**Mm/n**).

angeordnet) – $\text{Col}_{\text{h}(\parallel)}$ (aromatische Segmente parallel zu den polaren Säulen angeordnet) gefunden (S. Abb. 3).

Oligohydroxyalkylamide (Am/n). Hier wird eine Phasensequenz 3D hexagonal – $\text{Col}_{\text{sq}}(p4mm)$ – $\text{Col}_{\text{sq}}(p4gm)$ – $\text{Col}_{\text{h}(\perp)}$ (aromatische Segmente senkrecht zu den polaren Säulen

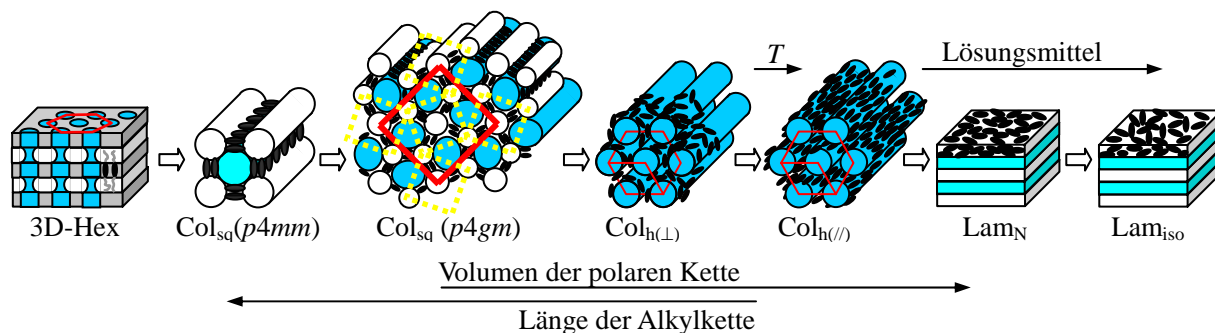


Abb. 3. Schematische Darstellung der Phasensequenz der Amide (**Am/n**).

Zusätzlich wurden in binären Mischungen aus **A4/4** und dem polaren, protischen Lösungsmittel Formamid zwei lyotrope Mesophasen gefunden. Es wird vermutet, daß es sich dabei um eine laminiert nematische Phase (Lam_N) und eine SmA (Lam_iso)-Phase handelt (Abb. 3).

Carbonsäuren (Hm/n). Eine Phasensequenz $\text{SmA} - \text{Col}_{\text{h}(\Delta)} - \text{Col}_{\text{h}(1)} - \text{Col}_{\text{sq}} (p4gm) - \text{Col}_{\text{h}}$ wurde bei Verkürzung der terminalen Alkoxyketten bzw. bei Vergrößerung des Volumens der polaren Kette gefunden (Abb. 4).

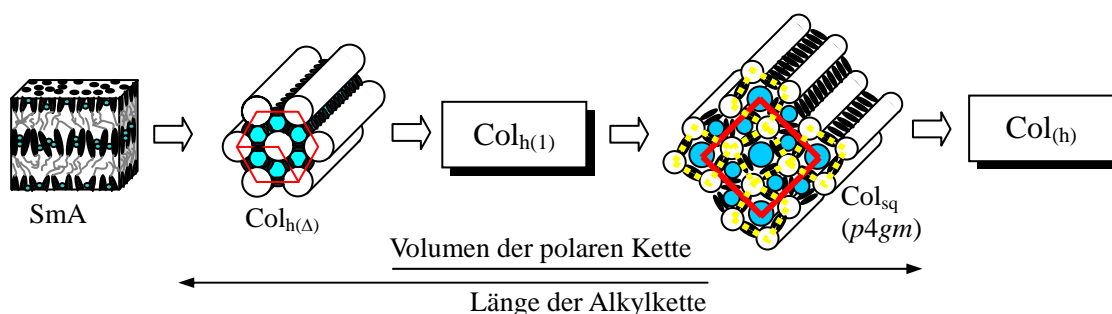


Abb. 4. Schematische Darstellung der Phasensequenz der Carbonsäuren (**Hm/n**); die Col_{h} -Phase konnte bisher durch Röntgenbeugungsexperimente nicht eindeutig bestätigt werden, $\text{Col}_{\text{h}(1)} =$ hexagonale kolumnare Phase mit grossem Gitterparameter.

Mindestens drei ausschlaggebende Faktoren bestimmen den Mesophasentyp: 1) Das Volumen der polaren lateralen Ketten; 2) die Länge der terminalen Alkylketten; 3) der Grad der Unverträglichkeit der lateralen Kette mit den anderen Molekülsegmenten.

Moleküle mit einer kurzen lateralen Kette bilden SmA-Phasen, in denen aromatische und aliphatische Subschichten alternieren. Jedoch separieren sich die polaren lateralen Ketten innerhalb der „aromatischen“ Unterschichten unter Bildung getrennter Domänen. Diese polaren Domänen sind zunächst zufällig verteilt, was zur Ausbildung einer „filled random mesh“-Phase (SmA_{frm}) führt. Mit abnehmender Temperatur organisieren sich die polaren Domänen in einem zweidimensionalen hexagonalen Gitter, was begleitet wird von einer Korrelation zwischen benachbarten Schichten in einer ABC-Anordnung und zur Bildung einer Rho ($\text{R}3m$)-Phase führt (Abb. 2). Mit zunehmendem Volumenanteil der lateralen polaren Ketten (durch Erhöhung der Anzahl der Oxyethyleneinheiten oder durch Verkürzung der terminalen Alkoxyketten) sind die polaren Domänen benachbarter Schichten befähigt, miteinander zu verschmelzen. Folglich wird eine 3D-Hex-Phase, bestehend aus perforierten aromatischen und lipophilen Schichten, welche senkrecht von hexagonal angeordneten Säulen durchdrungen werden, gebildet (Abb. 2).

Bei den Carbonsäuren (verringerte Unverträglichkeit mit den aromatischen Segmenten im Vergleich zu den Carboxylaten) führt eine Vergrößerung des Volumenanteils der lateralen polaren Kette direkt zu einem Aufbrechen der Schichtstruktur durch Bildung einer $\text{Col}_{\text{h}(\Delta)}$ -Phase. In dieser $\text{Col}_{\text{h}(\Delta)}$ -Phase bilden die aromatischen Segmente Zylinder mit dreieckigem Querschnitt, welche die polaren Säulen umschließen. Die Alkylketten sind in Säulen mit nahezu kreisförmigem Querschnitt segregiert. Diese Säulen sind hexagonal geordnet und befinden sich an den Kanten der dreieckigen Zylinder. Sie verknüpfen diese parallel miteinander, was zu Zylindernetzwerken führt. Durch weitere Vergrößerung des

Volumenanteils der lateralen polaren Kette wird eine Reorganisation eines Teils der rigiden Segmente zu einer quadratischen Anordnung induziert, was zur Ausbildung einer $\text{Col}_{\text{sq}} (p4gm)$ -Mesophase führt. In dieser $\text{Col}_{\text{sq}} (p4gm)$ -Phase haben die lipophilen Zylinder die Gestalt abgerundeter Pentagons (Abb. 4).

Die weitere Vergrößerung der lateralen Ketten durch Ersetzen der Carbonsäure-Funktion durch Polyhydroxygruppen, führt über eine Mesophase, bestehend ausschließlich aus quadratischen Zylindern [$\text{Col}_{\text{sq}} (p4mm)$] zu einer Mesophase aufgebaut aus fünfeckigen Zylindern [$\text{Col}_{\text{sq}} (p4gm)$] (Abb. 3). Diese $\text{Col}_{\text{sq}} (p4gm)$ -Phase ist die größte stabile polygonale Zylinderstruktur, die für die synthetisierten facialen Amphiphile gefunden wurde.

Eine Verkürzung der terminalen Alkylketten führt zum Verlust der Segregation dieser Ketten von den rigiden aromatischen Segmenten. Es resultiert ein Kontinuum der aromatischen und aliphatischen Segmente, in dem die polaren Säulen eine hexagonal dichteste Packung einnehmen, was zu Col_{h} -Phasen führt. In dem Kontinuum um die polaren Säulen herum besitzen die aromatischen Segmente jedoch noch eine Orientierungsfernordnung und diese Segmente sind entweder senkrecht (\perp) oder parallel (\parallel) zu den Säulenlängsachsen angeordnet. Dies führt zu zwei verschiedenen Col_{h} -Phasen ($\text{Col}_{\text{h}(\perp)}$ und $\text{Col}_{\text{h}(\parallel)}$, siehe Abb. 3).

Eine weitere Vergrößerung des polaren Molekülteils durch Solvation mit einem polaren Lösungsmittel (Formamid) führt zu einem Verschmelzen der Säulen zu Schichten und somit zur Bildung von lamellaren Phasen. In der Lam_{N} -Phase sollten die aromatischen Kerne eine Orientierungsfernordnung innerhalb der unpolaren Schichten besitzen. In der Lam_{iso} -Phase haben die aromatischen Segmente keine Fernordnung (Abb. 3).

Abbildung 5 faßt das Mesophasenverhalten aller Verbindungen zusammen. Die $\text{Col}_{\text{sq}} (p4gm)$ -Phasen sind dabei die bemerkenswertesten Mesophasen, da sie eine reguläre Organisation von Kolumnen mit fünfeckigem Querschnitt darstellen. Da eine periodische Anordnung von identischen regulären Fünfecken in einer Ebene unmöglich ist, müssen die Kolumnen einen nichtregulären pentagonalen Querschnitt aufweisen, d.h. die Kantenlängen und Winkel sind leicht verschieden. Solch eine Organisation kann mit wohldefinierten starren Bausteinen wie z.B. in kovalent gebundenen Strukturen oder in Koordinationspolymeren nicht realisiert werden.^[95,96] Folglich wurde bis heute noch keine reguläre und flache 2D-Organisation von Fünfecken beschrieben. Der flüssigkristalline Zustand, welcher Ordnung und Mobilität miteinander kombiniert, erlaubt eine solche Flexibilität und scheint daher eine wesentliche Voraussetzung für eine solche Organisation zu sein. Insgesamt wurden bisher vier verschiedene Typen solch einer regulären Organisation von pentagonalen Kolumnen in den flüssigkristallinen Phasen der T-förmigen ternären Amphiphile gefunden. Zwei dieser Mesophasen wurden für Bolaamphiphile mit unpolaren lateralen Ketten [$\text{Col}_{\text{r}} (p2gg)$ -Phasen] beschrieben^[70] und zwei neue Typen werden hier berichtet [$\text{Col}_{\text{sq}} (p4gm)$ -Phasen]. Dies zeigt, dass kolumnare Mesophasen, aufgebaut aus fünfeckigen Kolumnen, eine neue stabile Struktur in flüssigkristallinen Systemen repräsentieren.

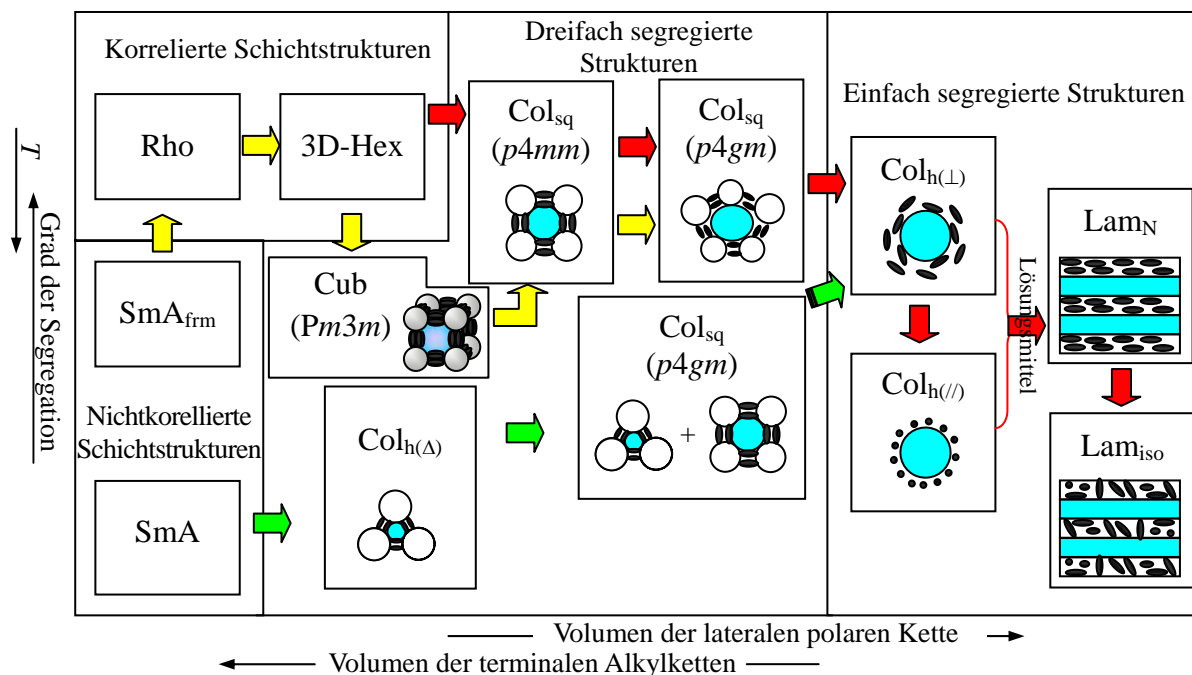


Abb. 5. Schematische Darstellung der Phasensequenz der facialis Amphiphile (gelber Pfeil: Metallcarboxylate; roter Pfeil: Amide; grüner Pfeil: Carbonsäuren)

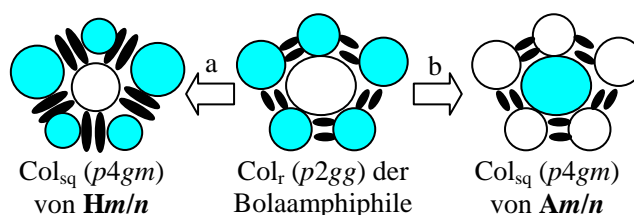


Abb. 6. Schematische Darstellung von drei verschiedenen kolumnaren Phasen mit einer fünfeckigen Querschnittsfläche (a: Wechsel der Orientierung der *rigid cores*; b: Austausch der Position der polaren und unpolaren Säulen).

Auch die $\text{Col}_{h(\Delta)}$ -Phase der Carbonsäuren **Hm/n** ist bemerkenswert, da in dieser Mesophase die polaren Säulen eine dreieckige Querschnittsfläche aufweisen, was hier zum ersten Mal gefunden wurde. Die $\text{Col}_{sq}(p4gm)$ -Phase von **Hm/n** ist sogar noch komplexer, da sie aus zwei verschiedenen Typen von polaren Säulen aufgebaut ist: Säulen mit dreieckigem und quadratischem Querschnitt. Auch dies stellt eine neue Organisationsform in flüssigkristallinen Phasen dar (Abb 7).

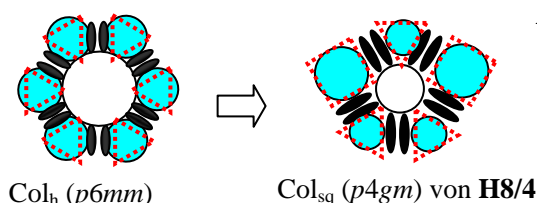


Abb. 7. Schematische Darstellung der Col_h -Phase und der $\text{Col}_{sq}(p4gm)$ -Phase; die polaren Säulen in der Col_h -Phase haben eine dreieckige Querschnittsfläche und in der $\text{Col}_{sq}(p4gm)$ -Phase dreieckige und quadratische Querschnittsflächen.

Die hier beschriebenen Moleküle weisen eine ternär amphiphile Struktur auf. Dreiblockcopolymeren^[44-57] repräsentieren eine weitere Klasse ternärer Amphiphile. Zum Beispiel zeigen ternäre sternförmige Blockcopolymeren Morphologien, welche vergleichbar mit den

Col_{sq} ($p4mm$)- und $\text{Col}_{\text{h}(\Delta)}$ -Phasen sind, aber auf einer signifikant größeren Längenskala.^[58] Jedoch ist für diese Polymere keine Organisation von fünfeckigen Säulen bekannt (Abb. 8).

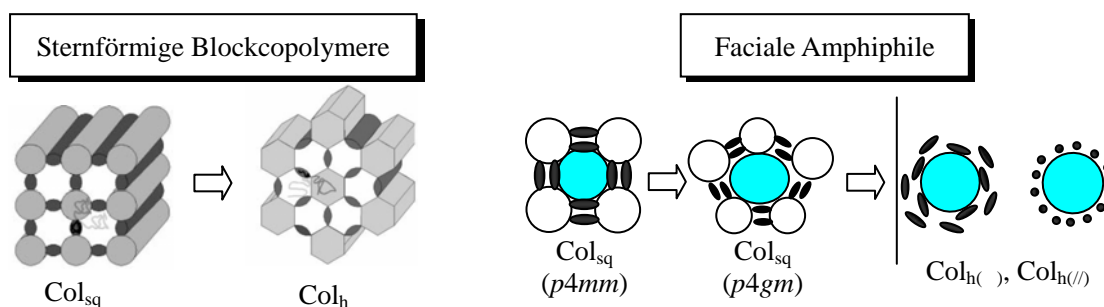


Abb. 8. Vergleich der Mesophasen von sternförmigen Blockcopolymeren und facialen Amphiphilen.

Die hier beschriebenen 3D-Phasen (Rho, 3D-Hex) können als korrelierte Schichtstrukturen aufgefasst werden. Sie können aber auch als korrelierte mesh-Phasen beschrieben werden. Mesh-Phasen wurden auch bei AB-Diblockcopolymeren,^[87] konventionellen binären Amphiphilen^[8-10] und Coil-rod-coil-Molekülen^[22-26] beobachtet. Die hier beschriebenen mesh-Phasen unterscheiden sich von den klassischen mesh-Phasen dadurch, dass die Hohlräume in einer der Subschichten von einer dritten inkompatiblen Komponente aufgefüllt sind, während in den mesh-Phasen binärer Verbindungen diese Hohlräume mit einem Überschuss der zweiten Komponente in den benachbarten Subschichten gefüllt sind.

Die Col_{sq} ($p4mm$)-Phase und die Col_{sq} ($p4gm$)-Phase der Verbindungen **Am/n** sind auch vergleichbar mit einigen Mesophasen, die für Bolaamphiphile mit unpolaren lateralen Ketten gefunden wurden,^[65-70] jedoch sind die Positionen der polaren und unpolaren Domänen im Vergleich zu diesen ausgetauscht. (siehe z. B. die $p2gg$ - und $p4gm$ -Phasen in Abb. 6).

Die beiden einfach segregierten Col_{h} -Phasen der Verbindungen **Am/n** ($\text{Col}_{\text{h}}()$ und $\text{Col}_{\text{h}}(//)$) unterscheiden sich von den inversen Col_{h} -Phasen binärer Amphiphile dadurch, dass in der kontinuierlichen Subphase eine zusätzliche Orientierungsfernordnung der p-Terphenyleinheiten vorliegt.

Die Position der lateralen polaren Kette an der p-Terphenyleinheit hat nur im Falle der Y-förmigen Natriumcarboxylate einen Einfluß auf die flüssigkristallinen Eigenschaften. Für diesen Verbindungstyp wurde eine bisher noch nicht näher charakterisierte Mesophase mit 3D-Gitter anstelle der 3D-Hex-Phase der analogen T-Amphiphile gefunden.

Alle experimentellen Ergebnisse zeigen, daß die kompetitive Kombination verschiedener Kräfte der Selbstorganisation in Multiblockmolekülen ein erfolgreicher Weg zu neuartigen Typen flüssigkristalliner Phasen ist.

Publications

- (1) "Liquid crystals with novel complex superstructures", **B. Chen**, X.-B. Zeng, U. Baumeister, S. Diele, G. Ungar, C. Tschierske, *Angew. Chem.*, **2004**, in press.
- (2) "Novel type of square columnar liquid crystalline phases formed by facial amphiphilic triblock molecules", **B. Chen**, U. Baumeister, S. Diele, X. -B. Zeng, G. Ungar, C. Tschierske, *J. Am. Chem. Soc.*, **2004**, 126, 8608.
- (3) "Complex mesophase morphologies of facial amphiphiles", **B. Chen**, U. Baumeister, S. Diele, X.-B. Zeng, G. Ungar, C. Tschierske, *32th Halle Arbeitstagung Flüssigkristalle, Halle (Saale)*, **2004**, Poster contributions 4.
- (4) "Novel Y-Shaped liquid crystals with complex mesophase morphologies", **B. Chen**, K. Das, S. Diele, A. G. Cook, C. Tschierske, *7th ECLC (Jaca)*, **2003**, Poster contributions 94.
- (5) H.-Y. Ma, Y. Zhang, **B. Chen**, et al, "Syndiospecific polymerization of styrene catalyzed by CpTiCl₂(OR) complexes", *Journal of Polymer science: Part A: polymer chemistry*, **2001**, 39, 1817.
- (6) H.-Y. Ma, **B. Chen**, J.-L. Huang, et al, "Steric and electronic effects of the R in IndTiCl₂(OR) catalysts on the syndiospecific polymerization of styrene", *Journal of Molecular Catalysis A: Chemical*, **2001**, 170, 67.
- (7) Z.-F. Feng, J Xie, **B. Chen**, et al, "The development of research on dinuclear metallocene catalysts", *Chinese J. Org. Chem.*, **2001**, 21 (1), 33.
- (8) Y.-L. Qian, **B. Chen**, J.-T. Jin, et al, "Ruthenium-Catalyzed ring-opening metathesis polymerization of norbornene initiated by O₂", *Acta Chim. Sinica*, **2000**, 58 (8), 1050.

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Erklärung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt habe. Den benutzten Werken wörtlich oder inhaltlich entnommene Stellen sind als solche kenntlich gemacht.

Diese Arbeit wurde bisher an keiner anderen Universität oder Hochschule vorgelegt. Ferner habe ich mich an keiner weiteren Institution um die Erlangung des Doktorgrades beworben.

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