Dendritic liquid crystals

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Abbreviations, symbols

2D	two-dimensional
abs.	absolute
Ar	aryl (group)
Bu	butyl group
CD	circular dichroism (spectroscopy)
Col_h	hexagonal columnar (phase)
Col_{obl}	oblique columnar (phase)
Col_r	rectangular columnar (phase)
Cr	crystalline (solid) state
D	director
d	layer thickness
DAB	diaminobutane
ΔH	phase transition enthalpy
DMF	dimethylformamide
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
eq.	equivalent
ESI	electron-spray ionisation
EtOAc	ethylacetate
EtOH	ethanol
HRMS	high-resolution mass spectrometry
Iso	isotropic (liquid) state
l	molecule legth
LC	liquid crystal

N	nematic (phase)
MS	mass spectrometry
N*	chiral nematic (phase)
N_D	discotic nematic (phase)
NMR	nuclear magnetic resonance
PAMAM	poly(amidoamine)
PEG	polyethylenglycol
PPI	poly(propyleneimine)
R_f	retention factor
RT	room temperature
SmA	smectic A (phase)
SmB	smectic B (phase)
SmC	smectic C (phase)
TEG	tetraethylene-gylcol moiety
T_I	isotropisation temperature
T_G	glass transition temperature
THF	tetrahydrofurane
TLC	thin layer chromatography
XRD	X-ray diffraction

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1 Literature overview

1.1 Liquid crystals

Since the initial discovery of Reinitzer[1] – and subsequent early pioneering work of Vorländer[2] and Friedel amongst others – the occasional existence of a transitional state of matter between the solid and the liquid phases has been established. This state is called mesomorphic state[3] (the degree of molecular order has an intermediate value between the long-range, three dimensional orientational and positional order of crystalline solids and the isotropic liquids). The states of matter during the transition from crystalline solid to isotropic liquid are the mesophases. If the long-range orientational order of the particles remains but the positional order is only partial or absent then the subgroup of substances is liquid crystalline. The liquid crystalline materials can be divided in two groups, the thermotropic and lyotropic liquid crystals. Thermotropic substances show mesophases in function of the temperature, while lyotropic systems are solutions having liquid crystalline behaviour depending on the temperature and the concentration of the solution. Substances that are both lyotropic and thermotropic are called amphotropic. Lyotropic systems are out of the scope of this thesis.

From very early on the 'fathers' of the liquid crystal research have recognized early that shape anisotropy of the molecules is necessary for the formation of mesophases. Early liquid crystal research has produced many examples of elongated, rod-like (so called calamitic) molecules. Most of them contained some rigid parts (aromatic rings in para substitution pattern) and flexible moieties (alkyl- or alkoxy-chains). This observation suggested a viable model for the molecular structure of the simplest mesophase called nematic phase (N). The molecules orient themselves in this phase to each other so that their long axis point on average in one direction (the director, D, Figure 1.1a). But otherwise the phase has much in common with the liquids, the substances are fluids, the molecules are moving rather free, rotation around the short and long axes are possible. Intramolecular mobility exists as well. From a macroscopic viewpoint the substances also exhibit anisotropy with respect to viscosity, optical properties, electrical and thermal conductivity. External stimuli like the presence of an electric or magnetic field can align the molecules which is the base of their most important application on the field of display technology[4,5,6]. The optical anisotropy and its consequences are an important identification tool

for liquid crystal phases as the image of a thin layer of a substance in the microscope with a heating stage illuminated with polarised light can be characteristic for a given mesophase. Chiral substances form chiral nematic mesophase (notation: N*, other name: cholesteric phase) which is a layered structure considering the molecular layers 'quasi-nematic'. The director of each layer is tilted with the previous one by the same angle giving rise to a twisted, helical structure.

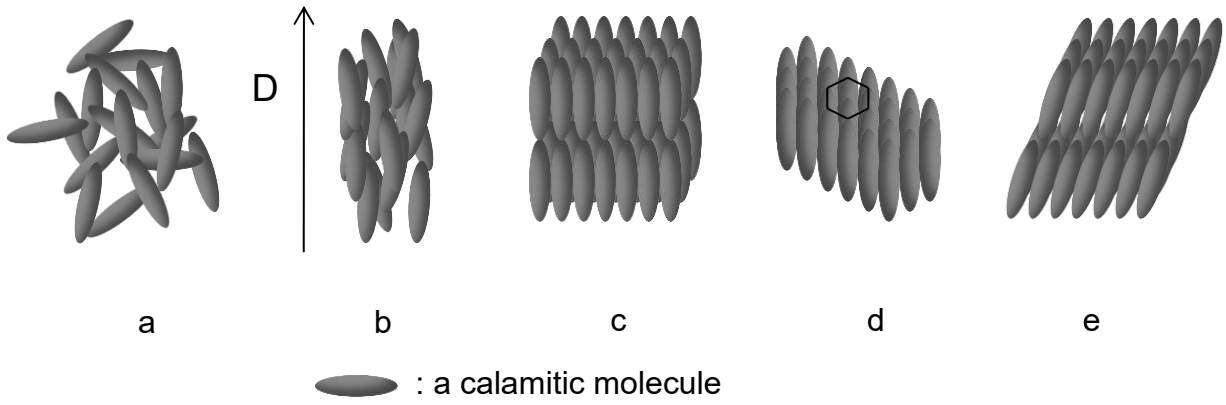


Figure 1.1 The schematic representation of the a) isotropic b) nematic c) smectic A d) smectic B e) smectic C mesophases.

Another phase may occur if the substance in the nematic state is cooled. This phase exhibits a higher order than the previous one because here formation of layers can be seen though other than in the case of N*. In this 'smectic' phase the molecules are preferentially parallel to each other in layers having an one-dimensional long-range order. The main driving force behind this is the microphase separation, *i.e.* the rigid parts of the calamitics associate to each other as well as the flexible ones forming the layers. In the smectic A phase (SmA) the director is perpendicular to the layer plane (Figure 1.1c) and the molecules retain freedom of translational diffusion, rotation around the short and long axes and there is no long-range positional order. X-ray diffraction measurements give a deeper insight in the structure of the correlated ones. The determined X-ray diffraction patterns show that in many cases of smectic A phases the layer distance seems to be smaller that the length of the molecule. The reason is that the terminal alkyl chains are in a 'molten' state[7], so their conformation is not all-trans (or all-anti), in consequence they have a shorter londitudinal extension. Another possibility is the intercalation of these 'liquid' chains between the molecular layers. Polar groups on the molecule like terminal cyano- or nitro-groups can lead to a bigger layer distance than the lenght of the molecule, explained by the polarity induced antiparallel orientation of the molecules.

The smectic C phase is similar to the smectic A but the director is not parallel to the layer normal (Figure 1.1e). The tilt angle is a function of the temperature, heating the sample further diminishes the angle between the director and the layer normal and forces the formation of smectic A phase if the substance is able to obtain this mesophase. The molecules enjoy almost the same degree of freedom in this phase as in the smectic A, though rotation around the long axis is more difficult.

Smectic B phase shows higher order than the above mesophases. Here the smectic A layer structure is maintained and additionally the molecules are in a hexagonal packing in the layers (Figure 1.1d). It applies only to the phases with a short-range positional order within the layers ('hexatic' smectic B phase). Chiral variants of the smectic phases also exist. Similar to the chiral nematic phase, periodic changes of properties can be seen in the layers. There is a plethora of different mesophases found up to now and with the development of the structure elucidation techniques further growth can be expected in the number of the distinguishable LC phases.

In 1977 Chandrasekhar and coworkers discovered[8] that beside the usual calamitics, disc shaped molecules can also form distinct mesophases. The structure of these mesophases has been explored and many similarities to the calamitics have been found. Discotic nematic (N_D) phase exist in which the molecular discs are ordered to that extent that the disc normals point on average in one direction (the director, D, see Figure 1.2b).

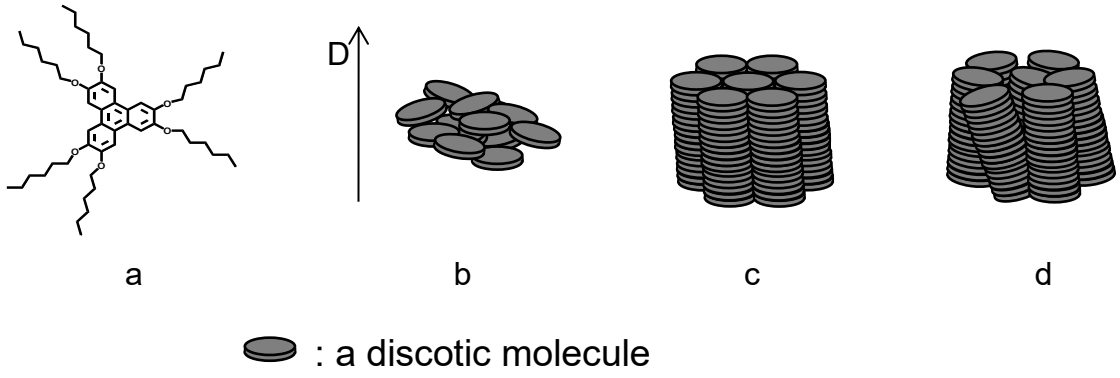


Figure 1.2 An example of a discotic mesogen (a). The schematic representation of the discotic phases: b) nematic, c) ordered, d) columnar nematic mesophases.

There is no additional order in this phase. If the discs organize themselves into columnar secondary structures, that can happen easily considering the different interactions in the inner

and outer parts of the discs, the discotic columnar phases are formed. An interesting mesophase is the columnar nematic phase in which the dics organize into columns but then the columns behave like the calamitic molecules in their nematic phase (Figure 1.2d). Interconnection of calamitic and discotic mesogens has been reported[9], too.

The above two classes of LC molecules possess shape anisotropy according to the general formula $z \neq x = y$. In the case of calamitics z represents the long axis, and with discotics z is the short axis. Both classes show rotational symmetry. If all three dimensions of the molecule are different, sanidic liquid crystalline systems may arise constituted by board-like molecules.

Among the many different molecular architectures that support the formation of mesophases[10,11] the bent-core molecules must be emphasized. They had been discovered in 1996[12] by a Japanese group and have been studied[13] intensively ever since. Their most exciting features are the ferroelectric or antiferroelectric switching behaviour due to special layer formation in a smectic-like arrangement.

The idea of connecting mesogens to a polymer backbone[14] afforded materials that – in a fortunate case - combined the advantageous properties of the polymers with the liquid crystals. The necessary mobility of the molecular segments (mesogenes) can usually be reached at elevated temperatures showing one of the drawbacks of these systems.

Interestingly, the incorporation of comparatively big, virtually incompatible moieties is also possible in a liquid crystalline system, as many examples of fullerene[15]- or ferrocene-containing[16,17] structures have been successfully prepared.

To answer the question 'Why do mesophases form?' one has to consider the intermolecular forces acting between the molecules[11,18]. The entropy driven general dispersion is counteracted by the van der Waals-forces, H-bonding, dipole-dipole interactions and electrostatic forces. Further repulsivity stems from the anisometry of the molecules and their amphipathic nature. Most of the LCs contain one or more aromatic moieties where π-π interactions play an important role. However, if the structure of the most common thermotropic LC classes is examined, it seems to be a plausible answer, that the cohesion caused by the associative forces of the rigid parts must be 'softened' by the chaotic, 'molten' nature of the mobile alkyl chains. If an equilibrium at a

certain temperature range is possible between the two opposite forces, liquid crystalline mesophase can form.

The liquid crystals were lacking practical applications for many years[2] but since the pioneering developments in the seventies of the last century a wide spectrum of practical applications[19,20,21] have emerged.

Further applications may arise from the idea of connecting mesogens to a polymer backbone[14] affording materials that – in a fortunate case - combine the advantageous properties of the polymers with the liquid crystals. The necessary mobility of the molecular segments (mesogenes) can usually be reached at elevated temperatures showing one of the drawbacks of these systems.

Interestingly, the incorporation of comparatively big, virtually incompatible moieties is also possible in a liquid crystalline system, as many examples of fullerene[15]- or ferrocene-containing[16,17] structures have been successfully prepared.

1.2 Dendrons, dendrimers

Dendrons are molecules with a repetitve, branched, tree-like backbone. The molecule is called a dendrimer if several, usually but not always identical dendrons are attached to a central core unit. Due to their extended structures, they possess a higher molecular mass than most of the molecules an organic chemist encounters. But their size and molar mass does not reach the polymer range. This intermediate position makes them interesting to many applications in chemistry.

Hyperbranched polymers are the forerunners of dendrimers. The monomer bears at least three complementary functionalities and during the polymerization these functional groups react forming the highly interwaved, irregular backbone (Figure 1.3. a).

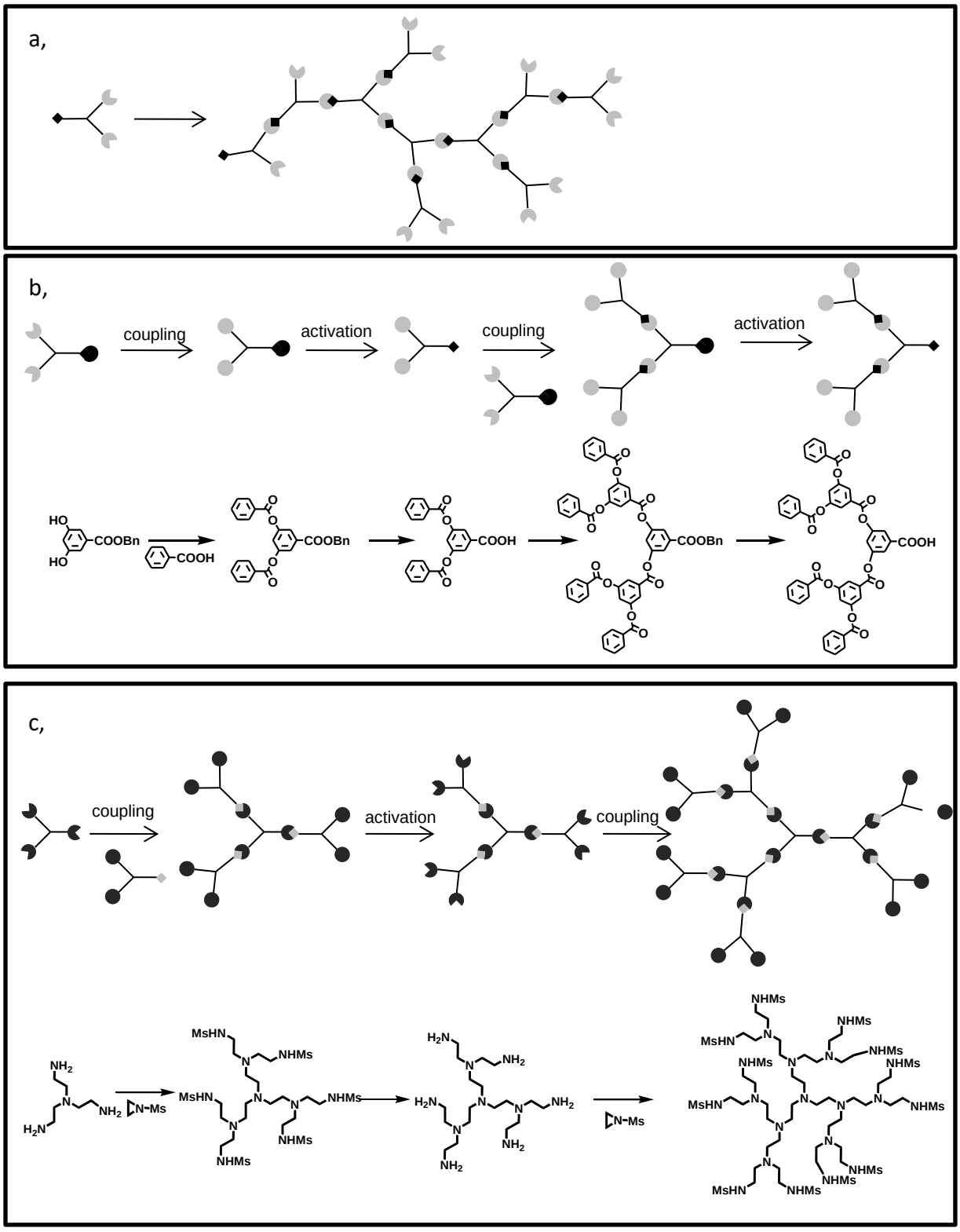


Figure 1.3 a) formation of a hyperbranched polymer b) convergent dendritic build-up with example c) divergent dendritic build-up with example

In contrast to this, the build up of the dendrons and dendrimers is a strictly controlled process yielding regular and tailorable structures that can be described by fractal-geometry[22]. The

synthesis requires two repeated, consecutive steps. The coupling step attaches the next building block layer to the previous structure and the activation step makes the next coupling step possible. Activation means the removal of a protecting group or some kind of functional group transformation that turns the previously necessarily inactive functionality to an active one. One of the two fundamental pathways to dendrons is the convergent growth (Figure 1.3b). In this case the later outer surface of the molecule is where the synthesis starts and the dendritic growth progresses inwards. When the necessary number of generations in a dendron have reached the synthesis may be finished or coupling to a core or a different entity (a polymer backbone[23], for instance) renders the desired molecule.

Dendritic generation or generation number shows how many layers of building block have been incorporated in the structure (Figure 1.4). It must be pointed out that there is no consensus where to start the numbering of the generations (at the core or at the surface).

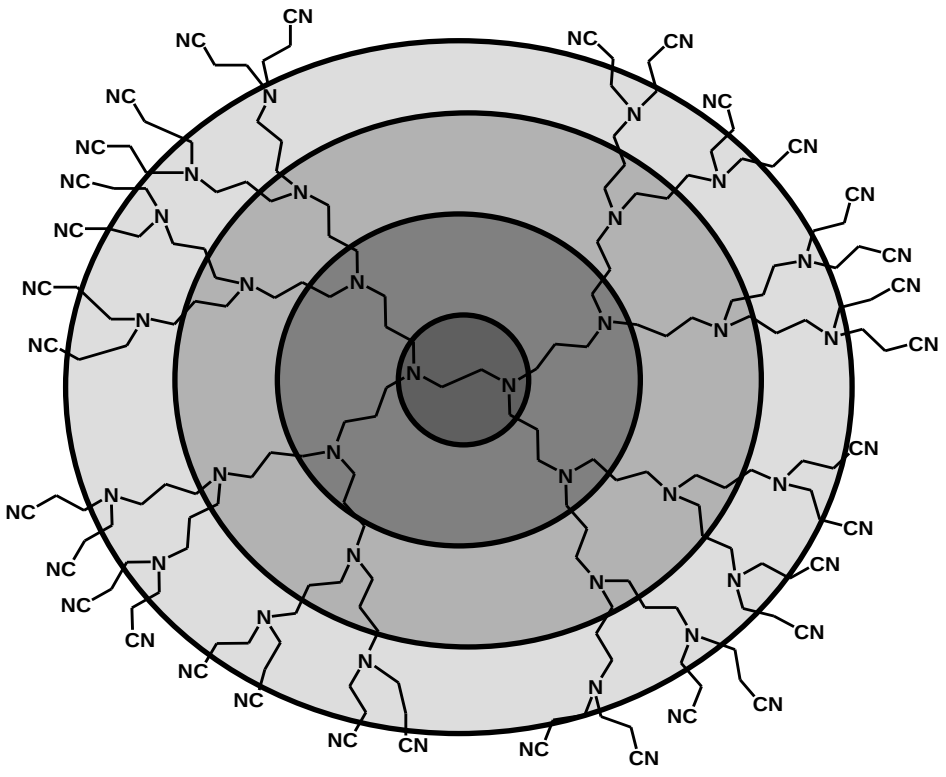


Figure 1.4 A 3rd generational dendrimer and its generations. The central circle covers the core and the fading coloured rings show the different generations

The divergent growth (Figure 1.3c) starts with a core unit to which the first generation of dendritic building block is attached. Then the obligatory activation and coupling delivers the

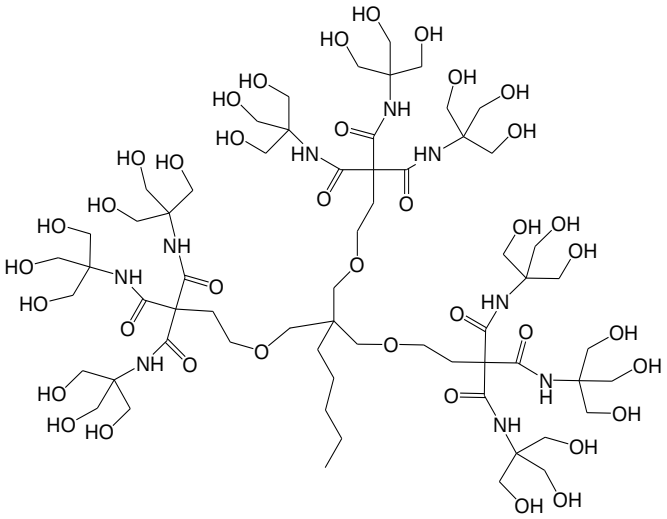
second generational dendrimer and so on. There were attempts to develop new dendrimer building startegies[24] different than the above two but they are used infrequently.

From the synthetic point of view, both pathways have advantages and disadvantages. By the divergent approach, different 'end-groups' can be attached to the appropriately functionalized surface of the divergent dendrimers, leading to multy-antennary dendrons and dendrimers. Some of these dendrimers are commercially available leading to frequent usage in the research, like the PAMAM or poly(amidoamine) dendrimers. The disadvantage here is that the divergent method always leads to a certain imperfection in the structure due to non-quantitative reaction of all end-groups. Purification of these compounds is challenging, considering polydisperse higher generations even more so, because of the relatively small polarity or molar mass difference between the compound and the 'impurity'. The normally high polarity and weight difference of the parent molecules and the product simplifies purification at the convergently grown dendrimers yielding perfect and monodisperse particles. The price one has to pay is the increased work effort of the synthesis with the convergent method.

The dendritic building block must always bear two sorts of functionalities. One of the reactive centers must be alone on the molecule and the other functionality must be present twice or three times. More than three of the same group used for coupling is unusual just because of steric factors.

The dendritic growth can not be infinite. The theroretical maximal size of a certain dendrimer is defined by the De Gennes-limit[25] which determines the size of a dendrimer with the tightest packing on the surface. This size can not be reached as the steric constraints increase with the increasing generation number.

Another point that must be mentioned is the problem of the nomeclature. Figure 1.5. shows a relatively simple dendrimer[22] having amide and ether branching points. The Chemical Abstracts compatible name is given. It is clear that the usage of the IUPAC nomenclature is inconvenient here. The simplified and practical naming convention is shown in Chapter 3.2.



1,19-dihydroxy-N, N',N'',N'''-tetrakis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]-10-[[4-[[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]amino]-3,3-bis[[[2-hydroxy-1,1-bis(hydroxymethyl)-ethyl]amino]carbonyl]-4-oxobutoxy]methyl]-2,2,18,18-tetrakis(hydroxymethyl)-4,16-dioxo-10-pentyl-8,12-dioxa-3,17-diazanonadecane-5,5,15,15-tetra-carboxamide

Figure 1.5 Example of a regular name for a dendrimer

Since the first attempts[26,27] to reach a regular structure instead of the polymer-like irregularity, a wide variety of branching possibilites have been used. Connections by ether-[28], ester-[29], amide-[30], double-[31] or triple-bonds[32] and even more particular connecting units[33,34] have been applied. Multicomponent and click reactions are also such a particular method.[35,36] Dendrimers that are held together by non-covalent interaction, e.g. ionic or coordinative forces have been synthesised, too. But not only this shows how versatile and flexible dendritic structures and synthestic protocols can be. Considering the different generations, incorporation of chirality[37], the possibility of different building blocks as different generations on the very same dendritic scaffold[38], the diverse functionalities that can be placed on the surface of a dendrimer, the manyfoldness of the useable core units, the possibility of attaching different dendrons on the same core, the production of dendrons with artificial defects or with grafted, differing parts can implement that the expression of 'tailoring' dendritic structures and function is not just an overused expression, like in some other fields of chemistry.

Different dendritic backbones have different properties. Molecules can be built up from perfect shape-persistency[33,39] to high flexiblility[40]. However, it is widely accepted that flexible dendrimers have a globular shape in solution or in vacuum. Increasing generation number forces the molecules increasingly in the globular shape under other circumstances as well. This is also

a reason why the outer surface of dendrimers is held to be the interface to the environment. Surface density and functionalization significantly determine the properties of the molecule. Dendrimers can associate to each other forming megamers[41] representing the next step towards macroscopic structures.

Applications[42,43] of dendrimers are also numerous. Among the features the catalytic carrier function is very prominent. The surface of the dendrimer or the internal cavities[44,45] in the structure can serve as catalytic centers. This application led to the concept of 'dendritic effect'[46]. According to it the dendritic structure enhances synergistically the effectivity of the individual catalytic centers and increases the efficiency beyond the sum of the individual efficiencies. In addition, similarities have been observed to the structural and self-organization possibilities of dendrimers and of the biomacromolecules[47]. Self-organization is also the basis of dendritic LC applications.

1.2.1 Fréchet-type dendrons and dendrimers

The well documented convergent approach leads to poly(benzyl-aryl-ether) dendrimers that are named after the discoverer Fréchet-type dendrimers[28,48]. They are synthesised using a simple building block, 3,5-dihydroxy benzylalcohol (Figure 1.6 a). The strategy utilizes the reactivity difference between the phenolic and alcoholic OH groups through a Williamson-type ether-synthesis as the coupling step. A part of an original Fréchet-type dendrimer can be seen on the Figure 1.6., a more complete impression can be won at the Scheme 3.2. The versatility of this approach has been attested by the many different building blocks[29,49,50,51,52,53,54,55,56] (Figure 1.6 c-i) used on a similar fashion to build up dendritic structures. Subsequent investigations of Fréchet and others led to surface modified dendrimers[57] transforming the original ester functionalities to free acids, amides, etc. The dendritic backbone is prepared by well known protocols and its chemical stability is notably.

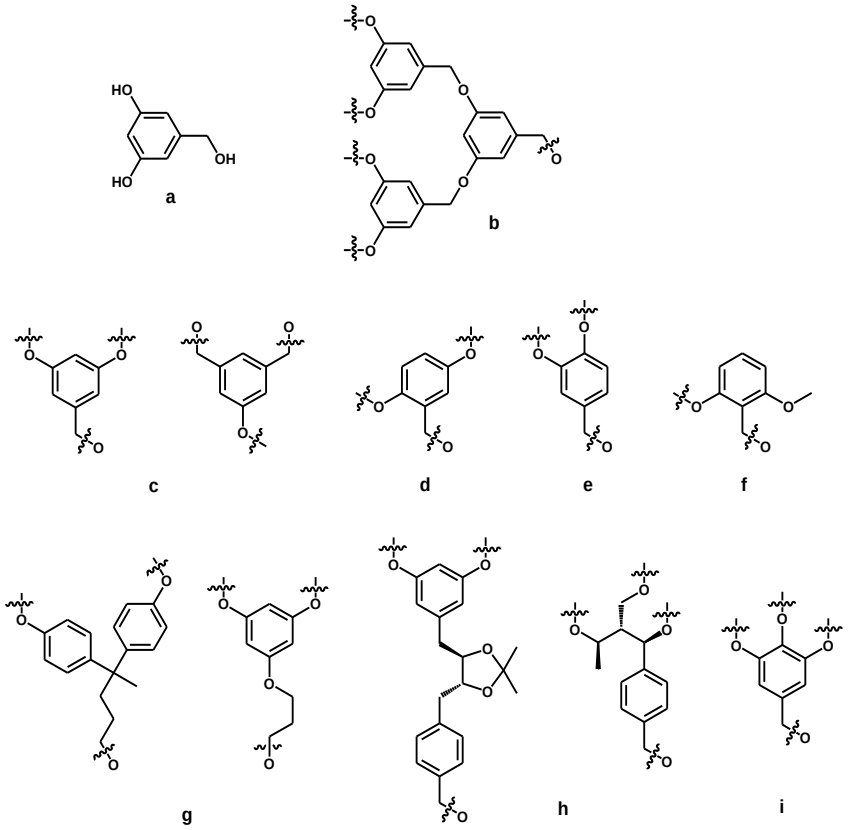


Figure 1.6 a) 3,5-dihydroxy benzylalcohol b) part of a Fréchet-type dendrimer c) normal and reversed connectivity d) 2,5-substitution e) 3,4-substitution f) 2,6 substitution (backfolding) g) building blocks with spacers h) chiral building blocks i) units with threefold branching

This explains the multitude of different applications like forming huge Janus-faced dendrimers having two hemispheres of opposite polarity on the surface[58], covering a photoactive ruthenium-bipyridyl core[59] with a nonpolar shell, the same with a phthalocyanine core[60] delivering a glass forming columnar mesogen, binding of dendrons on C_{60}[61,62] and even an uncommon incorporation of Fréchet-type dendrons in a polymer chain[63]. Non-covalent binding of C_{60} to cyclotriveratrylene centers[64] provided with Fréchet-type dendrons led to solubilization of the former. Self assembly of dendritic structures of this kind[41,65] have been investigated as well.

1.3 Liquid crystalline dendritic structures

It has been proven that the seemingly structurally non-compatible mesogens and long polymer chains do form materials with the retention of liquid crystallinity creating a new class of materials with advatageous properties[18,66,67,68,69]. The same has been achieved with dendrimers and mesogens[70,71,72,73,74]. One of the first attempts was to create hyperbranched polymeric liquid

crystals. This group of materials has an irregular, random structure but they can be seen as predecessors of the real dendritic LCs.

1.3.1 Hyperbranched polymeric liquid crystals

Percec and his colleagues had the pioneering role in this field. Their concept was that using appropriate monomers (Figure 1.8, **1**-**4**) having phenolic OH and alkyl bromide functionalities results in a formation of an interwoven polymeric structure[75,76]. Structural similarity exist between these substances and the regular main-chain LC polymers (Figure 1.7)

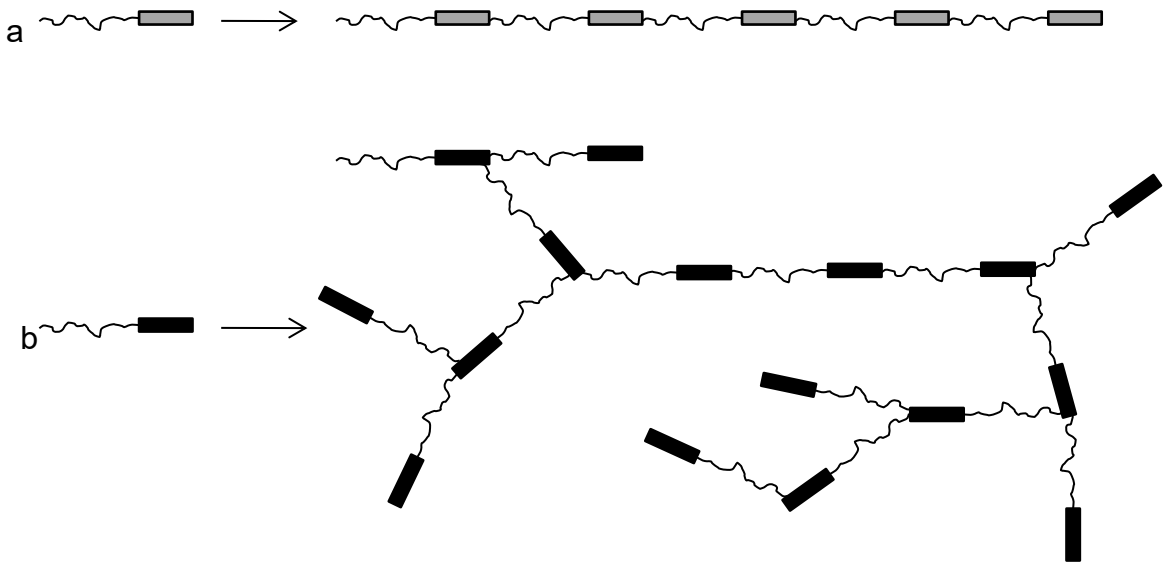


Figure 1.7 Schematic representation of a main-chain LC polymer (a) and a hyperbranched LC polymer (b)

The following monomers (Figure 1.8) have been prepared and polymerized.

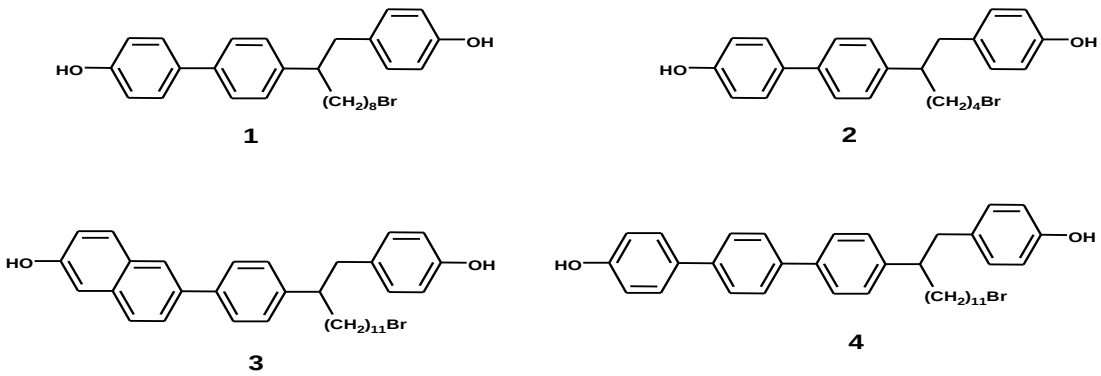


Figure 1.8 Monomers used to create hyperbranched polymeric LCs

The obligatory remaining free hydroxyls were capped with alkyl-substituents by ether-linkages in a subsequent step. In the majority of the formed polymers a nematic mesophase was determined between the glass-transition temperature and the clearing point. The phase transitions were sensitive to the alkyl chain length, to the size of the aromatic moiety and to the size of the polymer. A plausible explanation of the phase transition suggested by the authors is that the molecules have an 'extended' random conformation in the isotropic liquid or in a solution while in the nematic state the segments are rendered to a close packing, independently from the different secondary forces between the aromatic and aliphatic segments (Figure 1.9).

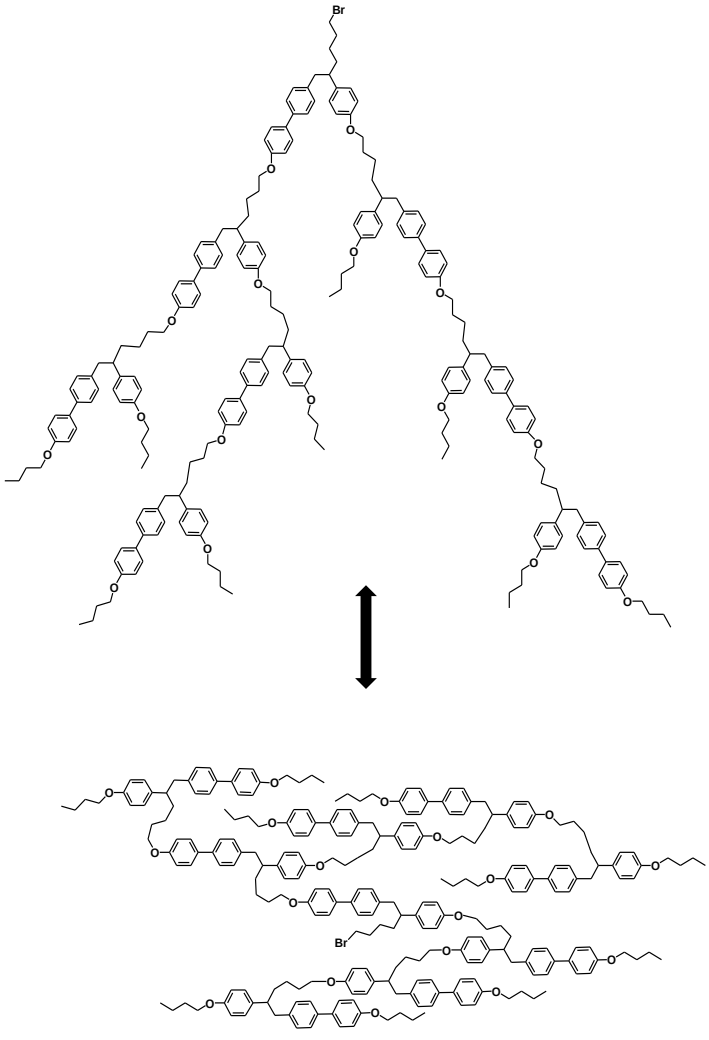


Figure 1.9 Isotropic and nematic states of a hyperbranched LC polymer

Subsequently, Percec also synthesised smaller condensation products (dimers, trimers and cyclic oligomers from cyclodimers to cyclopentamers) and studied their phase behaviour[77]. The presence of nematic phase could be attested again with more expressed odd-even effects due to

the smaller molecular size. The preparation of the regular dendritic structures from the same, though necesserily functionalised monomers was also achived[77,78,79], up to the fourth generation. The terphenyl containing building block (**4**) had an aliphatic OH function instead of bromine (see Figure 1.8) indispensable for the dendritic build up. Then here again the reactivity difference between phenolic and alcoholic hydroxyl groups was utilized during the dendritic synthesis. To the surprise of the authors smectic phases were determined here beside the nematic ones. The properties were again chainging along the growth of the dendritic generation number and a very low viscosity was seen in contrary to the polymers.

1.3.2. Supramolecular dendromesogens

Liquid crystalline self-organisation can proceed with supramolecular associations, e.g. molecular assemblies producing a higher degree of mesophase organisation. Again, Percecs group was explored first this field, starting with grafting of the later individually examined dendron on poly(methylsiloxane) backbone[80,81]. The unfolding the full potential of these dendrons yielding supramolecular assemblies came a few years later and was documented in numerous publications[50,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97]. The dendrons in question (Figure 1.10, a) have aryl-benzyl ether connectivities. The number of branching was varied using mono-, di- and trifunctional phenyl rings, substitution patterns were different (4-, 3,4-, 3,5-, 3,4,5-substitutions). The length of the terminal chains have been varied and partially fluorinated chains were also used[96,97] and diverse functional groups (carboxylate, primary alcohol, ester, oligoethylenglycol, crown ethers) constituted the focal points of the dendrons. Different generation numbers were achieved (from 1 to 5) and different layers of building blocks were present in some of the dendrons. Depending on the shape of the molecules diverse self-assemblies were formed. The sterically less demanding entities with monosubstitution in the structure were prone to forming discs by association with each other (Figure 1.10 b) due to their flat fan shape. The formed discs could constitute columns giving rise to different columnar LC phases. Rarely smectic phases were also seen to be formed by these molecules.

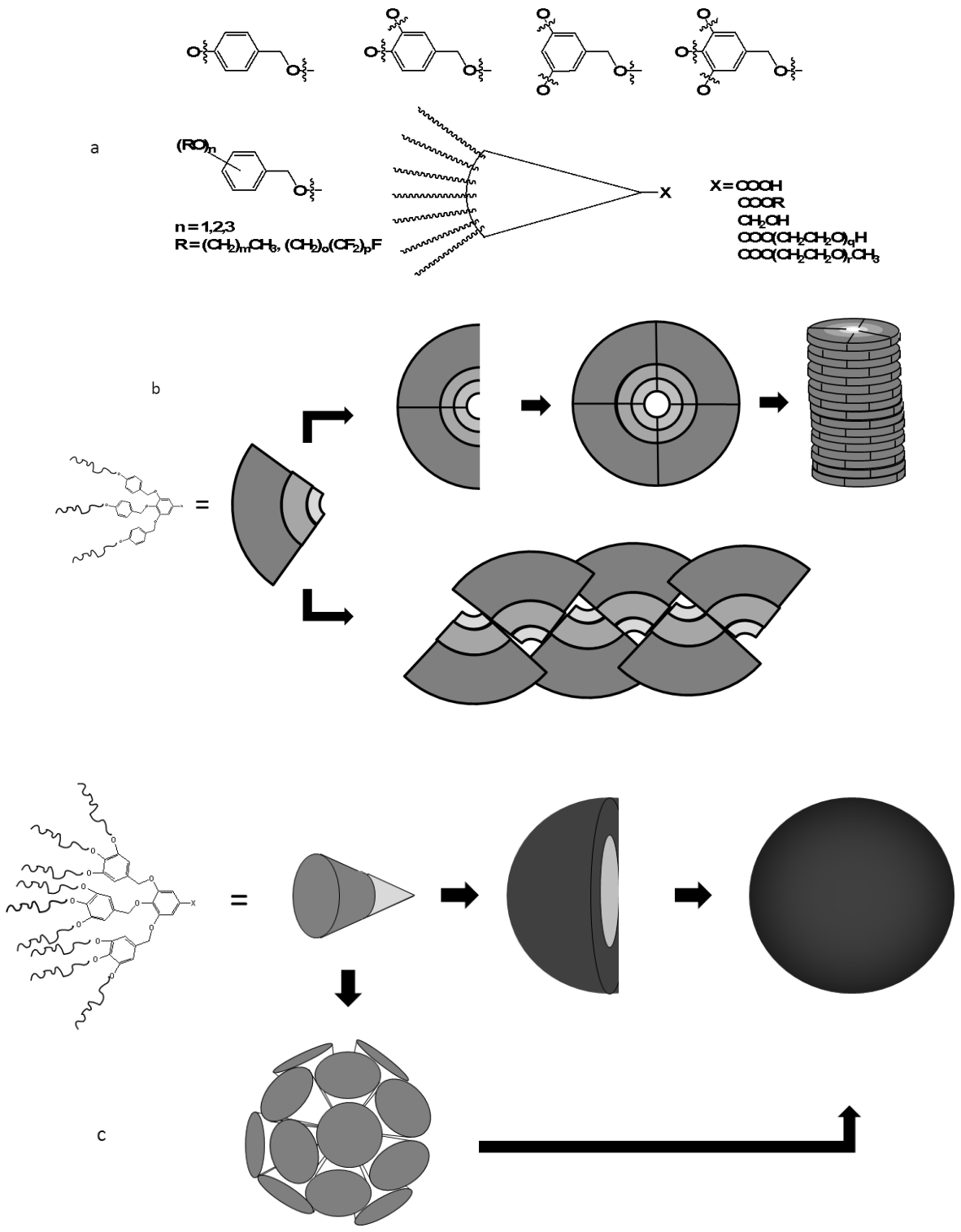


Figure 1.10 Variable parts of Percecs dendrons and formation of supramolecular structures (explanation in the text)

The higher density in the monodendron structure (di- and trisubstitution pattern, higher generation number) made the molecules tend to take a conical and with growing radius up to pseudospherical shapes (Figure 1.10 c). The association of these cones led to supramolecular

spheres[92,93,94,95] which in turn formed different cubic phases. A common feature was that the alkyl-chains covered the surface and the more polar focal groups were retained in the columns and the spheres forming polar ducts and cavities. Fluorinated alkyl chains[96,97] led to induction or stabilization of mesophase formation. Insertion of 4-oxy-benzyl elongative units in the dendritic arms[86] resulted in the stabilization of smectic and columnar phases compared to cubic frameworks. Chinese scientists found[98] that the ionic binding of dendrons very similar to the above mentioned ones to polymer chains, namely poly(ethyleneimine) or poly(allylamine hydrochloride) gave rise to lamellar smectic A or C phases and hexagonal columnar phases, respectively. Alignment of columnar phases built up of similar dendrons on surfaces with different polarity were examined[99], too.

Further research from Percecs group[100] yielded an extension to the above treated structures by the usage of biphenyl motivs instead of phenyl groups throughout the structures. Comprehensive libraries of dendrons up to the third generation with variety of attaching possibilites have been created. The dendrons were end-capped with n-dodecyloxy-groups, connected in 4-, 3,4- or 3,4,5-positions (Figure 1.11), while 3,4-, 3,5-, 3,4,5- branching patterns connected the biphenyl units to each other.

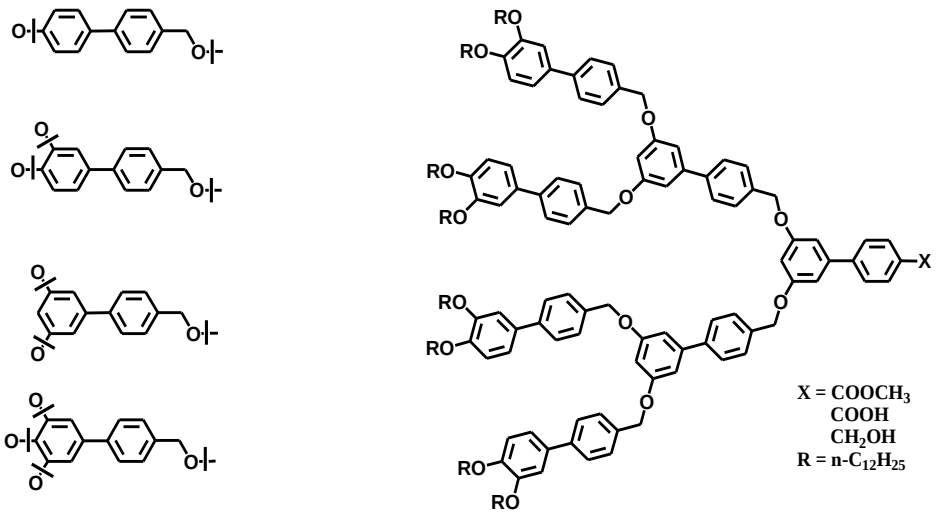


Figure 1.11 Biphenyl containing building blocks and an example of the derived Percec-type dendrons

The synthesis of the dendrons deviated from the Fréchet-standard although the same aryl-benzyl ether connections were achieved. The coupling step used DMF as solvent not applying the chemoselective approach in acetone as the building block bears ester functionality instead of

primary alcohol. Consequently, the activtation was a two step process reducing the ester first and then substituting the OH group with chloride. The altered interactions due to the extended rigid, aromatic parts led generally to a higher number of mesophases of the compounds. The formation of smectic phases was favoured in the small members while higher generations produced the variety of mesophases governed by structural features with emphasis on the polarity of the dendritic apex. Supramolecular spheres, circular and elliptical columns were formed at higher generations, some of the columnar organizations showing helical structures, giving rise to chirality proven by CD spectroscopy.

1.3.3. Main-chain liquid crystalline dendrimers

Main-chain LC dendrimers are analogous to main-chain LC polymers[101], *i.e.* the mesogenic units can be found throughout the dendritic scaffold unlike in side-chain LC dendrimers that carry the mesogens at the outer sphere of the dendritic structure (see Chapter 1.3.4.).

The earliest attempt[102] to prepare a main chain liquid crystalline dendrimer can be traced back to Fréchets coworker Wooley who created the building block (**5**), dendrons up to the second generation and dendrimers through attachment to different core units (Figure 1.12).

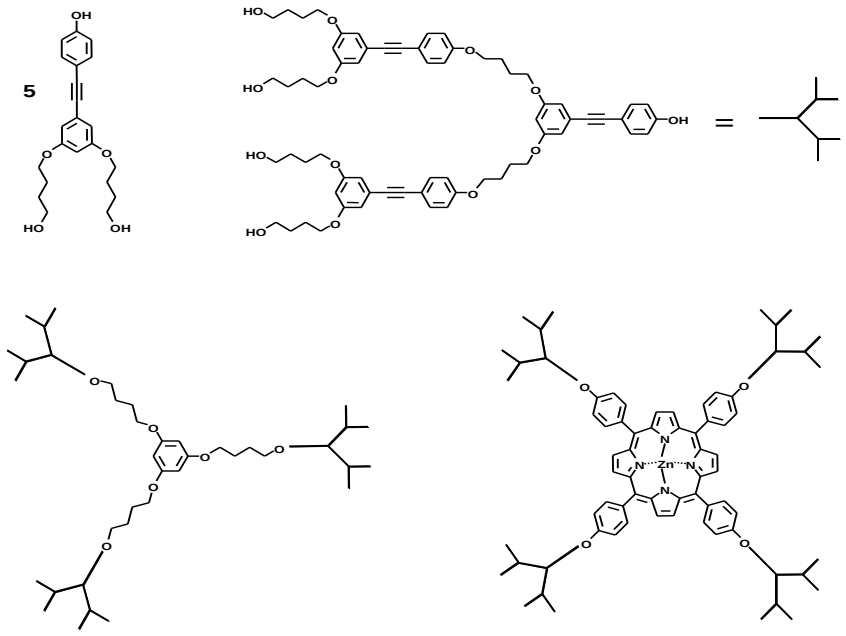


Figure 1.12 Wooleys building block, second generational dendron and dendrimers

Tetramethylene spacer were used in the structure and the 3,5,4'-substituted tolane-moiety serving as the rigid part of the mesogen. The formation of the dendrons proceeded under similar

circumstances as in the case of the original Fréchet-type dendrons. The end-groups of the dendrons were free hydroxy- or acetoxy-groups. Unfortunately the work has not been continued on this topic, so the promising LC-properties of the compounds remain unknown.

Dendrons composed of biphenyl units attached through aryl-benzyl ether connection has been prepared[103] up to the fourth generation. The dendritic building block (**6**) was deliberately grafted with two substituents of different polarities (Figure 1.13).

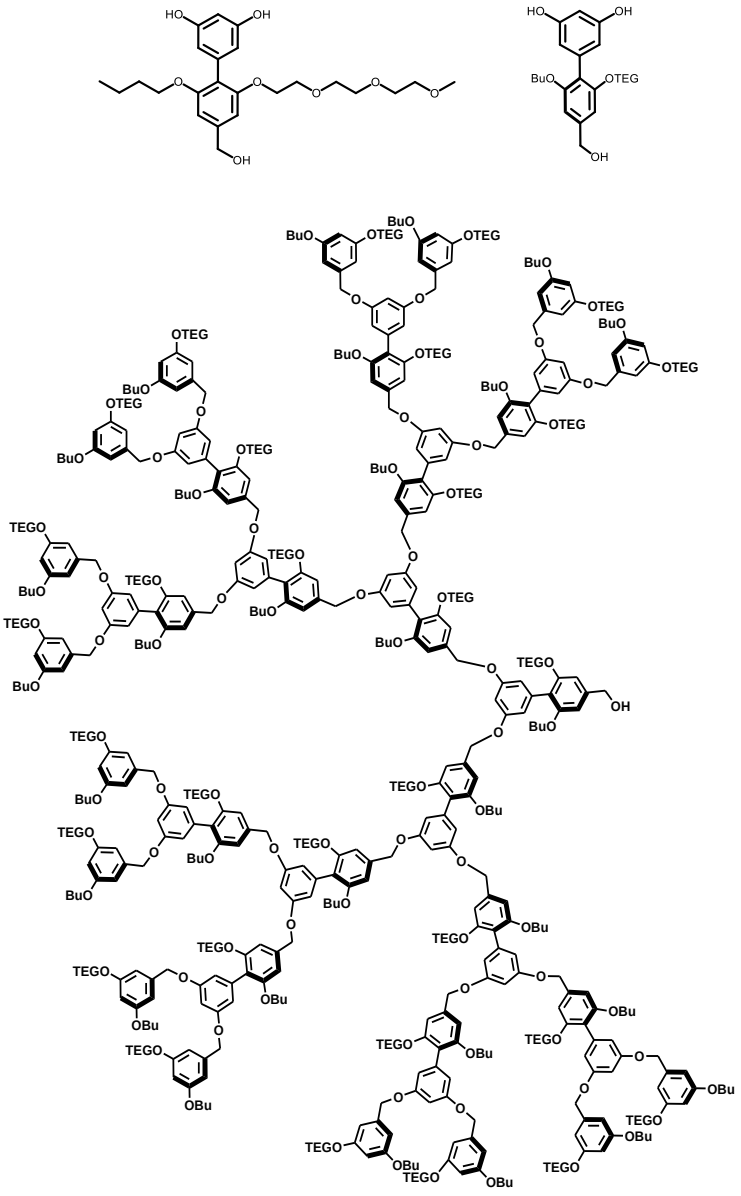


Figure 1.13 Biphenyl building block, its atropisomeric twist and a dendron made of it

The reason for this architecture is that these compounds should not serve as thermotropic liquid crystalline materials but the formation of amphiphilic dendritic structures changing

conformation according to the polarity of the solvent resembling the small-molecular facial amphiphiles was the aim of the synthesis. The rotationally restricted building blocks could react to the polarity change of the solvent by changing the whole shape of the dendron in an attempt to hide the polar groups in a nonpolar solvent and *vice versa*. The building block was generated through simple chemistry involving Suzuki-coupling, while the dendron building steps were the same as Fréchets. Solubility problems hindered the detailed study of the expected behaviour[104].

Another example utilizing biphenyls in a dendritic, tricatenar scaffold has been synthesized[105]. The building blocks (Figure 1.14) contained two biphenyl units connected by an aliphatic spacer. 3,4- and a 3,5-substitution patterns attached the aliphatic chains (from n-hexyl to n-dodecyl) to the outer end of the dendron and the opposite side bearing a phenolic OH was alkylated with the same alkyl chain. Benzyl-endcapped dendrons with 3,4- and 3,5-substitution pattern were coupled through a C_6-spacer to a rigid 1,3,5-triphenyl-benzene core whose purpose after removal of the benzyl protection was to be a starting point of a divergent dendritic growth. The dendrimers were not liquid crystalline but the dendrons were, indeed. The terminal 3,4-pattern resulted monotropic smectic A phases while 3,5-substitution gave rise to enantiotropic smectic A phases appearing at lower temperatures as with the former. Increasing terminal chain length led to decreasing phase stability due to decreasing clearing points.

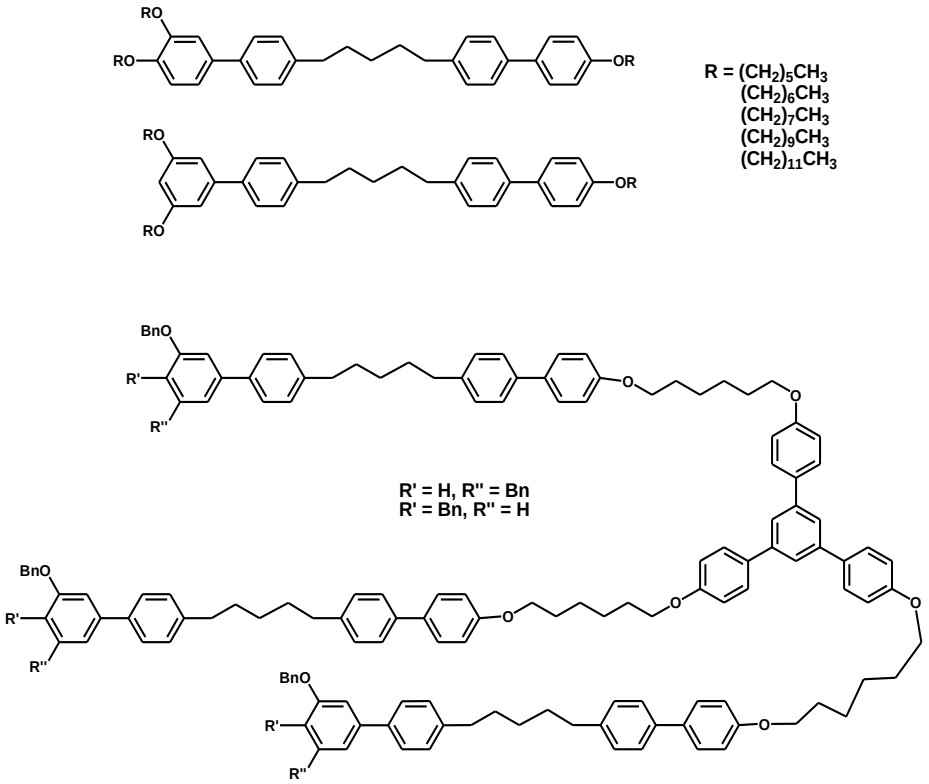


Figure 1.14 Tricatenar mesogenic dendrons and dendrimers

'Octopus' dendrimers feature main-chain liquid crystalline dendritic wedges[40,106,107] coupled to a relatively small core unit. Stilbene- and tolane moieties[108] represented the rigid aromatic parts and alkoxy chains connected them and served as terminal flexible moieties. If one terminal alkoxy-chain was present, the formed mesophase was a multilayer smectic one. The dendrimer occupied an elongated rod shape forming a unique sublevel structure of aliphatic layers of the terminal chains, followed by a layer-perpendicular then a tilted arrangment of rigid segments. More dense substitution of the termini led to aggregation of dendrons with oblate shape yielding discs that formed columnar phases. Effect of different core units on the LC properties was examined[40], too, but it turned out to be an insignificant factor as the hexagonal columnar phases were hardly influenced.

1.3.4. Side-chain liquid crystalline dendrimers

Side-chain LC dendrimers represent an important and in many cases easily accessible class of liquid crystalline material. The name stems from side-chain LC polymers again (Figure 1.15) mirroring the structural similarity.

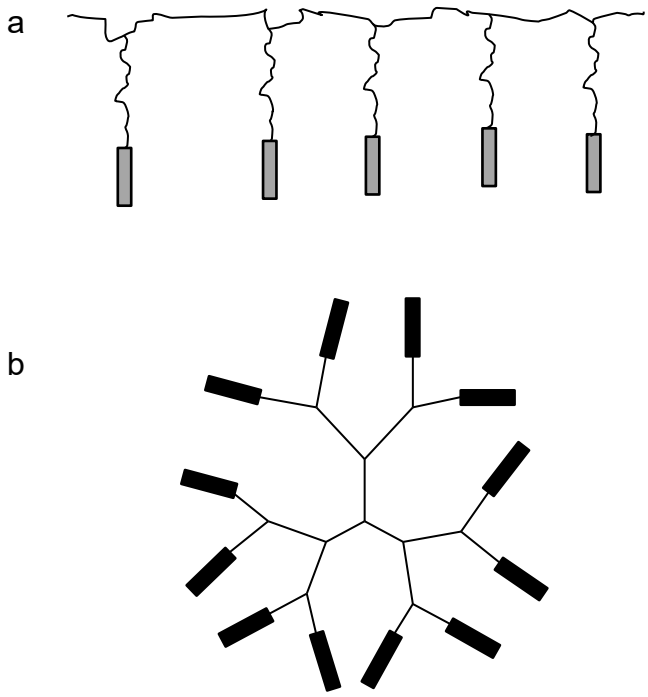


Figure 1.15 Side-chain LC polymers (a) and side-chain dendrimers (b)

The mesogenes are placed on the outer surface of a (mostly preformed) dendrimer with an effective coupling reaction. Commercially available dendrimers with appropriate funcionalities on the surface like poly(amidoamine) (PAMAM) or poly(propyleneimine) (PPI) were extensively attached to calamitic or discotic mesogens and studied[109,110]. Phase-transitional behaviour[111,112] of the class has been examined and elaborate molecular theoretical description[113] was attempted, too.

Silicon-containing dendrimers of siloxane-, carbosilane-, or carbosilazane type endowed with mesogens on the surface are a well-studied group of compounds. The existence of polysiloxane derived liquid crystalline material[114] and some early attempts[115,116,117] showed that the area was a promising one and Shibaevs research group contributed[118,119] significantly to the chemistry of the dendritic carbosilanes (Si-C connection) and they proposed a plausible model[120] to explain the particular mesophase occurrences of the systems.

The molecules synthesised by Shibaevs group include methoxyphenylbenzoate-[121], cyanobiphenyl-[118,122], and anisic acid-derived[123] mesogens. These were terminally attached through an efficiently long spacer to the carbosilane dendritic scaffolds (Figure 1.16).

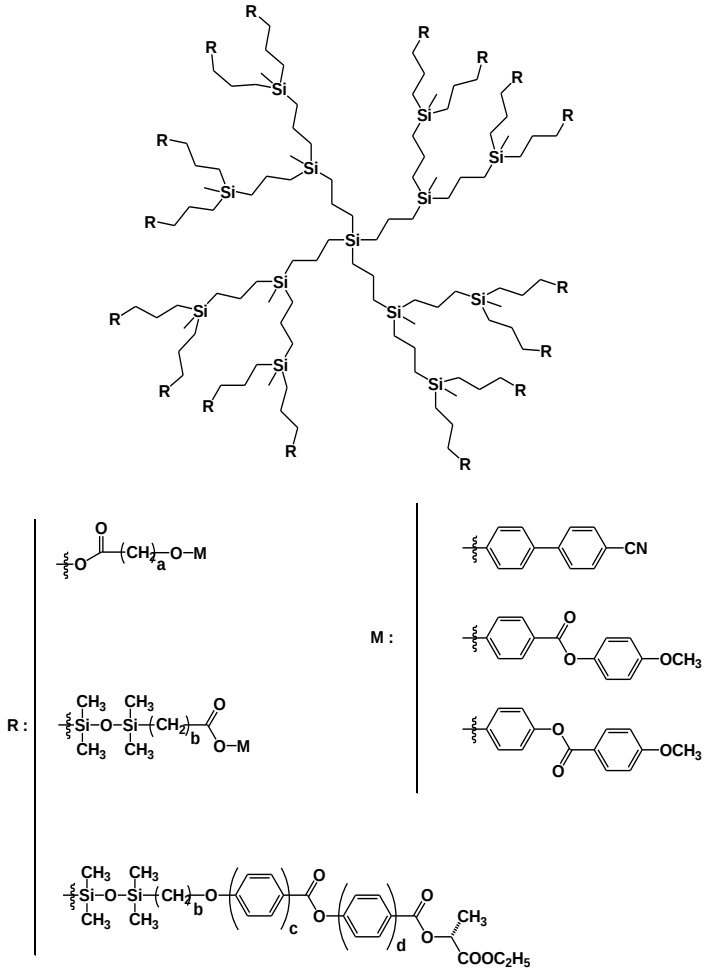


Figure 1.16 Carbosilane dendrimer (2nd generational) and the attached mesogens

The formed dendrimers exhibit smectic A and C phases from RT to around 90 °C. The layer thickness of the mesophases was not changing significantly from generation 1 to 4. It was explained with the cylindrical conformation of the dendrimers[120] (Figure 1.17).

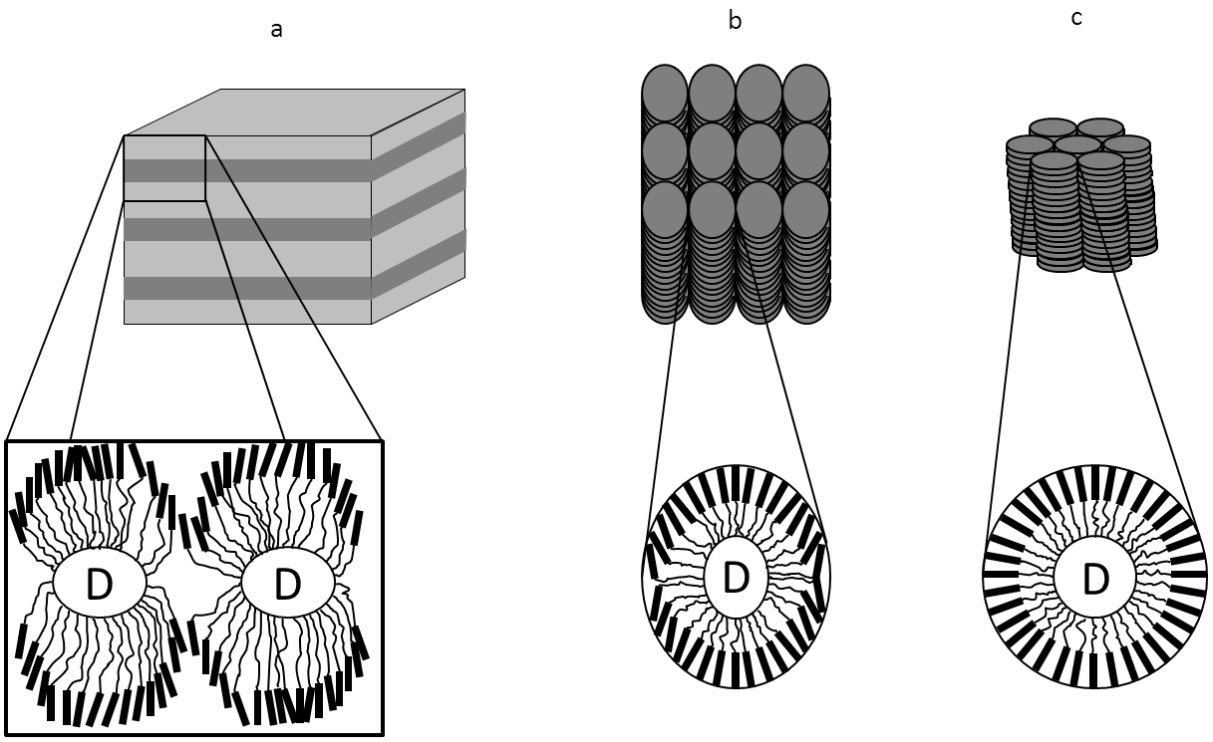


Figure 1.17 Structure of mesophases at different generations (D: dendritic part, further explanation in the text)

The calamitics associated to each other above and below the 'dendritic plane' where the necessarily distorted framework resided (Figure 1.17 a), the organisation resulting from microphase separation[124,125,126]. The distortion grew with the generation number to compensate the higher circumference of the mesogen-containing segment. In the fifth generation at lower temperature smectic phase was seen but increasing temperature led to the rise of rectangular and hexagonal columnar phases. The reason is according to the authors that the previous cylinders were not to maintain anymore and the systems response was another flat cylindrical shape having the mesogens at the perimeter and the dendritic moiety in the center of the disk. These oval discs formed the Col_r phase (Figure 1.17 b) while further increase of the temperature forced the discoid units to approximate a more symmetrical shape yielding the hexagonal columnar phase (Figure 1.17 c). This was proven by atomic force microscopic visualization of dendritic films[127]. Further structural investigations with X-ray diffraction and neutron scattering[128], dielectric relaxation measurements[129] and 2D-NMR techniques corroborated the theory[130]. It is an interesting example of a retrograde phase evolution, as columnar phases of dendrimers are characteristically form by cooling of layered structures like smectics.

Dendrimers at the beginning of their exploration were considered to have a more or less spherical shape. This might be true in vacuum or in a solution but in solid or liquid crystalline state shape anisometry must be assumed. But it is not the only factor. According to the now generally accepted and generalized theory, the keys to the mesophase formation are flexibility of the dendritic scaffold and spacers long enough to decouple the mesogens from the rest of the molecule[131,132].

Smaller dendrimers of similar structures having cyanobiphenyl units on the surface showed a decreasing smectic layer thickness by increasing the generation number[133]. The depth of intercalation of the cyanobiphenyls in the neighbouring layers was increasing with increasing temperature. Utilization of chiral mesogenic end-groups[134,135] gave ferroelectric dendrimers where chiral smectic C phase was observable over a wide temperature range. Photochromism of a second generational carbosilane LC dendrimer having cinnamoyl[136] or azobenzene-mesogens[137] was reported and the photochromism rate constants of the latter[138] were similar to low molecular substances leading to possible applications.

Siloxane-based LC dendrimers can be found as well in the side-chain LC dendrimer class. Goodbys structures[139] (Figure 1.18) represent zeroth generational dendrimers with cyanobiphenyl mesogens.

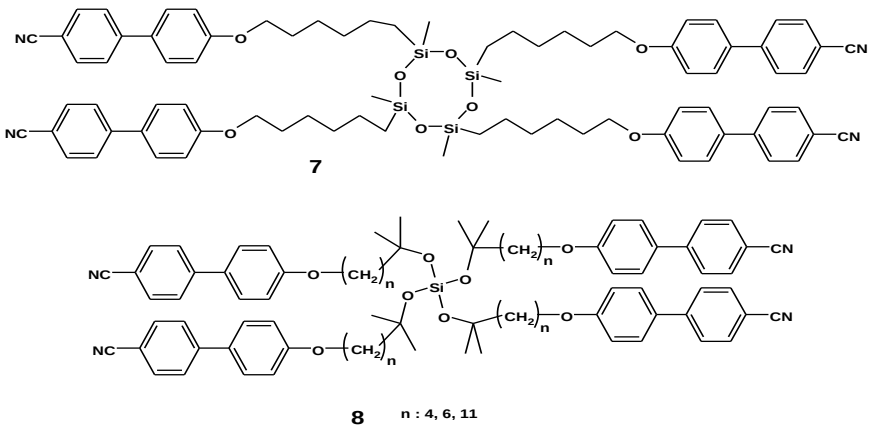


Figure 1.18 Siloxane based small dendrimers

An extended smectic A phase (more than 100 degree range from -10 °C) was observable at the compounds with a star-like core (**8**) while the ring-attachment (**7**) yielded a shorter LC temperature range (60 °C). The structure of the phase was reasoned on a similar way to Shibaevs

carbosilane dendrimers. The cubic silsesquioxane was also popular as core unit in this regard. It was substituted with cyanobiphenyl mesogens with changing length of the spacer[140] and the first generational dendrimer has been prepared[141], too (Figure 1.19).

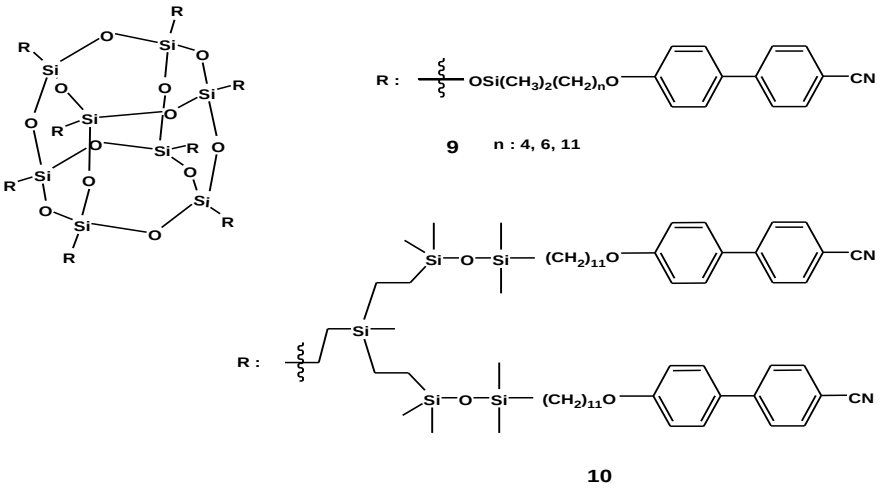


Figure 1.19 Silsesquioxane as core of LC dendrimers

The non-dendritic species (**9**) have shown a growing smectic A phase temperature range with growing spacer length while the first generational dendrimer (**10**) exhibited additional smectic C phase and a lowered glass transition temperature that is contrary to the usual polymeric systems. The presence of smectic phases in these and similar systems[142] proved that the silsesquioxane core was flexible enough to take part in the formation of the microphase separated lamellar structures.

The silsesquioxane core was shown to promote the formation of different mesophases. The attachment of a chiral, laterally substituted biphenyl-benzoate type unit on the second generational dendrimer with silsesquioxane core[143] helped the formation of hexagonal disordered columnar and rectangular disordered columnar phases beside the chiral nematic phase that was the only mesophase of the mesogen alone. Various models to explain the phases were developed, too. Attachment of the above mentioned chiral mesogen to one side of a Janus-like silicon containing dendritic core and substitution with cyanobiphenyl-derived small calamitic on the other side[144] gave Goodbys group the chance to study the effect of slight changes in the dendritic framework on the properties of the whole. The expected chiral nematic phases were present in both cases but one of the compounds showed chiral smectic C phase, as well, showing that insignificant changes can affect the materials properties profoundly.

This was shown by Tschierskes group, too, by the coupling of bent-core mesongens on various dendritic scaffolds made by the divergent procedure, like diaminobutane (DAB)[145], carbosilane and siloxane[146] containing ones. Decoupling of the mesogens from the dendritic matrix by long enough spacers was a prerequisite to LC state. The switch of antiferroelectric to ferroelectric phases encountered at the silicon-containing structures was reasoned with an elaborate, sandwich-like organization of the bent rigid moieties, aliphatic chains (spacer and terminal) and of the dendritic core.

There are still many examples of side-chain LC dendrimers that fit well into the above discussed model and were easily synthesized by using preformed (partly commercially available) dendritic cores[147,148,149,150,151,152]. The role of microphase separation is further highlighted as the preformed cores are usually polar compounds (amides, amines, etc.). Extreme polarity difference was seen at the *s*-triazine-based first- and second generational dendritic scaffolds that were connected by a PEG-chain and were attached to alkoxybiphenyl mesogens[153]. Smectic and nematic mesophases were seen and longer terminal chains did not change the T_G-T_I range but shifted it slighly downwards.

The last point of this literature overview shows the flexibility and efficacy of the organisatory principles of the liquid crystalline dendrimers, that is the incorporation of fullerenes (C_{60}) in the LC dendrimers.

Buckminsterfullerene has intriguing photophysical, magnetic and electrooptical properties and after early attempts to combine it with cholesteric mesogens[154] the coupling to short, alkoxy-substituted oligophenylenevinylene moiety containing first generational dendrons was reported[155] (Figure 1.20 a). No information is given about the possible LC properties but it has been pointed out that not electron- but energy-transfer occurs between the different molecular parts.

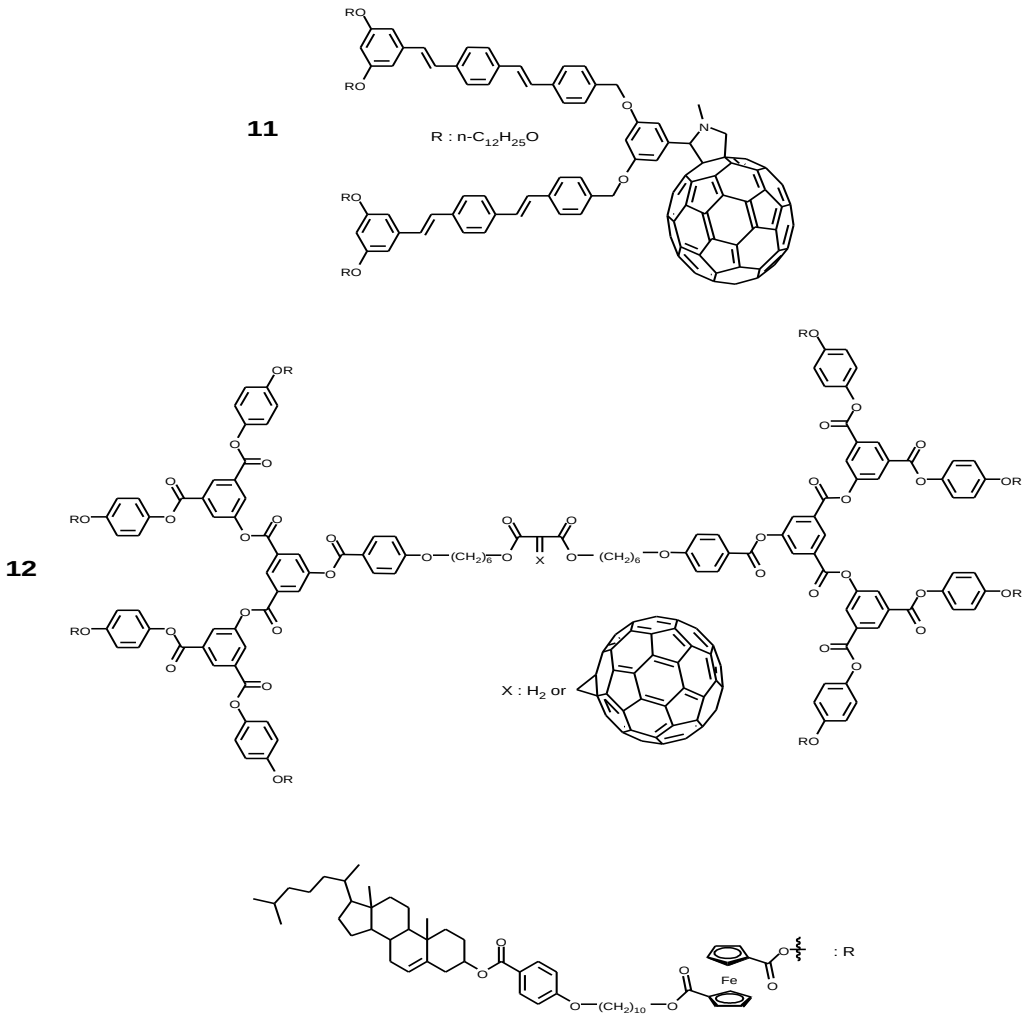


Figure 1.20 Fullerene-containing structures: with oligophenylenevinylene dendrons (**11**) and dendritic liquid crystalline C_{60}-derivative and antennae with cholesteryl mesogens (**12**)

A relatively complicated scaffold[156] (Figure 1.20, **12**) was used to incorporate the fullerene (electron acceptor) into a LC dendritic frame with ferrocene units (electron donors). Earlier attempts[157] attested the electron-transfer abilities of similar, more simple structures (**11**). Both of the molecules in Figure 1.20 showed enantiotropic smectic A phases over a wide temperature range. Consequently, the presence of the fullerene moiety did not disturb the formation of the mesophase as the precursors phase behaviour resembled the fullerene containing ones closely. That was explained by the relatively small size of the C_{60} compared to the whole molecule. Similar molecular structures were built up utilizing cyanobiphenyl-derived mesogens attached to an aromatic ester dendritic frame of first to fourth generation that had the fullerene in the focal point. Smectic A phases were here determined again and a proposal for the structure was delivered (Figure 1.21).

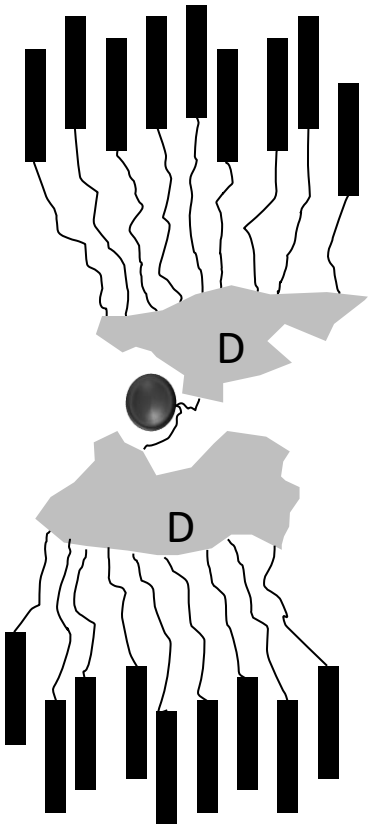


Figure 1.21 Fullerene containing LC dendrimer in smectic A phase (D: dendritic part)

When the attached mesogen was a laterally attached chiral biphenyl derivative[158] the formation of chiral nematic phase was observed. Even tailoring of the LC properties via forming Janus-type dendrimers with a C_{60} in the center was achieved. The difference in the two attached dendrons (cyanobiphenyl mesogen, poly(aryl-ester)-dendron *vs.* Percec-type alkoxy-terminated benzylether dendrons), their ratio considering the different generation numbers led to induction of smectic A/C phases and/or to columnar phases. Interestingly, the precursors (without C_{60}) and the fullerene containing compounds showed small differences in their phase behaviour. Therefore it was concluded that the presence of fullerene did not disturb the phase formation, though it was not necessary either. Investigations on the fullerene-substitution[159] proved that in smaller frameworks the way of substitution of the C_{60} can also influence the LC properties (fulleropyrrolidines are more flexibility restricting than methanofullerenes).

2 Objectives

The Fréchet-type dendritic framework is a well known and well established synthethic tool to connect dendritic structural elements to a wide variety of different functional units. Some liquid crystalline materials have been also achieved on this way. Studying the feasibility of the synthesis of small generational (1st through 3rd generations) poly(benzyl-aryl-ether) dendritic scaffolds with calamitic biphenyl mesogens on the outer surface seemed to be a niche in the dendritic liquid crystal field. As mesogenes alkoxy-substituted biphenyls were chosen and the length of the aliphatic spacers/terminaly alkyl chains have been systematically altered, having a chance to study the effects of decoupling of the mesogenes and the dendritic part. Connection of the dendrons to a core unit gave rise to another property changing modification of the original dendron structures.

The fragments used to establish the small molecular library are shown in Figure 2.1.

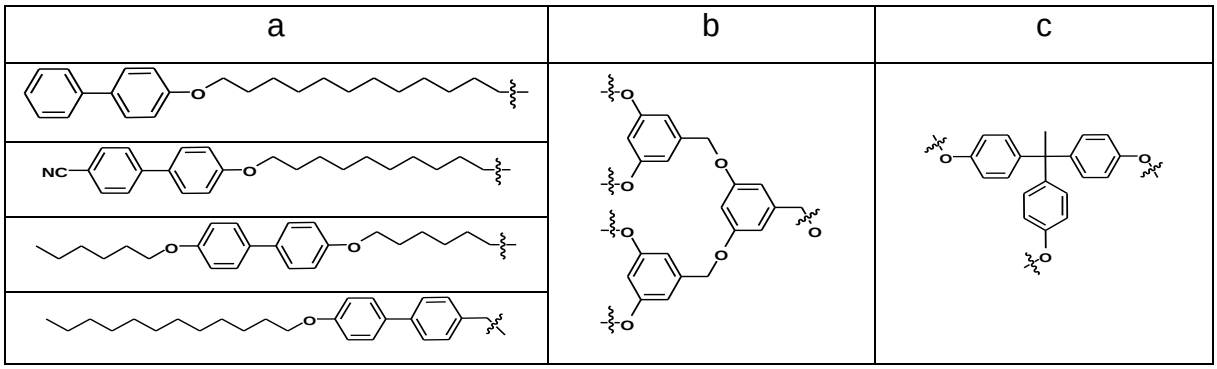


Figure 2.1 Target liqid crystalline dendrimers a, end-groups, b, dendritic scaffold, c, central core unit

The modification of the original building block (3,5-dihydroxy-benzilic alcohol) to bear a biphenyl-moiety (3,5-dihidroxy-4'-hydroxymethylene-biphenyl) also seemed to be promising in the LC field. The synthesis of this, at the beginning of the thesis not yet known[C33] compound (Figure 2.2 a) was an aim as well. It was requireed for building up the appropriate dendritic network.

Figure 2.2 a The biphenylic analogue (3,5-dihydroxy-4'-hydroxymethylene-biphenyl) of the original Freche-type building block, b the schematic view of a 'mixed' dendron.

The final aim of the study was to synthesise and study regarding their possible LC properties some 'mixed' dendrons and dendrimers, bearing two different end-groups on the dendritic building block (Figure 2.2. b).

3 Synthesis of the dendrons and dendrimers containing mesogenic groups

3.1 Building up the dendritic framework

3.1.1 General consideration to the proposed LC-dendrons and dendrimers

According to the aims of this thesis dendritic structures bearing mesogenic groups have been synthesised. The section 3.7 describes the synthesis of the a dendritic series having no mesogenic groups attached to the dendrons/dendrimers.

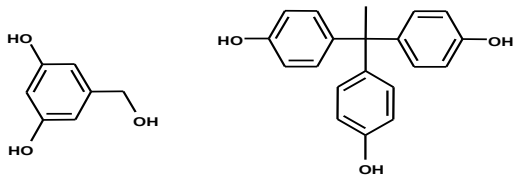
In the first four dendritic series the mesogenic groups were attached to that part of the dendrimeric skeleton that is on the outer surface resulting in a presumably growingly globular structure of the compounds with increasing generations. These so called Fréchet-type dendritic frameworks (with benzyl-ary-ether connections) were used owing to their chemically stable character and having a well known, often utilized and reliable synthesis. The convergent nature of the synthesis dictated that the attachment of the mesogenic groups to the primary building block was done first. The former process will be discussed in detail in the section 3.2.

The tailoring of the mesogenes has been done according to the following principles:

- the dendritic backbone is the standard Fréchet type dendron
- the core unit will be kept the same
- the overall length of the mesogenic moieties should be approximately the same
- the overall lenght of the alkyl chains should be sufficiently long to promise liquid crystalline properties
- only ether-bonds will be used

The fundamental molecules that served as building block and core unit in the formation of the Fréchet-type dendrimer synthesis[160] are 3,5-dihydroxybenzyl alcohol and 1,1,1-tris(4-hydroxyphenyl)-ethane (Scheme 3.1).

Synthesis



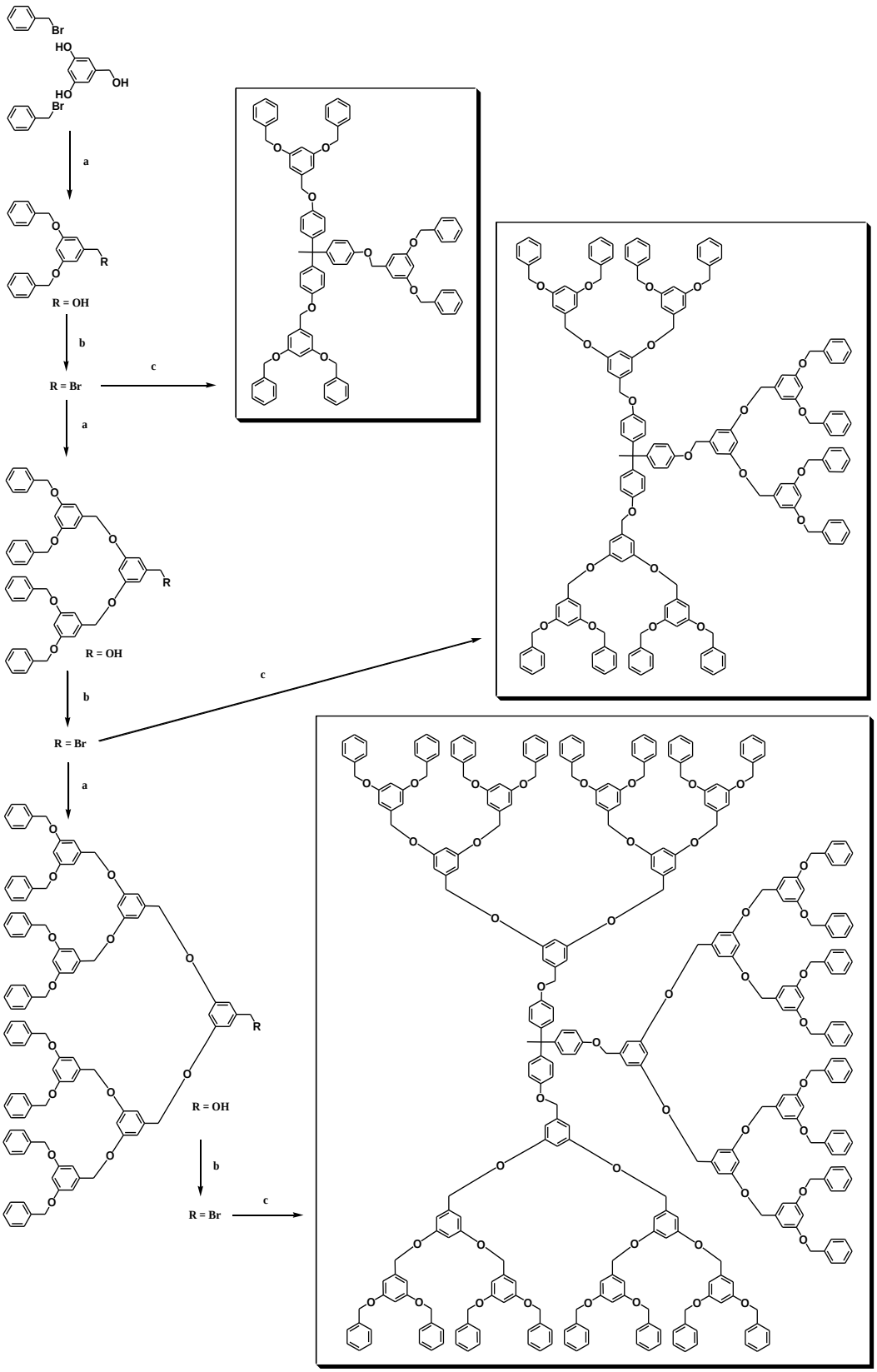
14 **15**

Scheme 3.1 Dendritic building block (3,5-dihydroxybenzyl alcohol, **14**) and core unit (1,1,1-tris(4-hydroxyphenyl)-ethane, **15**).

3.1.2 Fréchet-type dendrons and dendrimers

Presenting this group of compounds serves only the purpose of better understanding of the molecule building principles.

The scheme 3.2 shows the synthesis of the original dendritic structure that contains unsubstituted phenyl groups on the periphery. These terminal phenyl groups have been substituted with mesogenic units in our synthesis. The step (**a**) is the coupling step, the benzylic bromides are utilised to alkylate chemoselectively the phenolic hydroxyl groups of the building block. The carefully optimised conditions ensure the high selectivity of the reaction. The liberated HBr is neutralised by the base that is required in 2.5 eq. amount. The presence of too much base leads to partial decomposition of the benzyl bromide component. The reaction is carried out under phase-transfer conditions using 18-crown[6], an excellent and inexpensive phase-transfer catalyst when potassium salts are involved. 0.2 equivalents are sufficient to ensure the chemoselectivity. Working under absolute conditions (abs. acetone) proved to be of high importance. The presence of water can also induce undesired side reactions (for instance hydrolysis of the bromide) and can lead to very low yields. In the literature inert atmosphere (nitrogen) is also prescribed to avoid the colouration of the reaction medium due to oxidation products of the building block leading to drop in yield but only minor decrease was the consequence of avoiding this measure. Purification of the product was usually performed by column chromatography. Polarity differences of the (substituted) benzyl bromide, of non-reacted 3,5-dihydroxybenzyl alcohol and of the product made separation in an eluent containing dichloromethane usually easy.



Scheme 3.2 Overview of the synthetic path to the Fréchet-type dendrons and dendrimers. (**a**) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown[6], acetone, reflux, (**b**) CBr_4, PPh_3, THF, RT, (**c**) 1,1,1-tris(4-hydroxyphenyl)-ethane, K_2CO_3, 18-crown[6], acetone, reflux.

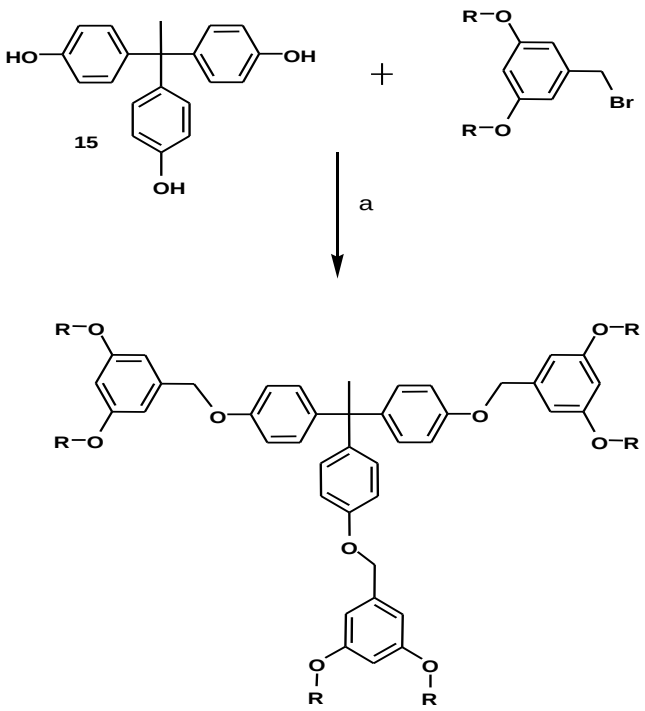
The following step (activation, **b**) is designated to the transformation of the preserved free benzylic hydroxy moiety to a bromide. This was achieved by means of the Appel reaction[161] that has been proven to be ideal for this purpose. The reaction involves carbon tetrabromide (or carbon tetrachloride resulting chlorides) and triphenylphosphine in a mechanism similar to the Mitsunobu coupling. Common point is triphenylphosphine being the oxygen acceptor forming triphenylphosphine oxyde. Tetrabromomethane is used in equimolar (or higher) amount. The reaction can be forced to completion in a reasonable rection time by adding 2 through 10 equivalents of the two reactants. This is necessary especially with high dendritic generation numbers due to a decreased reactivity. The reaction itself is of wide scope and applicable in the presence of numerous different functional groups. Aqueous workup, followed by column chromatographic purification delivers the bromide in the range of 70-90 % yield.

There is one practical aspect that has to be mentioned here, the removal of excess tetrabromomethane and the sideproduct bromoform ($CHBr_3$) proved to be essential. If the column chromatography is not done with care, the fractions containing the desired bromide might include small amounts of the two side products mentioned above. If so, the following reactions are accompanied by strong colouration of the medium, leading to reduction of the yield or even inhibiting the reaction entirely.

When the synthesis of the second and even more of the third generation had to be accomplished, the increasing nonpolar character of the reactants and products caused some solubility issues. Higher amounts of solvents were necessary to dissolve the reactants completely even under reflux conditions. During the dendron building steps using a less polar cosolvent was not favourable due to formation of sideproducts.

1.3 Attaching the dendrons to the core

Dendrons themselves are interesting materials on their own but attaching them to a central unit (core) may give rise to new properties. During our investigation the core unit was chosen to be 1,1,1-tris(4-hydroxymethyl)ethane (triphenylmethane core) and has not been varied throughout (Scheme 3.3). The aim was to keep the dendritic part of the molecule intact to see clearly the effect of variation of the mesogenic end groups on the properties.



Scheme 3.3 Attachment of dendrons to the core unit (**a**) K_2CO_3, 18-crown[6], acetone (and occasionally THF).

As the chemoselectivity was not a factor in the final coupling to the triphenylmethane core unit, a cosolvent was used here as the solubilty of the higher generational dendrons was relatively poor in pure acetone. Addition of relatively small amounts of abs. THF shifted the polarity of the solvent so that the reaction mixture became homogenous (not considering the insoluble particles of potassium carbonate). It decreased the otherwise extensively prolonged (in some attempts more than one week) reaction times to the usual range (1-2 days, determined by TLC monitoring). An excess of 3.3 equivalents of the dendritic bromides have been used in the reaction. The original procedure[48] recommended the removal of excess bromide by addition of many equivalents of the core unit to form patrially alkyalted (mono- or disubstituted) species which were easier to separate from the desired product during the column chromatographic purifying step. The reactions described here did not require this kind of treatment to be processed further properly, the polarity differences allowed the simple separation of the excess bromide and that of the dendrimer.

3.2 Synthesis of the mesogenic end groups

Owing to the naming difficulties of dendrons and dendrimers generally (as highlighted in the literature overview) the following notation will be used:

[X-1]-OH: the first generational dendron of the **X** series having free OH functionality

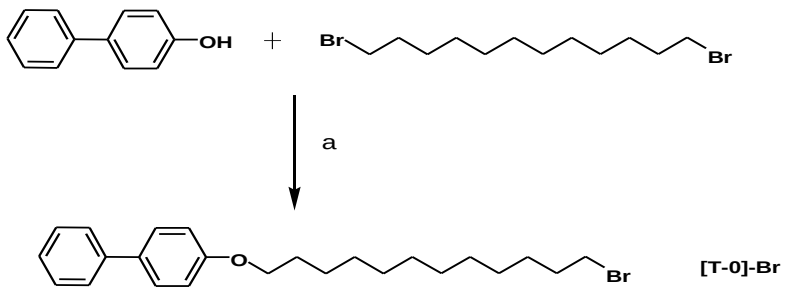
[Y-0]-Br: the zeroth generational dendron (the mesogenic unit itself) of the **Y** series having free Br functionality

[Z-2]-C: the second generational dendrimer (dendrons attached to the core unit) of the **Z** series

3.2.1 The mesogenic group of the **T** series

T stands for terminal, as the biphenyl unit is in these cases is most far from the central dendritic scaffold.

Scheme 3.4 shows the synthesis of the ω-bromo-alkoxy-biphenyl building block of the **T**-series **[T-0]-Br**.



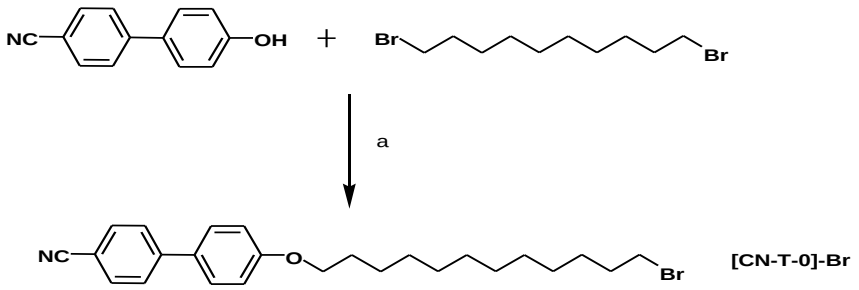
Scheme 3.4 Formation of **T**-mesogenic unit. (**a**) DMF, K_2CO_3, RT, 90 %.

The reaction can be performed in abs. dimethylformamide with carefully dried potassium carbonate at room temperature overnight. The key point is the monosubstitution of the bifunctional alkyl moiety by the phenolate ion derived from the 4-hydroxy-biphenyl. Monosubstitution can be enforced on the usual way, using excess of the bifunctional component lowering the probability of two consecutive reactions on the two ends of the same alkyl chain. In these of alkylation protocols the presence of three equivalents of the alkylating agent normally resulted in the formation of negligible amount of the disubstitution product that was easily separated by column chromatography. The potassium carbonate also was used in excess (9 eq.).

Working under absolute conditions proved to be crucial as well shown by the initial attempts resulting multicomponent product mixtures probably due to the competing hydrolysis and other processes.

3.2.2 The mesogenic group of the **CN-T** series

The group designation **CN-T** comes from 'cyano-substituted terminal biphenyl'. The cyanobiphenyl-group has shown its outstanding properties in the LC field. It was thus a good target to be attached to the dendritic skeleton, specially because the biphenyl lacking the cyano group was used for the same purpose in the **T** series. Synthetically the task was very similar to the one mentioned in 3.2.1 (Scheme 3.5).



Scheme 3.5 Synthesis of **CN-T** mesogenic unit. (**a**) DMF, K_2CO_3, RT, 81 %.

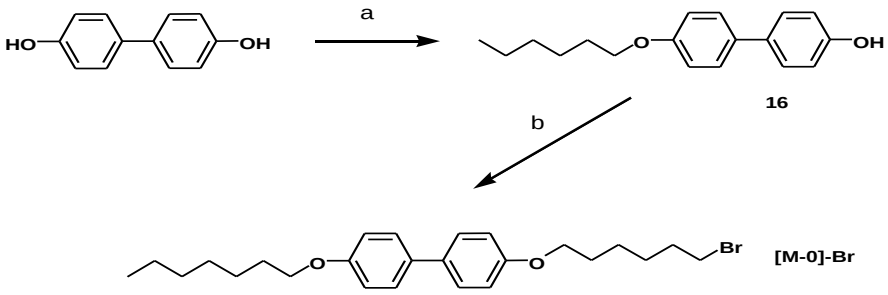
A different chain lenght (C_{10} instead of C_{12}) has been chosen for the alkyl spacer in order to keep the length of the whole mesogenic unit constant.

3.2.3 The mesogenic group of the **M** series

M is the abbreviation for middle, as the biphenyl moiety is here in the middle of the mesogenic unit.

The synthesis of the end group that contains the biphenyl unit which is inserted between two alkyl chains necessitated the usage of the above mentioned statistical approach (using excess of one reactant to drive the reaction to monosubstitution) twice (Scheme 3.6).

Synthesis



Scheme 3.6 Synthesis of the **M** mesogenic unit. (**a**) 1-bromo-hexane, NaOH, EtOH, reflux, 78 %, (**b**) Br-$(CH_2)_6$-Br, DMF, K_2CO_3, RT, 79 %.

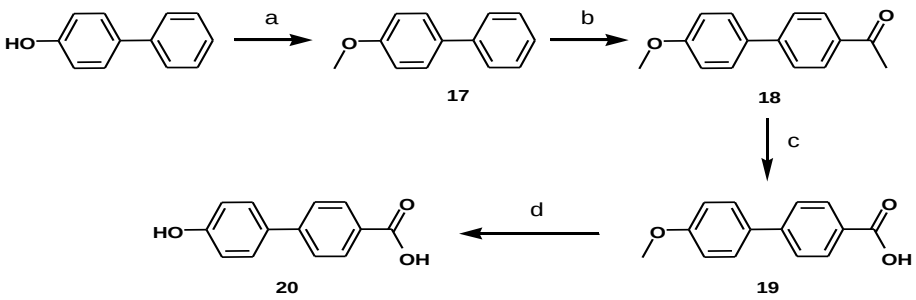
The chain lengths have been chosen again to stay in close proximity to the length of the (end)-dendritic mesogenic group. The first step has been carried out by a different type of a Williamson ether synthesis, the double phenoxyde ion formation was initiated by sodium hydroxyde and fivefold excess of the dihydroxy-biphenyl gave rise to some disubstitution products, but most of it remained unsubstituted yielding the monosubstitution product **16** in satisfactory amount. Separation in this case was relatively easy because of the significant differences in polarty of the non-, mono- and disubstituted compounds. The second alkylation required a threefold excess of the dibromide and has been achieved with the DMF/K_2CO_3 method, furnishing the mesogene **[M-o]-Br**.

3.2.4 The mesogenic group of the **S** series.

S stands for skeleton, as the biphenyl unit of the mesogenic group is here in close proximity to the dendritic skeleton.

3.2.4.1 Synthesis of the precursor 4-(4-hydroxyphenyl)-benzoic acid

Although the above mentioned compound is available commercially, it seemed to be economical to synthetise it from inexpensive starting materials and reagents. A known procedure[160] was adapted for the synthesis (see Scheme 3.7).

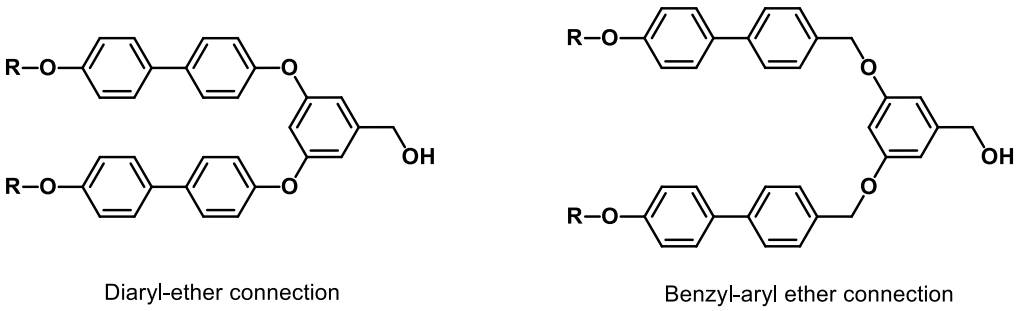


Scheme 3.7 Synthesis of the 4-(4-hydroxyphenyl)-benzoic acid (**20**) (**a**) CH_3I, NaOH, EtOH/water, reflux, 84 %, (**b**) CH_3COCl, $AlCl_3$, CH_2Cl_2, ice-bath→reflux, 43 %, (**c**) Br_2, NaOH, 1,4-dioxane/water, ice-bath→RT, 90 %, (**d**) CH_3COOH, 48 % HBr, reflux, 91 %.

The inexpensive starting material, 4-hydroxy biphenyl was methylated with methyl iodide to form **17** in order to protect the functional group and to hinder the *o*-substitution in the next step which is a standard Friedel-Crafts acylation (in this case acetylation) yielding **18**. The minor *o*-substituted product of the reaction was easily removed utilizing its good solubility in diethylether that is not the case for the desired *p*-product. The haloform reaction of the acetyl-group delivered the carboxylic acid **19** and the required intermediate **20** for the (core)-dendritic mesogenic unit was a result of a demethylation reaction with conc. hydrogen bromide.

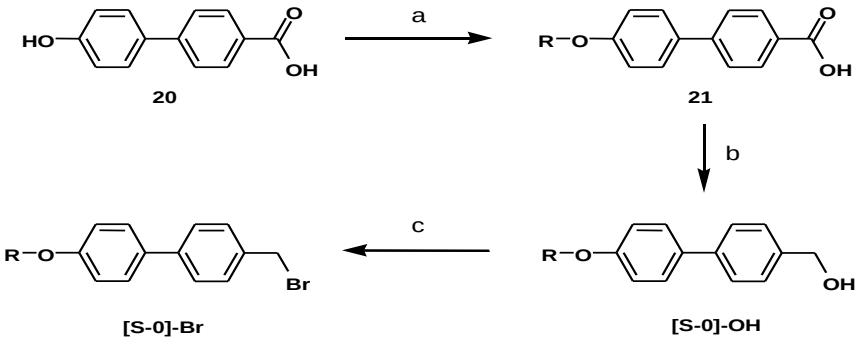
3.2.4.2 The mesogenic group of the **S** series

The aim of the preparation of this mesogenic group was to study how the mesogenic properties are influenced by the close proximity of the relatively rigid, aromatic dendritic network and the biphenyl unit of the end group. A strictly formal point of view might necessitate the more direct attachment of the two phenyl moieties through an oxygen link but instead of this (see Scheme 3.8) the benzyl-aryl ether connection has been chosen. It should be a more flexible structure and it reflects the main structural principle of the dendritic framework, the benzyl-aryl-ether connection (Section 3.1.2).



Scheme 3.8 Comparison of the two connection possibilities of the (core)-mesogenic unit to the dendritic framework

The synthesis started from the above mentioned 4-(4-hydroxyphenyl)-benzoic acid (**20**) and accomplished 4'-*n*-dodecyloxy-4-bromomethyl-biphenyl (**[S-0]-Br**) in only a few steps (Scheme 3.9).



Scheme 3.9 Preparation of the **S** mesogenic unit **[S-0]-Br** . **R** = CH_3-$(CH_2)_{11}$- (**a**) 1-bromo-dodecane, KOH, EtOH/water, reflux, (**b**) $LiAlH_4$, THF, reflux, 71 % over two steps, (**c**) CBr_4, PPh_3, THF, RT, 85 %.

The alkylation with a C_{12} aliphatic chain of the phenolic OH was achieved with a standard alkylation method[162] resulting in the formation of **21**. The reduction of the carboxylic function proceeded smoothly with lithium-aluminium-hydride in tetrahydrofurane yielding the precursor **[S-0]-OH**. The final step utilized the simple and effective Appel-reaction[161] to substitute the benzylic OH functionality to bromide (**[S-0]-Br**) which was required to the formation of the first generational dendron in this series.

3.3 Synthesis of the dendrons and dendrimers of series **T**, **CN-T**, **M** and **S**

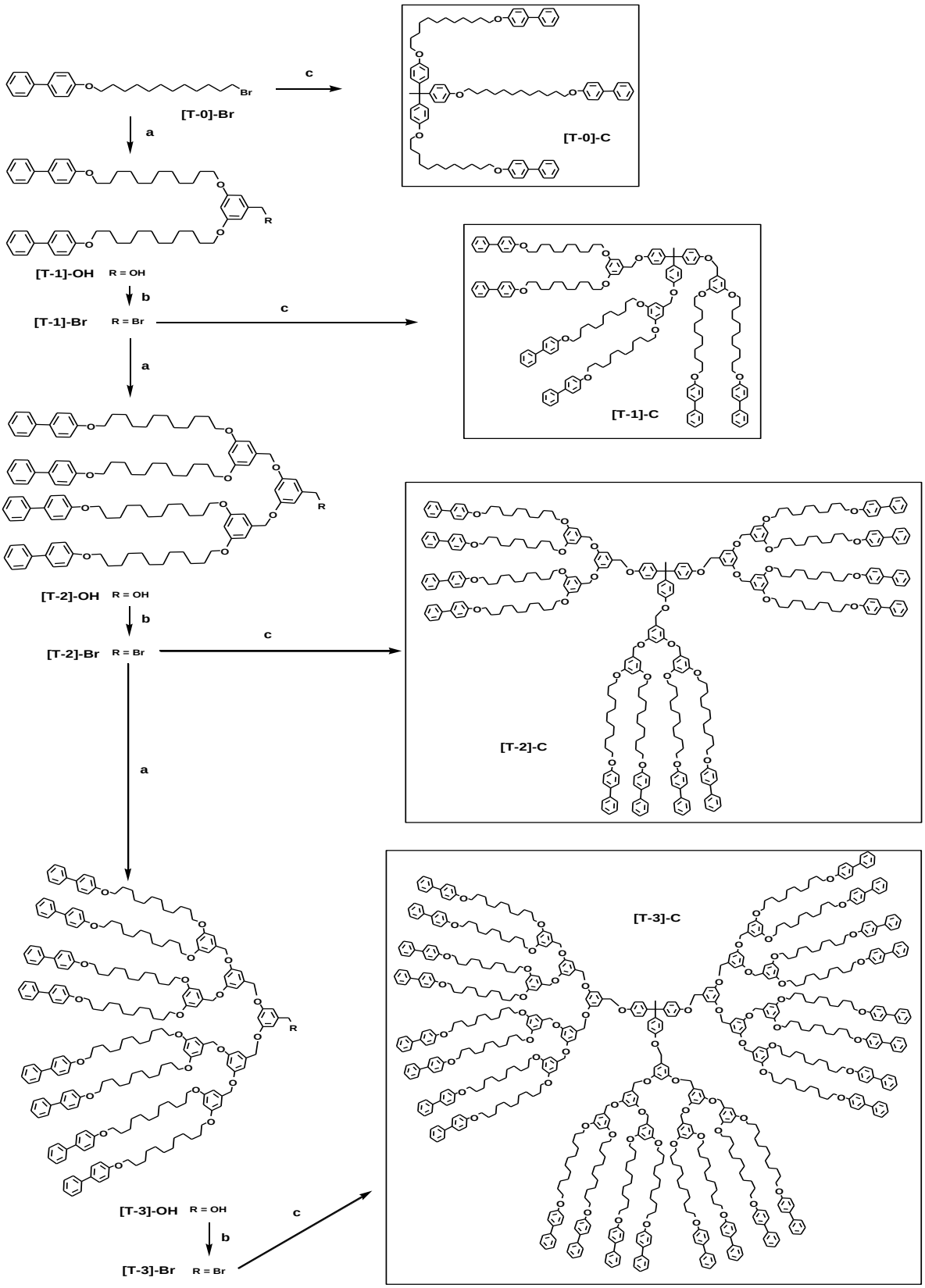
The following schemes (3.10, 3.11, 3.12, 3.13) show the synthesis of the members of the above indicated dendritic series.

The preparation of these dendrons/dendrimers was regarding most of the details very similar, though some differences at certain points were encountered. As the schemes show, the usual etherification procedure was used to attach the mesogenic groups to the first building block. The following synthesis itself went according to the optimised protocols, the only important point to mention is the necessity to start the synthesis with an appropriate mesogenic group. The literature[48] suggests that if the build up is carried out properly, the overall mass of the intermediates will be relatively constant due to the nature of the procedure, namely the increasing molar mass in the generations will counterbalance the loss caused by non-quantitative yield of reactions. So, a careful planning of the amount of starting material turned out to be of high relevance.

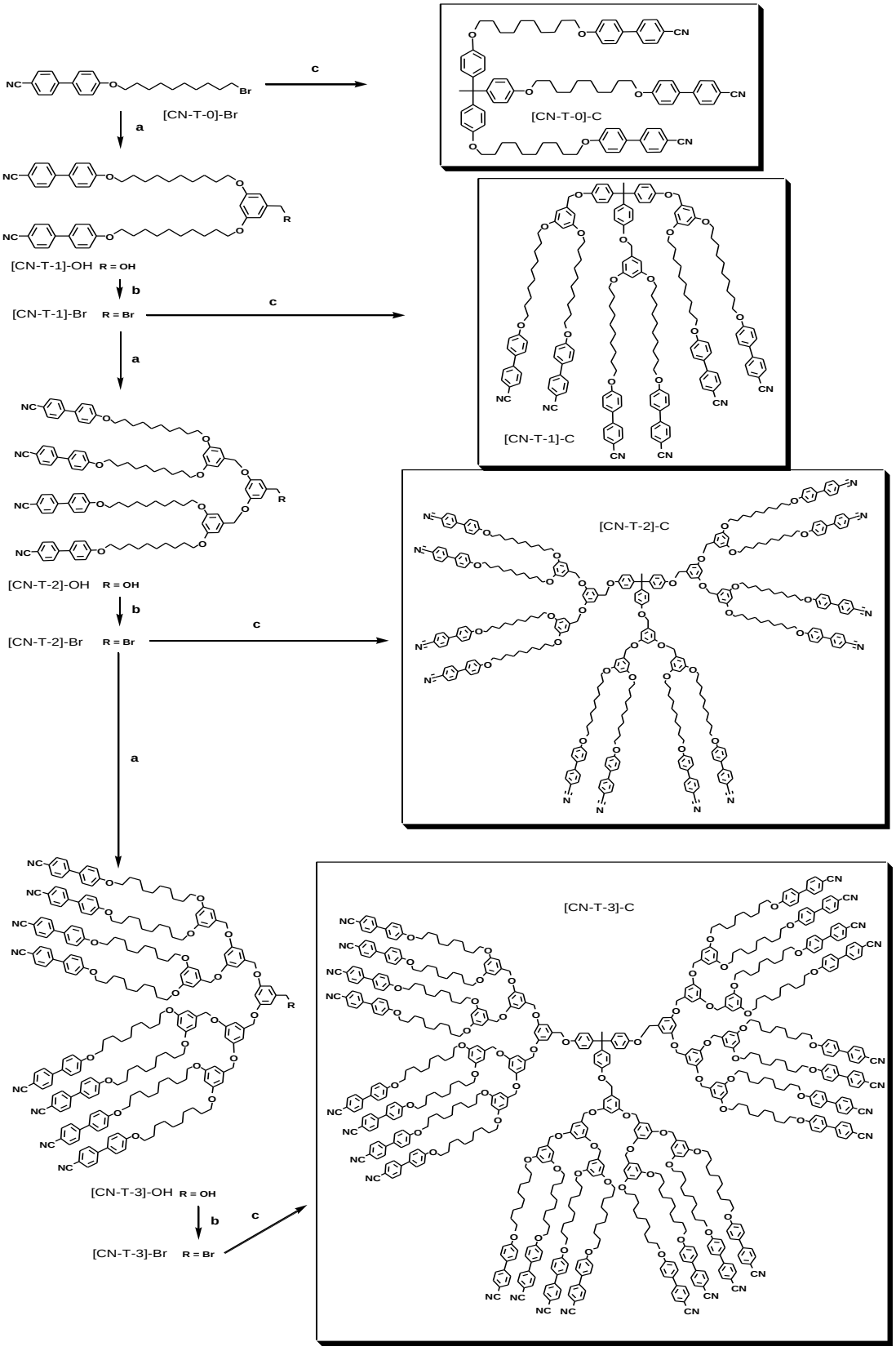
The yield of the individual steps does not show any trend that can be explained by the fact that the reactions were not optimised.

The first members (first generational dendrons) had a kind of a crystalline appearance but the higher generations can be characterised as amorphous materials.

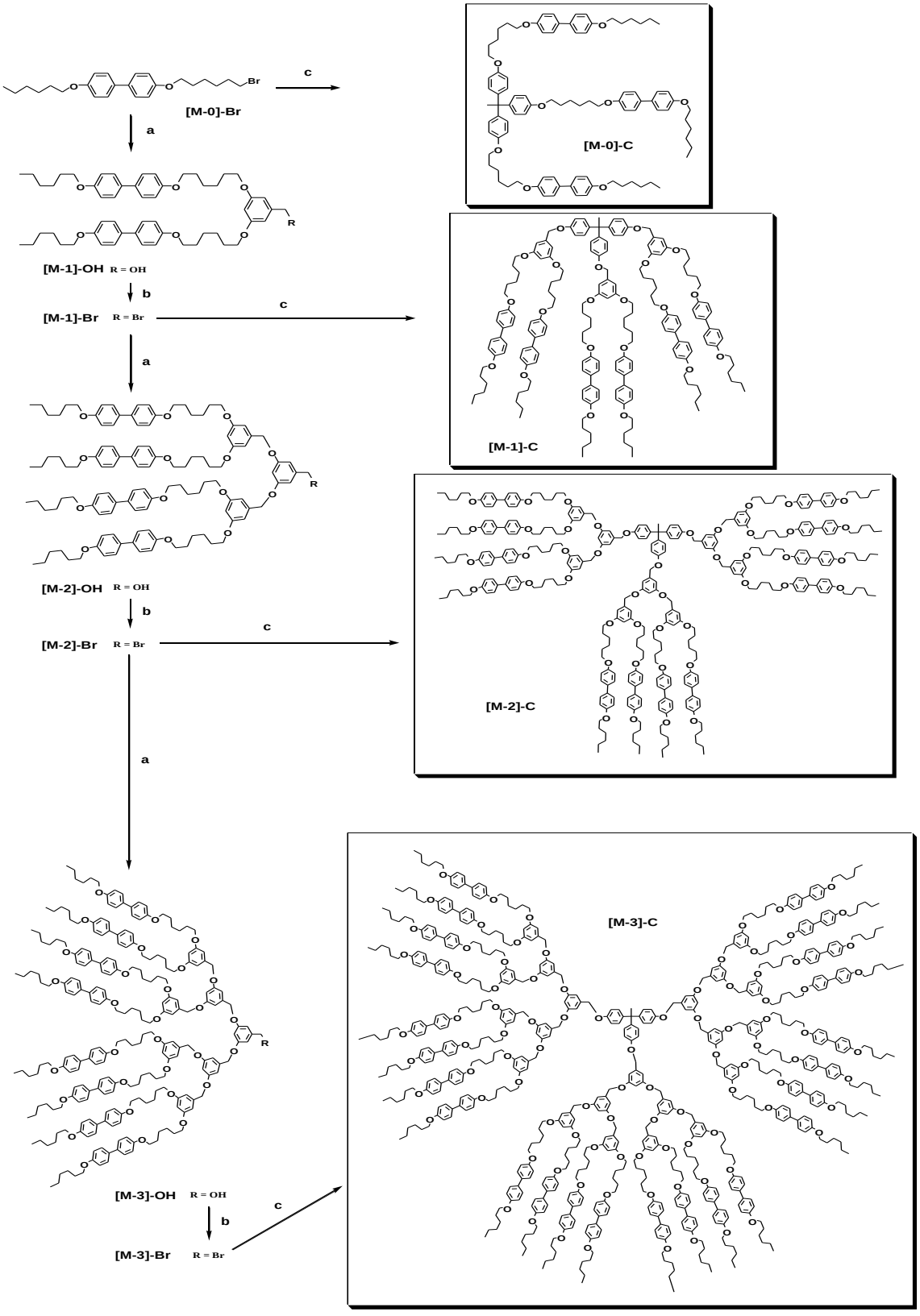
In the case of the **S** series (Scheme 3.13) the polarization microscopy examinations of the first (**[S-1]-OH**, **[S-1]-C**) and the second generation products (**[S-2]-OH**) showed unambigously that no liquid crystalline behavior can be expected from the substances. The synthesis has been interrupted. There was another relevant factor that made the synthetic work with the members of the **S** series uneasy. These compounds starting with **[S-1]-OH** and its derivatives demonstrated an unexpectedly low solubility in most of the usual organic solvents required for the synthetic manipulation. They have only shown good solubility in hot THF but recrystallizing efforts were of no success here either. Column chromatography worked only with very low load of the columns and generally the purification of the compounds in this series was a tedious procedure.



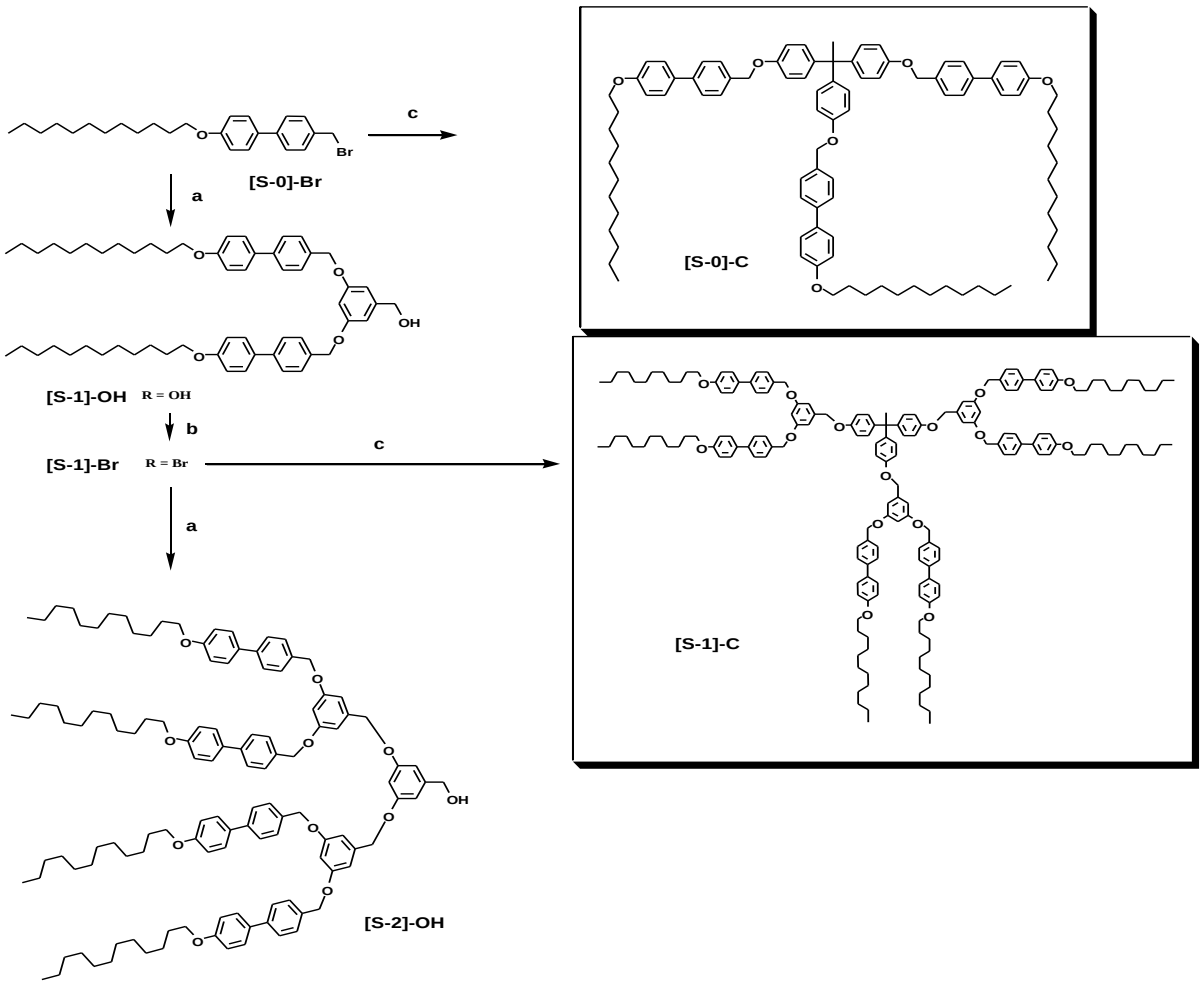
Scheme 3.10 Overview of the preparation of the **T** dendritic series (**a**) 3,5-dihydroxy-benzyl alcohol, K_2CO_3, 18-crown[6], acetone, reflux, (**b**) CBr_4, PPh_3, THF, RT, (**c**) 1,1,1-tris(4-hydroxyphenyl)-ethane (**15**), K_2CO_3, 18-crown[6], acetone (and occasionally THF), reflux.



Scheme 3.11 Overview of the preparation of the **CN-T** dendritic series (**a**) 3,5-dihydroxy-benzyl alcohol, K_2CO_3, 18-crown[6], acetone, reflux, (**b**) CBr_4, PPh_3, THF, RT, (**c**) 1,1,1-tris(4-hydroxyphenyl)-ethane (**15**), K_2CO_3, 18-crown[6], acetone (and occasionally THF), reflux.



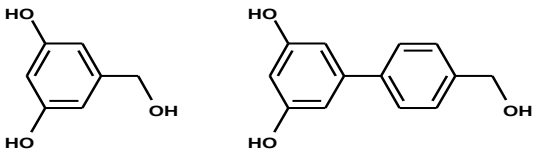
Scheme 3.12 Overview of the preparation of the **M** dendritic series (**a**) 3,5-dihydroxy-benzyl alcohol, K_2CO_3, 18-crown[6], acetone, reflux, (**b**) CBr_4, PPh_3, THF, RT, (**c**) 1,1,1-tris(4-hydroxyphenyl)-ethane (**15**), K_2CO_3, 18-crown[6], acetone (and occasionally THF), reflux.



Scheme 3.13 Overview of the preparation of the non complete **S** dendritic series (**a**) 3,5-dihydroxy-benzyl alcohol, K_2CO_3, 18-crown[6], acetone, reflux, (**b**) CBr_4, PPh_3, THF, RT, (**c**) 1,1,1-tris(4-hydroxyphenyl)-ethane (**15**), K_2CO_3, 18-crown[6], acetone, THF, reflux.

3.4 Synthesis of the building block and of the **B** dendritic series

Considering the pivotal role the biphenyl structural unit plays in the context of liquid crystals, it seemed to be of high interest to synthetize such a dendrimer which carry these biphenyl moieties not on the periphery but throughout its whole structure. 4-(3,5-dihydroxyphenyl)-benzyl alcohol (**13**) was chosen as building block that can be seen as an 'elongation' of the usual building block of Fréchet type dendrimers, 3,5-dihydroxy benzyl alcohol (**14**) with a *p*-phenylene group (Scheme 3.14).



14 **13**

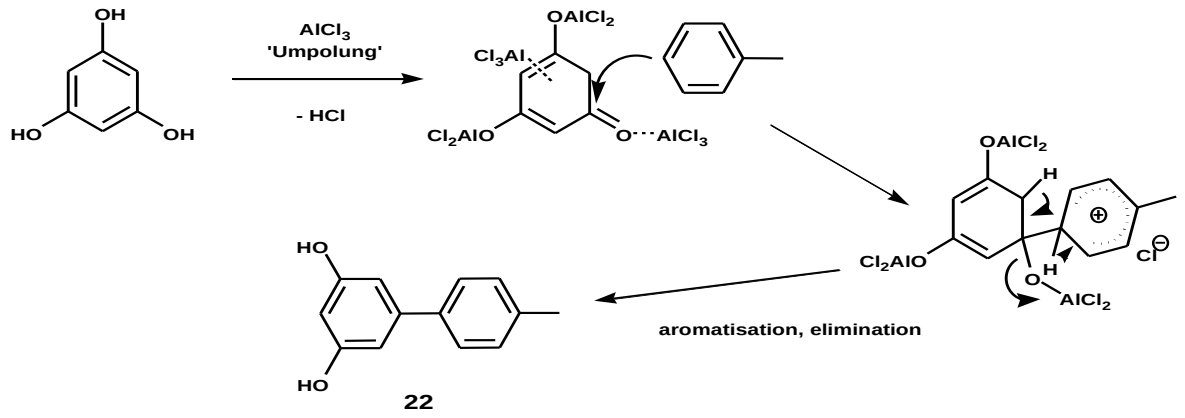
Scheme 3.14 3,5-dihydroxy-benzyl alcohol (**14**) as the traditional and 4-(3,5-dihydroxyphenyl)-benzyl alcohol (**13**), as the biphenyl based building block of Fréchet type dendrimers.

An independent and advantageous synthesis developed during the work on this thesis for the reported[163] building block 4-(3,5-dihydroxyphenyl)-benzyl alcohol will be presented first.

3.4.1 Synthesis of the biphenyl based dendritic building block

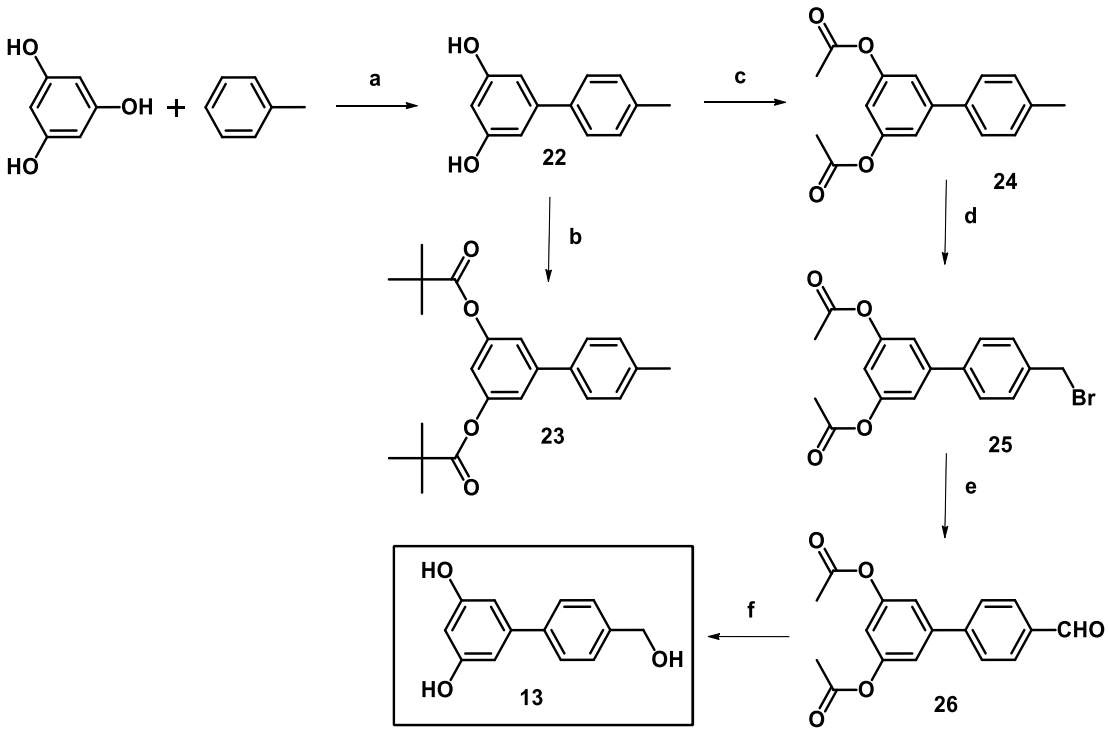
The synthesis of certain small molecules can sometimes be as challenging as the construction of relatively complicated, big molecular structures. A cheap and easy access path turned out to be necessary in order to be able to use the molecule as a dendritic building block.

There are a few reaction schemes that lead to this particular substitution pattern on the biphenyl carrier. They turned out to be ineffective and/or costly in our hands but serendipity and then revising some obscure articles of Russian authors gave the key to the molecule. The particular step of the synthesis is the „Anti-Friedel-Crafts"-type substitution between toluene and phloroglucinol[164] (Scheme 3.15)



Scheme 3.15 Proposed mechanism of the unconventional reaction between phloroglucinol and toluene via Lewis acid ($AlCl_3$) catalysis

The mechanism of the reaction has not been undoubtedly cleared yet but a putative mechanism can be drawn up. The hard Lewis acid aluminium ion is strongly attracted by the equally hard Lewis base oxygen atoms on the phloroglucinol yielding a stable complex. The phloroglucinol ring turns from an electron-rich state to an electron-deficient one and the carbonyl C of the complexated intermediates keto-tautomer gets sufficiently electrophilic for the aromatic π-cloud of toluene to attack. Rearomatisation occurs furnishing the biphenyl **22** with the desired 3,5-dihidroxy substitution. The reaction works well even on a 100 g scale and both starting materials as the reactant are economically viable. The regioselectivity of the reaction is excellent, no traces of sideproducts were detected in any attempt. Toluene serves as reactant and solvent at the same time. Two molar equivalents of aluminium chloride is required for the reaction to proceed.



Scheme 3.16 Reaction route towards the 4-(3,5-dihydroxyphenyl)-benzyl alcohol. (**a**) $AlCl_3$, RT, 70 %, (**b**) pivaloyl chloride, pyridine, ice-cooling→60 °C, 46 %, (**c**) $(CH_3CO)_2O$, pyridine, RT, 85 %, (**d**) N-bromo-succinimide, CCl_4, benzoyl peroxyde, reflux, 76 %, (**e**) CH_3COONa, DMSO, 70 °C, 85 %, (**f**) $LiAlH_4$, THF, reflux, 92 %.

In order to transform the methyl group to a hydroxymethyl, the phenolic OH functionalities of the formed 4-methyl-3,5-dihydroxy-biphenyl (**22**) must have been protected (Scheme 3.16). As first choice, pivaloyl protection to **23** was envisaged. The esterification step proved to be unsatisfactory in terms of yield and then this route was totally abandoned due to the very poor solubility of the pivaloyl protected compound in carbon tetrachloride indispensable to the next bromination step. Acetyl protection of **24** led to more promising results and the generally lower stability of the acetyl compared to pivaloyl did not have influence on the further steps. The acetyl-protected compound was brominated to **25** under the usual conditions, as indifferent solvent CCl_4 was used, thermal decomposition of benzoyl peroxyde delivered the radical initiation and N-bromo-succinimide was the source of bromine. The formed benzyl bromide was treated with an excess of sodium acetate in warm DMSO[165] (that served as reagent and solvent at the same time) which gave rise to the substituted benzaldehyde **26**. Sodium acetate was the base of choice as it did not interfere with the acetate protecting groups. In the last step the simultaneous removal of the acetyl protecting groups and reduction of the aldehyde to primary alcohol has

been achieved by the $LiAlH_4$ driven reduction in THF. The column chromatographic purification of the desired product **13** required understandably high polarity of the eluent.

The unusual coupling of phloroglucinol with aromatic nucleophiles could be extended to a certain degree. The further products of the reaction are shown below in Table 3.1.[164]

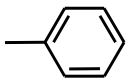
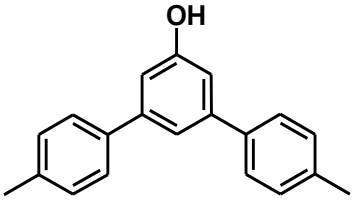
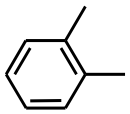
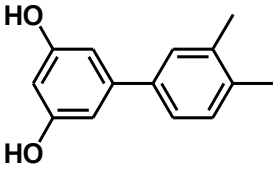
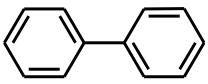
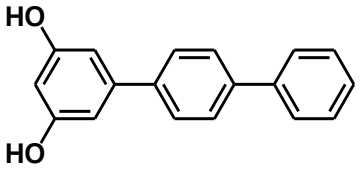
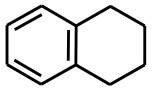
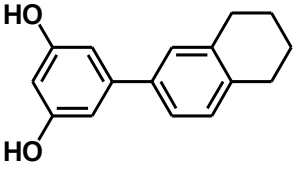
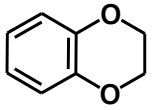
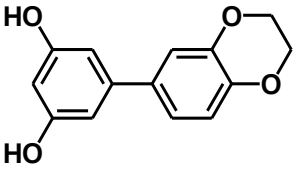
starting material	product
	
	
	
	
	

Table 3.1 Products of different subtrates with phloroglucinol under „Anti-Friedel-Crafts" conditions

Unfortunately the scope of the reaction is rather limited, acceptable results can be seen only with activated (or at least not deactivated) aromatic substrates and the functional groups must be able to resist the strong Lewis acid character of aluminium chloride. On the other side, too much activation (reactivity) is neither well tolerated, naphthalene as a pronounced nucleophile gives only tarry residues under the reaction conditions. As it can be seen from Table 3.1, disubstitution of the phloroglucinol is also possible, with four equivalents of aluminium chloride the reaction

could be forced to act on two toluene molecules but the yield of the disusbtitution product is significantly lower and the formation of considerable amounts of tarry sideproducts can be observed.

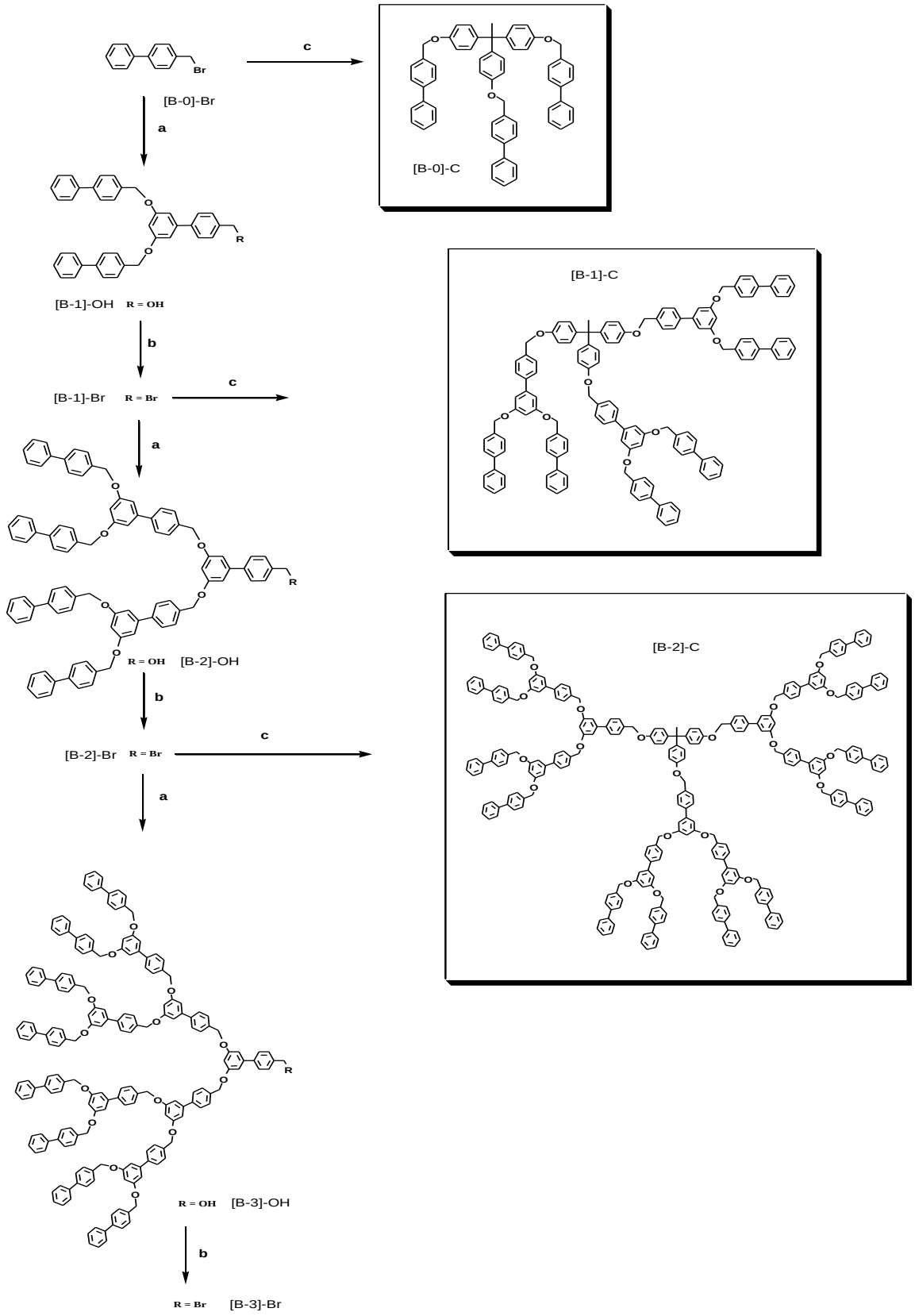
3.4.2 Synthesis of the biphenyl based dendrons/dendrimers (the incomplete **B** series).

The use of the biphenyl based, modified Fréchet-type dendron building process (Scheme 3.17) differed only at few points from the already described original. Solubility problems were only seen at the third generation at this series and the colouring of the reaction mixture was negligible during the reaction probably due to the lower tendency of the building block to oxidation.

As the core unit, again 1,1,1-tris(4-hydroxyphenyl)-ethane (**15**) was utilized.

Recrystallizing attempts as means of purification have usually failed in the cases of the end-group dendrimers (**T**, **CN-T**, **M** and **S** series) but here the structural resemblance to the original Fréchet type dendrimers were encouraging to try to purify the substances with simple recrystallising. In the case of the first two generational dendrons (**[B-1]-OH** and **[B-2]-OH**) it worked excellent. However, the rest (bromides and dendrimers) must have been purified by column chromatography.

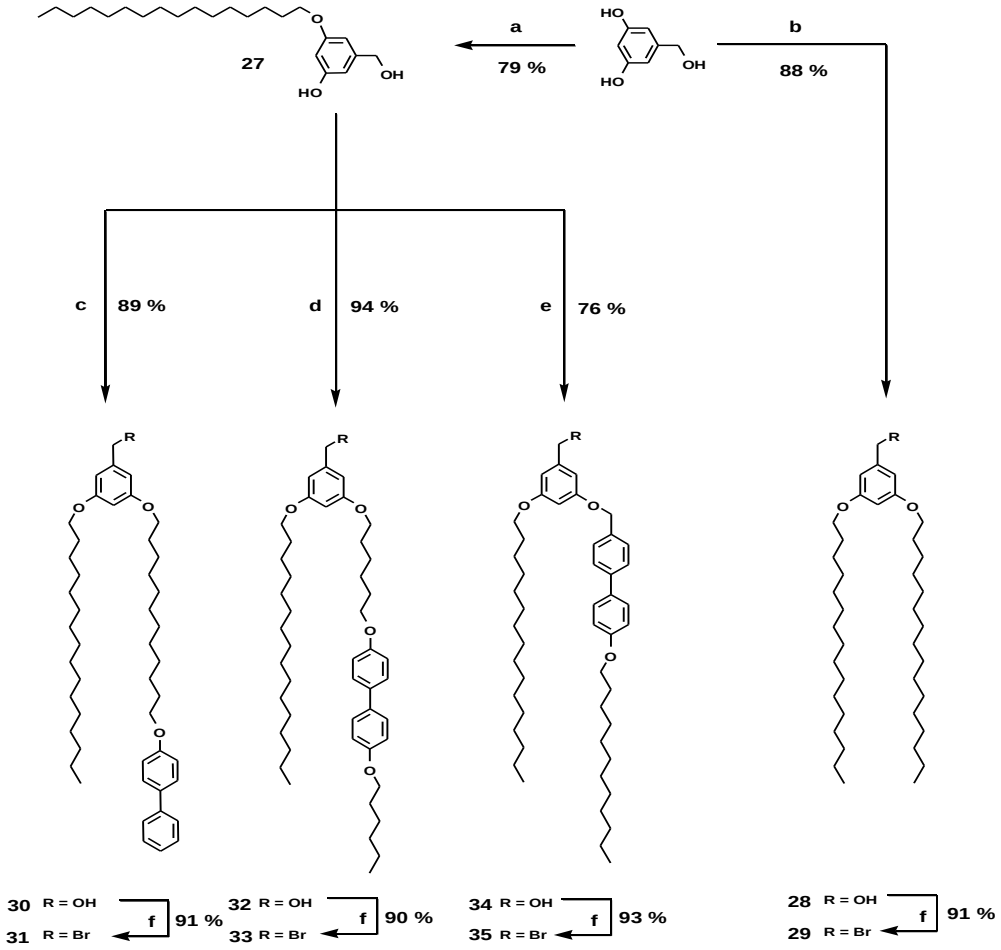
The synthesis of this series was interrupted as the examination of the liquid crystallinity of the prepared members showed that no LC behaviour was in sight in this group of compounds.



Scheme 3.17 Overview of the preparation of the non-complete **B** dendritic series (**a**) 4-(3,5-dihydroxy-phenyl)-benzyl alcohol (**13**), K_2CO_3, 18-crown[6], acetone, reflux, (**b**) CBr_4, PPh_3, THF, RT, (**c**) 1,1,1-tris(4-hydroxyphenyl)-ethane (**15**), K_2CO_3, 18-crown[6], acetone, THF, reflux.

3.5 Synthesis of the small 'mixed' dendrons and dendrimers

One of the big advantages of dendrons/dendrimers is the versatility concerning their structural features. Our interest was to incorporate two different units at the same aromatic moiety at the periphery, to 'mix' a previously used mesogenic group with a simple, long aliphatic chain on the same dendritic unit. The synthetic routes to the dendrons can be seen in Scheme 3.18.

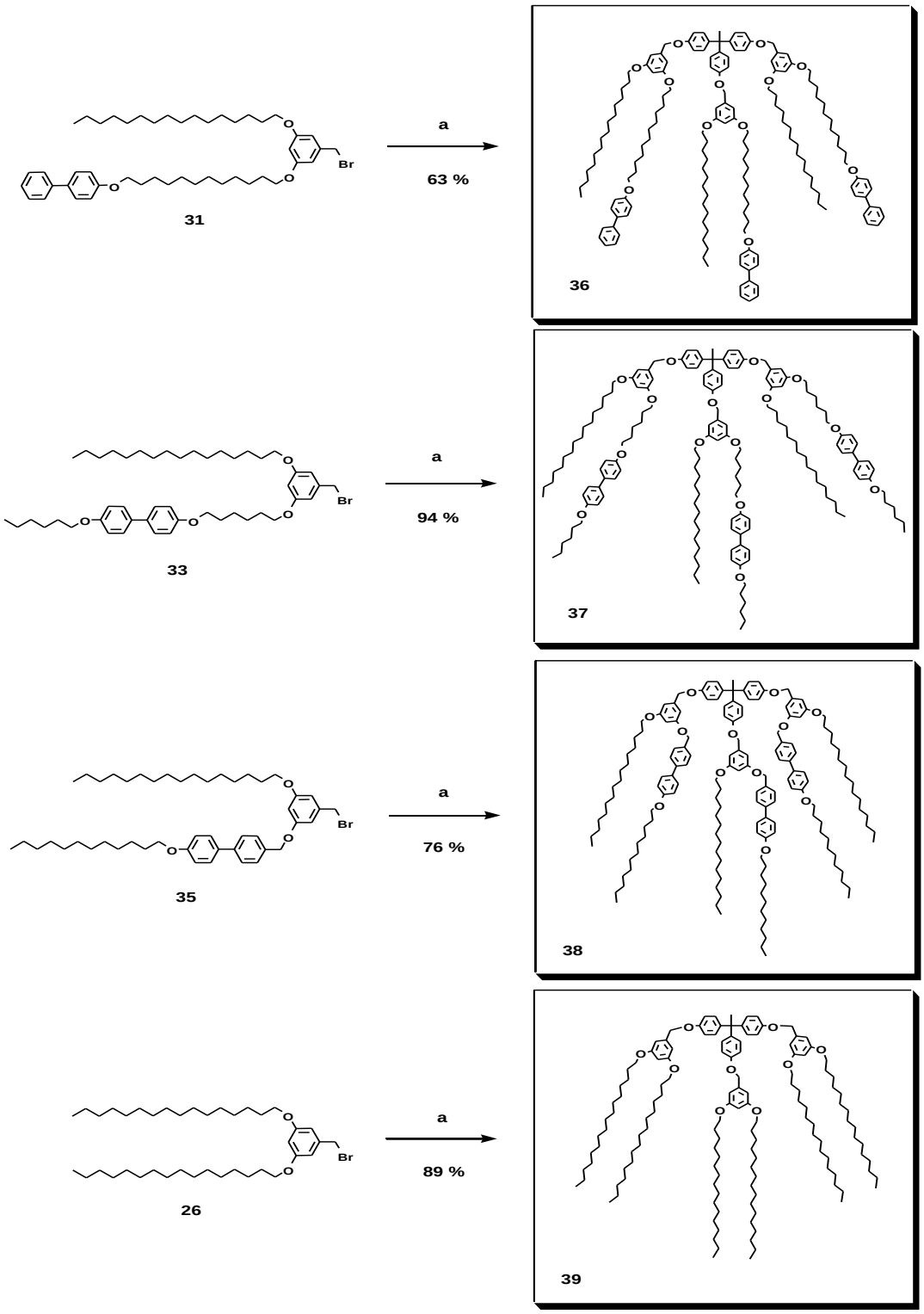


Scheme 3.18 Preparation of the asymmetrical dendrons and some related structures (**a**) 1-bromo-hexadecane, K_2CO_3, 18-crown[6], acetone, reflux (**b**) 1-bromo-hexadecane, K_2CO_3, 18-crown[6], acetone, reflux (**c**) **[T-o]-Br**, K_2CO_3, 18-crown[6], acetone, reflux (**d**) **[M-o]-Br**, K_2CO_3, 18-crown[6], acetone, reflux (**e**) **[S-o]-Br**, K_2CO_3, 18-crown[6], acetone, reflux (**f**) CBr_4, PPh_3, THF, RT.

Monoalkylation of the smaller building block (path **a, 27**) required fourfold excess of 3,5-dihydroxy-benzyl alcohol, formation of the disubstituted product could be observed in low amounts. The usual conditions (2.1 eq. of the halide, path **b**) delivered the disubstitution product **28**. The individual alkylations with the appropriate mesogenic unit were run with 1.1 eq. of the

zeroth generation dendritic bromides yielding the first generational mixed dendrons **30**, **32** and **34**. Transformation of the benzylic OH group to bromide was done under the conditions of the Appel reaction again yielding **29**, **31**, **33** and **35**.

Scheme 3.19 introduces the formed first generational dendrimers.



Scheme 3.19 Formation of the first generational dendrimers. (**a**) **15**, K_2CO_3, 18-crown[6], acetone, reflux

4 Liquid crystalline properties of the synthesised compounds

4.1 Investigation of the mesophases

The enthalpy values will be given in J/g units instead of the more common J/mol. The examined compounds have molecular masses of different magnitudes (from below 1000 g/mol to more than 10000 g/mol) so the data shown in J/mol were of little value due to their very limited comparability.

The groups of compounds described in this chapter are in order determined by the structure of the mesogenic units, starting with compounds having the mesogenic units directly attached to the dendritic core, followed by those involving longer aliphatic spacer units between mesogenic unit and dendritic/dendrimer core in the order 4-cyanobiphenyl, via nonsubstituted biphenyls to 4-hexyloxybiphenyls. The length of these groups including the aliphatic spacers is approximately the same for all compounds. In each group dendritic molecules are discussed first before attention is turned to the corresponding dendrimers involving three dendritic wedges.

The physical properties (optical microscopy, DSC, X-ray diffraction) have been measured in the group of and mesophase determinations have been made by Professor C. Tschierske.

The lengths of the molecules have been determined by the ChemOffice 2004 bundle ChemBio Ultra 8.0 software. The program provides the nanometer distances of selected atoms in the formulas drawn with ChemDraw and imported in ChemBio. The overall atomic distances (lengths of the molecules) were calculated as the sum of distances in molecular segments. The aliphatic moieties were measured in an extended, all-anti (or all-trans) conformational state, while the distances of atoms connected directly to aromatic moieties were easily determined due to the rigid nature of the aromatic rings, otherwise the molecular segments were chosen in the representation in which the closest arrangement of atoms to the sp^3-hybridised carbon with ideal bond angles could be assumed.

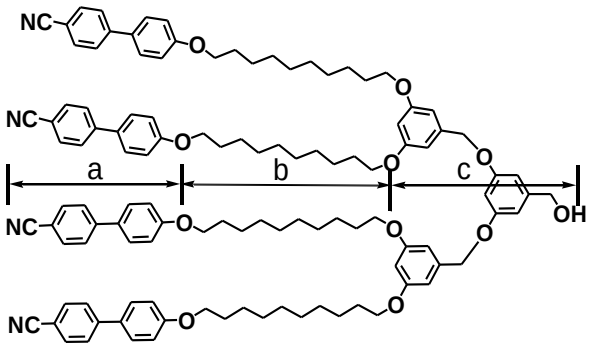


Figure 4.1 Example of intramolecular distance determination. The sum of the sequential values gave the length. a (terminal N of the cyano-group – O at the other end of the biphenyl) = 1.10 nm, b (the two oxygens at the ends of the decamethylene chain) = 1.36 nm, c („starting" O of the dendritic scaffold – H of the focal OH) = 0.98 nm. Length = a + b + c = 3.4 (3.44) nm.

It must be emphasised though that the „length of the molecule" cannot be understood on the same, clear way in the case of the dendrons and dendrimers as it is understood with the conventional calamitic liquid crystalline compounds. Even without approaching the De Gennes-limit[25] the steric repulsion forces some parts of the molecules in an angled orientation and here the distance of the focal atom and an atom on the periphery measured in the same direction will be obviously shorter than in the central branch of the structure (compare the cyano N – focal OH distance on the top branch with the central N – OH distance in the middle in Figure 4.1). Further effect encountered with dendrimers generally and here as well is the flexibility of certain molecular segments. Not only the ubiquitous „melting" of the alkyl chains can lead to virtually shorter molecular lengths than the calculated ones but the dendritic scaffold is also able to deform rather significantly adding to the length-flexibility of the compounds. There is even another factor that makes the usage of molecule length in the case of the dendritic molecules problematic (Figure 4.2).

It is highly reasonable to assume that the dendritic molecules, owing to their flexible nature, are not always organised as the usual representation displays them (Figure 4.2 a), dedritic arms/wedges showing in one direction but the opposite directional arrangment (Figure 4.2 b), reaching into different layers in a layer structure (most abundant with the described LC dendritics in this thesis). Different ratios of the mono- and bidirectional molecules can exist and even dynamic equilibrium between them is also a possibility. In the bidirectional case the physical length of the molecules do not correspond to a more or less exactly predetermined value. For the

sake of a uniform and reasonable reference system, the molecule length has been defined and used throughout this thesis as described before, the length of the molecules in the monodirectional (taper-shaped) conformation.

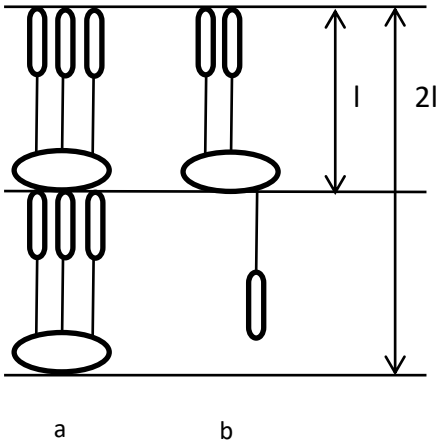


Figure 4.2 Representation of the possible arrangment of dendritic segments in layers. a, monodirectional wedges, molecule length applies, b, dendrons/moieties in different directions (probable in most of the cases), molecule length corresponds neither to l, nor to 2l.

The compounds were subjected to differential scanning calorimetry (DSC) measurements in the first place after initial confirmation of liquid crystalline behaviour by polarizing microscopic observation while being heated or cooled. Considering their structure and the knowledge gathered from similar compounds in the literature the presence of layered mesophases was probable and the utilisation of X-ray diffraction was the next logical step. To understand the relative nature of the differences observed by polarised optical microscopy with the present substances, take a closer look at one characteristic example, the examination results of the compound **[M-2]-C** (see Table 4.1)!

	Phase transitions (T/°C) ΔH (J/g)	phase	length of molecule (l) (nm)	layer thickness (d) (nm)	d/l
[M-2]-C	Cr ‹20 Col_r 76 SmB 91 SmA 114 Iso 0.6 3.7 9.2	SmA SmB Col_r	4.4	2.1 (100 °C) 4.2 (80 °C) *a = 4.7, b = 8.9 d = 4.5 (60 °C)	0.48 0.95 1.02

*: lattice parameters of the rectangular columnar phase

Table 4.1 Phase transition temperatures, transition enthalpies and other structural parameters of the compound **[M-2]-C**.

Figure 4.3 shows the optical microphotographs of the heated sample at three different temperatures.

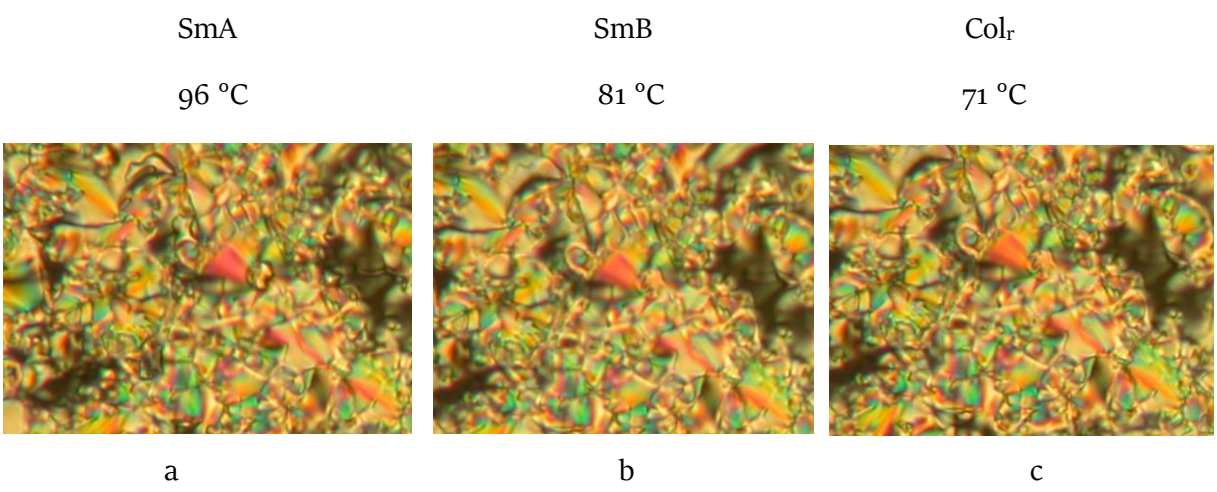


Figure 4.3 Polarised microscopy views of the different mesophases of compound **[M-2]-C**.

The fan-like texture seen at the highest temperature measurement (a) is an indicator of a possible smectic A phase (as it turned out from the X-ray results). Cooling the sample leads to a phase transition (according to DSC measurements) but the view of the substance under the microscope does not show any significant change. This is not unexpected (knowing that the observed phase is smectic B, b on the Figure) as the overall layer-structure is retained, and a paramorphotic fan-like texture is also retained in smectic B. Further cooling leads to the rectangular columnar mesophase (c) while the texture of the sample under the microscope changes again only very slightly. The structural difference is relatively small and the fan-like texture is a paramorphotic texture in this case, too.

The sole (only for the experts eyes recognisable) difference is the slight change of the birefringence.

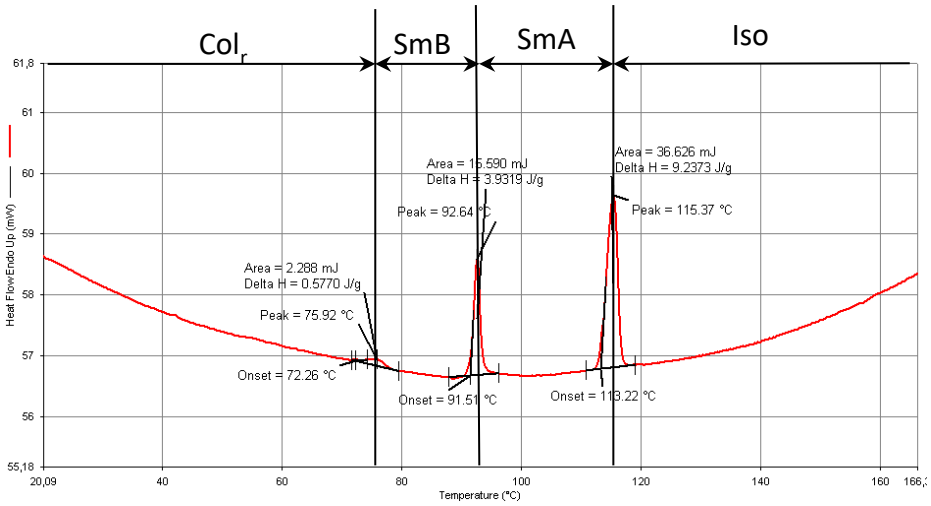


Figure 4.4 Differential scanning calorimetric curve of **[M-2]-C.** Second heating (10 K min-1).

The DSC curve of the second heating of this compound is shown in Figure 4.4. The DSC traces show all phase transitions mentioned above. The SmA-SmB transition is associated with a relatively large enthalpy change (below 3.9 J/g) indicating a significant structural change whereas no dramatic change in the organisation of the matter in the encountered at the SmB-Col$_r$ transition, having a much smaller enthalpy change. No crystallization is observed indicating that the material can be cooled in a liquid crystalline state to room temperature.

Figure 4.5 contain the decisive information about the mesophases.

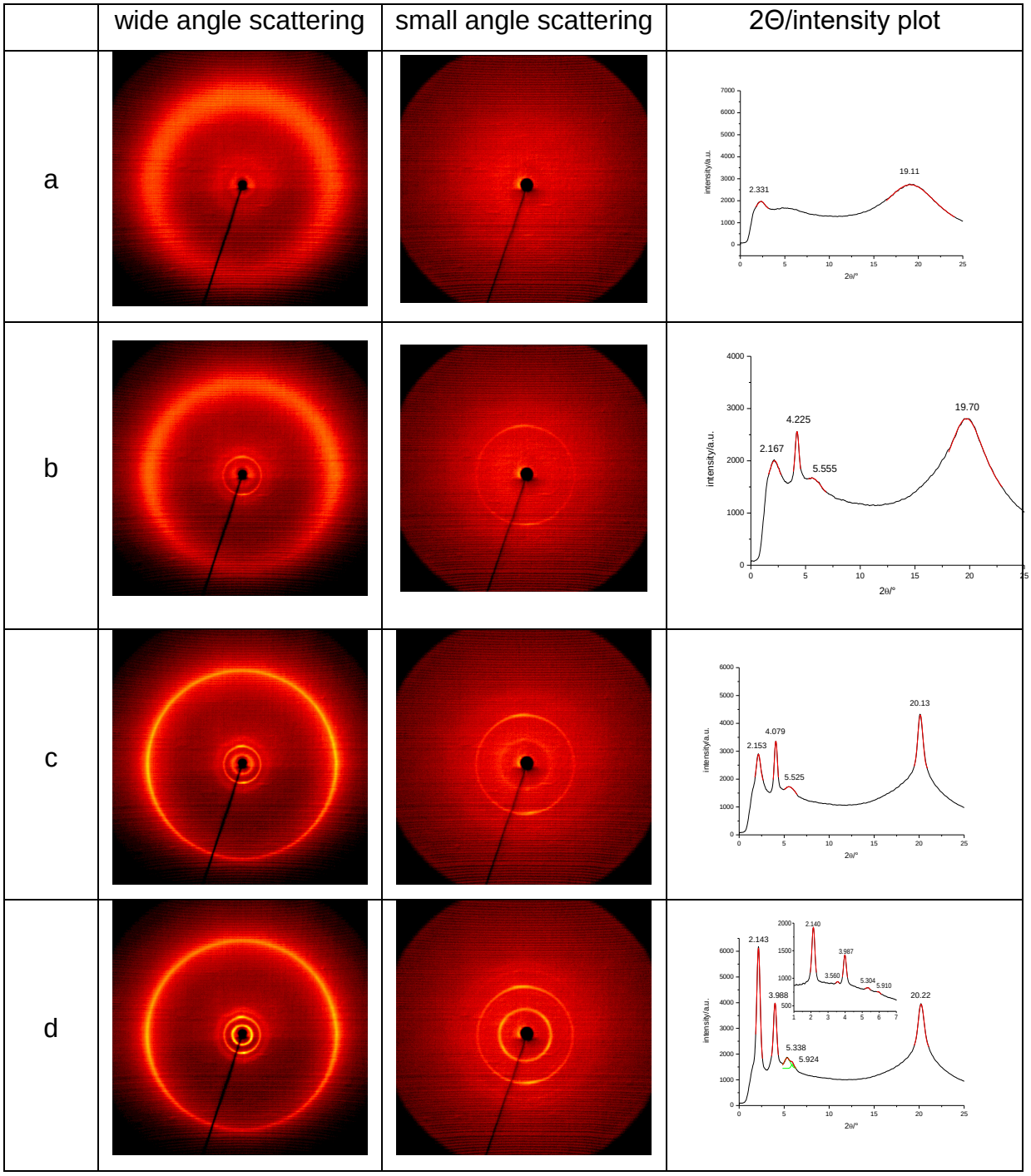


Figure 4.5 X-ray diffraction patterns of **[M-2]-C** at different mesophases. a, 120 °C, isotropic liquid, b, 100 °C, smectic A phase, c, 80 °C, smectic B phase, d, 60 °C, rectangular columnar phase

The XRD pattern in the isotropic state (a) shows only two blurred halos, one in the small angle range and a second one in the wide angle region, which indicates only short range order of the molecules. Cooling leads to the formation of the smectic A phase (b) showing a bit sharper but still fuzzy halo in the wide angle region and sharp peak in the small angle area, caused by the

development of a long range periodicity due to the organization of the molecules in the layers. The two additional diffuse scatterings in the small angle region is a special feature of the mesophases of this compound which will be discussed later in Section 4.7.2. Further cooling (c) leads to the smectic B phase, clearly visible by the sharpening of the wide angle scattering. Continued cooling leads to the rectangular columnar phase with the significant change in the small angle region yielding four reflections which can be indexed to a centered rectangular lattice. The wide angle diffraction patterns does not change at the SmB-Col_r transition, indicating that the Col_r phase represents a modulated SmB phase.

The *d*-values from XRD investigations were used as a main tool for the development of the structural models of the mesophases by comparison with the molecular dimensions as described in the following sections for the distinct classes of compounds.

4.2 Small 'mixed' dendrons and dendrimers (from Chapter 3.5).

None of the members of this group of compounds has shown mesophase forming activity at the preliminary optical microscopic examinations. The probable reason can be that the tethering of the long (C_{16}) alkoxy-chains with the mesogenic groups on the tight dendritic scaffold does not allow the necessary dissociation of the two fundamental functions of a calamitic-like mesogen components. It would be interesting though to see whether this behaviour might change at higher dendritic generational of the families.

4.3 Biphenyl based dendrons and dendrimers (**B** series, Chapter 3.4.2)

In this series of dendrons and dendrimers the absence of liquid crystalline behaviour was experienced, too. The probable reason is the stiffness of the structure, the attractive forces among the numerous aromatic rings due to the pronounced π-π interactions could not be counterbalanced by the limited flexibility offered by the benzyloxy joints between the dendritic generations. Incorporation of flexible linkers[77, 78, 79, 102] seems to be indispensable to experience mesophases, as the too tight coupling of the dendritic scaffold and the rigid parts of the mesogenes disrupt the necessary balance of molecular segments regarding flexibility vs. rigidity.

4.4 Alkoxy-biphenyl attached to dendrons and dendrimers (**S** series, Scheme 3.13)

The dramatically decreasing general solubility of the compounds in organic solvents with increasing generation number has foreshadowed the observed absence of liquid crystallinity in this group of dendrons and dendrimers. The too tight coupling of the dendritic moiety and the biphenyls probably lead to such a rigid structure that hinders formation of the mesophases. The theoretical possibility of mesophase formation was given, because for example the first generational dendrons **[S-1]-OH** structure is relatively close to some well-known and intensely researched 'banana-shaped' mesogenes. Probably the presence of the focal OH-group was one of the critical factors in the failure of the mesophase formation, this kind of substitution on the 5-ring banana-shaped molecules is uncommon and most likely disrupts the association of the aromatic segments in a herring bone alignment characteristic of the special kind of calamitics in question.

4.5 Cyano-biphenyl endgroup bearing dendrons and dendrimers (**CN-T** series, Scheme 3.11)

4.5.1. **CN-T** dendrons (**[CN-T-1]-OH**, **[CN-T-2]-OH**, **[CN-T-3]-OH**).

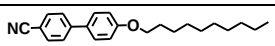
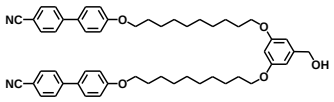
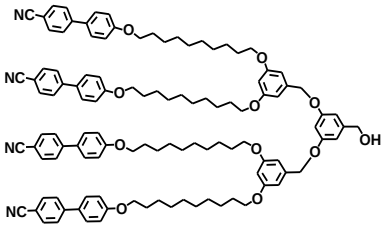
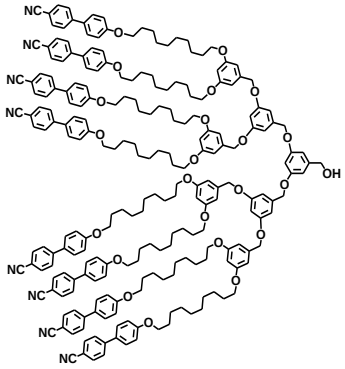
[CN-T-0]-H		
[CN-T-1]-OH	**[CN-T-2]-OH**	**[CN-T-3]-OH**
		

Table 4.2 Structures of the individual mesogen and of the cyanobiphenyl-derived dendrons.

	Phase transitions (T/°C) ΔH (J/g)	phase	molecule length (l) (nm)	layer thickness (d) (nm)	d/l
[CN-T-0]-H	Cr 61 N 84.5 Iso	N			
[CN-T-1]-OH	Cr 102 Iso 113.4	-	3.0	-	
[CN-T-2]-OH	Cr 105 (SmA 83 N 85) Iso 42.1 6.3 2.4	SmA	3.4	*	
[CN-T-3]-OH	Cr 105 (SmA 83) Iso 5.5 6.4	SmA	3.9	4.5	1.15

Table 4.3 Phase transition temperatures, transition enthalpies and other structural parameters of the cyanobiphenyl derived dendrons **[CN-T-*n*]-OH** *: no reflex visible in the small angle region

The individual mesogen (**[CN-T-0]-H**, 4-decyloxy-4'-cyano-biphenyl), known for a long time[167] shows only a nematic phase in a 20+ degree temperature range. In contrast, the first generational dendron of this series **[CN-T-1]-OH** did not show any mesophase, due to the high melting point, it melted to an isotropic liquid at 102 °C. The individual mesogen and the second- and third-generation dendrons have nearly the same clearing temperature. These dendrons show a relatively high melting point so that their mesophases are only monotropic. The second generational dendron **[CN-T-2]-OH** formes a monotropic SmA and a monotropic nematic phase in a narrow temperature range as well. The third generation dendrimer forms exclusively the SmA phase. The ratio of the determined layer thickness and molecule length (d/l) in the case of the third generational dendron **[CN-T-3]-OH** corresponds to the previously often seen behaviour of the cyanobiphenyl-mesogen containing calamitics, namely the intercalated bilayer structure as the layer thickness is somewhat greater than the length of the molecule. See the proposed layer structure in Figure 4.6. The lamellar structure develops as the generation number increases or the temperature is decreased, i.e. with increasing segregation of the aliphatic chains from the aromatic segments. Though the SmA phase of **[CN-T-2]-OH** is indicated by textural observations, there is no clear layer reflection in the XRD pattern. Also for the third generation dendrimer the layer reflection is only very weak, meaning that the interfaces between the segregated regions are still very diffuse in these SmA phases.

4.5.2. **CN-T** dendrimers (**[CN-T-0]-C**, **[CN-T-1]-C**, **[CN-T-2]-C**, **[CN-T-3]-C**).

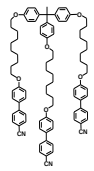
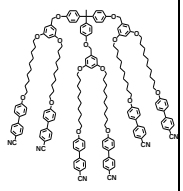
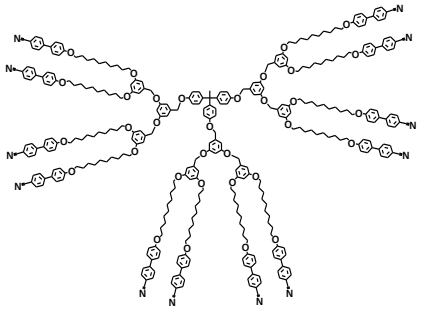
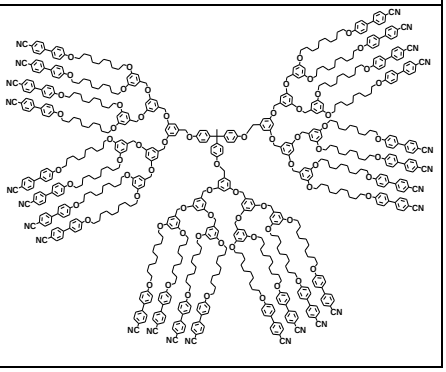
[CN-T-0]-C	[CN-T-1]-C	[CN-T-2]-C	[CN-T-3]-C
			

Table 4.4 Structures of the 4-cyanobiphenyl-derived dendrimers

	Phase transitions (*T*/°C) Δ*H* (J/g)	phase	length of molecule (*l*) (nm)	layer thickness (*d*) (nm)	*d*/*l*
[CN-T-0]-C	Cr 85 (SmA 68) Iso 35.7 8.1	SmA	3.2	4.1	1.28
[CN-T-1]-C	Cr ‹ 20 SmA 77 Iso 8.3	SmA	3.7	4.4	1.19
[CN-T-2]-C	Cr ‹ 20 SmA 87 Iso 7.7	SmA	4.2	4.77 (50 °C) 4.75 (70 °C)	1.14 1.13
[CN-T-3]-C	Cr ‹ 20 SmA 74 Iso 4.8	SmA	4.7	4.8	1.02

Table 4.5 Phase transition temperatures, transition enthalpies and other structural parameters of the cyanobiphenyl derived dendrimers **[CN-T-*n*]-C**

In contrast to the series **[CN-T-*n*]-OH** all compounds in the **[CN-T-*n*]-C** group show SmA phases. The zeroth generational dendrimer **[CN-T-0]-C** is the only one in this series which has only a monotropic smectic phase. The higher generations show enantriotropic smectic A phases over a relatively broad temperature range (60-70 degrees interval), starting from below room temperature. In this series of compounds the melting points are reduced by the dendritic structure in contrast to the **CN-T** dendron series where the attachment of the cyanobiphenyl mesogens to the dendron structures leads to much higher melting points (hydrogen bonding is

a possibile explanation). The phase transition enthalpy-changes being relatively small, always below 10 J/g, support the formation of the envisioned mesophases. According to the X-ray diffraction studies and in line with the similar *d/l* (layer thickness vs. molecule length) ratios, the structures of the formed mesophases can be explained on the simple model of an intercalated bilayer structure (Figure 4.6).

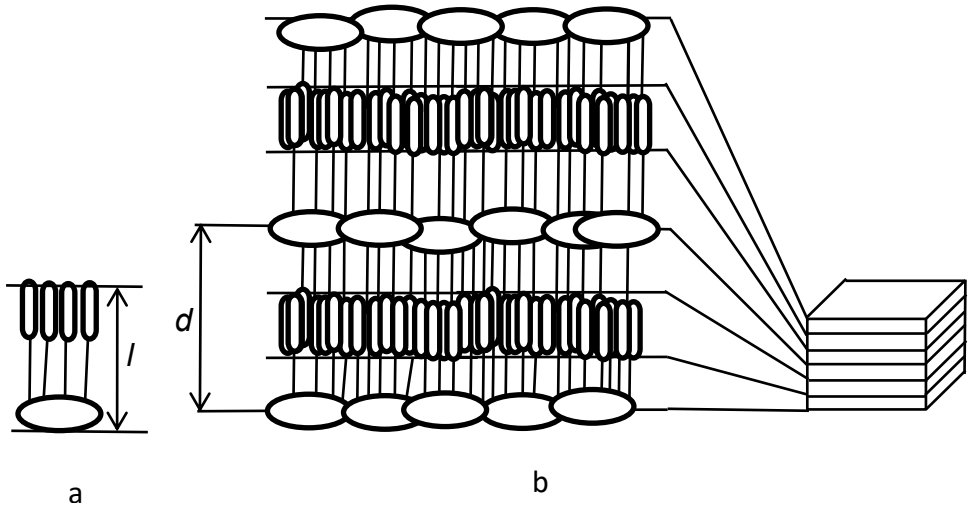


Figure 4.6 Schematic structure of the smectic A phases of the dendrons and dendrimers with cyanobiphenyl mesogenic units **CN-T**. a, representation of a single molecule (horizontal oval: dendritic moiety (dendron or dendrimer), black lines: C_{10} alkyl-chain, vertical oval: cyanobiphenyl unit), b, layer structure of the smectic phases. Here a structure with a full intercalation of the cyanobiphenyl units is shown, the actual intercalation is function of the temperature and depend on the actual molecular structure.

The microphase separation and the antiparallel packing of the molecules leads to the formation of aliphatic (alkyl chains) and separated aromatic (cyanobiphenyls on the one hand and dendritic moieties on the other hand) sublayers in the smectic structure. There is no order within a layer and the biphenyls and the dendritic segments do intercalate in their own layers though to a varying degree. The degree of intercalation and flexibility of the dendritic segments appears to increase with the increasing generation number shown by the decreasing *d/l*-ratios with higher generations.

General remarks to the **CN-T** series:

In contrast to the progenitor calamitic mesogen with a nematogenic tendency, an abundance of weakly defined smectic A layers was experienced among the members of this group. The dendritic structure acts as an organisatory framework helping the formation of more or less defined layers and boosting cooperativity of the cyanobiphenyls in contrary to the only one dimensional quasi-order of the original nematic phase of the mesogen. Smaller members of the series (dendron and dendrimer) do not tend to mesophase formation but when higher load of the calamitics is reached on the dendritic interface (spacer+biphenyl units on dendrimers, 1st generation: 6, 2nd generation: 12, 3rd generation: 24) monotropic (dendrons) or stable enantiotropic (dendrimers) smectic A layer structures are observed. The relatively similar clearing points of the compounds and the decreasing melting points at higher generations attest the property of the dendritic moiety that by lowering the melting point it gives a chance of the mesomorphic behaviour to appear, by not allowing the LC phase to transit earlier into a crystalline phase.

4.6 Biphenyl endgroup bearing dendrons and dendrimers (**T** series, Scheme 3.10)

The dendrons and dendrimers treated in this chapter differ at two sites from the previously described **CN-T** series. They do not bear the cyano group at the end of the biphenyl unit and the aliphatic chain length is increased by two methylene groups, to reach the approximately same overall molecule lengths as the members of the **CN-T** series.

4.6.1. **T** dendrons (**[T-1]-OH**, **[T-2]-OH**, **[T-3]-OH**).

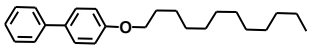
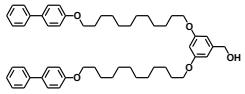
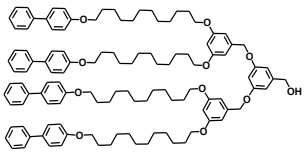
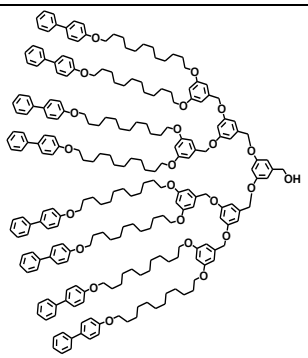
[T-0]-H		
[T-1]-OH	**[T-2]-OH**	**[T-3]-OH**
		

Table 4.6 Structures of the individual mesogen and of the biphenyl-derived dendrons

	Phase transitions (T/°C) ΔH (J/g)	phase	length of molecule (l) (nm)	layer thickness (d) (nm)	d/l
[T-1]-OH	Cr 103 Iso 115.8	-	3.1	-	
[T-2]-OH	Cr 100 (SmB 38 SmA 51) Iso 80.7 9.2 13.3	SmA SmB	3.6	3.34 (45 °C) 3.1 (35 °C)	0.93 0.86
[T-3]-OH	Cr 45 (SmB 35) SmA 51 Iso 17.9 5.7 11.8	SmA SmB	4.0	3.6 (40 °C) 3.4 (30 °C)	0.90 0.85

Table 4.7 Phase transition temperatures, transition enthalpies and other structural parameters of the biphenyl derived dendrons of the **T** group

The parent compound (**[T-0]-H**, 4-dodecyloxy-biphenyl) to the best of my knowledge is not a mesomorphic substance. I was not able to locate published reports of its liquid crystallinity. Some related compounds have been examined for liquid crystallinity (with C_{10}- and C_{16}-alkyl chains[169, 170]) but they were not mesomorphic, and most probably this is the case with the compound in question, too. Attachment to the dendritic framework is necessary for the appearance of mesomorphous state in this case. The first generational dendron in this series, just like the cyanobiphenyl analog, has a relatively high melting point and is not liquid crystalline. The second

generational member again is only able to form monotropic phases though smectic B - smectic A dimorphism makes the picture more colourful here. The third generation, having the lowest melting point, sees the appearence of an enantiotropic smectic A phase while the smectic B phase is still monotropic. The significant difference to the previous group is, that while in the case of the cyano-biphenyl-ending series the *d/l*-ratio was bigger than 1 (the layers were thicker than the molecule-length), here the opposite is true, the *d/l*-ratios are always smaller than 1. This indicates a mixed organization of the dendritic cores and the biphenyls in common layers, leading to a monolayer struture. In both smectic phases, the separated layers of alkyl chains and mixed layers formed by biphenyls+dendrons(+core) might be a good explanation for the phenomenon (Figure 4.7).

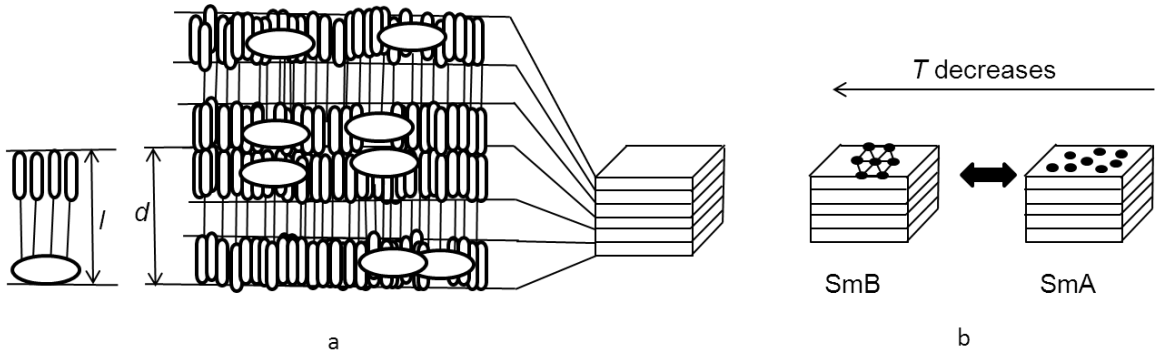


Figure 4.7 Schematic structure of the smectic A and B phases of the biphenyl-terminated dendrons. a, the representation of a single molecule (horizontal oval: dendritic moiety (dendron/dendrimer), black lines: C_{12} alkyl-chain, vertical oval: biphenyl unit) showing only the taper-shaped alignment, as mentioned before (Fig. 5.2) bidirectional arrangement of the dendritic wedges is possible,beside that layer structure of the smectic phases, b, smectic A – B transition.

The packing of the molecules in the layers is random. The smectic B phases appear at lower temperatures, mirroring the higher order of these phases called 'hexatic', with dense packing of the molecules on a two dimensional hexagonal lattice within the layers, but without bond-orientational order between the layers. Remarkably, the layer thickness decreases at the transition from SmA to SmB, though the increased packing density in the layers is expected to give rise to an extension of the molecules by the rigidification of the alkyl chains. This means that an even stronger intercalation occurs at the SmA-SmB transition, possibly involving a partial intercalation of biphenyls and alkyl chains.

4.6.2. **T** dendrimers (**[T-0]-C**, **[T-1]-C**, **[T-2]-C**, **[T-3]-C**).

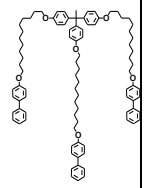
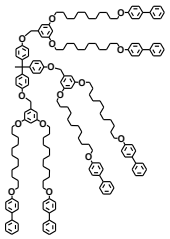
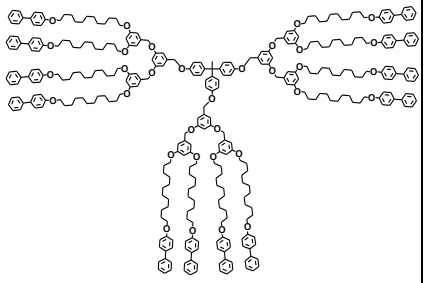
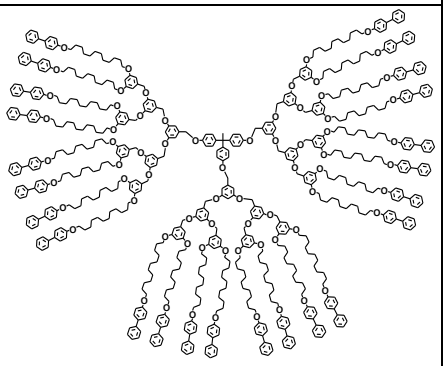
[T-0]-C	[T-1]-C	[T-2]-C	[T-3]-C
			

Table 4.8 Structures of the biphenyl-derived dendrimers

	Phase transitions (T/°C) ΔH (J/g)	phase	length of molecule (l) (nm)	layer thickness (d) (nm)	d/l
[T-0]-C	Cr 74 Iso 86.6	-	3.3	-	
[T-1]-C	Cr 54 (SmA 44) Iso 34.5 14.0	SmA	3.8	3.57 (35 °C)	0.94
[T-2]-C	Cr 45 (SmA 44) Iso 29.3 11.1	SmA	4.3	4.25 (36 °C)	0.99
[T-3]-C	Cr 58 (SmB 40) Iso 45.9 12.8	SmB	4.8	3.4 (30 °C)	0.71

Table 4.9 Phase transition temperatures, transition enthalpies and other structural parameters of the biphenyl derived dendrimers of the **T** group

Compared the the dendron counterparts, the dendrimers endcapped with a biphenyl mesogenic unit have lower phase transition temperature to the isotropic phase (all below 60 °C) and only monotropic mesophase formation could be experienced here. The 0th generational member is again not mesogenic at all. Monotropic smectic A phases were found in cases of the first and second generational dendrimers **[T-1]-C** and **[T-2]-C**, the d/l ratio is < 1 as also found for the dendrons **[T-n]-OH** and the layer structures can be assumed to correspond to those shown for these compounds in the model shown in Figure 4.8.

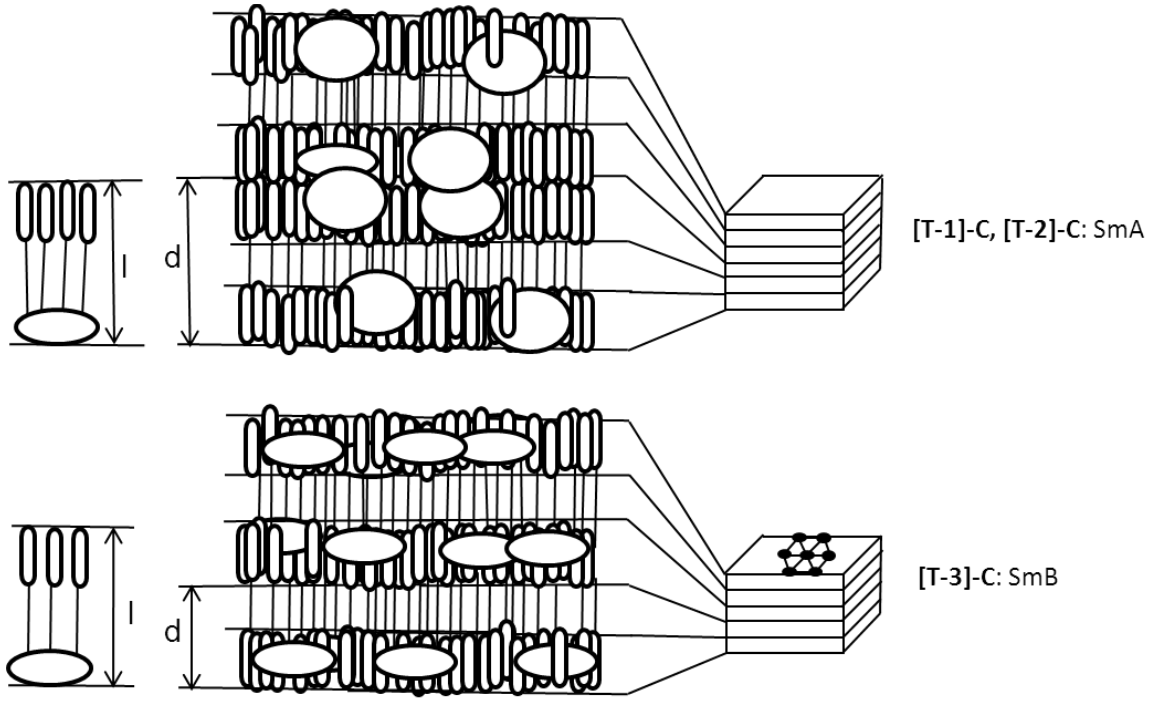


Figure 4.8 Schematic structures of the smectic A and B phases of the biphenyl-ending dendrimers (**T** dendrimers).

Also the formation of the SmB phase is associated with a reduction of the layer spacing, which can be explained in the same way as for the dendron **[T-3]-OH**.

General remarks to the **T** series:

The attachment to the dendritic scaffold allows the formation of mesophases with the otherwise not mesomorphic 4-alkoxybiphenyls. Formation of SmA and hexatic smectic B phases for the higher generation dendimers/dendrons dominates the LC phase behaviour. In contrast to related 4-cyanbiphenyl derived dendrimers/dendrons the aromatic molecular segments (dendritics and biphenyls) are mixed in common layers in the smectic mesophases of the compounds.

4.7.6-[4-(4'-Hexyloxy)-biphenyloxy)]-terminated dendrons and dendrimers (**M** series, Scheme 3.12)

The length of the mesogenic group (biphenyl + alkyl chains) attached to the denritic moiety was chosen to be equal with the previous groups (**T**-group, biphenyl + spacer), however, the biphenyl unit is in the middle of the alkyl chain, hence, the biphenyl unit has an additional terminal alkyl chain, being compatible with the aliphatic spacer units. There is an additional little difference due to the presence of one more oxygen atom in the chain, necessary for the ether-connectivity with the terminal alkyl chain. Anyhow, direct comparison of the related structures of the two series is possible.

4.7.1. **M** dendrons (**[M-1]-OH**, **[M-2]-OH**, **[M-3]-OH**).

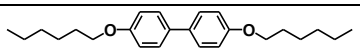
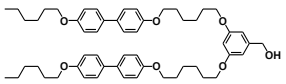
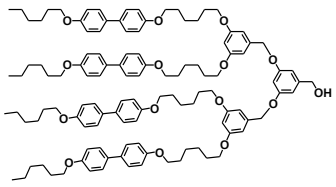
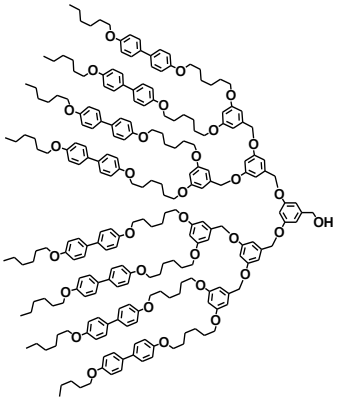
[M-0]-H		
[M-1]-OH	**[M-2]-OH**	**[M-3]-OH**
		

Table 4.10 Structures of 4,-4'-dihexyloxybiphenyl and the 4-hexyloxybiphenyl terminated dendrons

	Phase transitions (T/°C) ΔH (J/g)	phase	length of molecule (l) (nm)	layer thickness (d) (nm)	d/l
[M-0]-H	Cr 66 Sm 84 Iso	Sm			
[M-1]-OH	Cr 139 Iso 114.5	-	3.2	-	
[M-2]-OH	Cr 123 (SmB 98 SmA 117) Iso 53.9 5.4 12.4	SmA	3.6	3.1 (110 °C)	0.86
[M-3]-OH	Cr ‹20 Col_{ob} 83 SmB' 104 SmA 121 Iso 4.2 6.5 8.8	SmA SmB' Col_{ob}	4.1	3.6 (110 °C) 5.6 (90 °C) *a = 3.3, b = 5.9, $\gamma = 75^{o}$ d = 5.7 (70 °C)	0.88 1.37 1.39

*: lattice parameters of the columnar oblique phase

Table 4.11 Phase transition temperatures, transition enthalpies and other structural parameters of the biphenyl derived dendrons of the **M** group

The progenitor molecule of this series (**[M-0]-H**, 4,4'-di(hexyloxy)-biphenyl) is a smectogen, showing an (unidentified) smectic phase in a less than 20 degree temperature interval[168]. In the dendritic series the smallest member, the first generational dendron **[M-1]-OH** shows no mesophase. The importance of the reasonably sized focal aromatic segment is emphasised by this observation again. The second generational dendron **[M-2]-OH** does not show mesophase behaviour by melting but by cooling. The monotropic smectic A phase is followed by a monotropic smectic B phase at lower temperature. In the SmA phases the d/l ratio is <1 and smaller than for the previously discussed compounds **CN-T** and **T** dendrons and dendrimers. Essentially the same model as shown in Fig 4.7 can be assumed, i.e. there are layers of alkyl chain separarated by layers where biphenyl cores and dendritic units are easily mixed. As the terminal alkyl chains are mixed with the spacer units, a significant intercalation is achieved and therefore the d/l ratio is significantly smaller than for the related non-alkylated biphenyl derivatives (the appearent molecular length is reduced). No detailed information is available for the SmB phase of the 2nd generation dendron as the substance crystallised under the X-ray measurement conditions.

In the case of the third generational dendron **[M-3]-OH** a sequence of three different LC phases was found. The SmA phase at high *T* has a *d/l* ratio of 0.88, similar to that found for **[M-2]-OH** (0.86), indicates a mixed organization of biphenyls and dendritic cores. On decreasing temperature a SmB' phase is formed, in this case accompanied by a strong increase of *d*. The *d/l* ratio becomes significantly larger than 1 (1.37), indicating the formation of an intercalated bilayer structure (like Figure 4.6). The diffuse wide angle scattering in the X-ray diffraction of this phase has a reduced width compared to the SmA phase but still not so sharp as a clear SmB phase would be. That is why this mesophase should be seen as a particular SmB' phase with reduced coherence length of the in-plane order. On further decreasing the *T* a transition to a columnar phase is observed. The parameter *b* is close to the *d*-value in the SmB phase, thus it is likely to be a modulated version of the SmB' phase. There are numerous cases described in the literature for dendrons/dendrimers forming columnar phases[11, 166], as a way to adapt best to the thermodynamical driving forces by this specific kind of microseparation of their segments. The formed oblique columnar phase of compound **[M-3]-OH** (see Figure 1.3. c and Figure 4.9) can be best imagined by an organization of the dendritic scaffolds on an oblique 2D lattice. The 2D lattice could alternatively also appear due to the modulation of the aromatic layers and the correlation of the resulting ribbons to the twodimensional structure. As it is an accepted model for the formation of columnar phases of individual calamitics, we must not discard this possibility either, though with the examining techniques at hand it is not possible to decide which is the real reason of the behaviour of the molecules. The formation of the oblique columnar phase in the latter case would neccesitate the assumption of the uniform tilt of the biphenyl units in the layers. The difference to the SmB phase lays in the long range correlation of the dendritic moieties. The reason for the temperature dependent transition from the monolayer SmA phase to the interdigitated bilayer SmB phase (and finally to the Col_{ob} phase) with increasing dendrimer-core size is most probably the limited thickness of the biphenyl layers, which cannot be extended for accomodation of the larger dendrimer cores without simultaneous deintercalation of the biphenyls, i.e. with some unfavorable mixing of aromatics and alkyls.

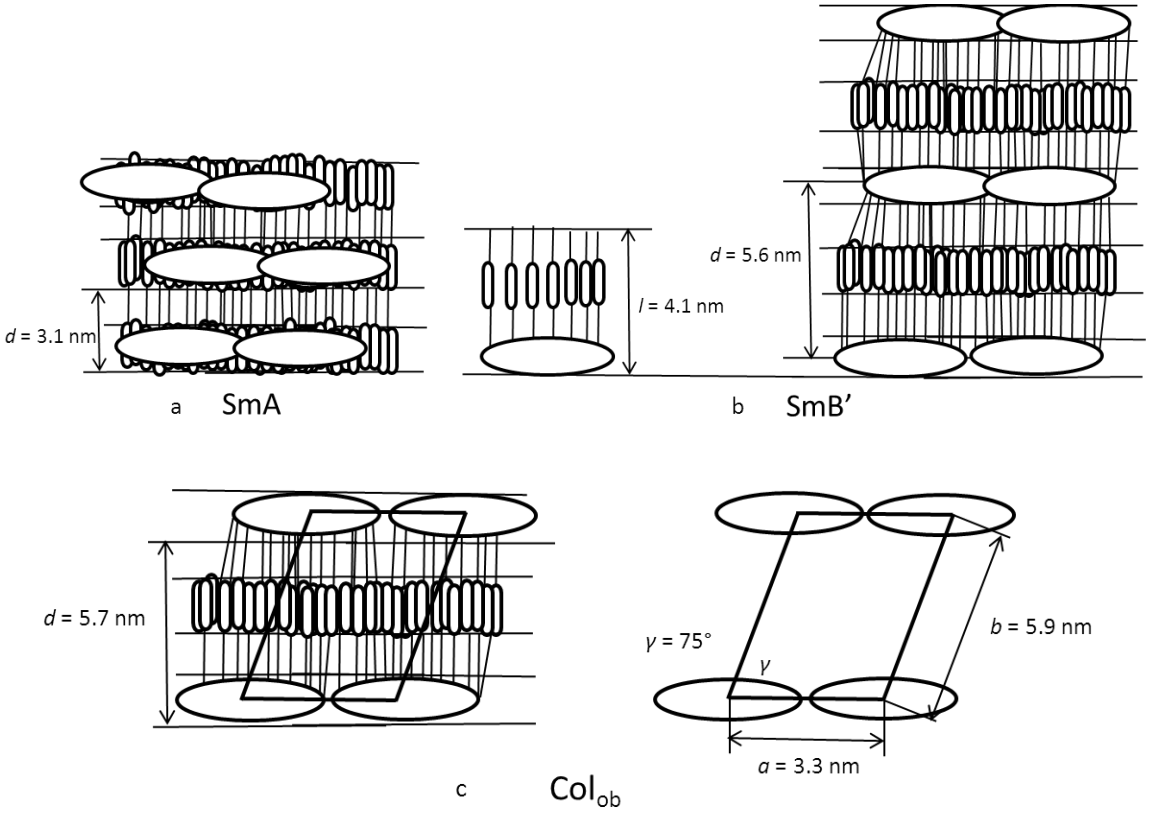


Figure 4.9 Schematic structure of the smectic and columnar LC phases of the compound **[M-3]-OH**. a, structure of the smectic A phase (horizontal oval: dendritic moiety, dendron/dendrimer, black lines: C_6 alkyl-chain, vertical oval: biphenyl unit), b, layer structure of the smectic B' phase, c, structure of the oblique columnar phase, with lattice parameters

4.7.2. **M** dendrimers (**[M-0]-C**, **[M-1]-C**, **[M-2]-C**, **[M-3]-C**).

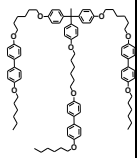
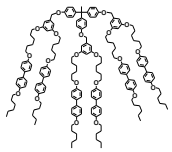
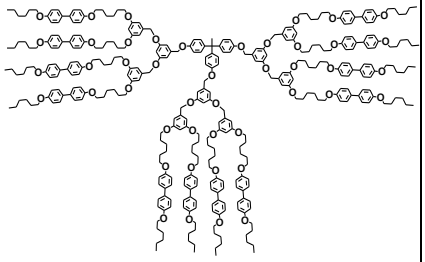
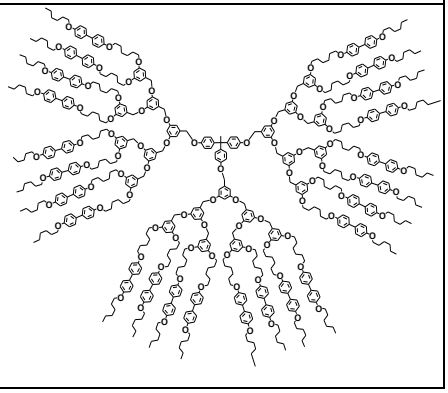
[M-0]-C	**[M-1]-C**	**[M-2]-C**	**[M-3]-C**
			

Table 4.12 Structures of the dendrimers with 4-hexyloxybiphenyl mesogenic units

	Phase transitions (T/°C) ΔH (J/g)	phase	length of molecule (l) (nm)	layer thickness (d) (nm)	d/l
[M-0]-C	Cr 151 (SmB 108 SmA 118) Iso 74.9 11.2 22.7	-	3.4	-	
[M-1]-C	Cr ‹20 Col_h 93 SmA 115 Iso 4.7 11.6	SmA Col_h	3.9	3.5 (105 °C) a = 3.7* d = 3.2 (60 °C)	0.90 0.82
[M-2]-C	Cr ‹20 Col_r 76 SmB 91 SmA 114 Iso 0.6 3.7 9.2	SmA SmB Col_r	4.4	2.1 (100 °C) 4.2 (80 °C) *a = 4.7, b = 8.9 d = 4.5 (60 °C)	0.48 0.95 1.02
[M-3]-C	Cr ‹20 $Col_?$ 86 SmB 92 SmA 119 Iso 1.4 2.6 7.3	SmA SmB	4.9	4.1 (100 °C) 4.3 (90 °C)	0.84 0.88

*: lattice parameters of the corresponding columnar phases

Table 4.13 Phase transition temperatures, transition enthalpies and other structural parameters of the dendrimers with 4-hexyloxybiphenyl mesogenic units.

The dendrimers formed by the previously mentioned dendrons of the 'chain-biphenyl-chain' end groups show even more interesting mesogenic properties than the previous series of compounds. All compounds form SmA phases at high temperature, having similar clearing temperatures for the distinct generations and they are followed by SmB and/or columnar phases on cooling. The zeroth generational dendrimer **[M-0]-C** shows unstable monotropic phases, presumably smectic A and B while cooling, according to the optical microscopy examinations. Unfortunately the X-ray diffraction experiment could not yield data, due to crystallisation tendencies of the substance. The first generational dendrimer **[M-1]-C** forms in a broad temperature range (from room temperature to 93 °C) a columnar phase. XRD indicates a ratio of the small angle reflections corresponding to a hexagonal lattice. However the optical texture is not typical for a Col_h phase and there is no significant change of it to the SmA phase at higher temperature. Therefore we assume that the lattice is pseudohexagonal, i.e. this is actually similar to the Col_{ob} phase of compound **[M-3]-OH** where the ratio of the parameters a/b by chance coincides with the ratio found in a hexagonal lattice and the oblique angle is ~60°. Thus, this is not a true hexagonal lattice and the structure is actually a rectangular columnar organization (c2mm), fundamentally

the same as as proposed for the for **[M-2]-C** (see below). In the Col_h phase and in the SmA phase the individual dendritic vs. biphenylic sheets are separated by the fluid alkyl chain layers.

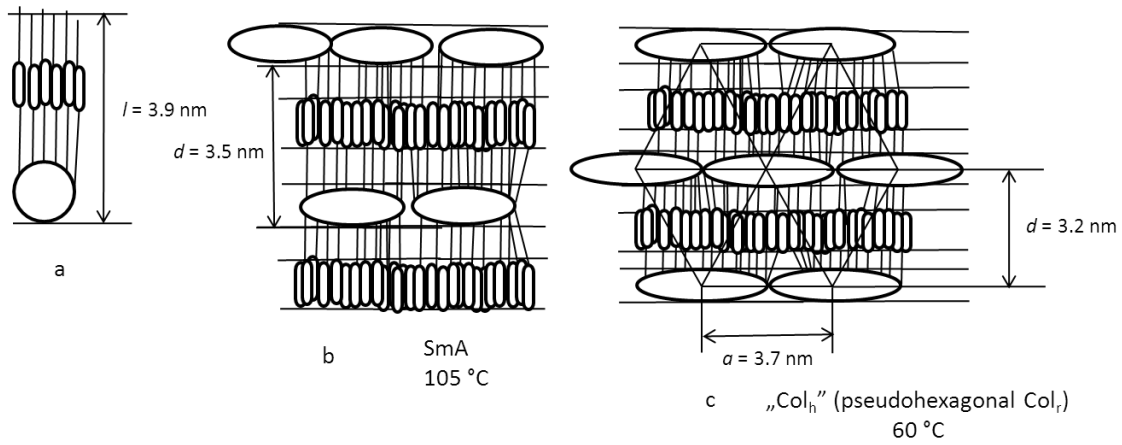


Figure 4.10 Schematic structure of the correlated (columnar) and non-correlated smectic phases of the compound **[M-1]-C**. a, representation of one molecule (circle: dendritic moiety, black lines: C_6 alkyl-chains, vertical oval: biphenyl unit), b, layer structure of the smectic A phase (horizontal oval: distorted dendritic moiety), c, structure of the pseudo-hexagonal columnar phase, with lattice parameters

The second generational dendrimer **[M-2]-C** also forms a columnar phase down to room temperature, here the rectangular columnar phase has been encountered (Figures 1.3, b, 4.11).

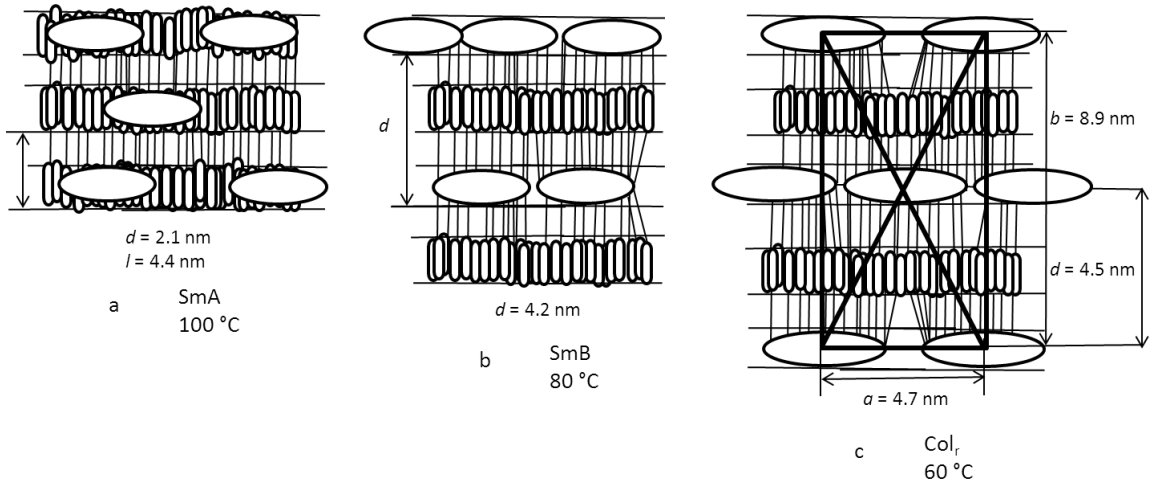


Figure 4.11 Schematic structure of the correlated (columnar) and non-correlated smectic phases of the compound **[M-2]-C**. a, structure of the smectic A phase (horizontal oval: dendritic moiety, black lines: C_6 alkyl-chains, vertical oval: biphenyl unit), b, layer structure of the smectic B phase, c, structure of the rectangular columnar phase, with lattice parameters

The stability of this phase is reduced compared to the pseudo-Col_h phase, as it transforms into smectic B phase first, at 76 degrees. This SmB-phase of **[M-2]-C** with $d/l \sim 1$ is envisioned as an intercalated bilayer structure having the biphenyls and aromatic dendrons/cores in different layers separated by the alkyl-chain layers, with a hexagonal in-plane lattice, while the SmA phase, appears to have the aromatic dendrimer cores and the biphenyls in a common layer as the layer thickness is practically the half of the SmB-case. The transition to the Col_r phase is associated with formation of a 2D lattice by correlation of the dendrimer cores between the layers in the SmB phase, as shown in Fig. 4.11. This proposed development of the phases is fully in line with the observations described in Section 4.7.1. In the XRD patterns (Fig. 4.11) the four small angle scatterings of the Col_r phase can already be found in the SmA and SmB phases, but some of them are diffuse, i.e. there is only short range correlation of the corresponding distances. Only the reflection around $\Theta = 4^\circ$, corresponding to the distance between the alkyl chain layers (or between the aromatic layers) is a sharp reflection in all three phases, thus indicating a fundamental layer structure. The sharpness increases with decreasing T, attesting an increasing definition of the aliphatic/aromatic interfaces, i.e. the layers become more perfect with decreasing T. In addition, the position of this reflection is continuously shifted to smaller scattering angles (= larger distances), in line with the growing packing density and stretching of the molecules (more trans conformation of the alkyl chains, increased orientational order of the biphenyls) on decreasing the temperature. At the SmA-SmB transition the scattering around $\Theta = 2.1^\circ$ becomes sharp (together with the wide angle scattering), indicating that the concentration of the dendritic cores in the aromatic layers becomes distinct and alternating between adjacent layers. That this reflection is observed already in the SmA phase as a diffuse scattering means that also in the SmA phase there is already a stacking of distinct layers (dendrimer-core rich and dendrimer-core pure), but this is only short range and becomes long range at the SmA-SmB transition, when the hexagonal order in the layers is formed. It appears that the dendritic units are largely expelled from the biphenyl layers at this transition to increased in-plane order. On further reducing the temperature the diffuse scattering around $q \sim 5.5$ nm becomes sharper and splits into two reflections, indicating the formation of a long range 2D lattice. But again, this lattice is already present as a short range lattice in the SmA and SmB phases. Hence, all LC phases have fundamentally the same structure, only wih different perfection and the structural changes are relatively small at the phase transitions, and this explains why nearly no textural changes

can be observed at the phase transitions (see Fig. 4.3). The major change is the increase of the in-plane packing density at the SmA-SmB transition which is associated with a significant enthalpy change (3.9 J/g, see Fig. 4.4). The transition of the 2D lattice from being short range to long range at the SmB-Col_r transition is a comparatively small structural change, associated with a very small transition enthalpy value (0.6 J/g). Even in the isotropic liquid there is already short range order resembling that in the LC phases, as indicated by the presence of the diffuse scatterings. This is a unique text-book-like example showing how soft self-assembly works on a molecular/supramolecular level.

The unusual observation that the birefringence increases slightly on going from the less ordered SmA phase to the SmB and Col_r phase with increrased orientational order parameter of the alkyl chains and biphenyl cores (see Fig. 4.3., the change of the large central fan from red to orange) might be explained by a competing effect of the organization of the dendritic cores. It appears that the high index axis of the aromatics in the dendritic cores (the benzylether units) is perpendicular to the biphenyls (where it is along the long axis), thus compensating the increase of birefringence provided by the increase of the orientational order parameter of the biphenyls. This might be a result of the meta substitution of the benzylether cores by two O atoms, providing the main conjugation pathway (O-Ar-O), i.e. the high index axis, being aligned „perpendicular" to the benzylether aromatics and thus parallel to the layer planes.

The third generational dendrimer **[M-3]-C** shows again a room temperature columnar phase of a kind not easy to uniequivocally indentify at the moment. The X-ray examination shows broad reflections, so a transitionary structure is probable here, not having the long range order of a true columnar phase but being still more ordered than a simple smectic one. Heating leads to a smectic B phase similar to the Figure 4.10.a, with the separated biphenyl and aromatic dendron/core layers.

Further heating leads to a smectic A phase with insignificant change of the *d*-value, being a bit smaller than in the previous LC phases. The stability of the columnar phase has increased compared to the 2nd generation but is still lower than in the case of the Col_h phase of the first generation dendrimer. The structure of the low temperature Col phase could not be resolved in this case.

General remarks to the **M**-series:

The smectogenic tendency of the parent calamitic dialkoxy-biphenyl is apparently a good basis for the plethora of mesophases shown by the members of this family of compounds (except for the smallest members). Beside the previously also seen smectic A and B phases, the lower temperature columnar phases show the uniqueness of the substace class. The smaller proximity or stronger coupling of the biphenyl segments to the aromatic dendron/core region and the presence of the terminal alkyl chains together affect the phase behaviour changes that lead to the formation of different types of columnar phases. The molecule size seem to determine the lattice type, with smaller generation favouring monolayer structures with mixed organization of biphenyls and dendritic cores being replaced by intercalated bilayer structures for the higher generations. The preorganization of the biphenyls by the dendritic cores facilitates their self-assembly by increasing cooperativity, thus favoring separation of aromatics and aliphatics with increasing generation number. Simultaneously the growing dendritic core with a non-linear shape distorts the self-assembly of the mesogenic units. Both effects increase with growing generation number and thus compensating each other. Therefore the mesophase stability is in the same range for all compounds, nearly independent on the generation number. Reducing the temperature increases the segregation of the rigid biphenyls from the flexible benzylether dendritic cores, providing formation of a 2D lattice perpendicular to the layers (formation of columnar phases, which actually represent modulated lamellar phases and could be considered as lamellocolumnar phases combining a lamellar organization of the biphenyls with a 2D lattice of the dendritic cores). Expelling the deorganising benzylether cores from the parallel aligned biphenyls and aliphatics (rigid-flexible segregation) allows the development of in-plane order (SmA-SmB transition). As the length of mesogenic biphenyl units is fixed and the size of the benzylether cores increases with generation number a mismatch of the layer thicknes of mesogen layers and benzylether layers arises for higher generations which additionally modify the self assembly. This leads to a partial deintercalation of the biphenyls, modifying the layer thickness and having a feed-back on the dendrimer-core self assembly, leading to different types of 2D lattice (rectangular, hexagonal, oblique).

4.8 Conclusions

The similarities and differences among the mesophases of the synthesised dendritic strucures allow the drawing some conclusions regarding the role and properties of the dendritic extension of the mesogenic units.

One important observation is that the separation of the semi-flexible dendritic moiety and the stiff biphenyl mesogenic unit by deformable alkyl chains is necessary to achieve mesophase formation. The few members of the non-mesogenic **S** series corroborate the statement and the low solubility of the compounds in almost all of the usual organic solvents points as well to the rigid nature of a considerable part of the molecular structure. This rigidity increases the melting temperatures and thus is not advantageous for the liquid crystalline behaviour either. The regular and fixed placement of the biphenyls on the dendritic surface cause probably strong π-π interactions between the above segments not sufficiently counterbalanced by flexible alkyl chains.

So, the separation of dendritic and biphenylic segments in the **CN-T**, **T** and **M** series by the alkyl linkers leads to the formation of liquid crystalline phases. Except for the appearence of a nematic phase in one case and only in a narrow temperature interval, the characteristic mesophase structure is an ordered or a disordered layered one. Smectic A and B phases are most often seen. Under certain circumstances (explained below) the transition of these smectic phases to columnar ones can be observed, as a possible adaptation of the system to the decreasing temperature and entropy. Obviously, the longer the molecule, the bigger the layer distance. As usual, the lower temperature phases contain thicker layers due to alkyl chain stretching and a simultaneously increasing orientational order parameter of the mesogenic units.

The mesophases of the dendrons/dendrimers ending in cyanobiphenyl units are nematic or SmA with diffuse interlayer interfaces, *i.e.* the layers are not well defined, as indicated by the weak layer reflection in XRD. Layer formation tendency increases with growing generation number. Exclusively smectic A phases, but no SmB or columnar phases were observed. The ratio of the layer distance and molecule length is always higher than 1. This can be explained easily with the known tendency of cyanobiphenyl segments to intercalate at the antiparallel alignment of the molecules in the layers. The degree of intercalation of the cyanobiphenyls can easily be modified.

Probably this variable intercalation is the reason of the uniform mesophase structure over generations of dendrons and dendrimers. Mixing of dendritic cores and cyanobiphenyl segments is not observed in this series, thus forming exclusively intercalated double layer SmA phases with different layers formed by the cyanobiphenyl and the dendritic cores, the alternating layers of the former two are always separated by an alkyl chain layer. The degree of intercalation of the cyanobiphenyls increases with growing generation number, as indicated by approaching the $d/l = 1$ limit for the 3rd generation dendrimer.

If we look at the mesogenic behaviour of the **T** series with a biphenyl moiety at the end of the alkyl chains, a more complex phase sequence is observed. Abundance of monotropic phases indicates the higher crystallization tendency of these cores without terminal substituent. Decreased phase stability (decreased clearing points) attest a weaker mesophase forming ability of this end-group. The observation of smectic B phases at increased generation number/reduced temperature shows an increased in-plane order in the layers. The d/l ratio <1 indicates a predominately mixed organization of dendritic cores and biphenyls in common layers. It is surprising that this mixed organization of flexible benzylether cores and rigid biphenyls allows the development of in-plane order. It could however be possible in this case that stretched alkyl chains and biphenyls (both having approximately the same length) are mixed in common layers with hexagonal in-plane order and the benzylether based dendritic cores form the more disordered layers separating them.

The **M** series having alkyl chain at both ends of the biphenyl cores show the widest variety of different LC phases, all of them derived from lamellar phases with alternating alkyl chain layers and aromatic layers. The increasing segregation of the soft dendritic cores from the rigid biphenyls provides a series of different phases (SmA, SmB, Col_r).

Generally all of the examined substance-groups share a few common properties:

- the low generations (zeroth/first) usually does not allow mesophase formation
- the generation number does not significantly affects the clearing point, but modifies the phase structure in most cases
- tethering of the individual calamitic mesogenes or even primarily non-mesomorphic moieties on a Fréchet-type dendritic surface supports the mesophase formation by

inhibiting crystallization and preorganization of the mesogenic units and leads to complex mesophases due to the competition between dendritic self-assembly and mesogen self-assembly.

The aim of the study was the systematic examination of zeroth to third generations of dendritic liquid crystals comparing generation number and different structures of the rod-like mesogenic unit. It would be though interesting to see the further increasing of the generation numbers in these series. Probably the further increase in the size of the molecules would lead to such a curvature of the aromatic-aliphatic interfaces that the formation of new types of columnar and also cubic mesophases could be approached.

5 Summary

The main aim of the work was the synthesis and liquid crystallinity examination of Fréchet-type small generational dendritic, potentially liquid crystalline molecules of different generations having different mesogenic units.

Of the planned compounds, some structural properties, like core unit in the case of the dendrimers, overall length of the molecules of the same generations, connectivity of the building blocks, were kept constant. Other properties, like the mesogenic units (four different kinds) and generation numbers of the dendrons/dendrimers (from zeroth through the third generation) were varied.

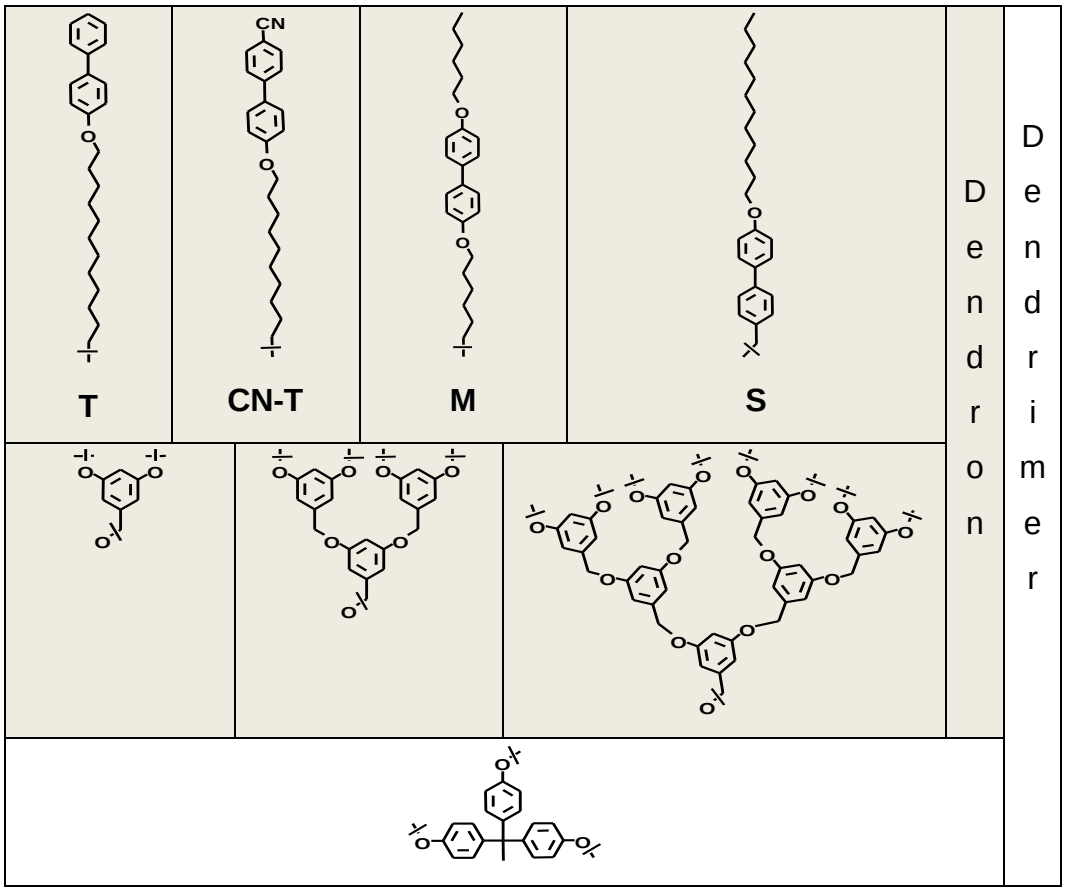


Figure 5.1 Mesogenic end-groups, dendritic generations and the core unit (applies only in the case of the dendrimers).

The synthesis of the planned structures started with the mesogenic end-groups, utilised mainly ether-bond forming reactions and having the appropriately functionalised units in hand allowed

the the sequential, convergent build-up of the dendritic frameworks according to the known procedure. In one case the physical properties of the intermediates toward the planned third generation prohibited the further build-up of the structure. Anyhow, the absence of liquid crystallinity in the precursors made it probable that the further efforts would be futile.

The other three dendritic families (**T**, **CN-T** and **M**) were indeed mostly liquid crystalline, the small generation dendrons/dendrimers usually not or only monotropic phases were encountered but at higher generation numbers the phase stability and versatility of the mesophases increased in all cases. The cyanobiphenyl-ending frameworks **CN-T** (beside a short glimpse of a nematic phase at one substance and in contrary to the inherent drive of alkoxycyanobiphenyls to form nematic phase) shown smectic A phases with different degrees of intercalation of the biphenyl units and due to adaptation of the alkyl- and dendritic-moieties differently distorted, flattened. The layered mesophases have been formed due to the organisatory effect of the dendritic and core moieties. The higher the dendritic generation, the more pronounced the organisatory effect. Antiparallel orientation of the cyanobiphenyl units to different degrees leads to thicker layers, than the molecule length only would dictate. Mixing of the cyanobiphenyl and dendritic aromatic parts were not seen here.

Members of the biphenyl terminated **T** series show more pronounced crystallisation tendencies and consequently lower phase stability of the formed smectic A and B phases. Presence of the more ordered smectic B phase points to an increased in-layer order here. Mixing of the aromatic segments (terminal biphenyl and dendritic/core moieties) can be assumed though aliphatic chains mixed with biphenyls and distinct, distorted dendritic arrangments can be also considered.

The decoupling of the biphenylic unit from the dendritic framework was important in the previous cases and maybe even so in the case of the **M** series, where the biphenylic mesogen component has an alkyl chain at the other end as well. This leads to increasing phase versatility, with higher temperature layered smectic phases that can gain higher organisation at decreasing temperature yielding columnar structures. The aromatics (biphenyl + dendritic/core units) are mixed in common layers here, separated by the alkyl-sheets. The size and intramolecular distances in a molecule can lead to different geometries of the columnar organisation,

demonstrated by the presence of oblique, rectangular and hexagonal lattices at different generations.

Generally, the bigger the molecule, the higher the drive to mesophase formation in all three series. Clearing points are significantly not affected by the size of the molecules. The dendritic frameworks organisatory effect is advantageous to mesophase formation, when the necessary detachment of the dendritic and other aromatic segments through alkyl chains is secured.

Higher then the achieved third dendritic generation would lead very probably to even newer organisatory forms.

The importance of the decoupling of the molecular segments is emphasised by the examples of the failed **S** and **B** series, in both cases the close proximity of the aromatic segments (biphenyl and dendritic part on the one hand, biphenylic dendritic building blocks without aliphatic moieties on the other hand) prevented any mesogenic property to be encountered.

The challenge of synthesising the appropriately functionalised building block to prepare the **B** series (4'-(Hydroxymethyl)biphenyl-3,5-diol, **13**) was achieved. The scope of the key step with the proposed „anti-Friedel-Crafts" type mechanism was widened using different arene nucleophiles in a reaction of synthetic chemical significance.

And attempt has been made with first generational dendrons and dendrimers to investigate the LC possibilities of mixing mesogenic end-groups of the above mentioned successful series with normal, long alkyl chains, unfortunately not yielding any liquid crystalline material.

Hopefully the further potential in changing structural parameters of the molecules can be exploited, as a way to better understand the regulating factors of mesophase-formation among the liquid crystalline dendrimers. Higher generation number dendrimers (despite the significant synthetic efforts) or incorporating functional moieties might provide materials with interesting properties and one day the true tailoring of these kind of molecules to the needs of applications might be possible.

6 Experimental

General remarks

Solvents and reagents were used as purchased. Diethylether and tetrahydrofurane were distilled freshly from lithium-aluminium-hydride. Abs. dichloromethane was prepared by distilling dichloromethane from phosphorus-pentoxide. Abs. DMF, pyridine, acetone, toluene, tetrachloromethane, DMSO were purchased from Sigma-Aldrich and were kept on molecular sieves.

For **column cromatography** Silica gel 60 (230-400 mesh, 0.040-0.063 mm) of Merck was the stationary phase on gravitational columns or with a slight overpressure (0.5 bar).

Analytical thin layer chromatography has applied silica gel plates on aluminium sheets (Merck, Silica gel 60 F_{254} with fluorescent dye). Detection of the spots was accomplished by:

- UV-light (extinction of the fluorescence at λ =254 nm or fluorescence at λ = 366 nm).
- Cerium-phosphomolybdic acid solution. The TLC-plates were immersed in the solution (5g of phosphoric acid, 2 g of cerium(IV)-sulfate, 16 ml cc. sulfuric acid and 180 ml water) then carefully heated.

NMR measurements

The following apparatuses have been used to measure NMR spectra of the compounds:

IPB-Halle: Varian Mercury 400

University of Pécs: Varian Unity Inova 400 WB

The chemical shifts (δ) in the NMR-spectra are given in ppm and they are referenced to the residual solvent signals of $CDCl_3$ (7.26 ppm in ^{1}H-spectra, 77.00 ppm in ^{13}C-spectra) or DMSO-*d6* (2.500 ppm in ^{1}H-spectra and 39.50 ppm in ^{13}C-spectra).

Multiplicity of ^{13}C signals were determined with the help of ^{13}C-APT-measurements. To characterise the splitting of the ^{1}H-signals the following symbols were used:

s singlet

d doublet

t triplet

q quartet

m multiplet

br broad signal

Reactions requiring dry solvents were performed in previously heated glassware.

High resolution mass spectrometry has been measured with a Bruker BioApex 70 eV FT-ICR-spectrometer with nitrogen as heated inert gas at 150 °C.

Elementary analyses were performed in the Microanalytical Laboratory of the Department Chemistry of the Martin-Luther University Halle.

MALDI-TOF spectra were obtained on an Autoflex II TOF/TOF spectrometer (Bruker Daltonics) in positive ion mode, using a 337 nm pulsed nitrogen laser (accelerating voltage: 20.0 kV). The samples were measured on a stainless steel target with dry droplet method, using 2,5-dihydroxybenzoic acid as matrix, dissolved in 30 % 0.1% TFA in water and 70% acetonitrile. The mass spectra were gained through the summary of 1000 shots per spot. External calibration were used to ensure the accuracy of the measurements in three different ranges, depending on the theoretical molecular masses.

Melting points were measured on an HMK hot-stage (Franz Küstner Nacht KG.) and are uncorrected.

Naming, substance codes: the more simple molecules have been named with the help of the naming function of the program Chemdraw Ultra 9.0. In the more complicated cases, knowing the difficulties of the IUPAC nomenclature on the molecules (see Figure 1.5) proper names have

been omitted. The dendrimer-based codes have been used instead (see Chapter 3.2 for the code-system and the Figures 3.10, 3.11, 3.12, 3.13, 3.17 for the structures).

The compounds in this chapter are listed in the order of

- first the ones with usual numbering (Chapter 6.1)
- then then dendritic ones with the dendrimer code-system (Chapter 6.2).

General procedure A (formation of the dendritic aryl-benzyl-ether bond):

The appropriate building block (with two phenolic and one benzylic OH functions) (1 eq.), alkyl bromide (2.1 eq.), K_2CO_3 (2.5 eq.) and 18-crown[6] (0.2 eq.) were boiled under reflux and stirred in abs. acetone for 48 h. The mixture was cooled and the solvent evaporated. The residue was taken up in dichloromethane, washed with water (three times), dried over anhydrous Na_2SO_4 and evaporated. The product was obtained after column chromatography purification or recrystallising.

General procedure B (Appel-reaction to form benzyl bromides from benzyl alcohols):
The appropriate benzyl alcohol (1 eq.) and tetrabromomethane (1.25 eq.) were stirred in the smallest amount of abs. THF necessary to dissolve them. Triphenylphosphine (1.25 eq.) was added at once and the mixture was stirred for 20 minutes. If TLC monitoring required, more bromide and phosphine were added in equimolar ratio (indicated at the individual substances). After completion water and dichloromethane were added and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with water, dried over anhydrous Na_2SO_4 and evaporated. Column chromatography delivered the product.

General procedure C (coupling of dendrons to the core-unit)

The appropriate benzyl bromide (3.6 eq.), 1,1,1-tris(4-hydroxyphenyl)-ethane (1 eq.), K_2CO_3 (4 eq.) and 18-crown[6] (0.3 eq.) were refluxed in dry acetone for 48 h. In some cases (shown at the individual compounds) THF as cosolvent was added, too. The liquids were evaporated and the residue taken up in water and dichloromethane. The aqueous layer was extracted with

dichloromethane three more times. The combined organic phases were washed with water (three times), dried over anhydrous Na_2SO_4 and evaporated. The product was purified via column chromatography.

General procedure D (ω-bromoalkylation of phenols):

The appropriate phenol (1 eq.), α,ω-dibromo-alkane (3 eq.), oven dried K_2CO_3 (9 eq.) were suspended in dry dimethylformamide and stirred overnight at romm temperature. The solvent was evaporated and the solid residue repeatedly washed with dichloromethane on the funnel. The mother liquor was transferred in a separatory funnel and extracted 5 times with water. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was purified by means of column chromatography.

6.1 Building blocks of the dentritics, other small molecules

4'-(Hydroxymethyl)biphenyl-3,5-diol (13)

10.0 g of 4'-formylbiphenyl-3,5-diyl diacetate (**330**) (33.6 mmol, 1 eq.) dissolved in 50 ml tetrahydrofurane was added dropwise to a stirred suspension of 2.60 g lithium-aluminium-hydride (68.6 mmol, appr. 8 eq.) in 200 ml tetrahydrofurane at RT. The solution was boiled under reflux for 1 hour and cooled. Ethylacetate, water and then 37 % HCl was added to the mixture that was extracted with 3x150 ml ethylacetate. The combined organic layers were washed with 3x150 ml water, with brine, then dried over $MgSO_4$ and evaporated. Purification by column chromatography (petrolether-ethylacetate 1:1).

6.69 g (92 %) pale brown solid.

R_f (petrolether–ethylacetate 1:2): 0.27

Melting point: 193-195 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 4.52 (d, 2H, *J* = 5.0 Hz, C$\underline{H}_2$OH), 5.20 (t, 1H, *J* = 5.5 Hz, OH), 6.22 (s, 1H, Ar-H), 6.47 (d, 2H, *J* = 1.9 Hz, Ar-H), 7.36 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.48 (d, 2H, *J* = 8.8 Hz, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 62.6, 101.5, 104.7, 126.1, 126.9, 139.0, 141.6, 142.0, 158.7.

$C_{13}H_{12}O_3$ (216.23)	calculated:	C 72.21	H 5.59
	found:	C 71.79	H 5.77

MALDI-TOF	$C_{13}H_{13}O_3$	$[M+H^+]$	calculated:	217.09
			found:	216.74

.4'-(Hexyloxy)biphenyl-4-ol (16)

19.02 g (102 mmol) 4,4'-Dihydroxy-biphenyl was dissolved in a solution of 8.16 g (204 mmol) NaOH in 200 ml 96 % EtOH. 8.42 g (51 mmol) 1-bromo-hexane was added and the mixture was boiled under reflux for 3 h. It was cooled to RT, the solvent evaporated and residue taken up in water-dichloromethane. The aqueous phase was extracted two more times with dichloromethane, the organic phases were discarded. The aqueous solution was acidified to pH 3, then extracted with dichloromethane again (three times). The combined organic phases were washed with water, with brine, dried over anhydrous Na_2SO_4 and evaporated. The solid residue was taken up in hot dichloromethane and addition of a minute amount of hexane delivered the product which was filtered and air-dried.

10.74 g (78 %), pale brown powder.

R_f (hexane-acetone 2:1): 0.43

Melting point: 158 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 3H, *J* = 6.7 Hz, CH_3), 1.26-1.54 (m, 6H, $(C\underline{H}_2)_3CH_3$), 1.80 8m, 2H, $C\underline{H}_2CH_2O$), 3.99 (t, 2H, *J* = 6.6 Hz, CH_2O), 6.88 (d, 2H, *J* = 8.5 Hz, Ar-H), 6.95 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.44 (m, 4H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 29.3, 31.6, 68.1, 114.8, 115.6, 127.7, 127.9, 133.2, 133.8, 154.5, 158.3.

HRMS (ESI)	$C_{18}H_{22}O_2$	$[M-H^+]$	calculated:	269.1542
			found:	269.1546

4-Methoxybiphenyl (17)

103.45 g (709 mmol, 1 eq.) 4-hydroxy-biphenyl was dissolved in a solution of 29.8 g (744 mmol, 1.05 eq.) NaOH in the mixture of 300 ml EtOH and 50 ml water. 110.7 g (780 mmol, 1.1 eq.)

methyl iodide was added and the solution was gently warmed to boiling. It was refluxed then for 8 hours. After cooling, the solvent was evaporated and the solid residue taken up in 600 ml dichloromethane. After filtration, the liquid phase was washed with water (three times, 150 ml each), then with brine, dried over anhydrous Na_2SO_4 and evaporated. The solid product war pure enough to be used without further purification.

109.57 g (84 %), white solid.

R_f (dichloromethane): 0.68

Melting point: 85 °C Lit[160] : 87-87.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.85 (s, 3H, CH_3), 6.98 (d, 2H, J = 8.8 Hz, Ar-H), 7.30 (t, 1H, J = 8.3 Hz, Ar-H), 7.41 (m, 2H, Ar-H), 7.54 (m, 4H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.7, 140.8, 159.1.

1-(4'-Methoxybiphenyl-4-yl)-ethanone (18)

103.23 g (561 mmol, 1 eq.) 4-methoxy-biphenyl was dissolved in 500 ml dichloromethane in a 2 L flask and the solution was cooled in an ice-bath. 89.0 g (667 mmol, 1.2 eq.) aluminium chloride was given in in two portions. 52.8 g (673 mmol, 1.2 eq.) acetyl chloride was added dropwise, over approximately an hour to the mixture, which was followed by refluxing for two hours. Cooled 37 % HCl-solution (400 ml) was then added to the solution, followed by the careful addition of water (350 ml). The phases were separated and the aqueous layer was washed with dichloromethane (three times, 100 ml each). The combined organic phases were washed with water (three times, 100 ml each), dried over anhydrous Na_2SO_4 and evaporated. The resulted solid was washed with diethylether (two times, 300 ml each) on a glass filter. The remaining solid was air-dried.

54.13 g (43 %), brown solid.

R_f (dichloromethane): 0.24

Melting point: 155 °C. Lit[160]: 153-154 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.63 (s, 3H, $COCH_3$), 3.86 (s, 3H, OCH_3), 7.00 (d, 2H, J = 8.8 Hz, Ar-H), 7.58 (d, 2H, J = 8.8 Hz, Ar-H), 7.64 (d, 2H, J = 8.4 Hz, Ar-H), 8.01 (d, 2H, J = 8.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.6, 55.4, 114.4, 126.6, 128.4, 128.9, 132.3, 135.3, 145.4, 159.9, 197.6.

4'-Methoxybiphenyl-4-carboxylic acid (19)

124.0 g (776 mmol, 40.0 ml) Br_2 was added very slowly to a well stirred, ice-cooled solution of 111.7 g (2.79 mol) NaOH in 528 ml water. The resulting sodium hypobromite solution was added slowly to a solution of 40.0 g 1-(4'-methoxybiphenyl-4-yl)-ethanone (**18**) in 1280 ml dioxane. After stirring for 15 minutes more, 61.6 g $NaHSO_3$ was added to the suspension. The mixture was treated with 20 % HCl-solution to reach pH 3, then the precipitate was collected by filtration and air-dried. It was sufficiently pure to use in the next step without further purification.

36.50 g (90 %), pale brown solid.

R_f (hexane-acetone-acetic acid 50:50:1): 0.34

Melting point: 254 °C. Lit[160]: 253-254 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 3.31 (s, 3H, CH_3), 7.05 (d, 2H, J = 8.7 Hz, Ar-H), 7.68 (d, 2H, J = 8.7 Hz, Ar-H), 7.74 (d, 2H, J = 8.3 Hz, 7.99 (d, 2H, J = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 55.1, 114.4, 126.0, 128.0, 128.8, 129.8, 131.1, 143.8, 159.4, 167.0.

4'-Hydroxybiphenyl-4-carboxylic acid (20)

36.50 g (160 mmol) 4'-methoxybiphenyl-4-carboxylic acid (**19**) was dissolved in 500 ml 96 % acetic acid, 280 ml 48 % HBr-solution was added and the mixture was boiled under reflux for 8 hours. Then it was cooled, poured in 2 l water and allowed to reach RT again. The resulting solid was filtered, washed with some water on the filter and air-dried. It was recrystallized from 70 % EtOH.

31.16 g (91 %), pale brown solid.

R_f (hexane-EtOAc-acetic acid 50:50:1): 0.45

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 6.88 (d, 2H, J = 8.6 Hz, Ar-H), 7.57 (d, 2H, J = 8.6 Hz, Ar-H), 7.70 (d, 2H, J = 8.3 Hz, Ar-H), 7.97 (d, 2H, J = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 115.8, 125.8, 128.0, 128.4, 129.6, 129.8, 144.3, 157.8, 167.2.

4'-Methylbiphenyl-3,5-diol (22)

50.40 g Phloroglucinol (0.40 mol, 1 eq.) was stirred in toluene (800 ml) for 10 minutes. Aluminium chloride powder (106.8 g, 0.8 mol, 2 eq.) was added in small portions and the suspension was stirred overnight. The two-phase mixture was poured on 400 g ice, 200 ml water was added and stirred until all the ice melted. The suspension was filtered and the filter cake was washed with diethylether. Air-drying resulted a solid, which was pure enough to use in the next step without further purification.

56.3 g (70 %), pale brown solid.

R_f (petrolether-ethylacetate 2:1): 0.34.

Melting point: 160-163 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 2.31 (s, 3H, CH_3), 6.25 (t, 1H, *J* = 2.1 Hz, Ar-H), 6.48 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.21 (d, 2H, *J* = 7.9 Hz, Ar-H), 7.42 (d, 2H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 20.7, 101.5, 104.7, 126.3, 129.4, 136.6, 137.8, 142.2, 158.8.

4'-Methylbiphenyl-3,5-diyl bis(2,2-dimethylpropanoate) (23)

27.84 g 4'-Methylbiphenyl-3,5-diol (**22**) (139 mmol, 1 eq.) was dissolved in 100 ml pyridine, the flask was cooled in an ice-bath and 35.22 g pivaloyl chloride (292 mmol, 2.10 eq.) was added dropwise to the stirred solution. After the addition the ice-bath was removed and the temperature was maitained at 60 °C for 24 h. The mixture was poured on 500 ml water, 300 ml diethylether was added. The phases were separated and the organic layer was washed five times with 300 ml water, three times with 200 ml 5% HCl solution then with water again, dried over Na_2SO_4 and evaporated. Column chromatography with petrolether-dichloromethane 1:1 yielded the product.

23.45 g (46 %), white solid.

R_f (dichloromethane): 0.80

Melting point: 130-133 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.37 (s, 18H, $C(CH_3)_3$), 2.39 (s, 3H, Ar-CH_3), 6.83 (t, 1H, *J* = 2.1 Hz, Ar-H), 7.14 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.23 (d, 2H, *J* = 7.9 Hz, Ar-H), 7.47 (d, 2H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.2, 27.2, 39.2, 113.7, 117.2, 126.9, 129.4, 136.5, 137.7, 143.1, 151.4, 176.1.

MALDI-TOF $C_{23}H_{28}O_4Na$ $[M+Na^+]$ calculated: 391.19
found: 390.90

4'-Methylbiphenyl-3,5-diyl diacetate (24)

56.3 g 4'-Methylbiphenyl-3,5-diol (**22**) (282 mmol, 1 eq.) was suspended in 114.9 g acetic anhydride (1.126 mol, 4 eq.). 3 ml Pyridine was added and the mixture was stirred overnight at RT. It was poured in 500 ml water, stirred for 2 h, then it was extracted three times with 200 ml diethylether. The combined organic phases were washed ten times with 300 ml water, dried over anhydrous Na_2SO_4 and the solvent was evaporated. Colunm chromatography of the resulted oil with dichloromethane eluent delivered the product.

68.05 g (85 %), colourless oil.

R_f (hexane-dichloromethane 1:1): 0.41

Melting point: 60 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.29 (s, 6H, Ar-$OOCCH_3$), 2.38 (s, 3H, Ar-CH_3), 6.88 (t, 1H, *J* = 2.1 Hz, Ar-H), 7.18 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.22 (d, 2H, *J* = 7.9 Hz, Ar-H), 7.44 (d, 2H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.2, 22.2, 113.7, 117.4, 126.8, 129.4, 136.3, 137.8, 143.2, 151.1, 168.8.

MALDI-TOF $C_{17}H_{16}O_4Na$ $[M+Na^+]$ calculated: 307.09
found: 306.72

4'-(Bromomethyl)biphenyl-3,5-diyl diacetate (25)

68.05 g 4'-Methylbiphenyl-3,5-diyl diacetate **(24)** (240 mmol, 1 eq.) and 44.83 g N-bromo-succinimide (252 mmol, 1.05 eq.) were dissolved in 600 ml abs. carbon tetrachloride. 1 g benzoyl-peroxid was added and the mixture was refluxed (TLC monitoring). When there was no more (**24**) present in the mixture, it was cooled down and filtered. The filtrate was evaporated. The residue was subjected to column chromatography (hexan-dichloromethane = 4:1).

66.09 g (76 %) colourless oil.

R_f (hexane-dichloromethane 1:1): 0.11

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.31 (s, 6H, Ar-OOCCH_3), 4.52 (s, 2H, CH_2Br), 6.94 (t, 1H, *J* = 2.1 Hz, Ar-H), 7.20 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.45 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.52 (d, 2H, *J* = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.2, 33.1, 114.3, 117.5, 127.3, 129.4, 137.4, 139.2, 142.4, 151.1, 168.8.

4'-Formylbiphenyl-3,5-diyl diacetate (26)

40.00 g 4'-(Bromomethyl)biphenyl-3,5-diyl diacetate **(25)** (110 mmol, 1 eq.) was stirred with 32.80 g sodium acetate (400 mmol, 3.6 eq.) in 100 ml dimethyl sulfoxide at 70 °C for 24 h. After cooling the mixture was poured on 500 ml water. It was extracted with diethylether (three times, 150 ml each) and the combined organic phases were extracted with water (five times, 200 ml each), with brine, dried over anhydrous Na_2SO_4 and evaporated. The resulted dark oil was purified by column chromatography (petrolether-ethylacetate 4:1).

27.90 g (85 %) brownish oil.

R_f (petrolether–ethylacetate 3:1): 0.32

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.23 (s, 6H, Ar-OOCCH_3), 6.95 (t, 1H, *J* = 1.6 Hz, Ar-H), 7.19 (t, 2H, *J* = 1.6 Hz, Ar-H), 7.59 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.83 (d, 2H, *J* = 8.1 Hz, Ar-H), 9.93 (s, 1H, CHO).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 20.7, 114.9, 117.5, 127.1, 129.7, 135.2, 141.4, 144.3, 151.0, 168.3, 191.1

3-(Hexadecyloxy)-5-(hydroxymethyl)phenol (27)

4.58 g (15 mmol, 1 eq.) 1-bromo-hexadecane, 6.30 g (45 mmol, 3 eq.) 3,5-dihydroxy-benzyl alcohol, 2.49 g (18 mmol, 1.2 eq.) K_2CO_3 and 750 mg (3 mmol, 0.2 eq.) 18-crown[6] were boiled under reflux in abs. acetone for 24 hours. The solvent was evaporated and the solid taken up in water-EtOAc. 5% HCl-solution was added until the aqueous layer reached pH 3. The aqueous phase was extracted three more times with EtOAc, the combined organic phases were washed with water (three times), with brine, dried over anhydrous Na_2SO_4 and evaporated. Column chromatography (hexane-acetone 2:1) yielded the product.

4.32 g (79 %), reddish powder.

R_f (hexane-acetone 1:1): 0.59

Melting point: 80-85 °C.

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 0.85 (t. 3H, *J* = 6.5 Hz, CH_3), 1.17-1.44 (m, 26 H, $(C\underline{H}_2)_{13}CH_3$), 1.66 (m, 2H, $C\underline{H}_2CH_2O$), 3.85 (t, 2H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.35 (s, 2H, $C\underline{H}_2OH$), 6.14 (t, 1H, *J* = 2.0 Hz, Ar-H), 6.29 (s, 1H, Ar-H), 6.32 (s, 1H, Ar-H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 13.8, 22.0, 25.4, 28.5, 28.6, 28.7, 28.9, 31.2, 62.8, 67.0, 99.8, 103.0, 105.5, 144.7, 158.1, 159.6.

HRMS (ESI)	$C_{23}H_{40}O_3$	$[M\text{-}H^+]$	calculated:	363.2899
			found:	363.2905

(3,5-Bis(hexadecyloxy)phenyl)methanol (28)

Prepared according to General procedure A.

2.72 g (8.93 mmol) 1-bromo-hexadecane, 0.50 g (3.57 mmol) 3,5-dihydroxy-benzyl alcohol, 1.48 g (10.7 mmol) K_2CO_3, 180 mg (0.7 mmol) 18-crown[6], 30 ml abs. acetone. Column chromatography (hexane-dichloromethane 2:3).

1.84 g (88 %), waxy solid

R_f (hexane-dichloromethane 1:2): 0.21

Melting point: 58 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.88 (t, 6H, *J* = 6.6 Hz, CH_3), 1.18-1.50 (m, 52H, $(C\underline{H}_2)_{13}CH_2CH_2O$), 1.71-1.81 (m, 4H, $C\underline{H}_2CH_2O$), 3.93 (t, 4H, *J* = 6.6 Hz, $CH_2C\underline{H}_2O$), 4.62 (s, 2H, $C\underline{H}_2OH$), 6.38 (t, 1H, *J* = 2.1 Hz, Ar-H), 6.50 (d, 2H, *J* = 2.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 65.5, 68.1, 100.6, 105.1, 143.2, 160.5.

MALDI-TOF $C_{39}H_{72}O_3Na$ $[M+Na^+]$ calculated: 611.54
found: 610.90

1-(Bromomethyl)-3,5-bis(hexadecyloxy)benzene (29)

Prepared according to General procedure B.

1.82 g (3.1 mmol, 1 eq.) (3,5-bis(hexadecyloxy)phenyl)methanol (**28**), 1.54 g (4.6 mmol, 1.5 eq.) carbontetrabromide, 1.21 g (4.6 mmol, 1.5 eq.) triphenylphosphine. Column chromatography (hexane-dichloromethane 4:1).

1.84 g (91 %), white solid.

R_f (hexane-dichloromethane 2:1): 0.60

Melting point: 62 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.88 (t, 6H, J = 6.4 Hz, CH_3), 1.20-1.49 (m, 52H, $(C\underline{H}_2)_{13}CH_2CH_2O$), 1.71-1.81 (m, 4H, $C\underline{H}_2CH_2O$), 3.93 (t, 6H, *J* = 6.5 Hz, CH_2O), 4.41 (s, 2H, CH_2Br), 6.38 (t, 1H, *J* = 2.0 Hz, Ar-H), 6.51 (d, 2H, *J* = 2.0 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.0, 29.2, 29.4, 29.5, 29.6, 29.7, 31.9, 33.8, 68.1, 101.4, 107.4, 139.5, 160.4.

HRMS (ESI) $C_{39}H_{72}O_3Na$ $[M+Na^+]$ calculated: 611.5379
found: 611.5381

(3-(12-(Biphenyl-4-yloxy)dodecyloxy)-5-(hexadecyloxy)phenyl)methanol (30)

739 mg (2.03 mmol, 1.3 eq.) 3-(hexadecyloxy)-5-(hydroxymethyl)phenol (**27**), 650 mg (1.56 mmol, 1 eq.) **[T-0]-Br**, 323 mg (2.34 mmol, 1.5 eq.) K_2CO_3 and 82 mg (0.3 mmol, 0.2 eq.) 18-crown[6] were boiled under reflux in 20 ml abs. acetone for 48 hours. The solvent was evaporated and the solid taken up in water-dichloromethane. The aqueous layer was extracted with dichloromethane three times, the combined organic phases were washed with water (three times), dried over anhydrous Na_2SO_4, and evaporated. Purification by column chromatography (dichloromethane).

972 mg (89 %), white solid.

R_f (dichloromethane): 0.45

Melting point: 74 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 3H, *J* = 6.6 Hz, CH_3), 1.21-1.54 (m, 42H, CH_2), 1.65 (t, 1H, *J* = 5.8 Hz, OH), 1.71-1.87 (m, 6H, C<u>H</u>$_2$CH$_2$O), 3.94 (t, 4H, *J* = 6.5 Hz, CH_2O), 4.00 (t, 2H, *J* = 6.6 Hz, CH_2O), 4.62 (d, 2H, *J* = 5.5 Hz, C<u>H</u>$_2$OH), 6.39 (s, 1H, Ar-H), 6.50 (d, 2H, *J* = 1.8 Hz, Ar-H), 6.97 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.30 (t, 1H, *J* = 7.3 Hz, Ar-H), 7.38-7.46 (m, 2H, *J* = 7.5 Hz, Ar-H), 7.52 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.46 (d, 2H, *J* = 7.2 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 65.5, 68.1, 100.5, 105.0, 114.7, 126.6, 126.7, 128.1, 128.7, 133.5, 140.9, 143.2, 158.7, 160.5.

HRMS (ESI)	$C_{47}H_{72}O_4Na$	[M+Na$^+$]	calculated:	723.5328
			found:	723.5334

4-(12-(3-(Bromomethyl)-5-(hexadecyloxy)phenoxy)dodecyloxy)biphenyl (31)

Prepared according to General procedure B.

1.06 g (1.51 mmol, 1 eq.) (**30**), 1.00 g (3.03 mmol, 2 eq.) tetrabromomethane, 0.79 g (3.03 mmol, 2 eq.) triphenylphosphine. Column chromatography (hexane-dichloromethane 4:1).

1.04 g (91 %), white solid

R_f (hexane-dichloromethane 2:1): 0.38

Melting point: 70 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 3H, J = 6.0 Hz, CH_3), 1.20-1.51 (m, 44H, CH_2), 1.71-1.87 (m, 6H, C<u>H</u>$_2$CH$_2$O), 3.93 (t, 4H, J = 6.5 Hz, CH_2O), 4.00 (t, 2H, J = 6.6 Hz, CH_2O), 4.41 (s, 2H, CH_2Br), 6.38 (s, 1H, Ar-H), 6.52 (s, 2H, Ar-H), 6.97 (d, 2H, J = 8.4 Hz, Ar-H), 7.30 (t, 1H, J = 7.5 Hz, Ar-H), 7.38-7.45 (m, 2H, Ar-H), 7.52 (d, 2H, J = 8.5 Hz, Ar-H), 7.56 (d, 2H, J = 7.9 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.7, 30.9, 31.9, 32.5, 33.8, 68.1, 101.4, 107.3, 114.7, 126.6, 126.7, 128.1, 128.7, 133.5, 139.5, 140.8, 158.7, 160.4.

MALDI-TOF	$C_{44}H_{71}BrO_3Na$	[M+Na$^+$]	calculated:	785.45
			found:	787.00

(3-(Hexadecyloxy)-5-(6-(4'-(hexadecyloxy)biphenyl-4-yloxy)hexyloxy)phenyl)methanol (32)

1.68 g (4.62 mmol, 1 eq.) (**27**), 2.59 g (6 mmol, 1.3 eq.) **[M-0]-Br**, 1.28 g (9.24 mmol, 2 eq.) K_2CO_3 and 50 mg 18-crown[6] were boiled under reflux in 30 ml abs. acetone for 48 hours. The solvent was evaporated and the solid taken up in water-dichloromethane. The aqueous layer was extracted with dichloromethane three times, the combined organic phases were washed with water (three times), dried over anhydrous Na_2SO_4, and evaporated. Purification by column chromatography (dichloromethane).

3.05 g (94 %), white solid.

R_f (dichloromethane): 0.29

Melting point: 70 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.90 (t, 3H, J = 6.5 Hz, CH_3), 0.93 (t, 3H, J = 6.2 Hz, CH_3), 1.20-1.62 (m, 36 H, CH_2), 1.70-1.89 (m, 8H, C<u>H</u>$_2$CH_2O), 3.90-4.04 (m, 8H, CH_2O), 4.62 (d, 2H, J = 3.5 Hz, C<u>H</u>$_2$OH), 6.39 (t, 1H, J = 2.1 Hz, Ar-H), 6.51 (d, 2H, J = 2.0 Hz, Ar-H), 6.95 (d, 4H, J = 8.6 Hz, Ar-H), 7.47 (d, 4H, J = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 14.1, 22.6, 22.7, 25.7, 25.9, 26.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.6, 31.9, 65.4, 67.8, 68.0, 100.5, 104.9, 105.0, 114.7, 127.6, 133.2, 133.3, 143.2, 158.1, 158.2, 160.4, 160.5.

HRMS (ESI)	$C_{47}H_{72}O_5Na$	$[M+Na^+]$	calculated:	739.5277
			found:	739.5284

4-(6-(3-(Bromomethyl)-5-(hexadecyloxy)phenoxy)hexyloxy)-4'-(hexyloxy)biphenyl (33)

Prepared according to General procedure B.

2.19 g (3.05 mmol) (**32**), 1.00 g (3.82 mmol) triphenylphosphine, 1.27 g (3.82 mmol) tetrabromomethane. Column chromatography (hexane-dichloromethane 2:1).

2.14 g (90 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.86

Melting point: 84 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 3H, *J* = 6.6 Hz, CH_3), 0.92 (t, 3H, *J* = 7.0 Hz, CH_3), 1.21-1.62 (m, 36H, CH_2), 1.72-1.89 (m, 8H, C<u>H</u>$_2$CH_2O), 3.90-4.05 (m, 8H, CH_2O), 4.41 (s, 2H, CH_2Br), 6.39 (t, 1H, *J* = 2.0 Hz, Ar-H), 6.52 (d, 2H, *J* = 2.0 Hz, Ar-H), 6.95 (d, 4H, *J* = 8.6

Hz, Ar-H), 7.46 (d, 4H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 14.1, 22.6, 22.7, 25.8, 25.9, 26.0, 29.1, 29.2, 29.3, 29.4, 29.6, 29.7, 31.6, 31.9, 33.7, 67.9, 68.0, 68.1, 68.2, 101.5, 107.4, 107.5, 114.7, 127.7, 133.3, 133.4, 139.6, 158.2, 158.3, 160.4, 160.5.

MALDI-TOF	$C_{47}H_{72}BrO_4$	$[M+H^+]$	calculated:	779.46
			found:	780.05
	$C_{47}H_{71Br}O_4Na$	$[M+Na^+]$	calculated:	801.44
			found:	801.07

(3-((4'-(dodecyloxy)biphenyl-4-yl)methoxy)-5-(hexadecyloxy)phenyl)methanol (34)

0.98 g (2.28 mmol, 1.1 eq.) **[S-0]-Br**, 754 mg (2.07 mmol, 1 eq.) (**27**), 572 mg (4.14 mmol, 2 eq.) K_2CO_3 and 100 mg (0.4 mmol, 0.2 eq.) 18-crown[6] were boiled under reflux in 20 ml abs. acetone for 48 hours. The solvent was evaporated and the solid taken up in water-dichloromethane. The aqueous layer was extracted with dichloromethane three times, the combined organic phases were washed with water (three times), dried over anhydrous Na_2SO_4, and evaporated. Purification by column chromatography (dichloromethane).

1.12g (76 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.12

Melting point: 73 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.85-0.94 (m, 6H, CH_3), 1.20-1.54 (m, 44H, CH_2), 1.70-1.86 (m, 4H, $C\underline{H}_2CH_2O$), 3.94 (t, 2H, *J* = 6.6 Hz, $CH_2C\underline{H}_2O$), 4.00 (t, 2H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.63 (d, 2H, *J* = 5.6 Hz, $C\underline{H}_2OH$), 5.07 (s, 2H, Ar-CH_2O-Ar), 6.50 (s, 1H, Ar-H), 6.55 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 6.97 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.47 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.52 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.57 (d, 2H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.0, 22.2, 22.3, 22.4, 22.5, 22.6, 22.7, 31.9, 65.4, 68.1, 69.8, 100.9, 105.2, 105.5, 114.8, 126.8, 128.0, 128.0, 133.0, 135.1, 140.6, 143.3, 158.8, 160.2, 160.5.

HRMS (ESI)	$C_{48}H_{74}O_4Na$	$[M+Na^+]$	calculated:	737.5485
			found:	737.5484

4-((3-(bromomethyl)-5-(hexadecyloxy)phenoxy)methyl)-4'-(dodecyloxy)biphenyl (35)

Prepared according to General procedure B.

1.10 g (1.54 mmol, 1 eq.) (**34**), 766 mg (2.31 mmol, 1.5 eq.) carbontetrabromide, 605 mg (2.31 mmol, 1.5 eq.) triphenylphosphine. Column chromatography (hexane-dichloromethane 3:1). 1.11 g (93 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.54

Melting point: 73 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.84-0.93 (m, 6H, CH_3), 1.19-1.52 (m, 44H, CH_2), 1.71-1.85 (m, 4H, C<u>H</u>$_2$CH_2O), 3.93 (t, 2H, *J* = 6.5 Hz, CH_2C<u>H</u>$_2$O), 4.00 (t, 2H, *J* = 6.6 Hz, CH_2C<u>H</u>$_2$O), 4.42 (s, 2H, CH_2Br), 5.06 (s, 2H, Ar-CH_2O-Ar), 6.49 (t, 1H, *J* = 2.1 Hz, Ar-H), 5.56 (s, 1H, Ar-H), 6.63 (s, 1H, Ar-H), 6.97 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.47 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.52 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.57 (d, 2H, *J* = 8.2 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 33.7, 68.1, 68.2, 70.0, 101.8, 107.6, 107.9, 114.8, 126.9, 128.1, 133.0, 134.9, 139.6, 140.7, 158.8, 160.1, 160.4.

MALDI-TOF	$C_{48}H_{73}BrO_3$	$[M^+]$	calculated:	776.47
			found:	776.28
	$C_{48}H_{73}BrO_3Na$	$[M+Na^+]$	calculated:	799.46
			found:	798.38

4,4',4''-(12,12',12''-(5,5',5''-(4,4',4''-(ethane-1,1,1-yl)tris(4,1-phenylene))tris(oxy)tris(methylene)tris(3-(hexadecyloxy)-5,1-phenylene))tris(oxy)tris(dodecane-12,1-diyl))tris(oxy)tribiphenyl (36)

Prepared according to General procedure C.

0.72 g (0.945 mmol) (**31**), 88 mg (0.286 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 158 mg (1.15 mmol) K_2CO_3, 15 mg (0.057 mmol) 18-crown[6], 30 ml abs. acetone. Column chromatography (hexane-dichloromethane 3:1).

424 mg (63 %), white solid

R_f (hexane-dichloromethane 3:1): 0.15

Melting point: 40 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.85-0.93 8m, 9H, CH_2CH_3), 1.23-1.52 (m, 126H, CH_2), 1.71-1.86 (m, 18H, C<u>H</u>$_2$CH$_2$O), 2.10 (s, 3H, CH_3), 3.94 (t, 12H, J = 6.4 Hz, CH_2O), 4.00 (t, 6H, J = 6.5 Hz, CH_2O), 4.95 (s, 6H, CH_2C<u>H</u>$_2$O), 6.41 (s, 3H, Ar-H), 6.56 (d, 6H, J = 1.5 Hz, Ar-H), 6.86 (d, 6H, J = 8.8 Hz, Ar-H), 6.97 (d, 6H, J = 8.7 Hz, Ar-H), 7.00 (d, 6H, 8.8 Hz, Ar-H), 7.29 (t, 3H, J = 7.3 Hz, Ar-H), 7.37-7.44 (m, 6H, Ar-H), 7.51 (d, 6H, J = 8.6 Hz, Ar-H), 7.55 (d, 6H, J = 7.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 22.8, 26.1, 29.3, 29.4, 29.6, 29.7, 30.8, 31.6, 32.0, 50.7, 68.1, 70.1, 100.9, 105.8, 114.0, 114.8, 126.6, 126.7, 128.1, 128.7, 129.7, 133.6, 139.4, 140.9, 142.1, 156.9, 158.8, 160.5.

4',4'',4'''-(6,6',6''-(5,5',5''-(4,4',4''-(ethane-1,1,1-triyl)tris(4,1-phenylene))tris(oxy)tris(methylene)tris(3-(hexadecyloxy)-5,1-phenylene))tris(oxy)tris(hexane-1,6-diyl))tris(oxy)tris(4-(hexyloxy)biphenyl) (37)

Prepared according to General procedure B.

990 mg (1.27 mmol) (**33**), 119 mg (0.39 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 216 mg (1.56 mmol) K_2CO_3, 30 mg 18-crown[6], 25 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:1).

881 mg (94 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.23

Melting point: 53 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 9H, *J* = 7.0 Hz, CH_2C<u>H</u>$_3$), 0.93 (t, 9H, *J* = 6.7 Hz, CH_3), 1.22-1.60 (m, 108H, CH_2), 1.72-1.87 (m, 24H, C<u>H</u>$_2$CH$_2$O), 2.11 (s, 3H, CH_3), 3.91-4.04 (m, 24H, CH_2C<u>H</u>$_2$O), 4.96 (s, 6H, Ar-CH_2O-Ar), 6.41 (t, 3H, *J* = 2.1 Hz, Ar-H), 6.57 (d, 6H, *J* = 2.1 Hz, Ar-H), 6.86 (d, 6H, *J* = 8.9 Hz, Ar-H), 6.94 (d, 12H, *J* = 8.7 Hz, Ar-H), 7.00 (d, 6H, *J* = 8.9 Hz, Ar-H), 7.46 (d, 12H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 14.1, 22.6, 22.7, 25.8, 25.9, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.8, 31.6, 31.9, 50.7, 67.9, 68.1, 70.1, 100.8, 105.7, 105.8, 114.0, 114.8, 127.6, 129.6, 133.3, 133.4, 139.4, 142.0, 156.9, 158.2, 158.3, 160.4, 160.

4',4'',4'''-(5,5',5''-(4,4',4''-(ethane-1,1,1-triyl)tris(4,1-phenylene))tris(oxy)tris(methylene)tris(3-(hexadecyloxy)-5,1-phenylene))tris(oxy)tris(methylene)tris(4-(dodecyloxy)biphenyl) (38)

Prepared according to General procedure C.

1.07 g (1.38 mmol) (**35**), 128 mg (0.42 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 232 mg (1.68 mmol) K_2CO_3, 22 mg (0.082 mmol) 18-crown[6], 20 ml abs. acetone, 5 ml abs. THF. Column chromatography (hexane-dichloromethane 4:1).

765 mg (76 %), waxy solid

R_f (hexane-dichloromethane 3:1): 0.38

Melting point: 53 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.86-0.95 (m, 24H, $CH_2C\underline{H}_3$), 1.22-1.55 (m, 132H, CH_2), 1.73-1.87 (m, 12H, $C\underline{H}_2CH_2O$), 2.13 (s, 3H, CH_3), 3.96 (t, 6H, J = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.01 (t, 6H, J = 6.6 Hz, $CH_2C\underline{H}_2O$), 4.99 (s, 6H, Ar-CH_2O-Ar), 5.08 (s, 6H, Ar-CH_2O-Ar), 6.53 (t, 3H, J = 2.0 Hz, Ar-H), 6.62 (s, 3H, Ar-H), 6.70 (s, 3H, Ar-H), 6.88 (d, 6H, J = 8.9 Hz, Ar-H), 6.98 (d, 6H, J = 8.8 Hz, Ar-H), 7.02 (d, 6H, J = 8.8 Hz, Ar-H), 7.49 (d, 6H, J = 8.2 Hz, Ar-H), 7.53 (d, 6H, J = 8.7 Hz, Ar-H), 7.59 (d, 6H, J = 8.2 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 30.8, 31.9, 50.6, 68.1, 69.9, 70.0, 101.1, 105.9, 106.2, 114.0, 114.8, 126.8, 128.0, 129.6, 133.0, 135.1, 139.4, 140.6, 142.0, 156.8, 158.8, 160.1, 160.5.

MALDI-TOF $C_{164}H_{234}O_{12}Na$ [$M+Na^+$] calculated: 2418.76 found: 2418.66

5,5',5''-(4,4',4''-(ethane-1,1,1-triyl)tris(4,1-phenylene))tris(oxy)tris(methylene)tris(1,3-bis(hexadecyloxy)benzene (39)

Prepared according to General prcedure C.

1.70 g (2.61 mmol) (**29**), 242 mg (0.8 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 442 mg (3.2 mmol) K_2CO_3, 42 mg (0.16 mmol) 18-crown[6], 20 ml abs. acetone. Column chromatography (hexane-dichloromethane 3:1).

1.43 g (89 %), white waxy solid

R_f (hexane-dichloromethane 3:1): 0.29

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 18H, J = 6.4 Hz, $CH_2C\underline{H}_3$), 1.19-1.52 (m, 156H, $(C\underline{H}_2)_{13}CH_2CH_2O$), 1.71-1.82 (m, 12H, $C\underline{H}_2CH_2O$), 2.11 (s, 3H, CH_3), 3.94 (t, 12H, J = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.95 (s, 6H, Ar-CH_2O-Ar), 6.41 (s, 3H, Ar-H), 6.56 (s, 6H, Ar-H), 6.86 (d, 6H, J = 8.8 Hz, Ar-H), 7.00 (d, 6H, J = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.8, 31.9, 50.6, 68.0, 70.0, 100.7, 105.7, 113.9, 129.6, 139.3, 142.0, 156.8, 160.5.

MALDI-TOF $C_{137}H_{228}O_9Na$ $[M+Na^+]$ calculated: 2040.73 found: 2041.05

6.2 Build-up of the dendrons and dendrimers

6.2.1 The **T** compound family (Scheme 3.10)

[T-o]-Br

Prepared according to General procedure D.

2.55 g (15 mmol) 4-hydroxy-biphenyl, 14.75 g (45 mmol) 1,12-dibromododecane, 18.66 g (135 mmol) K_2CO_3, 70 ml abs. DMF. Column chromatography (petrolether-dichloromethane 3:1).

5.62 g (90 %), white crystalline solid.

R_f (petrolether-dichloromethane): 0.79

Melting point: 87 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.24-1.57 (m, 16 H, $(C\underline{H}_2)_8CH_2CH_2Br$), 1.76-1.94 (m, 4H, $C\underline{H}_2CH_2Br$, $OCH_2C\underline{H}_2$), 3.42 (t, 2H, *J* = 6.9 Hz, CH_2Br), 4.01 (t, 2H, *J* = 6.7 Hz, OCH_2), 6.98 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.31 (t, 1H, *J* = 7.2 Hz, Ar-H), 7.43 (m, 2H, Ar-H), 7.50-7.60 (m, 4H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 28.2, 28.8, 29.3, 29.4, 29.5, 29.6, 29.7, 32.9, 34.1, 68.0, 114.6, 126.5, 126.6, 128.0, 128.6, 133.4, 140.7, 158.5.

MALDI-TOF	$C_{24}H_{34}BrO$	$[M+H^+]$	calculated:	417.18
			found:	417.88

[T-o]-C

Prepared according to General procedure C.

184 mg (0.6 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 901 mg (2.16 mmol) **[T-o]-Br**, 200 mg (1.44 mmol, 7.2 eq.) K_2CO_3 and 48 mg (0.18 mmol) 18-crown[6], 10 ml abs. acetone. Column chromatography (hexane-dichloromethane 3:1).

607 mg (77 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.39

Melting point: 74 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.28-1.57 (m, 48H, $(C\underline{H}_2)_8CH_2CH_2O$), 1.80 (m, 12H, $C\underline{H}_2CH_2O$), 2.12 (s, 3H, CH_3), 3.94 (t, 6H, *J* = 6.4 Hz, CH_2O), 4.01 (t, 6H, *J* = 6.5 Hz, CH_2O), 6.79 (d, 6H, *J* = 8.6 Hz, Ar-H), 7.00 (m, 12H, Ar-H), 7.31 (t, 3H, *J* = 7.2 Hz, Ar-H), 7.43 (m, 6H, Ar-H), 7.53 (d, 6H, *J* = 8.5 Hz, Ar-H), 7.57 (d, 6H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 26.1, 29.3, 29.4, 29.6, 30.8, 50.6, 67.9, 68.1, 113.6, 114.8, 126.6, 126.7, 128.1, 128.7, 129.6, 133.5, 140.9, 141.7, 157.1, 158.7.

MALDI-TOF	$C_{92}H_{114}O_6Na$	$[M+Na^+]$	calculated:	1337.85
			found:	1337.82

[T-1]-OH

Prepared according to General procedure A.

5.50 g (13.2 mmol) **[T-o]-Br**, 0.88 g (6.28 mmol) 3,5-dihydroxy-benzyl alcohol, 2.17 (15.7 mmol) g K_2CO_3, 0.33 g (1.26 mmol) 18-crown[6], 40 ml abs. acetone. Recrystallized from toluene-hexane 3:1.

4.68 g (92 %), white solid.

R_f (dichloromethane): 0.40

Melting point: 103 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.24-1.53 (m, 32H, (C<u>H</u>$_2$)$_8$C<u>H</u>$_2$C<u>H</u>$_2$O), 1.80 (m, 8H, C<u>H</u>$_2$C<u>H</u>$_2$O), 3.95 (t, 4H, *J* = 6.5 Hz, CH$_2$C<u>H</u>$_2$O), 4.01 (d, 4H, *J* = 6.5 Hz, CH$_2$C<u>H</u>$_2$O), 4.62 (d, 2H, *J* = 5.3 Hz, C<u>H</u>$_2$OH), 6.39 (s, 1H, Ar-H), 6.51 (d, 2H, *J* = 1.8 Hz, Ar-H), 6.97 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.30 (t, 2H, *J* = 7.5 Hz, Ar-H), 7.42 (m, 4H, Ar-H), 7.52 (d, 4H, *J* = 8.6 Hz, Ar-H), 7.56 (d, 4H, *J* = 7.8 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 29.2, 29.3, 29.4, 29.6, 65.5, 68.0, 68.1, 100.6, 105.1, 114.8, 126.6, 126.7, 128.1, 128.7, 133.5, 140.9, 143.2, 158.7, 160.6.

HRMS (ESI)	$C_{55}H_{72}O_5Na$	[M+Na$^+$]	calculated:	835.5277
			found:	835.5274

[T-1]-Br

Prepared according to General procedure B.

4.68 g (5.76 mmol) **[T-1]-OH**, 1.89 g (7.2 mmol) triphenylphosphine, 2.39 g (7.2 mmol) tetrabromomethane. Column chromatography (hexane-dichloromethane 4:1).

4.63 g (92 %), white crystalline solid.

R_f (hexane-dichloromethane 2:1): 0.68

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.26-1.58 (m, 32H, (C<u>H</u>$_2$)$_8$C<u>H</u>$_2$C<u>H</u>$_2$O), 1.79 (m, 8H, C<u>H</u>$_2$C<u>H</u>$_2$O), 3.93 (t, 4H, *J* = 6.5 Hz, CH$_2$C<u>H</u>$_2$O), 4.00 (d, 4H, *J* = 6.6 Hz, CH$_2$C<u>H</u>$_2$O), 4.41 (s, 2H, CH$_2$Br), 6.38 (t, 2H, *J* = 2.1 Hz, Ar-H), 6.52 (d, 2H, *J* = 2.1 Hz, Ar-H), 6.97 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.30 (t, 2H, *J* = 7.2 Hz, Ar-H), 7.41 (m, 4H, Ar-H), 7.51 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.55 (d, 4H, *J* = 7.2 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 29.2, 29.3, 29.4, 29.6, 33.8, 68.1, 101.5, 107.4, 114.8, 126.6, 126.7, 128.1, 128.7, 133.6, 139.5, 140.9, 158.7, 160.4.

HRMS (ESI)	$C_{55}H_{71}BrO_4Ag$	[M+Ag$^+$]	calculated:	981.3587
			found:	981.3576

[T-1]-C

Prepared according to General procedure C.

89 mg (0.29 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 837 mg (1.04 mmol) **[T-1]-Br**, 160 mg (1.17 mmol) K_2CO_3, 20 mg 18-crown[6], 20 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:1)

631 mg (81 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.25

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.26-1.57 (m, 96H, (C<u>H</u>$_2$)$_8$CH$_2$CH$_2$O), 1.81 (m, 24H, C<u>H</u>$_2$CH$_2$O), 2.12 (s, 3H, CH_3), 3.96 (t, 12H, *J* = 6.5 Hz, CH$_2$C<u>H</u>$_2$O), 4.01 (t, 12H, *J* = 6.5 Hz, CH$_2$C<u>H</u>$_2$O), 4.97 (s, 6H, Ar-CH$_2$O-Ar), 6.43 (m, 3H, Ar-H), 6.59 (d, 6H, *J* = 2.0 Hz, Ar-H), 6.88 (d, 6H, *J* = 8.9 Hz, Ar-H), 6.98 (d, 12H, *J* = 8.7 Hz, Ar-H), 7.02 (d, 6H, *J* = 8.8 Hz, Ar-H), 7.31 (t, 6H, *J* = 7.4 Hz, Ar-H), 7.43 (m, 12H, Ar-H), 7.53 (d, 12H, *J* = 8.7 Hz, Ar-H), 7.57 (d, 12H, *J* = 8.0 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 29.2, 29.3, 29.4, 29.6, 30.8, 50.7, 68.1, 70.1, 100.8, 105.8, 114.0, 114.8, 126.5, 126.7, 128.1, 128.7, 129.6, 133.5, 139.3, 140.9, 142.0, 156.9, 158.7, 160.5.

MALDI-TOF $C_{185}H_{228}O_{15}Na$ [M+Na$^+$] calculated: 2712.70

found: 2710.59

[T-2]-OH

Prepared according to general procedure A.

4.23 g (4.83 mmol) **[T-1]-Br**, 0.32 g (2.3 mmol) 3,5-dihydroxy-benzyl alcohol, 0.80 g (5.76 mmol) K_2CO_3, 0.12 g (0.45 mmol) 18-crown[6], 30 ml abs. acetone. Column chromatography (petrolether-dichloromethane 1:1).

2.35 g (59 %), white solid.

R_f (dichloromethane-petrolether 3:1): 0.39

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.25-1.53 (m, 64H, (C<u>H</u>$_2$)$_8$CH$_2$CH$_2$O), 1.79 (m, 16H, C<u>H</u>$_2$CH$_2$O), 3.94 (t, 8H, *J* = 6.5 Hz, CH$_2$C<u>H</u>$_2$O), 4.00 (t, 8H, *J* = 6.6 Hz, CH$_2$C<u>H</u>$_2$O), 4.62 (d, 2H, *J* = 5.9 Hz, C<u>H</u>$_2$OH), 4.96 (s, 4H, Ar-CH$_2$O-Ar), 6.42 (s, 2H, Ar-H), 6.56 (m, 5H, Ar-H), 6.62 (m, 2H, Ar-H), 6.97 (d, 8H, *J* = 8.7 Hz, Ar-H), 7.30 (t, 4H, *J* = 7.4 Hz, Ar-H), 7.41 (m, 8H, Ar-H), 7.52 (d, 8H, *J* = 8.8 Hz, Ar-H), 7.55 (d, 8H, *J* = 7.9 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 29.2, 29.3, 29.4, 29.6, 65.3, 68.1, 70.1, 100.9, 101.4, 105.7, 114.8, 126.6, 126.7, 128.1, 128.7, 133.5, 139.0, 140.9, 143.4, 158.7, 160.2, 160.5.

[T-2]-Br

Prepared according to General procedure B.

2.27 g (1.31 mmol) **[T-2]-OH**, 0.43 g (1.64 mmol) triphenylphosphine, 0.54 g (1.64 mmol) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:1).

2.02 g (86 %), white solid.

R_f (petrolether-dichloromethane 1:1): 0.35

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.30-1.59 (m, 64H, $(C\underline{H}_2)_8CH_2CH_2O$), 1.82 (m, 16H, $C\underline{H}_2CH_2O$), 3.98 (t, 8H, *J* = 6.5 Hz, CH_2O), 4.02 (t, 4H, *J* = 6.5 Hz, CH_2O), 4.43 (s, 2H, CH_2Br), 4.98 (s, 4H, Ar-CH_2O-Ar), 6.46 (s, 2H, Ar-H), 6.59 (s, 5H, Ar-H), 6.66 (d, 2H, *J* = 1.8 Hz, Ar-H), 7.00 (d, 8H, *J* = 8.6 Hz, Ar-H), 7.33 (t, 4H, *J* = 7.3 Hz, Ar-H), 7.44 (m, 8H, Ar-H), 7.55 (d, 8H, *J* = 8.6 Hz, Ar-H), 7.59 (d, 8H, *J* = 7.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.2, 29.3, 29.4, 29.6, 33.5, 68.1, 70.2, 100.9, 102.2, 105.7, 108.1, 114.8, 126.5, 126.6, 128.0, 128.6, 133.5, 138.8, 139.7, 140.8, 158.7, 160.0, 160.5.

MALDI-TOF	$C_{117}H_{147}BrO_{10}$	$[M^+]$	calculated:	1791.02
			found:	1791.09
	$C_{117}H_{147}BrO_{10}Na$	$[M+Na^+]$	calculated:	1814.01
			found:	1815.47

[T-2]-C

Prepared according to General procedure C.

895 mg (0.50 mmol) **[T-2]-Br**, 46 mg (0.151 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 105 mg (0.758 mmol) K_2CO_3, 10 mg (0.038 mmol) 18-crown[6], 20 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:1).

600 mg (73 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.65

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.25-1.54 (m, 192H, $(C\underline{H}_2)_8CH_2CH_2O$), 1.72-1.87 (m, 48H, $C\underline{H}_2CH_2O$), 2.13 (s, 3H, CH_3), 3.95 (t, 24H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.00 (t, 24H, *J* = 6.6 Hz, $CH_2C\underline{H}_2O$), 4.96 (s, 18H, Ar-CH_2O-Ar), 6.43 (s, 6H, Ar-H), 6.56-6.62 (m, 15H, Ar-H), 6.71 (d, 6H,

J = 1.6 Hz, Ar-H), 6.88 (d, 6H, *J* = 8.8 Hz, Ar-H), 6.97 (d, 24H, *J* = 8.7 Hz, Ar-H), 7.04 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.31 (t, 12H, *J* = 7.4 Hz, Ar-H), 7.39-7.46 (m, 24H, Ar-H), 7.52 (d, 24H, *J* = 8.7 Hz, Ar-H), 7.56 (d, 24H, *J* = 7.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 29.2, 29.3, 29.4, 29.6, 30.9, 50.7, 68.1, 69.9, 70.1, 100.9, 101.5, 105.8, 106.5, 114.0, 114.7, 126.5, 126.7, 128.0, 128.7, 129.6, 133.5, 138.9, 139.5, 140.9, 142.1, 156.8, 158.7, 160.1, 160.5.

[T-3]-OH

Prepared according to General procedure A.

1.64 g (0.916 mmol) **[T-2]-Br**, 61 mg (0.436 mmol) 3,5-dihydroxy-benzyl alcohol, 181 mg (1.31 mmol) K_2CO_3, 23 mg (0.087 mmol) 18-crown[6], 30 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:9).

1.06 g (68 %), white solid.

R_f (dichloromethane): 0.65

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.29-1.57 (m, 128H, $(C\underline{H}_2)_8CH_2CH_2O$), 1.75-1.89 (m, 32H, $C\underline{H}_2CH_2O$), 3.97 (t, 16H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.01 (t, 16H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.64 (d, 2H, *J* = 5.7 Hz, $C\underline{H}_2OH$), 4.96-5.03 (m, 12H, Ar-CH_2O-Ar), 6.46 (s, 4H, Ar-H), 6.57-6.66 (m, 13H, Ar-H), 6.72 (d, 4H, *J* = 1.5 Hz, Ar-H), 7.00 (d, 16H, *J* = 8.7 Hz, Ar-H), 7.33 (t, 8H, *J* = 7.3 Hz, Ar-H), 7.44 (m, 16H, *J* = 7.5 Hz, Ar-H), 7.55 (d, 16H, *J* = 8.7 Hz, Ar-H), 7.59 (d, 16H, *J* = 7.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.3, 29.4, 29.6, 65.2, 68.0, 69.9, 70.1, 100.8, 101.2, 101.5, 105.7, 106.2, 114.7, 126.5, 126.6, 128.0, 128.6, 133.4, 138.9, 139.2, 140.8, 143.4, 158.7, 160.0, 160.1, 160.4.

[T-3]-Br

Prepared according to General procedure B.

0.93 g (0.261 mmol, 1 eq.) **[T-3]-OH**, 173 mg (0.522 mmol, 2 eq.) tetratbromomethane, 137 mg (0.522 mmol, 2 eq.) triphenylphosphine. Column chromatography (hexane-dichloromethane 1:1).

832 mg (88 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.20

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.24-1.53 (m, 128H, (C<u>H</u>$_2$)$_8$$CH_2CH_2O$), 1.70-1.86 (m, 32H, C<u>H</u>$_2$$CH_2O$), 3.94 (t, 16H, *J* = 6.5 Hz, CH_2C<u>H</u>$_2O$), 3.99 (t, 16H, *J* = 6.5 Hz, CH_2O), 4.41 (s, 2H, CH_2Br), 4.96 (s, 12H, Ar-CH_2O-Ar), 6.42 (s, 4H, Ar-H), 6.54-6.61 (m, 11H, Ar-H), 6.63 (d, 2H, *J* = 1.9 Hz, Ar-H), 6.68 (d, 4H, *J* = 1.8 Hz, Ar-H), 6.97 (d, 16H, *J* = 8.7 Hz, Ar-H), 7.30 (t, 8H, *J* = 7.3 Hz, Ar-H), 7.38-7.45 (m, 16H, Ar-H), 7.52 (d, 16H, *J* = 8.6 Hz, Ar-H), 7.56 (d, 16H, *J* = 7.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 29.3, 29.4, 29.6, 33.6, 68.0, 70.1, 70.2, 100.8, 101.6, 102.1, 105.7, 106.4, 108.2, 114.7, 126.5, 126.6, 128.0, 128.7, 133.5, 138.8, 138.9, 139.7, 140.8, 158.7, 160.0, 160.1, 160.5.

[T-3]-C

Prepared according to General procedure C.

900 mg (0.248 mmol) **[T-3]-Br**, 23 mg (0.075 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 41 mg (0.300 mmol) K_2CO_3, 4 mg (0.015 mmol) 18-crown[6], 10 ml abs. acetone, 5 ml abs. THF. Column chromatography (hexane-dichloromethane 1:2).

602 mg (73 %), white solid.

R_f (hexane-dichloromethane 1:4): 0.75

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.23-1.56 (m, 384H, (C<u>H</u>$_2$)$_8$$CH_2CH_2O$), 1.72-1.89 (m, 96H, C<u>H</u>$_2$$CH_2O$), 2.13 (s, 3H, CH_3), 3.96 (t, 48H, *J* = 6.4 Hz, CH_2C<u>H</u>$_2O$), 4.01 (t, 48H, *J* = 6.5 Hz, CH_2C<u>H</u>$_2O$), 4.95 (s, 42H, Ar-CH_2O-Ar), 6.44 (m, 12H, Ar-H), 6.55 (m, 33H, Ar-H), 6.65 (m, 18H, Ar-H), 6.87 (d, 6H, *J* = 8.8 Hz, Ar-H), 6.94-7.05 (m, 54 H, Ar-H), 7.31 (t, 24H, *J* = 7.4 Hz, Ar-H), 7.38-7.46 (m, 48H, Ar-H), 7.53 (m, 48H, Ar-H), 7.55 (d, 48H, *J* = 7.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.1, 30.9, 50.7, 68.0, 68.1, 69.5, 70.0, 70.1, 100.8, 101.5, 106.2, 106.5, 113.9, 114.7, 126.5, 126.7, 128.0, 128.7, 129.6, 133.5, 139.0, 139.2, 139.4, 140.7, 141.9, 157.0, 158.7, 160.0, 160.5.

6.2.2 The **CN-T** compound family (Scheme 3.11)

[CN-T-o]-Br

Prepared according to General procedure D.

9.36 g 4-cyano-4'-hydroxy-biphenyl (48 mmol, 1 eq.), 43.2 g 1,10-dibromodecane (144 mmol, 3 eq.), 59.68 g K_2CO_3 (432 mmol, 9 eq.), 200 ml DMF. Column chromatography: petrolether – dichloromethane = 4:1.

16.00 g (81 %), white crystalline solid.

R_f (dichloromethane): 0.70

Melting point: 75 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.25-1.52 (m, 12H, (C<u>H</u>$_2$)$_6$CH$_2$CH$_2$Br), 1.76-1.92 (m, 4H, OCH$_2$C<u>H</u>$_2$, C<u>H</u>$_2$CH$_2$Br), 3.41 (t, 2H, *J* = 6.8 Hz, CH$_2$Br), 4.01 (t, 2H, *J* = 6.5 Hz, OCH$_2$), 6.99 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.53 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.64 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.69 (d, 2H, *J* = 8.2 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 28.1, 28.7, 29.2, 29.3, 29.4, 29.5, 32.8, 34.0, 68.2, 110.1, 115.1, 119.1, 127.1, 128.3, 131.3, 132.5, 145.3, 159.8.

HRMS (ESI) $C_{23}H_{28}BrNOK$ [M+K$^+$] calculated: 452.0991
found: 452.0994

[CN-T-o]-C

Prepared according to General procedure C.

184 mg (0.6 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 820 mg (1.98 mmol) **[CN-T-o]-Br**, 312 mg (2.4 mmol) K_2CO_3, 48 mg (0.18 mmol) 18-crown[6]. Column chromatography (dichloromethane).

532 mg (68 %), white solid.

R_f (dichloromethane): 0.45

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.29-1.54 (m, 36 H, (C<u>H</u>$_2$)$_6$CH$_2$CH$_2$O), 1.71-1.87 (m, 12H, C<u>H</u>$_2$CH$_2$O), 2.10 (s, 3H, CH_3), 3.93 (t, 6H, *J* = 6.5 Hz, CH$_2$O), 4.01 (t, 6H, *J* = 6.5 Hz, CH$_2$O), 6.78 (d, 6H, *J* = 8.9 Hz, Ar-H), 6.98 (d, 6H, *J* = 8.8 Hz, Ar-H), 6.99 (d, 6H, *J* = 8.8 Hz, Ar-H), 7.52 (d, 6H, *J* = 8.8 Hz, Ar-H), 7.64 (d, 6H, *J* = 8.6 Hz, Ar-H), 7.68 (d, 6H, *J* = 8.5 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 26.1, 29.2, 29.3, 29.5, 30.8, 50.6, 67.9, 68.2, 110.0, 113.6, 115.1, 119.1, 127.0, 128.3, 129.6, 131.2, 132.5, 141.7, 145.3, 157.1, 159.8.

MALDI-TOF $C_{89}H_{99}N_3O_6Na$ [M+Na$^+$] calculated: 1328.74
found: 1328.39

[CN-T-1]-OH

Prepared according to General procedure A.

7.90 g (19.1 mmol) **[CN-T-0]-Br**, 1.27 g (9.1 mmol) 3,5-dihydroxy-benzyl alcohol, 3.14 g (22.8 mmol) K_2CO_3, 400 mg 18-crown[6], 90 ml abs. acetone. Purified by column chromatography, petrolether-dichloromethane = 2:1.

6.78 g (92 %), white solid.

R_f (dichloromethane-diethylether 9:1): 0.68

Melting point: 102 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.30-1.54 (m, 24H, (C<u>H</u>$_2$)$_6$(CH$_2$)$_2$O), 1.69 (t, 1H, *J* = 6.0 Hz, OH), 1.72-1.87 (m, 8H, OCH$_2$C<u>H</u>$_2$), 3.94 (t, 4H, *J* = 6.5 Hz, OC<u>H</u>$_2$CH$_2$), 4.01 (t, 4H, *J* = 6.5 Hz, OC<u>H</u>$_2$CH$_2$), 4.62 (d, 2H, *J* = 5.8 Hz, C<u>H</u>$_2$OH), 6.38 (t, 1H, *J* = 2.1 Hz, Ar-H), 6.51 (, d, 2H, *J* = 2.1 Hz, Ar-H), 6.99 (d, 4H, *J* = 8.8 Hz, Ar-H), 7.53 (, d, 4H, *J* = 8.8 Hz, Ar-H), 7.63 (d, 4H, *J* = 8.6 Hz, Ar-H), 7.68 (d, 4H, *J* = 8.5 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.1, 29.2, 29.3, 29.4, 65.4, 68.0, 68.2, 100.6, 105.0, 110.0, 115.1, 119.1, 127.0, 128.3, 131.2, 132.5, 143.2, 145.3, 159.8, 160.5.

HRMS (ESI) $C_{53}H_{62}N_2O_5Na$ [M+Na$^+$] calculated: 829.4556
found: 829.4549

[CN-T-1]-Br

Prepared according to General procedure B.

6.56 g (8.14 mmol) **[CN-T-1]-OH**, 2.67 g (10.2 mmol) triphenylphosphine, 3.38 g (10.2 mmol) tetrabromomethane. Column chromatography: petrolether-dichloromethane 2:1.

6.93 g (98 %) white crystalline solid.

R_f (hexane-dichloromethane 1:1): 0.40

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.30-1.54 (m, 24H, (C<u>H</u>$_2$)$_6$CH$_2$CH$_2$O), 1.72-1.87 (m, 8H, C<u>H</u>$_2$CH$_2$O), 3.93 (t, 4H, *J* = 6.5 Hz, CH$_2$O), 4.01 (t, 4H, *J* = 6.5 Hz, CH$_2$O), 4.41 (s, 2H, CH$_2$Br), 6.38 (t, 1H, *J* = 2.0 Hz, Ar-H), 6.52 (d, 2H, *J* = 2.0 Hz, Ar-H), 6.99 (d, 4H, *J* = 8.7 Hz, Ar-H), 7.53 (d, 4H, *J* = 8.6 Hz, Ar-H), 7.64 (d, 4H, *J* = 8.3 Hz, Ar-H), 7.69 (d, 4H, *J* = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.2, 29.3, 29.5, 33.7, 68.1, 68.2, 101.5, 107.4, 110.1, 115.1, 119.1, 127.0, 128.3, 131.3, 132.5, 139.5, 145.3, 159.8, 160.4.

HRMS (ESI)	$C_{53}H_{61}BrN_2O_4Ag$	$[M+Ag^+]$	calculated:	975.2866
			found:	975.2858

[CN-T-1]-C

Prepared according to General procedure C.

765 mg (0.88 mmol) **[CN-T-1]-Br**, 83 mg (0.27 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 150 mg (1.08 mmol) K_2CO_3, 20 mg 18-crown[6], 30 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:9).

454 mg (63 %), white solid.

R_f (hexane-dichloromethane 1:9): 0.25

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.27-1.54 (m, 72 H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.80 (m, 24 H, $C\underline{H}_2CH_2O$), 2.10 (s, 3H, CH_3), 3.44 (t, 12H, *J* = 6.5 Hz, CH_2O), 4.01 (d, 12H, *J* = 6.5 Hz, Ar-H), 4.96 (s, 6H, Ar-CH_2O-Ar), 6.42 (t, 3H, *J* = 1.9 Hz, Ar-H), 6.57 (d, 6H, *J* = 2.0 Hz, Ar-H), 6.87 (d, 6H, *J* = 8.9 Hz, Ar-H), 6.99 (d, 12H, *J* = 8.7 Hz, Ar-H), 7.00 (d, 6H, *J* = 8.6 Hz, Ar-H), 7.52 (d, 12H, *J* = 8.7 Hz, Ar-H), 7.63 (d, 12H, *J* = 8.5 Hz, Ar-H), 7.67 (d, 12H, *J* = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.1, 29.2, 29.3, 29.4, 30.8, 50.6, 68.0, 68.1, 70.0, 100.8, 105.7, 110.0, 114.0, 115.1, 119.0, 127.0, 128.2, 129.6, 131.2, 132.5, 139.3, 142.0, 145.2, 156.8, 159.8, 160.5.

MALDI-TOF	$C_{179}H_{198}N_6O_{15}Na$	$[M+Na^+]$	calculated:	2694.48
			found:	2692.60

[CN-T-2]-OH

Prepared according to General procedure A.

6.22 g (7.16 mmol) **[CN-T-1]-Br**, 0.46 g 3,5-dihydroxy-benzyl alcohol (3.25 mmol), 1.13 g K_2CO_3 (8.13 mmol), 0.18 g (0.65 mmol) 18-crown[6], 50 ml abs. acetone. Purified by column chromatography (dichloromethane-diethylether 20:1).

5.00 g (90 %), white solid.

R_f (dichloromethane-*t*-butyl-methyl-ether 20:1): 0.63

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.28-1.53 (m, 48H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.79 (m, 16H, $C\underline{H}_2CH_2O$), 3.93 (t, 8H, *J* = 6.5 Hz, CH_2O), 4.00 (t, 8H, *J* = 6.5 Hz, CH_2O), 4.62 (s, 2H, $C\underline{H}_2OH$), 4.95 (s, 4H, Ar-CH_2O-Ar), 6.40 (t, 2H, *J* = 2.1 Hz, Ar-H), 6.55 (m, 5H, Ar-H), 6.61 (d, 2H, *J* = 2.1 Hz, Ar-H), 6.98 (d, 8H, *J* = 8.8 Hz, Ar-H), 7.52 (d, 8H, *J* = 8.8 Hz, Ar-H), 7.63 (d, 8H, *J* = 8.8 Hz, Ar-H), 7.68 (d, 8H, *J* = 8.5 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.2, 29.3, 29.4, 29.5, 65.3, 68.0, 68.1, 70.1, 100.7, 101.3, 105.7, 110.0, 115.0, 119.1, 127.0, 128.3, 131.2, 132.5, 138.9, 143.4, 145.2, 159.7, 160.1, 160.5.

MALDI-TOF	$C_{113}H_{128}N_4O_{11}Na$	$[M+Na^+]$	calculated:	1739.95
			found:	1739.60

[CN-T-2]-Br

Prepared according to General procedure B.

4.50 g (2.62 mmol) **[CN-T-2]-OH**, 1.52 g (4.59 mmol, 1.75 eq.)) tetrabromomethane, 1.20 g (4.59 mmol, 1.75 eq.) triphenylphosphine. Column chromatography (dichloromethane).

3.50 g (75 %), white solid.

R_f (dichloromethane): 0.41

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.24-1.53 (m, 48H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.79 (m, 16H, $C\underline{H}_2CH_2O$), 3.94 (t, 8H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.00 (t, 8H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.40 (s, 2H, Ar-CH_2O-Ar), 4.94 (s, 4H, Ar-CH_2O-Ar), 6.41 (t, 2H, *J* = 2 Hz, Ar-H), 6.55 (m, 5H, Ar-H), 6.63 (d, 2H, *J* = 2.0 Hz, Ar-H), 6.99 (d, 8H, *J* = 8.7 Hz, Ar-H), 7.52 (d, 8H, *J* = 8.7 Hz, Ar-H), 7.63 (d, 8H, *J* = 8.5 Hz, Ar-H), 7.68 (d, 8H, *J* = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.1, 29.2, 29.3, 29.5, 68.1, 68.2, 70.2, 100.9, 102.2, 105.8, 108.1, 110.0, 115.1, 119.0, 127.0, 128.3, 131.2, 132.5, 138.8, 139.7, 145.2, 159.8, 160.0, 160.5.

[CN-T-2]-C

Prepared according to General procedure C.

510 mg (0.287 mmol) **[CN-T-2]-Br**, 27 mg (0.087 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 48 mg (0.348 mmol) K_2CO_3, 5 mg 18-crown[6], 10 ml abs. acetone, 5 ml abs. THF. Column chromatography (dichloromethane-diethylether 50:1).

282 mg (60 %), white solid.

R_f (dichloromethane): 0.37

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.31-1.54 (m, 144H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.80 (m, 48H, $C\underline{H}_2CH_2O$), 2.13 (s, 3H, CH_3), 3.96 (t, 24H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.00 (t, 24H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.97 (s, 18H, Ar-CH_2O-Ar), 6.44 (m, 6H, Ar-H), 6.59 (m, 15H, Ar-H), 6.72 (m, 6H, Ar-H), 6.89 (d, 6H, *J* = 8.8 Hz, Ar-H), 6.99 (d, 24H, *J* = 8.7 Hz, Ar-H), 7.04 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.52 (d, 24H, *J* = 8.7 Hz, Ar-H), 7.62 (d, 24H, *J* = 8.5 Hz, Ar-H), 7.66 (d, 24H, *J* = 8.5 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 25.9, 29.0, 29.1, 29.2, 29.3, 30.7, 50.5, 67.9, 68.0, 69.8, 70.0, 100.7, 101.4, 105.6, 106.3, 109.8, 113.9, 114.9, 118.9, 126.8, 128.1, 129.5, 131.0, 132.4, 138.8, 139.4, 141.9, 145.0, 156.7, 159.7, 160.0, 160.4.

[CN-T-3]-OH

Prepared according to General procedure A.

3.43 g (1.93 mmol) **[CN-T-2]-Br**, 0.123 g (0.88 mmol) 3,5-dihydroxy-benzyl alcohol, 0.304 g (2.20 mmol) K_2CO_3, 46 mg (0.18 mmol) 18-crown[6], 30 ml abs. acetone. Column chromatography (dichloromethane-diethylether 50:1).

2.16 g (69 %), white amorphous solid.

R_f (dichloromethane-diethylether 19:1): 0.89

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.25-1.53 (m, 96H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.78 (m, 32H, $C\underline{H}_2CH_2O$), 3.93 (t, 16H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 3.99 (t, 16H, *J* = 6.5 Hz, $C\underline{H}_2CH_2O$), 4.61 (d, 2H, *J* = 5.3 Hz, $C\underline{H}_2OH$), 4.95 (m, 12H, Ar-CH_2O-Ar), 6.40 (s, 4H, Ar-H), 6.55 (m, 11H, Ar-H), 6.60 (s, 2H, Ar-H), 6.67 (s, 4H, Ar-H), 6,97 (d, 16H, *J* = 8.6 Hz, Ar-H), 7.51 (d, 16H, *J* = 8.6 Hz, Ar-H), 7.61 (d, 16H, *J* = 8.3 Hz, Ar-H), 7.66 (d, 16H, *J* = 8.2 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.2, 29.3, 29.4, 29.5, 65.2, 68.1, 68.2, 70.0, 70.2, 100.9, 101.3, 101.6, 105.7, 106.3, 110.1, 115.1, 119.0, 127.0, 128.3, 131.2, 132.5, 138.9, 139.3, 143.5, 145.2, 159.8, 160.1, 160.2, 160.5.

MALDI-TOF	$C_{223}H_{260}N_8O_{23}Na$	$[M+Na^+]$	calculated:	3560.93
			found:	3560.08

[CN-T-3]-Br

Prepared according to General procedure B.

0.97 g (0.274 mmol) **[CN-T-3]-OH**, 90 mg (0.343 mmol) triphenylphosphine, 114 mg (0.343 mmol) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:2).

750 mg (76 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.33

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.27-1.51 (m, 96H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.78 (m, 32H, $C\underline{H}_2CH_2O$), 3.94 (t, 16H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 3.99 (t, 16H, *J* = 6.5 Hz, $C\underline{H}_2CH_2O$), 4.40 (s, 2H, CH_2Br), 4.95 (m, 12H, Ar-CH_2O-Ar), 6.41 (s, 4H, Ar-H), 6.56 (m, 11H, Ar-H), 6.63 (d, 2H, J = 2.0 Hz, Ar-H), 6.67 (d, 4H, J = 1.9 Hz, Ar-H), 6.98 (d, 16H, *J* = 8.8 Hz, Ar-H), 7.51 (d, 16H, *J* = 8.7 Hz, Ar-H), 7.62 (d, 16H, *J* = 8.3 Hz, Ar-H), 7.67 (d, 16H, *J* = 8.5 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.1, 29.2, 29.3, 29.4, 33.5, 53.4, 68.0, 68.1, 70.1, 70.2, 100.9, 101.7, 102.2, 105.8, 106.4, 108.2, 110.0, 115.1, 119.0, 127.0, 128.3, 131.2, 132.5, 138.9, 139.0, 139.8, 145.2, 159.8, 160.0, 160.2, 160.5.

[CN-T-3]-C

Prepared according to General procedure C.

710 mg (0.20 mmol) **[CN-T-3]-Br**, 19 mg (0.061 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 34 mg (0.24 mmol) K_2CO_3, 10 mg 18-crown[6], 10 ml abs. acetone, 10 ml abs. THF. Column chromatography (hexane-dichloromethane 1:2).

437 mg (66 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.72

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.21-1.49 (m, 288H, $(C\underline{H}_2)_6CH_2CH_2O$), 1.75 (m, 96H, $C\underline{H}_2CH_2O$), 2.07 (s, 3H, CH_3), 3.89 (t, 48H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 3.95 (t, 48H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.91 (s, 42H, Ar-CH_2O-Ar), 6.38 (m, 12H, Ar-H), 6.54 (m, 33H, Ar-H), 6.67 (m, 18H, Ar-H), 6.86 (d, 6H, *J* = 8.7 Hz, Ar-H), 6.94 (d, 48H, J = 8.7 Hz, Ar-H), 7.00 (d, 6H, *J* = 8.8 Hz, Ar-

H), 7.48 (d, 48H, *J* = 8.7 Hz, Ar-H), 7.58 8(d, 48H, *J* = 8.4 Hz, Ar-H), 7.63 (d, 48H, *J* = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.0, 29.1, 29.2, 29.3, 29.5, 31.7, 50.7, 68.0, 68.1, 69.5, 70.0, 70.1, 100.8, 101.4, 101.6, 105.8, 106.5, 110.0, 113.9, 115.1, 119.0, 127.0, 128.2, 129.7, 131.2, 132.4, 138.9, 139.0, 139.4, 142.1, 145.1, 156.8, 159.8, 160.1, 160.2, 160.5.

6.2.3 The **M** compound family (Scheme 3.12)

[M-o]-Br

Prepared according to General procedure D.

10.00 g (37 mmol) (**16**), 27.09 g (111 mmol) 1,6-dibromo-hexane, 46.02 g (333 mmol) K_2CO_3, 200 ml abs. DMF. Column chromatography (petrolether-dichloromethane 3:1).

12.65 g (79 %), white solid.

R_f (petrolether-dichloromethane 2:1): 0.47

Melting point: 115 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 3H, *J* = 6.9 Hz, CH_3), 1.35 (m, 4H, CH_2), 1.43-1.58 (m, 6H, CH_2), 1.80 (m, 4H, CH_2), 1.91 (m, 2H, CH_2), 3.43 (t, 2H, *J* = 6.8 Hz, CH_2Br), 3.99 (m, 4H, CH_2O), 6.94 (m, 4H, Ar-H), 7.46 (d, 4H, *J* = 8.6 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.3, 25.7, 27.9, 29.1, 29.3, 31.6, 32.7, 33.8, 67.8, 68.1, 114.7, 127.6, 133.3, 133.5, 158.1, 158.3.

MALDI-TOF	$C_{24}H_{34}BrO_2$	$[M^+]$	calculated:	433.17
			found:	433.91

[M-o]-C

Prepared according to General procedure C.

1.59 g (3.68 mmol) **[M-o]-Br**, 313 mg (1.02 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 565 mg (4.09 mmol) K_2CO_3, 53 mg (0.2 mmol) 18-crown[6], 25 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:1).

945 mg (68 %), white solid.

R_f (dichloromethane): 0.43

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.94 (t, 9H, *J* = 6.9 Hz, $CH_2C\underline{H}_3$), 1.32-1.63 (m, 30H, CH_2), 1.84 (m, 18H, $C\underline{H}_2CH_2O$), 2.13 (s, 3H, CH_3), 3.97 (m, 18H, CH_2O), 6.81 (d, 6H, *J* = 8.8 Hz, Ar-H), 6.96 (d, 12H, *J* = 8.3 Hz, Ar-H), 7.01 (d, 6H, *J* = 8.8 Hz, 7.48 (d, 12H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 26.0, 29.3, 30.8, 31.6, 50.6, 67.7, 67.9, 68.1, 113.6, 114.7, 127.6, 129.6, 133.3, 133.4, 141.7, 157.0, 158.1, 158.2.

MALDI-TOF	$C_{92}H_{114}O_9Na$	$[M+Na^+]$	calculated:	1385.84
			found:	1385.69

[M-1]-OH

Prepared according to General procedure A.

9.85 g (22.8 mmol) **[M-0]-Br**, 1.46 g (10.4 mmol) 3,5-dihydroxy-benzyl alcohol, 3.59 g (26 mmol) K_2CO_3, 0.48 g (1.8 mmol) 18-crown[6], 50 ml abs. acetone. Recrystallized from hexane-dichloromethane 2:1.

5.70 g (65 %), white solid.

R_f (dichloromethane): 0.42

Melting point: 139 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 6H, *J* = 7.0 Hz, 1.32-1.63 (m, 20H, CH_2), 1.82 (m, 12H, $C\underline{H}_2CH_2O$), 3.99 (m, 12H, $CH_2C\underline{H}_2O$), 4.62 (d, 2H, *J* = 4.1 Hz, $C\underline{H}_2OH$), 6.40 (m, 1H, Ar-H), 6.52 (d, 2H, *J* = 2.1 Hz, Ar-H), 6.95 (d, 8H, *J* = 8.5 Hz, Ar-H), 7.46 (d, 8H, *J* = 8.6 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 29.1, 29.2, 29.3, 31.6, 65.4, 67.9, 68.1, 100.6, 105.1, 114.8, 127.6, 133.3, 133.4, 143.3, 158.2, 158.3, 160.5.

HRMS (ESI)	$C_{55}H_{72}O_7Na$	$[M+Na^+]$	calculated:	867.5176
			found:	867.5170

[M-1]-Br

Prepared according to General procedure B.

6.34 g (7.51 mmol) **[M-1]-OH**, 2.95 g (11.3 mmol, 1.5 eq.) triphenylphosphine, 3.73 g (11.3 mmol, 1.5 eq.) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:1)

5.11 g (75 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.52

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 6H, J = 7.0 Hz, CH_3), 1.31-1.64 (m, 20H, CH_2), 1.82 (m, 12H, C<u>H</u>$_2$CH$_2$O), 3.96 (t, 6H, J = 6.0 Hz, CH_2O), 4.01 (t, 12H, J = 6.5 Hz, CH_2O), 4.41 (s, 2H, CH_2Br), 6.40 (t, 1H, J = 2.1 Hz, Ar-H), 6.53 (d, 2H, J = 2.1 Hz, Ar-H), 6.95 (d, 8H, J = 8.7 Hz, Ar-H), 7.46 (d, 8H, J = 8.6 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 29.1, 29.2, 29.3, 31.6, 33.7, 67.9, 68.0, 68.1, 101.5, 107.4, 114.8, 127.6, 133.3, 133.4, 139.6, 158.2, 158.3, 160.4.

MALDI-TOF	$C_{55}H_{71}BrO_6$	$[M^+]$	calculated:	906.44
			found:	906.35
	$C_{55}H_{70}BrO_6Na$	$[M+Na^+]$	calculated:	929.43
			found:	929.31

[M-1]-C

Prepared according to General procedure C.

89 mg (0.29 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 880 mg (1.04 mmol) **[M-1]-Br**, 160 mg (1.17 mmol) K_2CO_3, 20 mg 18-crown[6], 15 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:2).

710 mg (88%), white solid.

R_f (hexane-dichloromethane 1:3): 0.69

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.91 (t, 18H, *J* = 6.9 Hz, CH_2C<u>H</u>$_3$), 1.31-1.62 (m, 60H, CH_2), 1.81 (m, 36H, C<u>H</u>$_2$CH$_2$O), 2.09 (s, 3H, CH_3), 3.97 (m, 36H, CH_2O), 4.94 (s, 6H, Ar-CH_2O-Ar), 6.40 (t, 3H, *J* = 1.8 Hz, Ar-H), 6.56 (d, 6H, *J* = 1.9 Hz, Ar-H), 6.85 (d, 6H, *J* = 8.9 Hz, Ar-H), 6.93 (d, 24H, *J* = 8.6 Hz, Ar-H), 6.98 (d, 6H, *J* = 8.9 Hz, Ar-H), 7.44 (d, 24H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.8, 25.9, 29.2, 29.3, 30.8, 31.6, 50.7, 67.9, 68.1, 70.1, 100.9, 105.8, 114.0, 114.8, 127.6, 129.6, 133.3, 133.4, 139.4, 142.1, 156.9, 158.2, 158.3, 160.5.

MALDI-TOF	$C_{185}H_{228}O_{21}Na$	$[M+Na^+]$	calculated:	2808.67
			found:	2806.37

[M-2]-OH

Prepared according to General procedure A.

3.11 g (3.43 mmol) **[M-1]-Br**, 218 mg (1.56 mmol) 3,5-dihydroxy-benzyl alcohol, 539 mg (3.9 mmol) K_2CO_3 and 82 mg 18-crown[6], 35 ml abs. acetone. Column chromatography (dichloromethane).

2.43 g (87 %), white solid.

R_f (dichloromethane): 0.41

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 12H, *J* = 6.9 Hz, CH_3), 1.30-1.59 (m, 40 H, CH_2), 1.81 (m, 24H, $C\underline{H}_2CH_2O$), 3.98 (m, 24H, $CH_2C\underline{H}_2O$), 4.62 (d, 2H, *J* = 5.9 Hz, $C\underline{H}_2OH$), 4.96 (s, 4H, Ar-CH_2O-Ar), 6.41 (s, 2H, Ar-H), 6.60 (m, 5H, Ar-H), 6.61 (d, 2H, *J* = 1.9 Hz, Ar-H), 6.93 (d, 16H, *J* = 8.6 Hz, Ar-H), 7.45 (d, 16H, *J* = 8.6 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 29.1, 29.2, 29.3, 31.6, 65.3, 67.9, 68.1, 70.1, 100.8, 101.4, 105.7, 114.7, 127.6, 133.3, 133.4, 139.1, 143.4, 158.1, 158.2, 160.1, 160.5.

MALDI-TOF $C_{117}H_{148}O_{15}Na$ $[M+Na^+]$ calculated: 1816.07
found: 1815.52

[M-2]-Br

Prepared according to General procedure B.

3.69 g (2.06 mmol, 1 eq.) **[M-2]-OH**, 1.079 g (4.12 mmol, 2 eq.) triphenylphosphine, 1.362 g (4.12 mmol, 2 eq.) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:1).

3.29 g (86 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.35

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.93 (t, 12H, *J* = 7.0 Hz, CH_3), 1.31-1.62 (m, 40H, CH_2), 1.83 (m, 24H, $C\underline{H}_2CH_2O$), 3.92-4.04 (m, 24H, $CH_2C\underline{H}_2O$), 4.41 (s, 2H, CH_2Br), 4.96 (s, 4H, Ar-CH_2O-Ar), 6.43 (t, 2H, *J* = 2.1 Hz, Ar-H), 6.60 (m, 5H, Ar-H), 6.64 (d, 2H, *J* = 2.1 Hz, Ar-H), 6.95 (d, 16H, *J* = 8.7 Hz, Ar-H), 7.46 (d, 16H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 29.1, 29.2, 29.3, 32.6, 33.6, 67.9, 68.1, 70.2, 100.9, 102.3, 105.8, 108.2, 114.7, 127.6, 133.3, 133.4, 138.8, 139.7, 158.2, 158.3, 160.0, 160.5.

MALDI-TOF	$C_{117}H_{147}BrO_4Na$	$[M+Na^+]$	calculated:	1877.99
			found:	1878.43

[M-2]-C

Prepared according to General procedure C.

800 mg (0.43 mmol) **[M-2]-Br**, 40 mg (0.13 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 267 mg (1.94 mmol) K_2CO_3, 23 mg (0.086 mmol) 18-crown[6], 10 ml abs. acetone, 5 ml abs. THF. Column chromatography (hexane-dichloromethane 1:1).

256 mg (35 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.25

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.98 (t, 36H, *J* = 6.8 Hz, $CH_2C\underline{H}_3$), 1.36-1.64 (m, 120H, CH_2), 1.86 (m, 72H, $C\underline{H}_2CH_2O$), 2.17 (s, 3H, CH_3), 4.01 (m, 72H, $CH_2C\underline{H}_2O$), 5.01 (m, 18H, Ar-CH_2O-Ar), 6.48 (m, 6H, Ar-H), 6.63 (m 15H, Ar-H), 6.75 (m, 6H, Ar-H), 6.92 (d, 6H, *J* = 8.8 Hz, Ar-H), 6.98 (d, 48H, *J* = 8.4 Hz, Ar-H), 7.07 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.50 (d, 48H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.8, 29.1, 29.2, 29.3, 30.8, 31.6, 51.0, 67.8, 68.0, 69.8, 70.0, 100.8, 101.5, 105.7, 106.3, 113.9, 114.6, 127.5, 129.6, 133.1, 133.2, 138.9, 139.5, 142.0, 156.7, 158.1, 158.2, 160.0, 160.4.

[M-3]-OH

Prepared according to General procedure A.

1.90 g (1.02 mmol) **[M-2]-Br**, 65 mg (0.46 mmol) 3,5-dihydroxy-benzylalcohol, 191 mg (1.38 mmol) K_2CO_3, 24 mg (0.092 mmol) 18-crown[6], 20 ml abs. acetone. Column chromatography (hexane-dichloromethane 1:9).

1.17 g (69 %), white solid.

R_f (dichloromethane): 0.35

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 24H, *J* = 6.8 Hz, CH_3), 1.30-1.61 (m, 80H, CH_2), 1.75-1.86 (m, 48H, $C\underline{H}_2CH_2O$), 3.91-4.02 (m, 48H, $CH_2C\underline{H}_2O$), 4.59 (d, 2H, *J* = 5.6 Hz, $C\underline{H}_2OH$),

4.96 (s, 12H, Ar-CH_2O-Ar), 6.42 (s, 4H, Ar-H), 6.51-6.60 (m, 13H, Ar-H), 6.67 (d, 4H, *J* = 1.6 Hz, Ar-H), 6.89-6.98 (m, 32H, Ar-H), 7.45 (d, 32H, *J* = 8.6 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 29.1, 29.2, 29.3, 31.6, 65.2, 67.9, 68.1, 69.9, 70.1, 100.9, 101.3, 101.6, 105.7, 106.3, 114.7, 127.6, 133.2, 133.3, 139.0, 139.3, 143.5, 158.1, 158.2, 160.0, 160.1, 160.4.

MALDI-TOF $C_{241}H_{300}O_{31}Na$ $[M+Na^+]$ calculated: 3713.18

found: 3711.71

[M-3]-Br

Prepared according to General procedure B.

1.03 g (0.354 mmol, 1 eq.) **[M-3]-OH**, 278 mg (1.06 mmol, 3 eq.) triphenylphosphine, 352 mg (1.06 mmol, 3 eq.) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:2).

1.03 g (78 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.21

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.92 (t, 24H, *J* = 6.9 Hz, CH_3), 1.28-1.32 (m, 80H, CH_2), 1.73-1.87 (m, 48H, $C\underline{H}_2CH_2O$), 3.90-4.03 (m, 48H, $CH_2C\underline{H}_2O$), 4.39 (s, 2H, CH_2Br), 4.95 (s, 12H, Ar-CH_2O-Ar), 6.41 (s, 4H, Ar-H), 6.52-6.59 (m, 11H, Ar-H), 6.61 (d, 2H, *J* = 1.9 Hz, Ar-H), 6.67 (d, 4H, *J* = 1.8 Hz, Ar-H), 6.88-6.97 (m, 32H, Ar-H), 7.44 (d, 32H, *J* = 8.7 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.0, 22.6, 25.7, 25.9, 29.2, 29.3, 31.6, 33.6, 67.9, 68.1, 70.1, 70.2, 100.9, 101.7, 102.2, 105.8, 106.4, 108.2, 114.7, 127.6, 133.3, 133.4, 139.0, 139.8, 158.1, 158.2, 160.0, 160.1, 160.5.

[M-3]-C

Prepared according to General procedure C.

810 mg (0.216 mmol) **[M-3]-Br**, 20 mg (0.080 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 50 mg (0.405 mmol) K_2CO_3, 10 mg (0.038 mmol) 18-crown[6], 10 ml abs. acetone, 5 ml abs. THF. Column chromatography (hexane-dichloromethane 1:4).

583 mg (64 %), white solid.

R_f (hexane-dichloromethane 1:9): 0.65

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.98 (t, 72H, *J* = 6.8 Hz, CH_3), 1.33-1.64 (m, 240H, CH_2), 2.15 (s, 3H, CH_3), 4.00 (m, 144H, $CH_2C\underline{H}_2O$), 5.03 (m, 42H, Ar-CH_2O-Ar), 6.45 (m, 12H, Ar-H), 6.60 (m, 33H, Ar-H), 6.72 (m, 18H, Ar-H), 6.90 (d, 6H, *J* = 8.7 Hz, Ar-H), 6.97 (d, 96H, *J* = 8.4 Hz, Ar-H), 7.03 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.49 (d, 96H, *J* = 8.4 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.6, 29.1, 29.3, 30.8, 31.6, 51.1, 67.8, 68.1, 69.5, 69.7, 70.0, 100.8, 101.7, 105.8, 106.3, 106.5, 113.9, 114.6, 114.7, 127.5, 127.6, 129.5, 133.3, 133.4, 138.9, 139.1, 139.5, 141.8, 156.9, 158.0, 158.1, 160.1, 160.3, 160.4.

6.2.4 The **S** compound family (Scheme 3.13)

[S-o]-OH

2.46 g (44mmol) KOH was dissolved in 70 ml 90 % EtOH, 4.28 g (20 mmol) 4-hydroxy-4'-carboxy-biphenyl (**20**), 5.48 g (22 mmol) dodecyl-1-bromide were added and the mixture boiled under reflux for 20 hours. Then 4.80 g KOH and 20 ml water were added and boiled under reflux for four more hours. After cooling, the mixture was poured on icewater and 20 % HCl was added until pH 3 was reached. The resulted white solid was collected by filtration. It was purified by recrystallizing from 96 % EtOH.

The tetrahydrofurane solution of the product of the previous reaction was added slowly to a stirred suspension of 0.60 g $LiAlH_4$ (15.8 mmol) in THF. When the addition was complete, the mixture was boiled under reflux for 2 h. After cooling, careful addition of acetone, water and 10 % H_2SO_4 rendered the mixture ready for extraction with EtOAc (three times 150 ml). The combined organic phases were washed with water (three times 200 ml), with brine, dried over anhydrous Na_2SO_4 and the solvent evaporated. No further purification was necessary.

5.23 g (71 % over two steps), white solid.

R_f (hexane-acetone 1:1): 0.58

Melting point: 133 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 3H, *J* = 6.4 Hz, CH_3), 1.29-1.56 (m, 18H, $(C\underline{H}_2)_9CH_3$), 1.81 (m, 2H, $C\underline{H}_2CH_2O$), 4.00 (t, 2H, *J* = 6.6 Hz, $CH_2C\underline{H}_2O$), 4.73 (s, 2H, $C\underline{H}_2OH$), 6.97 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.42 (d, 2H, *J* = 7.9, Ar-H), 7.51 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.55 (d, 2H, *J* = 7.9 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 65.2, 68.2, 114.8, 126.9, 127.5, 128.0, 133.1, 139.2, 140.4, 158.8.

MALDI-TOF	$C_{25}H_{37}O_2$	$[M+H^+]$	calculated:	369.28
			found:	369.00

[S-o]-Br

Prepared according to General procedure B.

5.13 g (13.9 mmol) **[S-o]-OH**, 5.77 g (17.4 mmol) tetrabromomethane, 4.56 g (17.4 mmol) triphenylphosphine. Column chromatography (petrolether-dichloromethane 3:1).

5.83 g (85 %), white solid.

R_f (petrolether-dichloromethane 1:1): 0.81

Melting point: 98 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.91 (t, 3H, *J* = 6.5 Hz, CH_3), 1.22-1.60 (m, 18H, ($C\underline{H}_2$)$_9CH_3$), 1.82 (m, 2H, $OCH_2C\underline{H}_2$), 4.01 (t, 2H, *J* = 6.6 Hz, OCH_2), 4.56 (s, 2H, CH_2Br), 6.98 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.44 (d, 2H, *J* = 8.4, Ar-H), 7. 51 (d, 2H, J = 6.7 Hz, Ar-H), 7.54 (d, 2H, *J* = 6.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.2, 22.8, 26.1, 29.3, 29.4, 29.5, 29.7, 29.8, 32.0, 33.6, 68.1, 114.7, 126.9, 127.9, 129.3, 132.5, 135.9, 140.9, 158.8.

MALDI-TOF	$C_{25}H_{36}BrO$	$[M+H^+]$	calculated:	431.19
			found:	431.90

[S-o]-C

Prepared according to General procedure C.

113 mg 1,1,1-tris(4-hydroxyphenyl)-ethane (0.37 mmol, 1 eq.), 449 mg (1.22 mmol, 3.3 eq.) **[S-o]-Br**, 800 mg (5.8 mmol) K_2CO_3, 69 mg (0.26 mmol) 18-crown[6], 10 ml abs. acetone, 5 ml abs. THF. Column chromatography (hexane-dichloromethane 1:1).

84 mg (17 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.47

Melting point: 157 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.87 (t, 9H, *J* = 6.6 Hz, $CH_2C\underline{H}_3$), 1.20-1.53 (m, 54 H, $(C\underline{H}_2)_9CH_2CH_2O$), 1.81 (m, 6H, $C\underline{H}_2CH_2O$), 2.13 (s, 3H, CH_3), 4.00 (t, 6H, J = 6.6 Hz, $CH_2C\underline{H}_2O$), 5.06 (s, 6H, Ar-CH_2O-Ar), 6.89 (d, 6H, *J* = 8.7 Hz, ar-H), 6.97 (d, 6H, *J* = 8.6 Hz, Ar-H), 7.02 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.47 (d, 6H, *J* = 8.0 Hz, Ar-H), 7.51 (d, 6H, *J* = 8.6 Hz, Ar-H), 7.56 (d, 6H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.9, 31.9, 50.7, 68.1, 69.9, 114.0, 114.8, 126.9, 128.0, 128.1, 129.7, 133.1, 135.4, 140.6, 142.1, 156.9, 158.8.

MALDI-TOF	$C_{95}H_{120}O_6Na$	[M+Na^+]	calculated:	1379.90
			found:	1379.81

[S-1]-OH

Prepared according to General procedure A.

5.13 g (11.9 mmol) **[S-o]-Br**, 0.757 g (5.41 mmol) 3,5-dihydroxy-benzyl alcohol, 1.86 g (13.5 mmol) K_2CO_3, 0.29 g (1.1 mmol) 18-crown[6], 100 ml abs. acetone. Column chromatography (dichloromethane).

4.04 g (89 %), white solid.

R_f (dichloromethane): 0.52

Melting point: 132 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 6H, *J* = 6.6 Hz, CH_3), 1.21-1.52 (m, 36H, $(C\underline{H}_2)_9CH_3$), 1.81 (m, 4H, $C\underline{H}_2CH_2O$), 4.00 (t, 4H, *J* = 6.6 Hz, $CH_2C\underline{H}_2O$), 4.65 (d, 2H, *J* = 6.5 Hz, $C\underline{H}_2OH$), 5.08 (s, 4H, Ar-CH_2O-Ar), 6.59 (t, 1H, *J* = 2.2 Hz, Ar-H), 6.65 (d, 2H, *J* = 2.2 Hz, Ar-H), 6.97 (d, 4H, *J* = 8.8 Hz, Ar-H), 7.46 (d, 4H, *J* = 8.2 Hz, Ar-H), 7.51 (d, 4H, *J* = 8.8 Hz, Ar-H), 7.56 (d, 4H, *J* = 8.3 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 31.9, 65.4, 68.2, 70.0, 101.4, 105.9, 114.9, 126.9, 128.0, 128.1, 133.1, 135.1, 140.7, 143.5, 158.9, 160.2.

MALDI-TOF	$C_{57}H_{76}O_5Na$	[M+Na^+]	calculated:	863.56
			found:	863.50
	$C_{57}H_{76}O_5K$	[M+K^+]	calculated:	879.53
			found:	879.35

[S-1]-Br

Prepared according to General procedure B.

10.95 g (13.0 mmol) **[S-1]-OH**, 5.98 g (21.7 mmol, 1.75 eq.) triphenylphosphine, 7.56 g (21.7 mmol, 1.75 eq.) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:1).

8.69 g (74 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.24

Melting point: 118 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.86 (t, 6H, *J* = 6.2 Hz, CH_3), 1.21-1.54 (m, 36H, $(C\underline{H}_2)_9CH_3$), 1.81 (m, 4H, $C\underline{H}_2CH_2O$), 4.00 (t, 4H, *J* = 6.5 Hz, CH_2O), 4.43 (s, 2H, CH_2Br), 5.06 (s, 4H, Ar-CH_2O-Ar), 6.59 (t, 1H, *J* = 2.1 Hz, Ar-H), 6.67 (d, 2H, *J* = 2.1 Hz, Ar-H), 6.97 (d, 4H, *J* = 8.6 Hz, Ar-H), 7.46 (d, 4H, *J* = 8.1 Hz, Ar-H), 7.51 (d, 4H, *J* = 8.6 Hz, Ar-H), 7.57 (d, 4H, *J* = Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 33.6, 68.1, 70.0, 102.2, 108.2, 114.8, 126.9, 128.1, 133.0, 134.9, 139.8, 140.8, 158.8, 160.1.

MALDI-TOF $C_{57}H_{75}BrO_4Na$ [$M+Na^+$] calculated: 925.47

found: 925.59

[S-1]-C

Prepared according to General procedure C.

800 mg (0.887 mmol) **[S-1]-Br**, 90 mg (0.296 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 170 mg (1.2 mmol) K_2CO_3, 20 mg (0.060 mmol) 18-crown[6], 30 ml abs. acetone, 10 ml abs. THF. Column chromatography (hexane-dichloromethane 2:1).

238 mg (29 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.45

Melting point: 105 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.97 (t, 18H, *J* = 6.4 Hz, $CH_2C\underline{H}_3$), 1.29-1.61 (m, 108H, $(C\underline{H}_2)_9CH_3$), 1.86 (m, 12H, $C\underline{H}_2CH_2O$), 2.15 (s, 3H, CH_3), 4.04 (t, 12H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 5.01 (s, 6H, Ar-CH_2O-Ar), 5.09 (s, 12H, Ar-CH_2O-Ar), 6.66 (s, 3H, Ar-H), 6.77 (m, 6H, Ar-H), 6.91 (d,

6H, *J* = 8.7 Hz, Ar-H), 7.01 (d, 12H, *J* = 8.6 Hz, Ar-H), 7.06 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.50 (d, 12H, *J* = 8.1 Hz, Ar-H), 7.56 (d, 12H, *J* = 8.6 Hz, Ar-H), 7.61 8d, 12H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 30.7, 31.9, 50.6, 68.0, 69.9, 101.5, 106.4, 114.0, 114.8, 126.8, 128.0, 129.6, 133.0, 135.0, 139.6, 140.6, 142.0, 156.7, 158.8, 160.2.

[S-2]-OH

Prepared according to general procedure A.

7.92 g (8.78 mmol) **[S-1]-Br**, 0.56 g (4.00 mmol) 3,5-dihydroxy-benzyl alcohol, 1.66 g (12.00 mmol) K_2CO_3, 211 mg (0.8 mmol) 18-crown[6], 100 ml abs. acetone. Column chromatography (dichloromethane).

3.86 g (54 %), white solid.

R_f (dichloromethane): 0.39

Melting point: 164 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 0.89 (t, 12H, *J* = 6.4 Hz, CH_3), 1.22-1.56 (m, 72H, $(C\underline{H}_2)_9CH_2CH_2O$), 1.80 (m, 8H, $C\underline{H}_2CH_2O$), 3.99 (t, 8H, *J* = 6.5 Hz, $CH_2C\underline{H}_2O$), 4.60 (d, 2H, J = 5.7 Hz, $C\underline{H}_2OH$), 5.00 (s, 4H, Ar-CH_2O-Ar), 5.07 (s, 8H, Ar-CH_2O-Ar), 6.54 (m, 1H, Ar-H), 6.61 (m, 4H, Ar-H), 6.99 (d, 4H, *J* = 1.6 Hz, Ar-H), 6.95 (d, 8H, *J* = 8.7 Hz, Ar-H), 7.44 (d, 8H, *J* = 8.1 Hz, Ar-H), 7.50 (d, 8H, *J* = 8.6 Hz, Ar-H), 7.54 (d, 8H, *J* = 8.1 Hz, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 31.9, 65.3, 68.2, 70.1, 101.5, 101.8, 106.0, 106.5, 114.9, 126.9, 128.0, 128.1, 133.1, 135.2, 139.5, 140.7, 143.5, 158.9, 160.2, 160.3.

6.2.5 The **B** compound family (Scheme 3.17)

[B-0]-Br

Prepared according to General procedure B.

7.36 g (40 mmol, 1 eq.) 4-phenyl-benzyl alcohol, 13.10 g (50.0 mmol, 1.25 eq.) triphenylphosphine, 16.58 g (50.0 mmol, 1.25 eq.) tetrabromomethane. Column chromatography: hexane-dichloromethane 3:1.

8.79 g (89 %) white crystalline solid.

R_f (hexane-dichloromethane 1:1): 0.69

Melting point: 84 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.58 (s, 2H, CH_2), 7.40 (t, 1H, *J* = 7.3 Hz, Ar-H), 7.44-7.54 (m, 4H, Ar-H), 7.58-7.66 (m, 4H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 33.3, 127.1, 127.4, 127.5, 128.8, 129.4, 136.7, 140.4, 141.3.

[B-o]-C

Prepared according to General procedure C.

459 mg 1,1,1-tris(4-hydroxyphenyl)-ethane (1.5 mmol, 1 eq.), 1.22 g (4.95 mmol, 3.3 eq.) **[B-o]-Br**, 850 mg (6.2 mmol) K_2CO_3, 10 mg (0.030 mmol) 18-crown[6], 30 ml abs. acetone, 10 ml abs. THF.

Column chromatography (hexane-dichloromethane 2:1).

977 mg (81 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.38

Melting point: 190 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.13 (s, 3H, CH_3), 5.09 (s, 6H, CH_2), 6.90 (d, 6H, *J* = 8.9 Hz, Ar-H), 7.03 (d, 6H, *J* = 8.8 Hz, Ar-H), 7.35 (t, 3H, *J* = 7.3 Hz, Ar-H), 7.45 (m, 6H, Ar-H), 7.51 (d, 6H, *J* = 8.1 Hz, Ar-H), 7.60 (m, 12H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 30.9, 69.8, 110.0, 114.0, 127.1, 127.3, 128.0, 128.8, 129.7, 136.2, 140.8, 141.0, 142.1, 156.9.

MALDI-TOF	$C_{59}H_{48}O_3Na$	$[M+Na^+]$	calculated:	827.35
			found:	827.37

[B-1]-OH

Prepared according to General procedure A.

6.18 g (25 mmol) **[B-o]-Br**, 2.57 g (11.9 mmol) 4-(3,5-dihydroxy-phenyl)-benzyl alcohol (**13**), 4.11 g (29.8 mmol) K_2CO_3 and 628 mg 18-crown[6] (2.38 mmol). Recrystallized from hexane-toluene 1:3.

5.15 g (79 %), white solid.

R_f (dichloromethane-methanol 19:1): 0.72

Melting point: 185 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.76 (d, 2H, *J* = 5.3 Hz, C$\underline{H}_2$OH), 5.16 (s, 4H, Ar-CH_2O-Ar), 6.69 (t, 1H, *J* = 2.2 Hz, Ar-H), 6.88 (d, 2H, *J* = 2.2 Hz, Ar-H), 7.36 (m, 2H, Ar-H), 7.42-7.48 (m, 6H, Ar-H), 7.53 (d, 4H, *J* = 8.1 Hz, Ar-H), 7.56-7.66 (m, 10H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 65.1, 70.0, 101.0, 106.7, 127.1, 127.4, 128.0, 128.8, 135.8, 140.3, 140.5, 140.8, 141.0, 143.1, 160.3.

HRMS (ESI) $C_{39}H_{32}O_3Ag$ $[M+Ag^+]$ calculated: 655.1402
found: 655.1399

[B-1]-Br

Prepared according to General procedure B.

7.43 g (13.6 mmol, 1 eq.) **[B-1]-OH**, 4.45 g (17.0 mmol, 1.25 eq.) triphenylphosphine, 5.64 g (17.0 mmol, 1.25 eq.) tetrabromomethane. Column chromatography: petrolether-dichloromethane 2:1.

7.64 g (92 %) white crystalline solid.

R_f (hexane-dichloromethane 1:1): 0.33

Melting point: 148 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.55 (s, 2H, CH_2Br), 5.15 (s, 4H, OCH_2), 6.69 (t, 1H, *J* = 2.1 Hz, Ar-H), 6.86 (d, 2H, *J* = 2.1 Hz, Ar-H), 7.36 (t, 2H, *J* = 7.3 Hz, Ar-H), 7.45 (m, 6H, Ar-H), 7.54 (m, 6H, Ar-H), 7.62 (m, 8H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 33.2, 70.0, 101.3, 106.8, 127.1, 127.4, 127.6, 128.0, 128.8, 129.5, 135.8, 137.1, 140.8, 141.1, 141.2, 142.7, 160.3.

HRMS (ESI) $C_{39}H_{31}O_2BrAg$ $[M+Ag^+]$ calculated: 717.0558
found: 717.0556

[B-1]-C

Prepared according to General procedure C.

123 mg (0.4 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 806 mg (1.32 mmol) **[B-1]-Br**, 208 mg (1.50 mmol) K_2CO_3, 50 mg 18-crown[6], 30 ml abs. acetone. Column chromatography (hexane-dichloromethane 2:1).

622 mg (82 %), white solid.

R_f (hexane-dichloromethane 1:1): 0.36

Melting point: 97-100 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.14 (s, 3H, CH_3), 5.09 (s, 6H, CH_2), 5.16 (s, 12H, CH_2), 6.69 (s, 3H, Ar-H), 6.89 (d, 6H, *J* = 1.4 Hz, Ar-H), 6.91 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.04 (d, 6H, *J* = 8.6 Hz, Ar-H), 7.36 (t, 6H, *J* = 7.8 Hz, Ar-H), 7.41-7.57 (m, 30 H, Ar-H), 7.58-7.69 (m, 30H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 30.8, 50.7, 69.8, 70.0, 101.1, 106.7, 114.0, 127.1, 127.4, 127.9, 128.0, 128.8, 129.7, 135.8, 136.5, 140.8, 141.0, 142.1, 143.1, 156.9, 160.3.

[B-2]-OH

Prepared according to General procedure A.

7.60 g (12.4 mmol) **[B-2]-OH**, 1.28 g (5.92 mmol) 4-(3,5-dihydroxy-phenyl)-benzyl alcohol (**13**), 2.05 g (14.8 mmol) K_2CO_3 and 200 mg 18-crown[6] (0.76 mmol) in 80 ml abs. acetone. Recrystallized from hexane-toluene 1:3.

6.65 g (88 %), white solid.

R_f (dichloromethane): 0.45

Melting point: 140-145 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.75 (s, 2H, $C\underline{H}_2OH$), 5.15 (s, 12H, CH_2O-Ar), 6.69 (m, 3H, Ar-H), 6.89 (m, 6H, Ar-H), 7.36 (t, 4H, *J* = 7.3 Hz, Ar-H), 7.45 (m, 12H, Ar-H), 7.53 (m, 12H, Ar-H), 7.57-7.68 (m, 20H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 65.1, 70.0, 101.0, 101.1, 106.7, 127.1, 127.4, 128.0, 128.8, 135.8, 136.2, 140.3, 140.4, 140.7, 140.8, 141.0, 143.0, 143.1, 160.3.

MALDI-TOF	$C_{91}H_{72}O_7Na$	$[M+Na^+]$	calculated:	1299.52
			found:	1299.58

[B-2]-Br

Prepared according to General procedure B.

2.73 g (2.14 mmol) **[B-2]-OH**, 876 mg (3.20 mmol, 1.5 eq.) triphenylphosphine, 1.11 g (3.20 mmol, 1.5 eq.) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:1).

1.98 g (69 %), white powder.

R_f (hexane-dichloromethane 1:1): 0.19

Melting point: 145-150 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.55 (s, 2H, CH_2Br), 5.16 (s, 12H, CH_2O), 6.70 (t, 3H, *J* = 2.1 Hz, Ar-H), 6.87 (d, 2H, *J* = 2.0 Hz, Ar-H), 6.90 (s, 4H, *J* = 2.1 Hz, Ar-H), 7.37 (t, 4H, *J* = 7.1 Hz, Ar-H), 7.46 (m, 12H, Ar-H), 7.53 (m, 12H, Ar-H), 7.62 (m, 20H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 33.2, 70.0, 101.1, 101.3, 106.7, 127.1, 127.4, 127.5, 127.9, 128.0, 128.8, 129.4, 135.8, 136.1, 137.1, 140.8, 140.9, 141.0, 141.1, 142.7, 143.0, 160.3.

[B-2]-C

Prepared according to General procedure C.

42 mg (0.136 mmol) 1,1,1-tris(4-hydroxyphenyl)-ethane, 600 mg (0.448 mmol) **[B-2]-Br**, 94 mg (0.680 mmol) K_2CO_3, 20 mg 18-crown[6], 15 ml abs. acetone, 5 ml abs. THF. Column chromatography (hexane-dichloromethane 1:2).

305 mg (55 %), white solid.

R_f (hexane-dichloromethane 1:2): 0.41

Melting point: 125-130 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.14 (s, 3H, CH_3), 5.08 (s, 6H, CH_2O), 5.14 (s, 36H, CH_2O), 6.69 (m, 9H, Ar-H), 6.89 (m, 24H, Ar-H), 7.05 (d, 6H, *J* = 8.7 Hz, Ar-H), 7.36 (t, 12H, *J* = 7.1 Hz, Ar-H), 7.45 (t, 24H, *J* = 7.3 Hz, Ar-H), 7.58-7.67 (m, 120H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 30.8, 50.7, 69.7, 70.0, 101.1, 106.7, 114.0, 127.1, 127.3, 128.0, 128.1, 128.8, 129.7, 135.8, 136.2, 136.5, 140.7, 140.8, 141.0, 142.1, 143.0, 143.1, 156.8, 160.3.

[B-3]-OH

Prepared according to General procedure A.

2.78 g (2.08 mmol) **[B-2]-Br**, 214 mg (0.989 mmol) 4-(3,5-dihydroxy-phenyl)-benzyl alcohol (**13**), 341 mg (2.47 mmol) K_2CO_3, 50 mg 18-crown[6], 30 ml abs. acetone, 30 ml abs. THF. Column chromatography (dichloromethane).

1.59 g (59 %), white solid.

R_f (dichloromethane): 0.47

Melting point: 125-130 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.73 (d, 2H, *J* = 5.5 Hz, C$\underline{H}_2$OH), 5.13 (s, 28H, CH_2O), 6.67 (s, 7H, Ar-H), 6.87 (s, 14H, Ar-H), 7.35 (t, 8H, *J* = 7.2 Hz, Ar-H), 7.44 (m, 18H, Ar-H), 7.51 (m, 30H, Ar-H), 7.60 (m, 40H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 65.1, 70.0, 101.1, 106.7, 127.1, 127.4, 128.0, 128.0, 128.7, 135.8, 136.2, 140.3, 140.4, 140.7, 140.8, 141.0, 143.0, 160.3.

[B-3]-Br

Prepared according to General procedure B.

1.18 g (0.432 mmol) **[B-3]-OH**, 226 mg (0.864 mmol, 2 eq.) triphenylphosphine, 287 mg (0.864 mmol, 2 eq.) tetrabromomethane. Column chromatography (hexane-dichloromethane 1:3).

1.01 g (83 %), white solid.

R_f (hexane-dichloromethane 1:4): 0.42

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.53 (s, 2H, CH_2Br), 5.13 (s, 28H, Ar-CH_2O-Ar), 6.67 (t, 7H, J = 2.1 Hz, Ar-H), 6.82-6.90 (m, 14H, Ar-H), 7.35 (t, 8H, J = 7.3 Hz, Ar-H), 7.39-7.65 (m, 100H, Ar-H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 33.2, 70.0, 101.1, 106.7, 127.1, 127.4, 127.5, 128.0, 128.1, 128.8, 129.4, 135.8, 136.2, 140.7, 140.8, 141.0, 143.0, 160.3.

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8 List of publications*

*: in some of the publications my authorname (Gergely Gulyás-Fekete) is used.

Related to the present thesis:

G. Gulyás-Fekete, C. J. Boluda, B. Westermann, L. A. Wessjohann
Anti-Friedel-Crafts-Type Substitution to form Biaryl Linkages
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Erklärung

Hiermit erkläre ich an Eides Statt, dass ich die vorliegende Arbeit selbstständig und nur unter Verwendung der angegebenen Literatur und Hilfsmittel angefertigt habe. Diese Arbeit wurde bisher an keiner anderen Institution zur Erlangung eines akademischen Grades vorgelegt.

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