

Syntheses and Mesophase Characterizations

of Novel Bent-Core Molecules



Dissertation

zur Erlangung des akademischen Grades
doctor rerum naturalium (Dr. rer. nat.)

vorgelegt der

**Mathematisch-Naturwissenschaftlich-Technischen Fakultät
(mathematisch-naturwissenschaftlicher Bereich)
der Martin-Luther -Universität Halle-Wittenberg**

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geb. am 7. November 1965 in Shanghai, V. R. China**

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Halle(Saale), Deutschland, 11. September. 2000.

Acknowledgment

This work was carried out at the institute of organic chemistry, Martin-Luther University Halle-Wittenberg, from April 1997 till June 2000 under the direction of Prof. C. Tschierske.

My sincerest thanks go to Prof. C. Tschierske for the chance of finishing this work in his working group, for his most valuable advice and encouragement in research, and constant support at all stages of my Ph.D. studies.

I am gratefully thankful to Dr. S. Diele and his group for the X-ray investigations, I thanks also heartily Prof. G. Pelzl and Miss I. Wirth for the valuable discussion and advice on the electrooptical study, Prof. H. Kresse and Dr. H. Schmalfuss for the dielectric investigation.

My appreciation is also extended to all of the colleague in the working group for their discussion and helping, the colleague at the institute of organic chemistry for their most valuable service.

Thanks are due to my family and my friends for their support and encouragement.

The Educational Committee of China and the Kultusministerium des Lands Sachsen-Anhalt are gratefully acknowledged for their financial support.

Abbreviations

The following abbreviations are used in this work:

Ar	Aromatic
n-Bu	n-Butyl group
t-Bu	tert-Butyl group
CMC	<i>N</i> -Cyclohexyl- <i>N'</i> -(2-morpholinoethyl)carbodiimide methyl- <i>p</i> -toluolsulfonat
Col _r	Rectangular columnar phase
Cr	Crystalline phase
DHP	3,4-Dihydro-2H-pyran
DMAP	4-Dimethylaminopyridine
DMF	<i>N,N</i> -Dimethylformamide
DMSO	Dimethyl sulfoxide
Et	Ethyl
EtOH	Ethanol
Iso	Isotropic phase
MCPBA	<i>m</i> -Chloroperbenzoic acid
MeOH	Methanol
N	Nematic phase
NLO	Non linear optics
P	Polarization
Ps	Spontaneous polarization
PTSA	<i>p</i> -Toluenesulphonic acid
RT	Room temperature (25 °C)
SmA	Smectic A phase
SmC	Smectic C phase
SmC*	Chiral smectic C phase
SmCP _A	Tilted smectic phase with a polar order of the molecules within the layers and an antiferroelectric interlayer correlation
Sm _{intercal}	Intercalated smectic phase
THF	Tetrahydrofuran

THP	Tetrahydropyranyl
Sm _b	Optically biaxial smectic phase of unknown precise structure
SmC _b	Tilted smectic phase built up by biaxial molecules
SmC _(b)	Tilted smectic phase built up by uniaxial or biaxial molecules (SmC or SmC _b)
SmC _M	McMillan phase (SmA phase built up by biaxial molecules)

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Supplement

Zusammenfassung

I Introduction

1 Liquid crystalline phases

Matter can have three different states: solid, liquid and gaseous. If a solid is heated, it usually melts at a fixed temperature and transforms into the liquid state. However there are also some substances which have no direct transition between the solid and the liquid state. Intermediate states between solid and liquid states can be found for these substances which are called mesophases. These mesophases can be plastic crystals or liquid crystalline phases.¹ In the solid state, the molecules have a long range positional and orientational order whereas in the liquid state the molecules have only a short range order and the individual molecules are mobile. In the liquid crystalline phases, the molecules have lost some degree of order of the solid state, and have got some degree of mobility, so they have some characteristics of the solid state and of the liquid state, for example, anisotropic physical properties and

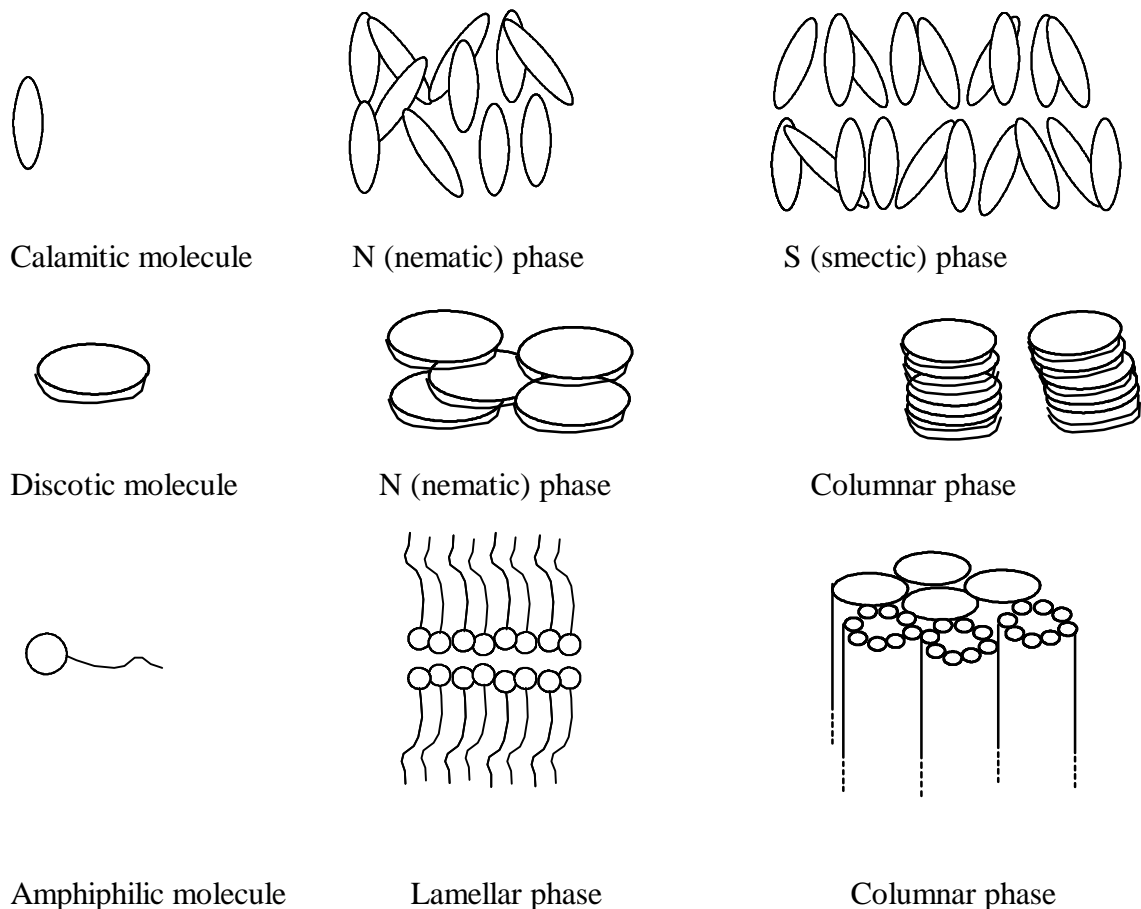


Figure 1-1 Examples of liquid crystalline molecules and phases.

mobility.² A proper molecular structure is required for molecules to be liquid crystals. Liquid crystalline materials have developed to a large family and they have quite different structures. Usually they are divided into two groups:³ Materials which form liquid crystalline phase as pure materials only in dependence on the temperature are thermotropic liquid crystals. If the mesophases are induced by a solvent in a certain temperature interval, they are called lyotropic liquid crystals. Usually, thermotropic liquid crystalline phases are formed by rod-like (calamitic) molecules and by disc-like (discotic) molecules. Both of them can form nematic phase in which molecules have only a long range orientational order. Calamitic molecules can exhibit additional smectic phase in which molecules are ordered in layers whereas discotic molecules can exhibit columnar phase in which molecules are stacked one on top of one another to build up columns. Lyotropic liquid crystals can be formed by amphiphilic molecules, in (mostly protic) solvent. Here we can distinguish lamellar, columnar and different cubic mesophases. Nematic phases are quite rare in lyotropic systems (figure 1-1). These classic molecular structures can be modified in different ways to obtain special features. For example, if the molecules are chiral, then chiral phases can exist in place of the non-chiral phases.⁴ For calamitic molecules, chiral nematic (cholesteric) and chiral smectic C-phases (SmC*) replace the usual nematic (N) and smectic C-phase (SmC) respectively.⁵ SmC* phases are of special interest because of their ferroelectric properties which can be used for technical applications, for example, in fast-switching electrooptic devices.⁶

2 Ferroelectricity

The concept of ferroelectricity first came from solid state physics. It was found that some crystals have a spontaneous polarization even without an external electric field. If the direction of this spontaneous polarization can be changed with the changing of the direction of an external field, the material has ferroelectricity.⁷ Ferroelectricity in liquid crystals was first found by Meyer.⁸ In 1975 Meyer reported about ferroelectricity occurring in a fluid liquid crystalline phase which is based on a tilted arrangement of homochiral molecules in layers (e.g. smectic C-phase) which generates C_{2v} symmetry and allows the occurrence of a spontaneous electric polarization. The polarization results from the parallel alignment of that part of the molecular dipole moments which is directed along the C_2 -axis (ferroelectric order).⁹ The direction of the layer dipole changes slightly from layer to layer so that a helical

structure is generated. In this way the system escapes from a macroscopic polarization. By surface alignment, the helical structure can be unwound, and a macroscopic polar phase is formed (see figure 1-2). Later on, antiferroelectricity and ferroelectricity¹⁰ were also found in liquid crystals. In the antiferroelectric phases the polarization cancels out from layer to layer, whereas in ferroelectric phases the polarization in subsequent layers is only partially compensated (figure 1-3).

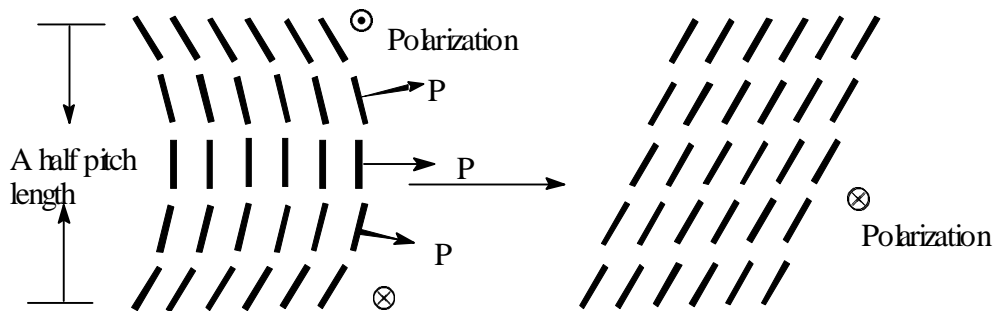


Figure 1-2 Chiral smectic C- phase (SmC*) Ferroelectric phase

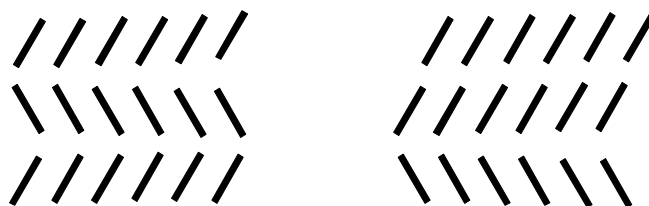


Figure 1-3 Antiferroelectric phase Ferroelectric phase

3 Ferroelectricity and chirality in liquid crystals

Because of the potential industrial application, ferroelectricity in liquid crystals attracted considerable interest as soon as it was discovered. The first ferroelectric liquid crystals were obtained with chiral molecule organized in SmC^* phases. A lot of such new chiral ferroelectric liquid crystals have been synthesized during the last decades.¹¹ Based on these experiments, chirality was believed to be essential for liquid crystalline molecules to have ferroelectric properties.¹² But this is not the fact. The basic requirement for a material to be ferroelectric is that the system must be non-centrosymmetric. Then, a macroscopic polarization can exist in the system. So the essentiality of ferroelectricity in liquid crystals is the polar arrangement, not the chirality. If rod-like molecules have some sufficiently incompatible subunits, and the lateral attraction between indential segments of adjacent

molecules is sufficiently strong, then it is also possible for the molecules to form non-centrosymmetric structures, although these molecules are achiral (polyphilic molecules).¹⁵ This was already predicted by theory,^{13,14} but for a long time ferroelectricity was only found with chiral molecules in practice.

In the last decade great effort has been made to find achiral molecules forming switchable phases. For example, polyphilic molecules¹⁵ and bowl-shaped molecules¹⁶ have been designed to obtain non-chiral ferroelectric fluid (figure 1-4).

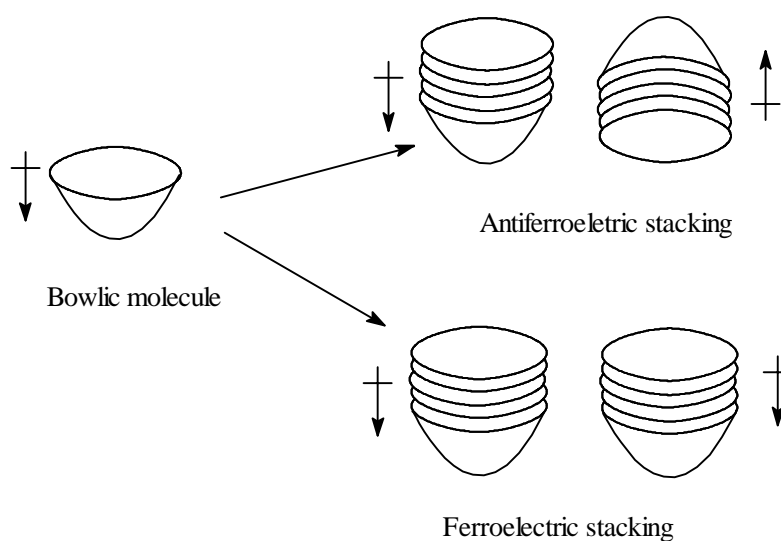


Figure 1-4 Parallel and antiparallel packing of columns of bowl-shaped molecules.

4 Bent-core molecules and their special liquid crystalline phases

The earliest report on bent-core molecules goes back to Schröter and Vorländer in 1925,¹⁷ who reported that the five ring bisesters **I** of the isophthalic acid have mesophases above 250 °C, but the type of the mesophases were not identified. This example confirmed the Vorländer's hypothesis that liquid crystallinity can be realized even in the case of strong non-linearity in the center of the mesogenic unit.¹⁸

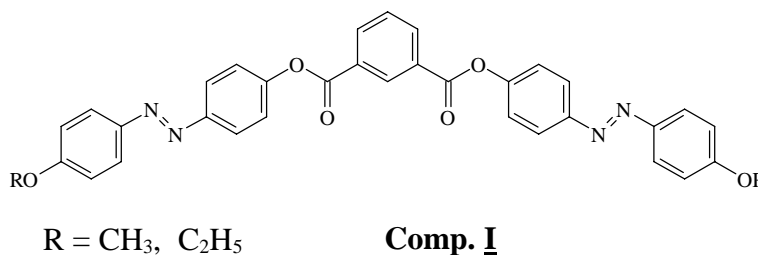
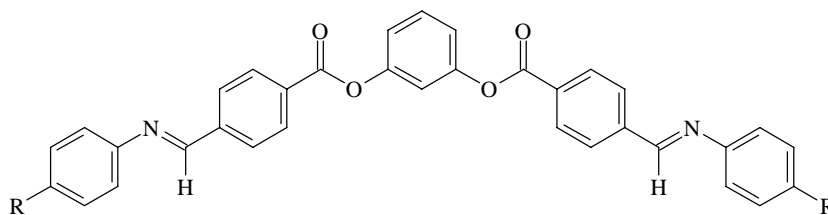


Figure 1-5 Bis-[4-(4-alkoxyphenylazo)phenyl]isophthalate (Schröter, 1925).

In 1994 Matsunaga and colleagues reported on an other homologous series of bent-core molecules.¹⁹ They synthesized 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoates] **II** and related compounds.



Comp. II: R = OC_nH_{2n+1}, **Comp. III:** R = C_nH_{2n+1} n: 1-16

Figure 1-6 1,3-Phenylene bis{4-[4-alkyl(oxy)phenyliminomethyl]benzoates }
(Matsunaga et. al. 1994).

They have observed that compounds **II** have mesomorphic behavior. All homologues having methoxy to hexadecyloxy terminal chains exhibit thermodynamically stable smectic phases with fan-shaped textures, and the butoxy to octyloxy homologues have an additional more ordered mesophase. They identified the high temperature smectic phase as a smectic C-phase (SmC), and used X-ray investigations of a homologous series to argue that the tails are nearly normal to the smectic layers whereas the cores are tilted. The occurrence of mesophases was significantly reduced by reversal of the direction of the iminomethyl linkage. Introduction of a chloro-substituent into the 4-position of the 1,3-phenylene moiety has destabilized the smectic C-phase and lead to remarkable broad nematic phases.

Current interest in bent-core molecules was promoted by investigations of Niori et. al. in 1996 revealing ferroelectricity in the mesophases of such banana-shaped molecules.²⁰ They investigated the switching behavior of this class of molecules and reported that the 1,3-phenylene bis[4-(4-alkylphenyliminomethyl)benzoates] **III** have ferroelectric properties. Two different smectic phases were detected, but only the high temperature smectic phase was switchable. One current peak was recorded during a half period by applying a triangular voltage. Based on this observation they claimed that the molecules are closely packed and aligned parallel with the bending direction pointing in the same direction in each layer, giving rise to a macroscopic polar order (see figure 1-7a).²¹ Later, they suggested that the mesomorphic ground state should have a helical structure to escape the macroscopic polarization (figure 1-7b).²² This was the first obvious example that ferroelectricity with a significant

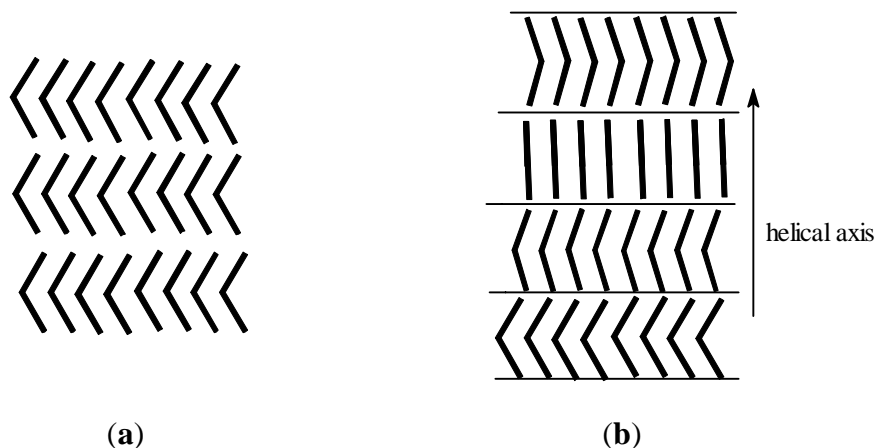


Figure 1-7 Arrangement of banana-shaped molecules in the ferroelectric phase and helical structure as suggested by Sekine et. al.

spontaneous polarization can exist in practice in a liquid crystal consisting of achiral molecules and therefore immediately arose significant interest. More detailed studies on such and related molecules have shown that these molecules have rather complicated mesomorphic and electrooptic properties. Firstly, several different mesophases were identified,²³ none of them is miscible with the conventional SmA and SmC phases of calamitic molecules. Considering the biaxiality and the bent shape of such molecules, their phase structures are not as simple as the smectic phases of calamitic molecules. So, bent-core (banana-shaped) molecules and their mesophases represent a new subfield of thermotropic liquid crystals. Because their exact structures were unknown, they were denoted as B1, B2, B3, B4, B5, B6, B7, respectively, according to the sequence of their discovery.²⁴

Secondly, Weissflog et. al. and Heppke et. al. have found that the switchable B2 phase, first

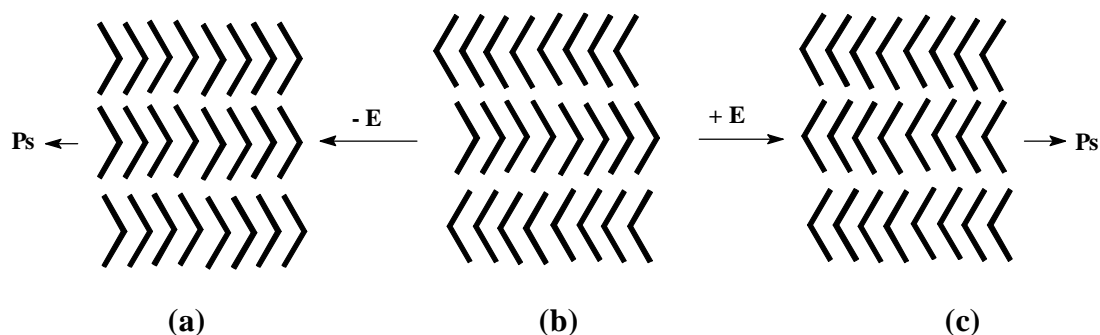


Figure 1-8 Antiferroelectric arrangement of the molecules in the ground state of the B2 phase (b) and ferroelectric switchable states (a, c).

identified as ferroelectric by Niori, has an antiferroelectric switching behavior, as two current

peaks can be observed during one half period by applying a triangular voltage.^{25,26} This was confirmed by Link et. al.. Thus, an antiferroelectric structure for the B2 phase was proposed (figure 1-8).

The following mesophases have been identified in the homologous series of compounds **II** and **III**.²⁷

B1: This mesophase was found only for the homologues **II** with short terminal chains ($n < 6$), It has a flower-like mosaic texture and a higher viscosity compared with the B2 phase. X-ray investigations have shown that it has a two dimensional structure, which can be regarded as a columnar ribbon phase.

B2: The antiferroelectric switchable smectic phase was found in both homologous series. It has a nonspecific schlieren texture. The viscosity is comparable with conventional SmA or SmC phases.

B3: This is a crystalline phase found as low temperature phase below the B2 phase.

B4: This crystalline phase has an intensive blue color. Domains of a different degree and a different sign of optical activity is the characteristic feature of this phase.

The most interesting and most often investigated mesophase formed by such banana-shaped molecules is the B2 phase because of its distinct electrooptic properties.

Link et. al. used the depolarized reflected light microscopy (DRLM) method to study thin freestanding films of the B2 phase structure more deeply.²⁸ A striking odd-even effect was observed in dependence on the number of layers (N) in the thin films. Odd-N regions were ferroelectric with c oriented normal to the electric field and the even-N regions did not respond to the field and thus are not ferroelectric. So it was proposed that the ground state of the B2 phase is actually antiferroelectric. The molecules arrange in layers whereby the layer polarization alternates from layer to layer. The resulting smectic phase is biaxial whereby one optical axis is tilted relative to the layer normal. Thus, the B2 phase was designated as SmCP_A phase, a tilted smectic phase (SmC) with antiferroelectric polar order of the molecules (P_A) within the layers. The switching behavior was investigated between crossed polarizers in regions with a well aligned focal conic texture where the smectic layers are essentially normal to the glass plates. Two types of regions, R regions (racemic) and H regions (homogeneously chiral) (figure 1-9) were coexistent.

Regions R have distinct stripes running parallel to the smectic layers and typically occupy the majority of the sample. Regions H appear with textures similar to SmA phases. Regions R

and H behave differently by applying a triangular electric field. In regions R, the texture changes to pink brushes but the brushes do not rotate. In regions H, extinction brushes rotating clockwise and anticlockwise were observed. Based on these experiments, it was proposed that the B2 phase has coexisting racemic R regions and homochiral H regions, whereby the racemic structure is the lower energy state.

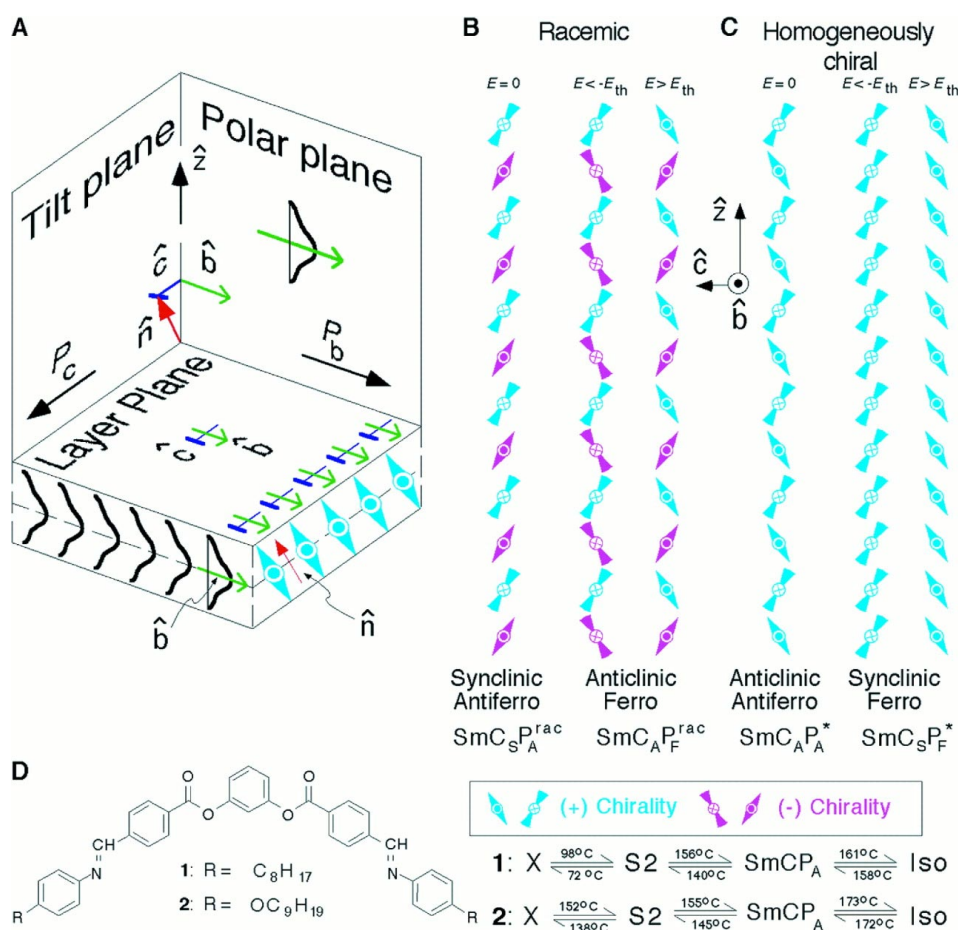


Figure 1-9 Proposed arrangement of the molecules in the H and R regions.²⁸

Weissflog et. al. have modified the basic molecules by introduction of substituents at the central unit (figure 1-10) or by replacing the phenyliminomethylbenzoate rigid cores by phenylbenzoate rigid cores.²⁹ Generally, the introduction of small substituents into the central 1,3-disubstituted phenyl ring proved to be a possibility for the synthesis of mesogens with novel B phases and for shifting the existence region of B-phases to lower temperatures.

For compounds with methyl substituents at the 2-position of the central 1,3-phenylene core ($R_2 = CH_3$) the B5 phase was formed below the B2 phase.³⁰ The enthalpy of the transition from B2 to B5 is very small and the change of the texture is also insignificant. By applying an

electric field, the B5 phase shows an electrooptical response comparable with that one of the B2 phase. If a nitro group was induced at the 2-position of the central unit ($R_2 = \text{NO}_2$),³¹

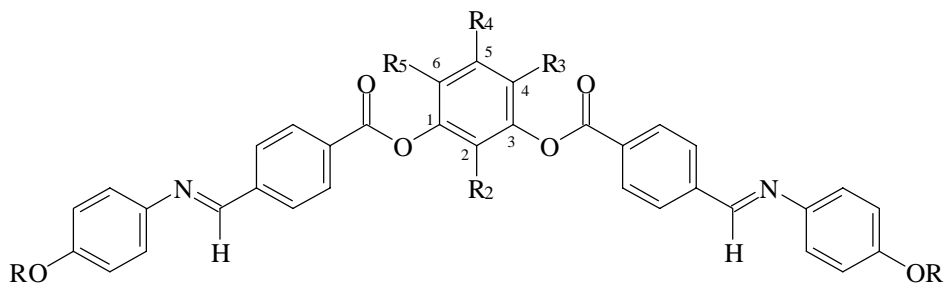
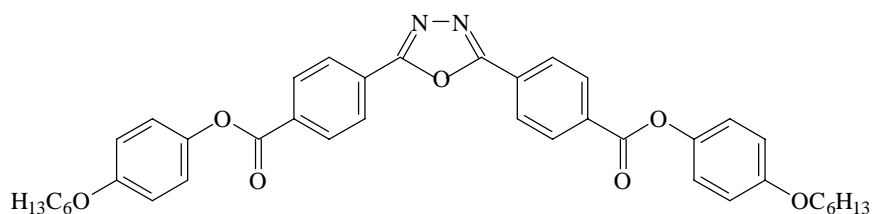


Figure 1-10 Banana-shaped molecules with substituted group in central unit
(Weissflog et. al.).

the molecules form a helix structure designed as B7 phase which was also observed for some molecules with chloro substituted aromatic rings³² and compounds with sulfur atom in the terminal chains.³³ The B7 phase exhibits quite unusual textures in which spiral domains can be seen and has also an antiferroelectric switching behavior, but the structure is still unclear. The replacement of the iminomethyl linkages by ester groups, leads to the replacement of the B2 phase by other B phases.



Cr 220 °C SmC 235 °C SmA 295 °C Iso.

Figure 1-11 Bent-core 1,3,4-oxadiazole derivative (Klaus. et. al. 1998).

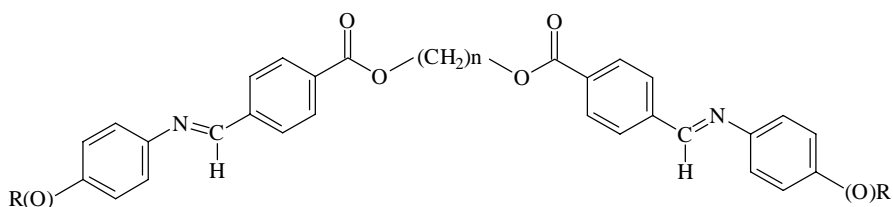


Figure 1-12 Mesogenic dimesogens incorporating odd numbered alkylene spacers
(Choi et. al. 1998).

Bent-core molecules with 2,5-disubstituted 1,3,4-oxadiazole central cores can form biaxial SmA phases³⁴ and mesogenic dimesogens with odd numbered alkylene spacers can form single layer, or double layer smectic phases as well as frustrated layer structures depending on the length of the central chains and the terminal alkyl chains.³⁵ Antiferroelectricity was detected for some representatives of this group.

Recently, very large second order NLO-effect have been measured in the switched (ferroelectric) states of B2 phases.³⁶ Hence an interesting application of such materials could be in switchable nonlinear optical devices.

5 Objectives

At the beginning of our work all banana-shaped (bent-core) molecules with antiferroelectric switchable SmCP_A phases incorporated at least one Schiff-base unit. Therefore, a major drawback of these compounds is their limited thermal, hydrolytic and photochemical stability. Furthermore, in most cases, these special mesophases occur at rather high temperatures. Additionally, the principal relationships between the molecular structure and mesomorphic properties were essentially unknown. Therefore, the main targets of this work were the design of novel stable and low-melting bent core liquid crystals without Schiff-base units and the investigation of the general structure-property relationships in this novel class of mesogens.

For simplicity, we consider the banana-shaped molecules as built up by three distinct parts, a bent central unit A, two linear rigid cores B and two terminal chains. In order to investigate the general relationship between molecular structures and mesomorphic properties, all three parts of the molecules should be changed systematically. The central cores A, will be gradually enlarged. Different rigid cores will be used (figure 1-13). The length of the terminal chains ($n = 4-14$) and the type of their connection with the rigid cores (CH₂ or O) will be changed. So, novel banana-shaped molecules with the following structural units will be synthesized, their mesomorphic properties and their switching behavior will be studied.

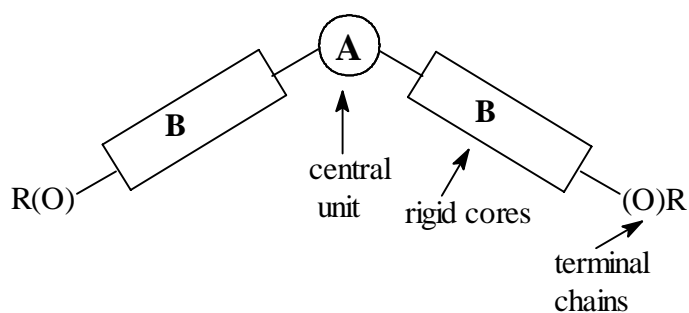
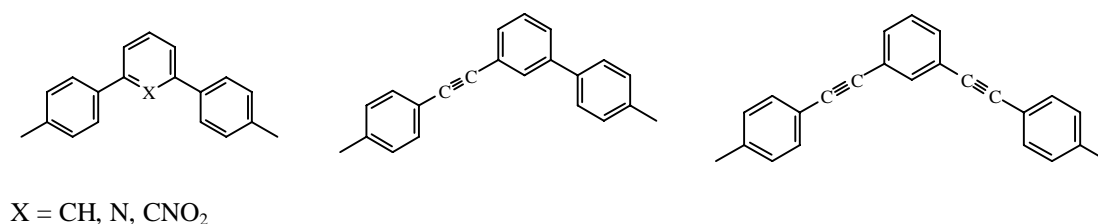
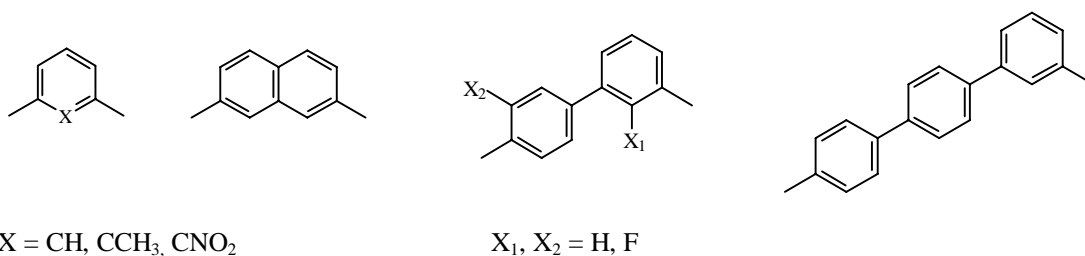
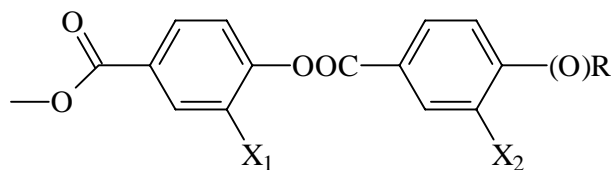
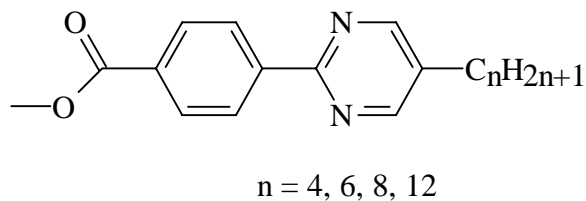


Figure 1-13 General structure of the banana-shaped molecules.

Central units (A)



Rigid cores (B)-(O)alkyl



$X_1, X_2 = H, Cl$ $R = C_nH_{2n+1}, (CH_2)_mC_nF_{2n+1}$ $n = 4, 6-14$

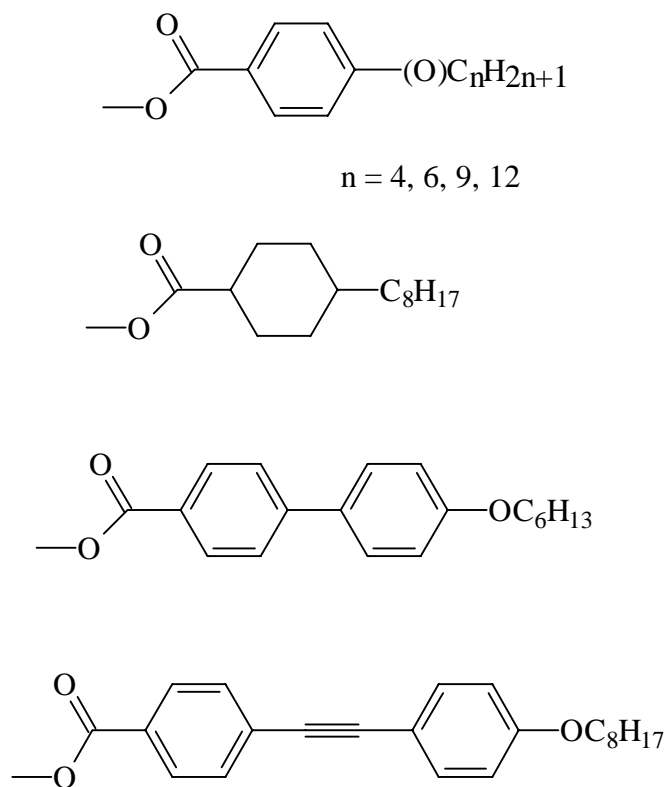


Figure 1-14 Structures of the central unit A and the rigid cores B of the novel bent-core molecules.

II Synthesis

1 Bent-core molecules with two identical rigid cores

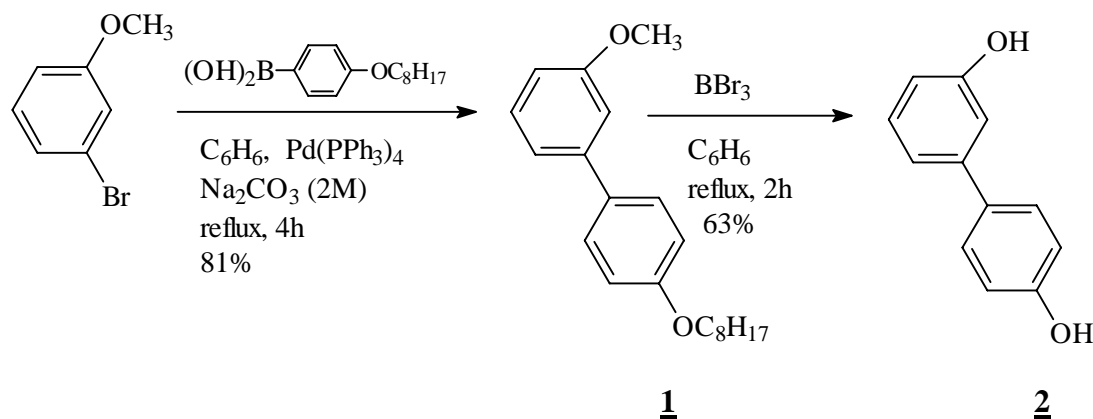
The synthesis of the compounds incorporates three distinct steps:

1. Synthesis of the central angular units (A) which in most cases represent divalent phenols.
2. Synthesis of the rigid rod segments (B) and
3. Combination of A and B to give the bent-core molecules.

1.1 Synthesis of divalent phenols

1.1.1 3,4'-Dihydroxybiphenyl 2

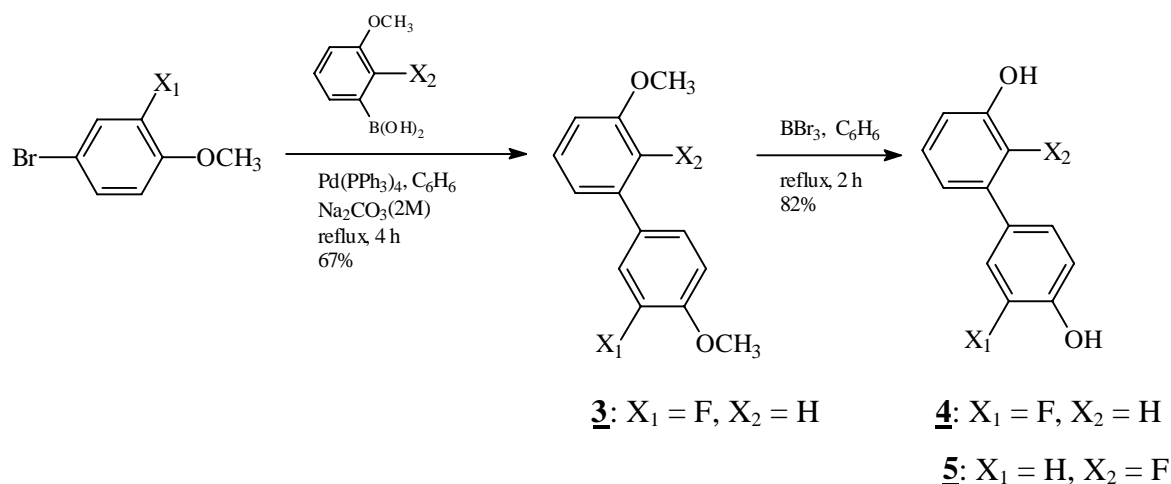
3,4'-Dihydroxybiphenyl was synthesized as shown in scheme 2-1. The first step was the Pd⁰-catalyzed Suzuki cross-coupling³⁷ of 3-bromoanisole with octyloxyphenylboronic acid. The obtained diether 1 was then cleaved with BBr₃ in benzene.³⁸



Scheme 2-1 Synthesis of the 3,4'-dihydroxybiphenyl 2.

1.1.2 3-Fluoro-4,3'-dihydroxybiphenyl 4 and 2-fluoro-3,4'-dihydroxybiphenyl 5

3-Fluoro-4,3'-dihydroxybiphenyl 4 was obtained according to scheme 2-2, similar to the synthesis of 3,4'-dihydroxybiphenyl 2 from 3-methoxyphenylboronic acid and 4-bromo-2-fluoroanisole whereas 2-fluoro-3-methoxyphenylboronic acid and 4-bromoanisole were used for the synthesis of 2-fluoro-3,4'-dihydroxybiphenyl 5.



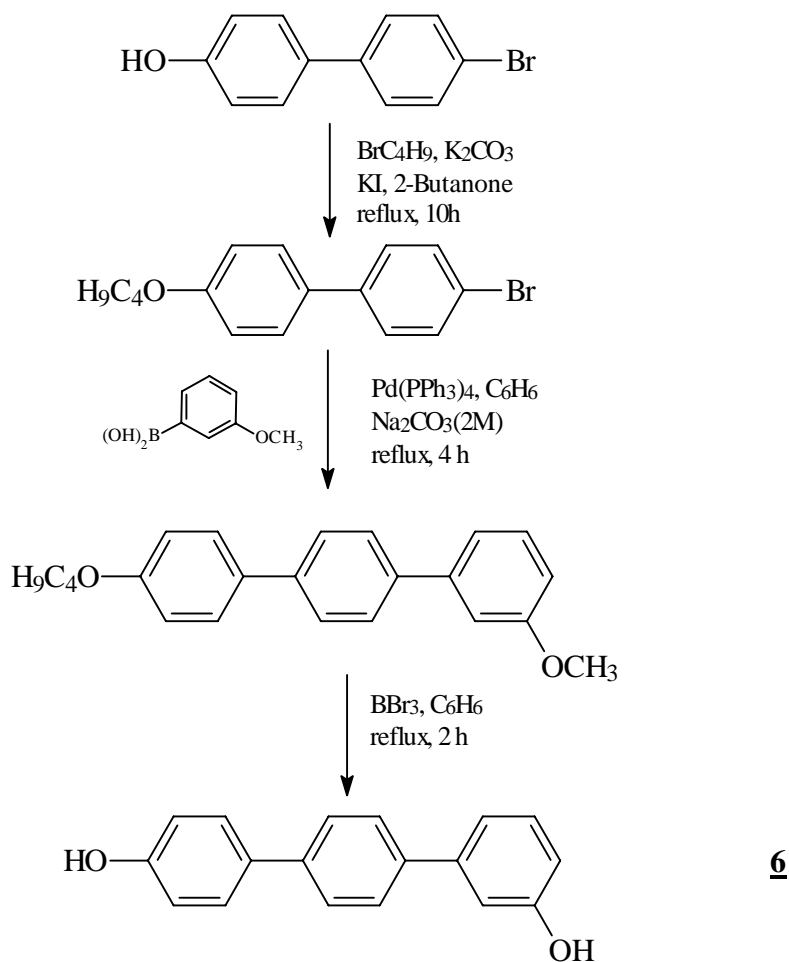
Scheme 2-2 Synthesis of 3-fluoro-4,3'-dihydroxybiphenyl **4** and 2-fluoro-3,4'-dihydroxybiphenyl **5**.

1.1.3 3,4''-Dihydroxy-1,1':4',1''-terphenyl **6**

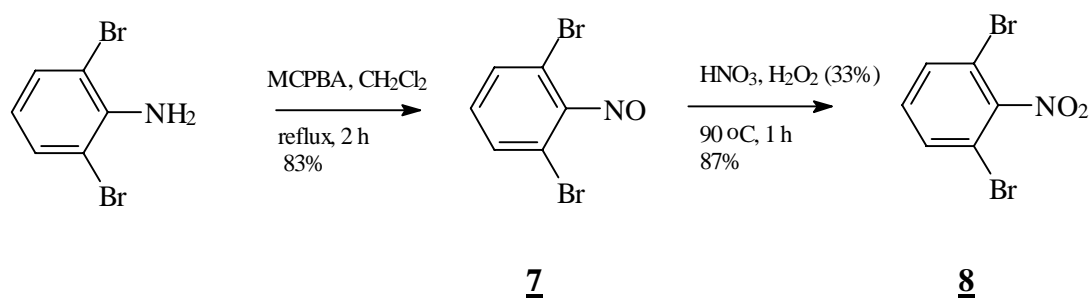
3,4''-Dihydroxy-1,1':4',1''-terphenyl was synthesized according to scheme 2-3. 4'-Bromo-4-hydroxybiphenyl was first etherified with 1-bromobutane, and then coupled with 3-methoxyphenylboronic acid to give the diether. The obtained ether was cleaved by BBr₃ to give the divalent phenol **6**.

1.1.4 4,4''-Dihydroxy-1,1':3',1''-terphenyl and 2,6-bis(4-hydroxyphenyl)pyridine

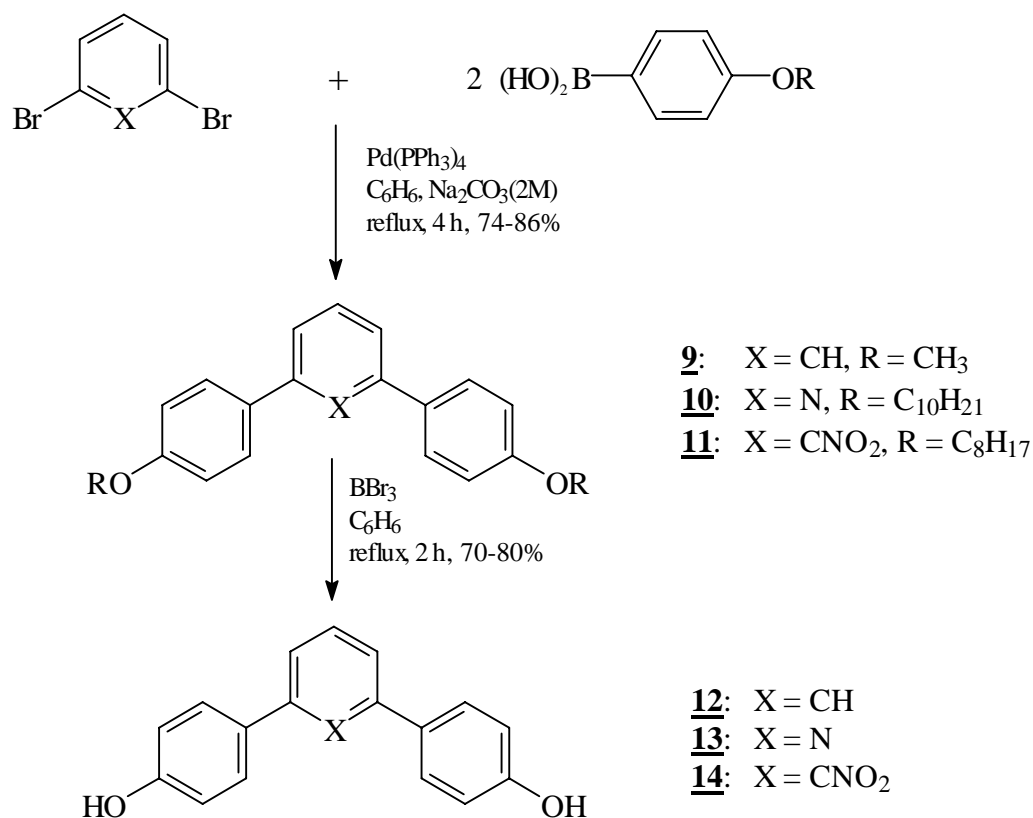
4,4''-Dihydroxy-1,1':3',1''-terphenyl **12**,³⁹ 2,6-bis(4-hydroxyphenyl)pyridine **13** and 4,4''-dihydroxy-2'-nitro-1,1':3',1''-terphenyl **14** were obtained by Pd⁰-catalyzed Suzuki cross-coupling of 1,3-dibromobenzene, 2,6-dibromopyridine or 1,3-dibromo-2-nitrobenzene, respectively, with 4-alkoxyphenylboronic acids followed by cleaving of the ethers with BBr₃ as shown in scheme 2-5. 2,6-Dibromonitrobenzene **8** was obtained by a two step oxidation.⁴⁰ At first 2,6-dibromoaniline was oxidized by MCPBA to give 2,6-dibromonitrosobenzene **7**, followed by oxidation with nitric acid to give 2,6-dibromonitrobenzene **8** (scheme 2-4). 2,6-Dibromopyridine and 1,3-dibromobenzene were commercially available.



Scheme 2-3 Synthesis of 3,4''-dihydroxy-1,1':4',1''-terphenyl **6**.



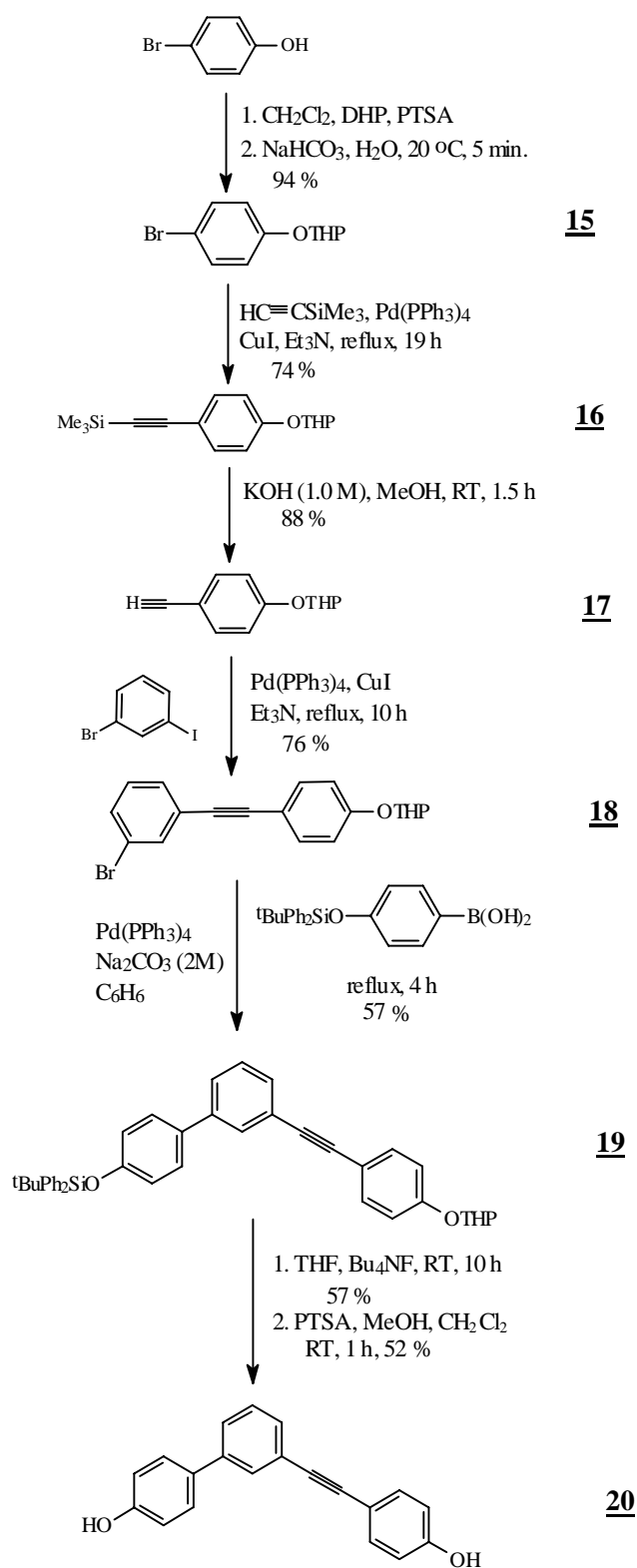
Scheme 2-4 Synthesis of 2,6-dibromonitrobenzene **8**.



Scheme 2-5 Synthesis of 4,4''-dihydroxy-1,1':3',1''-terphenyl **12** and the related divalent phenols **13** and **14**.

1.1.5 4'-Hydroxy-3-(4-hydroxyphenylethynyl)biphenyl **20**

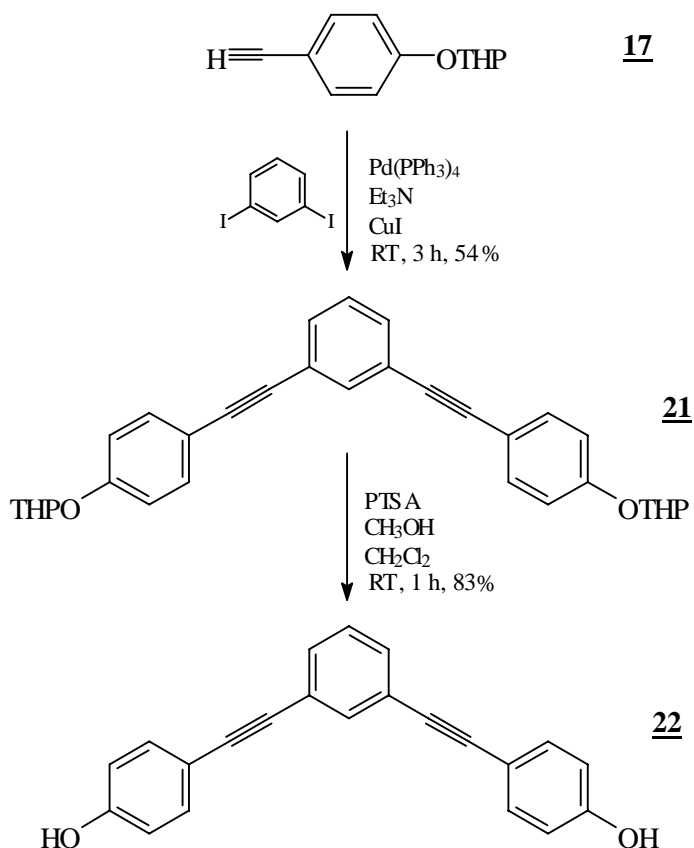
4'-Hydroxy-3-(4-hydroxyphenylethynyl)biphenyl **20** was synthesized according to scheme 2-6. Because the triple bond gives rise to serious side reactions during ether cleavage with BBr₃, the tetrahydropyranyl group was used as protective group instead of simple alkyl ethers.⁴¹ Hence, 1-bromo-4-tetrahydropyranyloxybenzene **15** was coupled with trimethylsilylacetylene under the joint influence of Pd(PPh₃)₄ and CuI. Cleavage of the C-Si bond was achieved with potassium hydroxide in methanol. The obtained 4-tetrahydropyranyloxyphenylacetylene **17** was first coupled with 1-bromo-3-iodobenzene at the iodo group. Because of the higher reactivity of the iodo group than the bromo group, only one coupling reaction takes place. Then, the resulting bromobenzene derivative **18** was coupled by Suzuki coupling with 4-(tert-butyl-diphenylsilyloxy)phenylboronic acid. Stepwise deprotection of the ether intermediate **19** with tetrabutylammonium fluoride⁴² followed by acidolysis gave the divalent phenol **20**.



Scheme 2-6 Synthesis of 4'-hydroxy-3-(4-hydroxyphenylethynyl)biphenyl **20**.

1.1.6 1,3-Bis(4-hydroxyphenylethynyl)benzene 22

The synthesis of 1,3-bis(4-hydroxyphenylethynyl)benzene 22 is shown in scheme 2-7. 4-Tetrahydropyranoxyphenylacetylene 17 was cross-coupled with 1,3-diiodobenzene. Acidolytic cleavage of the THP ether 21 gave the phenol 22.

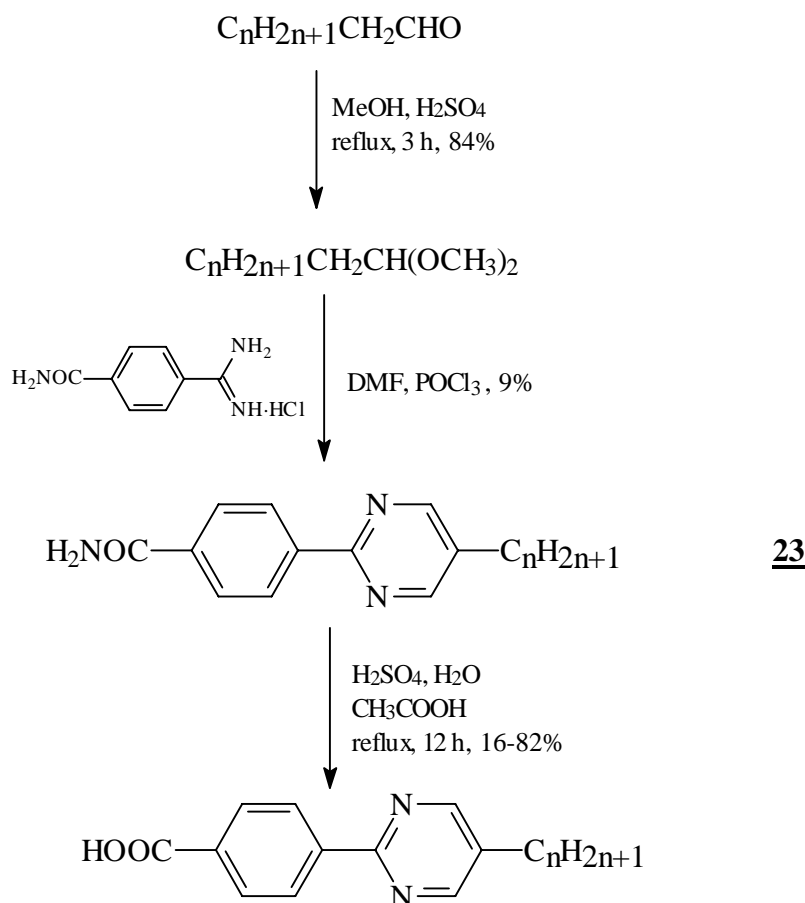


Scheme 2-7 Synthesis of 1,3-bis(4-hydroxyphenylethynyl)benzene 22.

1.2 Synthesis of the 4-substituted benzoic acids

1.2.1 4-(5-Alkylpyrimidine-2-yl)benzoic acids 24-27

4-(5-Alkylpyrimidine-2-yl)benzoic acids were synthesized according to scheme 2-8.⁴³



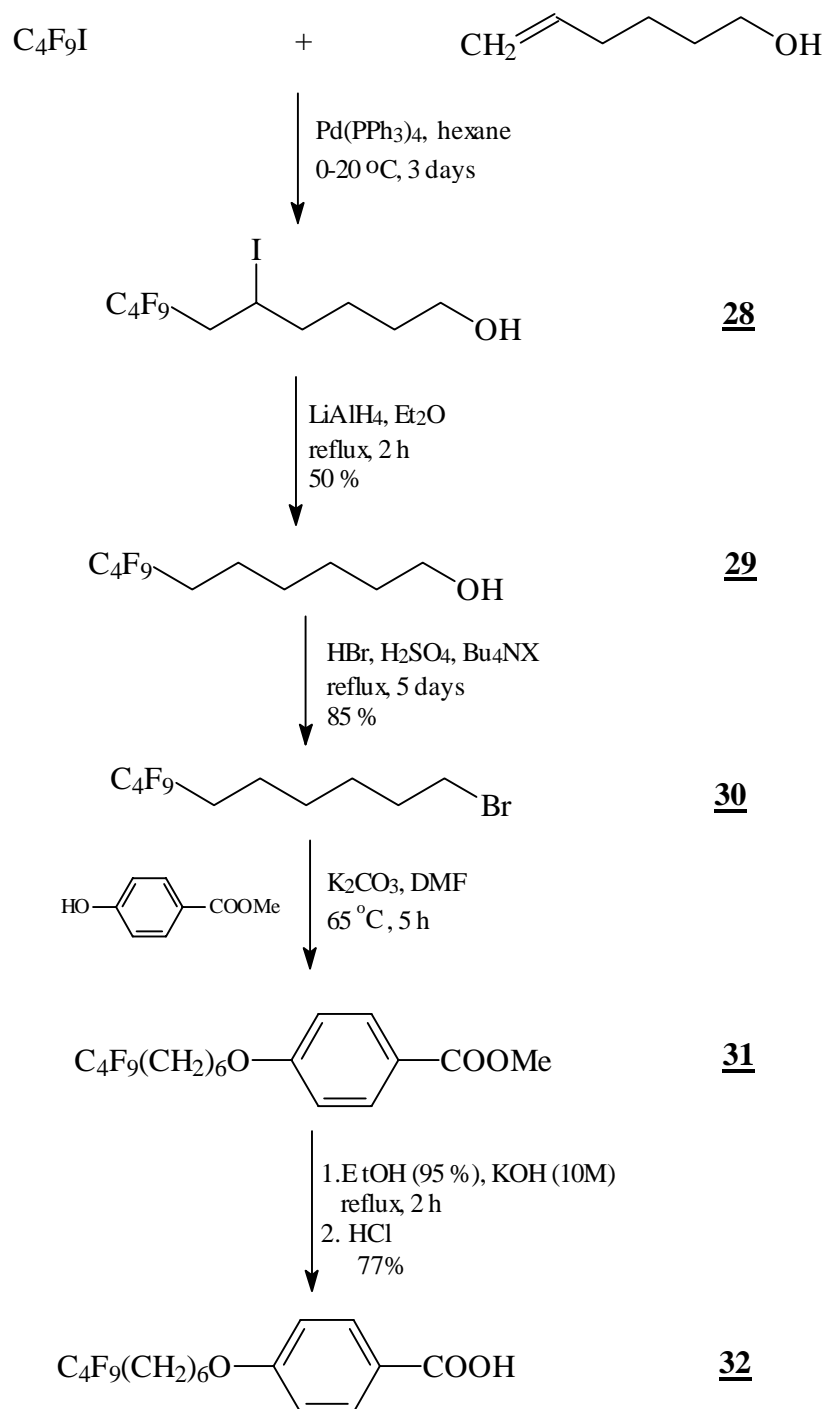
24: n = 4, 25: n = 6, 26: n = 8, 27: n = 12

Scheme 2-8 Synthetic route to the 4-(5-alkylpyrimidine-2-yl)benzoic acids.

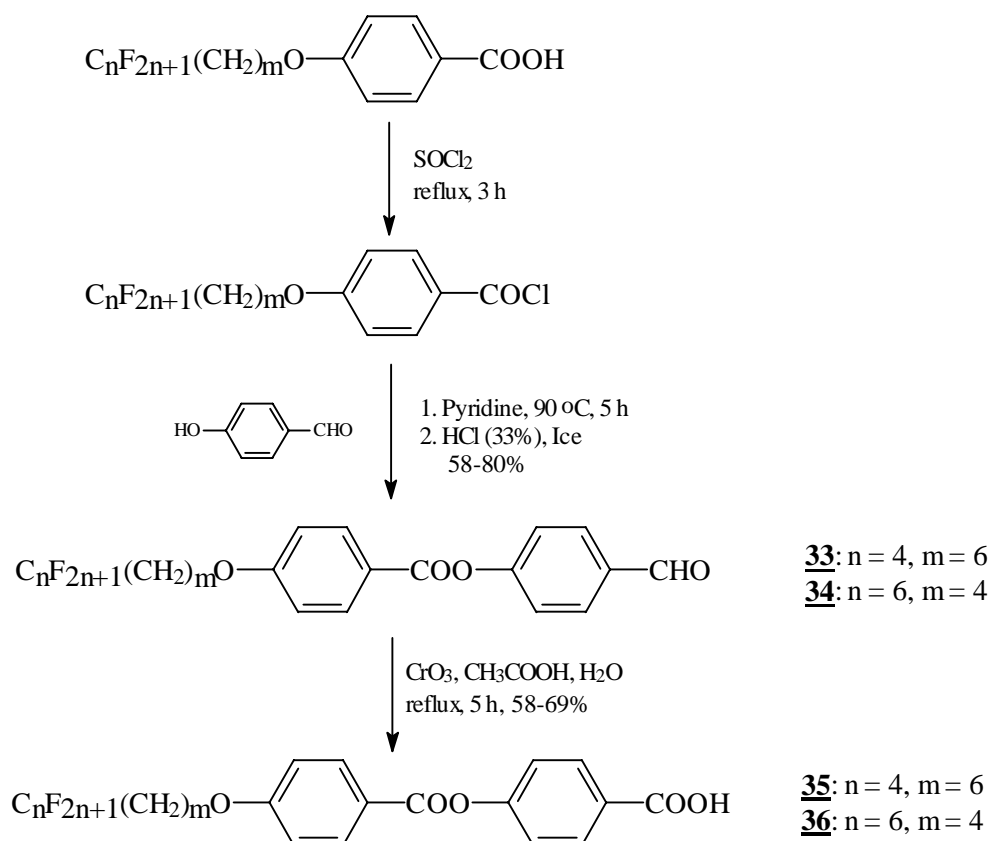
4-Amidinobenzamide hydrochloride was cyclized with 1,1-dimethoxyalkanes in DMF and POCl_3 to form 4-(5-alkylpyrimidine-2-yl)benzamides, which were then hydrolyzed to the corresponding 4-(5-alkylpyrimidine-2-yl)benzoic acids 24, 25, 26 and 27 with glacial acetic acid, and sulfuric acid. The 1,1-dimethoxyalkanes were obtained by the condensation of aldehydes with methanol under catalysis of sulfuric acid.

1.2.2 4-Benzoyloxybenzoic acids 35 and 36

All of the synthesized 4-benzoyloxybenzoic acids were obtained in the same way by oxidation of the corresponding 4-benzoyloxybenzaldehydes with CrO_3 in acetic acid.⁴⁴ As an example, the synthesis of the semifluorinated 4-(4-alkoxybenzoyloxy)benzoic acids is shown in schemes 2-9 and 2-10.



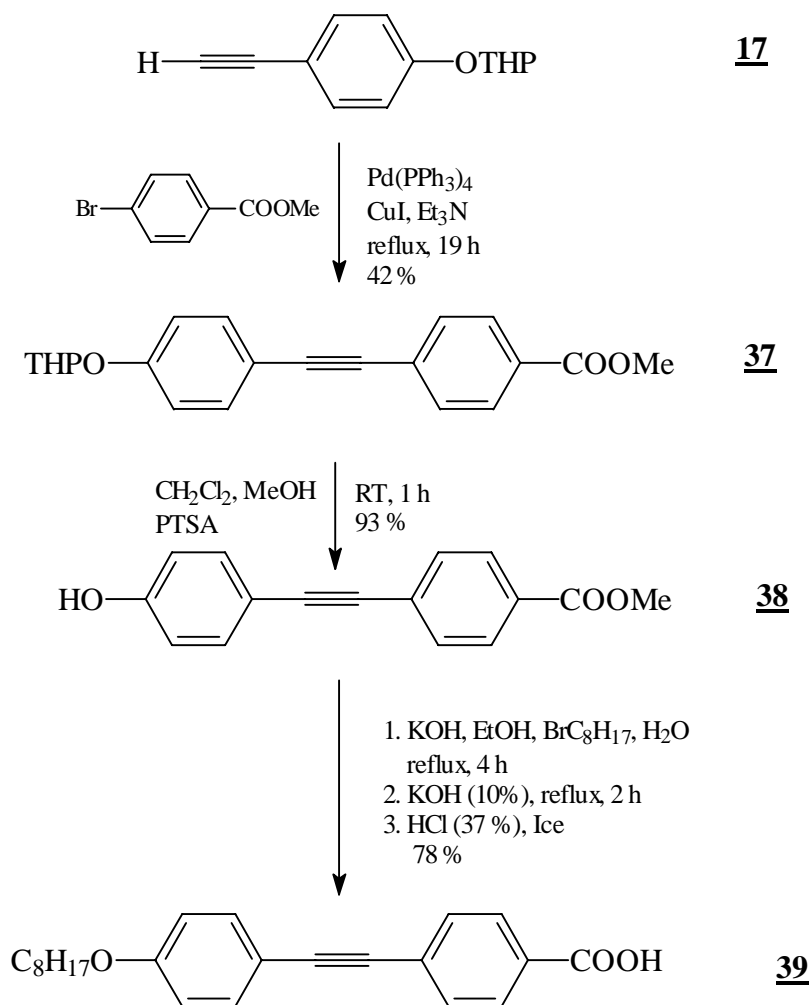
Scheme 2-9 Synthesis of 4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoic acid.



Scheme 2-10 Synthesis of semifluorinated 4-benzoyloxybenzoic acids **35** and **36**.

The semifluorinated 4-alkoxybenzoic acids were synthesized according to scheme 2-9.⁴⁵ The appropriate 1-iodoperfluoroalkanes were added to ω -alkenols by means of $Pd(PPh_3)_4$ as a catalyst. The obtained iodides were then reduced with $LiAlH_4$, the hydroxy group was brominated with HBr and the obtained semifluorinated 1-bromoalkanes were etherified with methyl 4-hydroxybenzoate to give the semifluorinated methyl 4-alkoxybenzoates. By hydrolysis of the ester first with base and then acidification with hydrochloric acid the semifluorinated 4-alkoxybenzoic acids were obtained. They were treated with $SOCl_2$ and the resulting acid chlorides were esterified with 4-hydroxybenzaldehyde. The obtained 4-benzoyloxybenzaldehydes **33** and **34** were then oxidized by CrO_3 in aqueous acetic acid to form the semifluorinated benzoyloxybenzoic acids **35** and **36**.

1.2.3 4-(4-Octyloxyphenylethynyl)benzoic acid **39**



Scheme 2-11 Synthesis of 4-(4-octyloxyphenylethynyl)benzoic acid **39**.

4-(4-Octyloxyphenylethynyl)benzoic acid **39** was synthesized by cross-coupling of ⁴⁶ 4-tetrahydropyranyloxyphenylacetylene **17** with methyl 4-bromobenzoate with the catalysts $\text{Pd(PPh}_3)_4$ and CuI in Et_3N (see scheme 2-11). The THP group of the resulting THP ether **37** was cleaved with PTSA in methanol, and then the deprotected phenol **38** was first etherified with 1-octylbromide under basic conditions. Afterwards, the benzoate was separated and finally acidified with concentrated hydrochloride acid to give the desired acid **39**.

1.3 Synthesis of the final bent-core molecules

1.3.1 Isophthalates 4/6-9/8

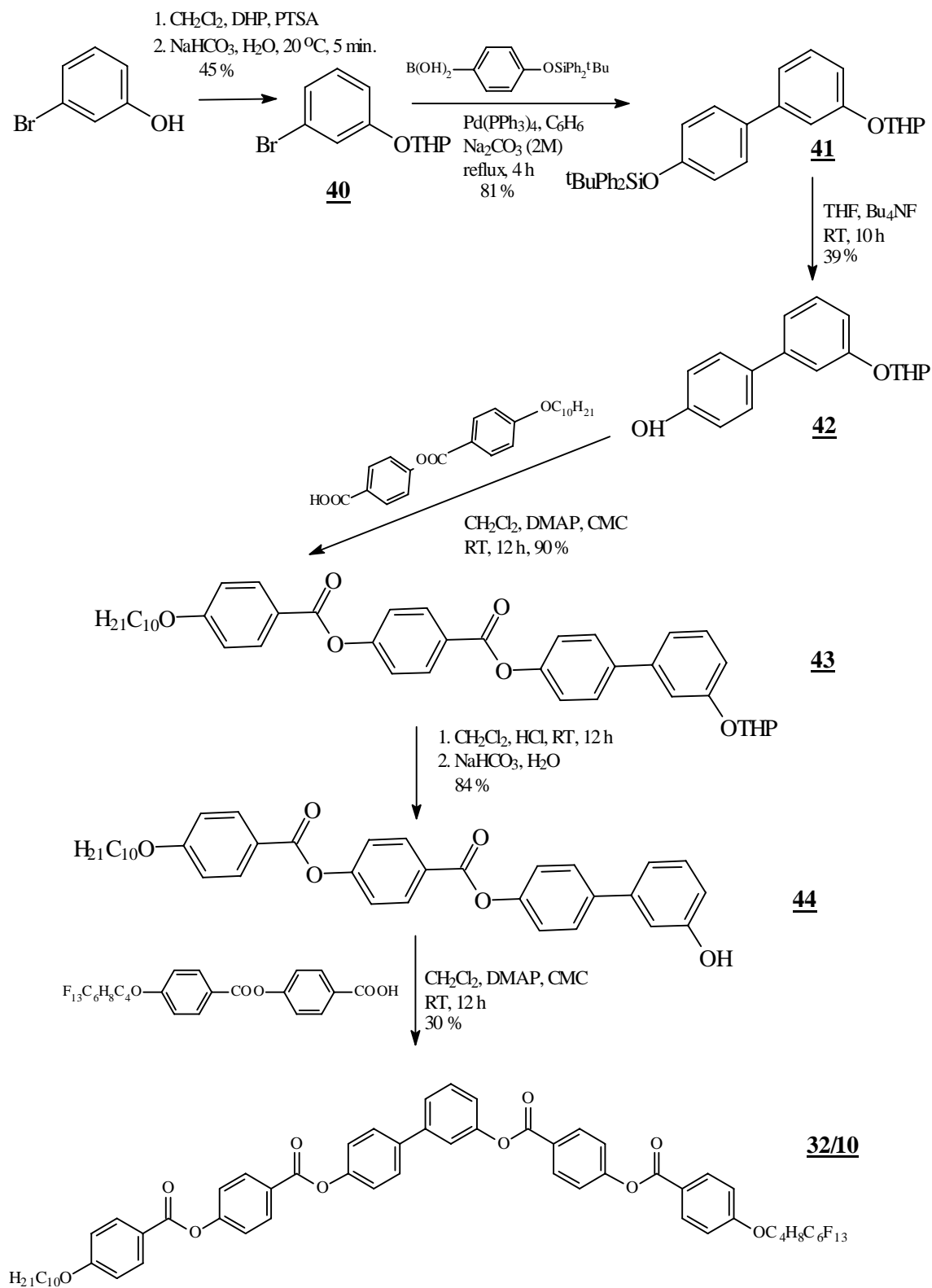
The isophthalate compounds were obtained by esterification of isophthaloyl dichloride with appropriate phenols in dry pyridine and toluene. Isophthaloyl dichloride was commercially available. The 4-(5-alkylpyrimidine-2-yl)phenols, the 4-(5-alkyl-1,3,4-thiadiazole)phenols, 4-(5-heptyl-2,2,2-bicyclooctyl)phenol, and 4-(4-octyloxybenzoyloxy)phenol were available in the working group. The final products were purified by column chromatography (Silica gel 60, eluent CHCl₃: MeOH = 10: 1.0), and then recrystallized from toluene.

1.3.2 Bisbenzoates of divalent phenols

These compounds were obtained by esterification of the appropriate divalent phenols resocinol, 2-nitroresocinol, 2-methylresocinol, **2**, **4-6**, **12-14**, **20** and **22** with the substituted benzoic acids **24-27**, **35**, **36** and **39** using the carbodiimide method. The water-soluble carbodiimide *N*-cyclohexyl-*N'*-(2-morpholinoethyl)carbodiimide methyl-*p*-toluenesulfonate (CMC) was used as condensating agent. Resorcinol, 2-nitroresorcinol and 2-methylresocinol were commercially available. The other divalent phenols were synthesized as described above. The final products were purified by column chromatography (Silica gel 60, eluent CHCl₃: MeOH = 10: 0.5) and then recrystallized from ethyl acetate.

2 Bent-core molecules incorporating two non-identical rigid cores

The synthetic route to one of these compounds is shown in scheme 2-12. In order to differentiate the two phenolic OH-groups, two orthogonal sets of protecting groups (THP and ^tBuPh₂Si) were used, which can be deprotected under different conditions. The ^tBuPh₂Si protecting group was first deprotected by Bu₄NF, while the THP group was maintained. The obtained phenols were then esterified with the appropriate 4-substituted benzoic acids to give the THP-protected intermediates. Then the THP group was deprotected under acidic condition and the obtained phenol was esterified with the other substituted benzoic acid so that bent-core compounds with two non-identical rigid cores were obtained.



Scheme 2-12 Synthesis of compound **32/10** as an example for the synthesis of bent-core molecules with two different rigid cores.

III Mesomorphic behavior and phase structures

1 1,3-Phenylene derivatives

Considering the original banana-shaped molecules they are molecules incorporating five aromatic rings whereby the central aromatic ring is a 1,3-substituted one. Because there was no knowledge about the relationship between the molecular structure and the mesogenic properties, in a first step of this work novel bent-core molecules incorporating different structural unit were synthesized. Furthermore compounds with additional substituents at the central unit and also molecules incorporating a 2,7-disubstituted naphthalene ring system as central unit were synthesized and studied.

All members of this group of bent-core molecules are crystalline solids without mesomorphic properties. Their melting points are summarized in table 3-1. A methyl group in the 2-position at the central unit leads to the increase of the melting points whereas the nitro group decreases the melting points. Comparison of the 1,3-phenylene derivative **1/6** with the 2,7-dihydroxynaphthalene derivative **10/6** shows a significant increase of the melting point on replacing the central benzene unit by a 2,7-disubstituted naphthalene unit. Because of the unfavorable properties provided by these central units, and considering that other 1,3-phenylene derivatives without Schiff-base unit reported by Weissflog have also no switchable B2 phase,²⁹ they were not combined with other rigid cores.

2 3,4'-Biphenyl derivatives

2.1 Mesomorphic properties of bent-core molecules with alkylsubstituted phenylbenzoate rigid cores

Because of the unfavorable properties of all 1,3-substituted phenylene compounds, the molecular structure was further modified by using the larger 3,4'-biphenyl unit as bent central unit. The combination of this bent unit with two phenylbenzoate rigid cores was a significant breakthrough for this work, because they exhibit broad regions of liquid crystalline phases.

Table 3-1 Melting temperatures ($T / ^\circ\text{C}$) of the 1,3-phenylene derivatives **1/n-9/8**.

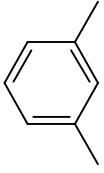
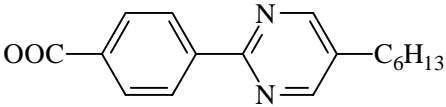
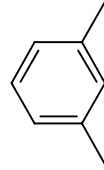
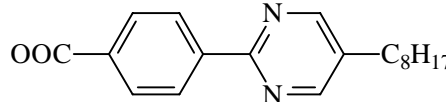
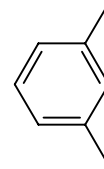
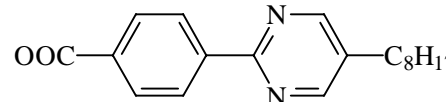
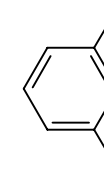
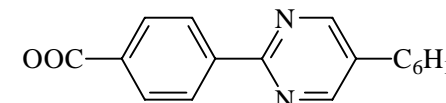
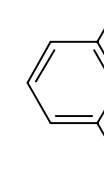
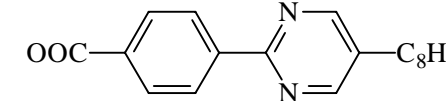
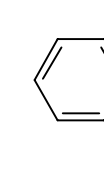
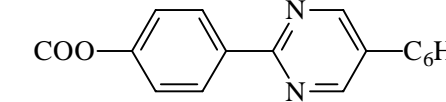
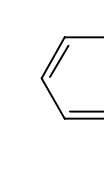
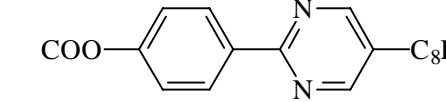
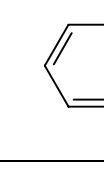
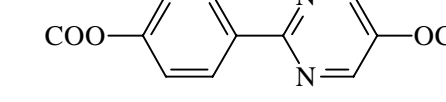
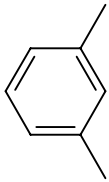
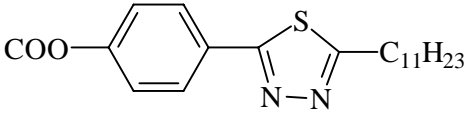
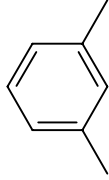
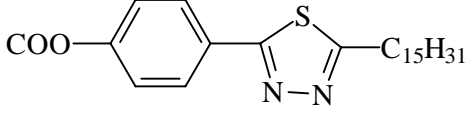
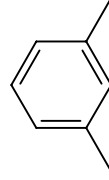
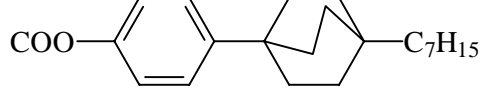
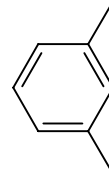
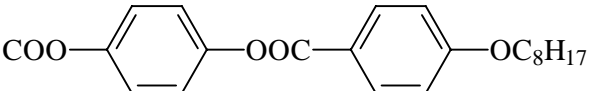
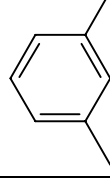
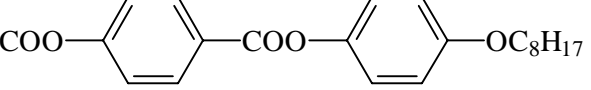
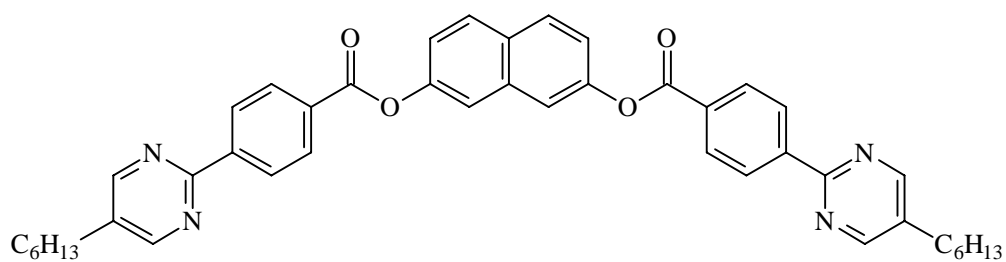
Comp.	Central unit (A)	Rigid core (B)	mp / $^\circ\text{C}$
1/6			160
1/8			130
2/8			166
3/6			145
3/8			106
4/6			139
4/8			142
5/8			155

Table 3-1 continued:

6/11			179
6/15			181
7/7			227
8/8			159
9/8			202



10/6 mp 215 °C

Naphthalene-2,7-diylbis[4-(5-hexylpyrimidine-2-yl)benzoate]

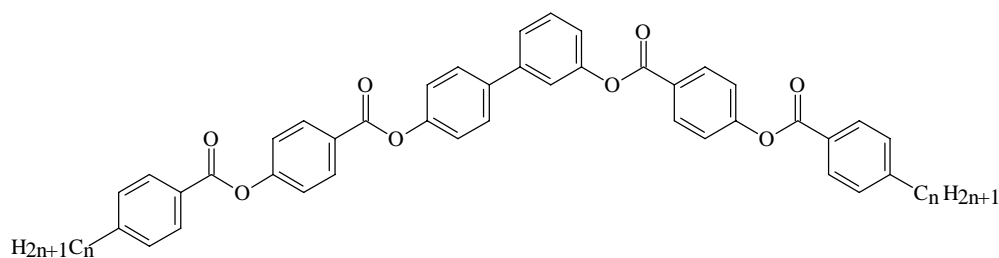


Table 3-2 Transition temperatures ($T/^\circ\text{C}$) and corresponding enthalpy values ($\Delta H/\text{kJ mol}^{-1}$, lower lines in *italics*) of compounds **11/n**.

Comp.	n	Phase transitions
11/4	4	Cr ₁ 82 Cr ₂ 161 (Col _r 153) Iso <i>12.3 34.2 (11.7)</i>
11/6	6	Cr 119 Col _r 158 Iso <i>12.4 14.6</i>
11/7	7	Cr ₁ 89 Cr ₂ 129 Col _r 167 Iso <i>8.7 21.1 18.8</i>
11/8	8	Cr ₁ 68 Cr ₂ 85 SmX 86 SmCP _A 152 Iso <i>2.8 9.2 (6.3) 19.6</i>
11/8^a	8	Iso 152 Col _r 147 SmCP _A 86 SmX <i>-16.2 -3.4 -6.3^b</i>
11/9	9	Cr 99 Col _r 158 Iso <i>18.5 19.1</i>
11/10	10	SmX 79 SmCP _A 148 Iso <i>9.2 18.4</i>
11/10^a	10	Iso 148 Col _r 147 SmCP _A 79 SmX
11/11	11	Cr ₁ 67 Cr ₂ 88 (SmX 87) SmCP _A 157 Iso <i>5.2 10.3 (6.7) 21.6</i>
11/12	12	SmX 78 SmCP _A 156 Iso <i>6.3 20.7</i>

^a: Phase sequence obtained on cooling, these transition temperatures were determined by microscopy between crossed polarizers.

^b: Determined from the DSC cooling scan.

SmX: Highly ordered smectic phase of unknown precise structure.

Two homologous series with alkyl and alkoxy terminal chains (**11/n**, **12/n**) were synthesized and studied. Their transition temperatures and the corresponding enthalpy values are summarized in tables 3-2 and 3-5. In figure 3-1 the dependence of the mesomorphic properties of the homologous series of the alkylsubstituted compounds **11/n** ($n = 4, 6-12$) on the chain length is shown schematically.

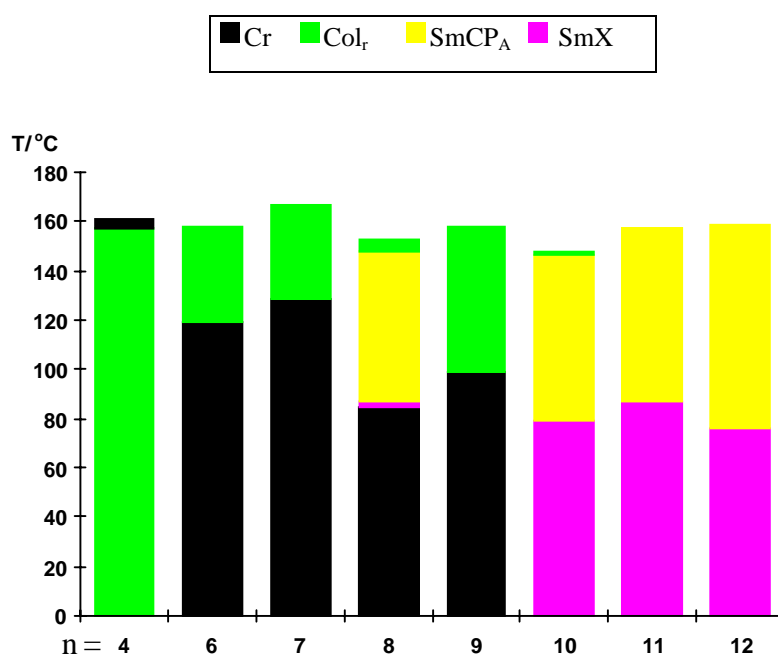


Figure 3-1 Transition temperatures ($T/^\circ\text{C}$) of compounds **11/n** in dependence on the length of the alkyl chains. The Col_r phases of the compounds $n = 4, 8$ and 10 are monotropic (i.e. they can only be observed on cooling from the isotropic liquid state). The crystalline phase of compound **11/11** is not shown.

Three different mesophases were found. The short chain molecules **11/4-11/7** exhibit only one mesophase. On cooling from the isotropic liquid state it can be detected by the formation of small batonnets which coalesces into a mosaic-like texture (see figure 3-2). Some times also spherulitic domains can be observed. The same texture was found for **11/9** with nonyl side chains and for the high temperature mesophases of **11/8** and **11/10**. These textures are the same as those which were detected for the short chain derivatives of Schiff's-base derived banana-shaped molecules.²³ It was designated as B1 phases and a rectangular columnar structure was proposed for this mesophase.²¹

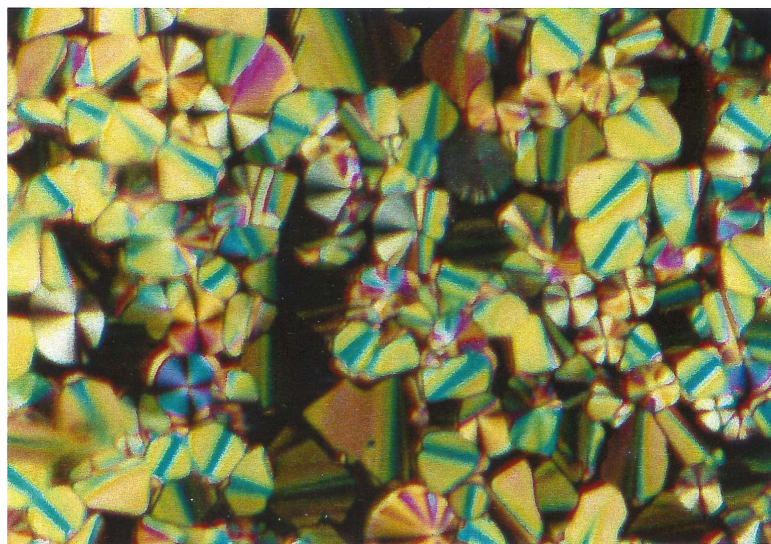


Figure 3-2 Optical photomicrograph (crossed polarizers) of Col_r phase of compound **11/8** as obtained by cooling from the isotropic liquid at 152 °C.

The X-ray diagrams of compounds **11/4-11/9** show two reflections in the small angle region in addition to a diffuse wide angle scattering (table 3-3). The pattern of an oriented sample of compound **11/4** displays Bragg-spots out of the meridian as well as Bragg-spots at the meridian, which point to the existence of a two-dimensional rectangular cell (figure 3-3) . It supposes to index the first reflection of the powder-like pattern by (101) and the second one by (002). The calculated lattice constants are given in table 3-4. The outer diffuse scattering is splitted off, too, and is arranged symmetrically to the equator. It yields to an angle of $\alpha = 126$ degree, which can be attributed to the bending angle of the two half-parts of the molecules.

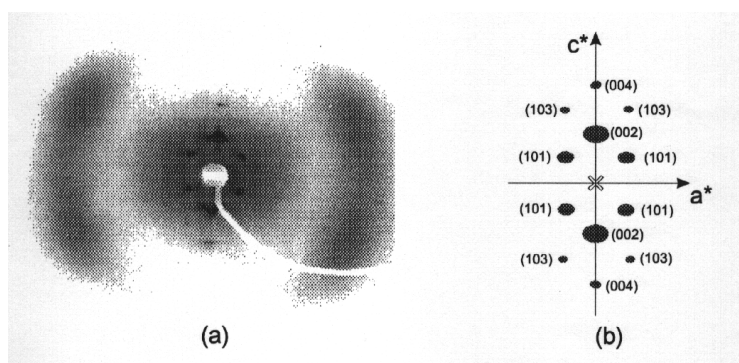


Figure 3-3 (a) X-ray pattern of a monodomain of the Col_r phase of compound **11/4** at 120 °C (supercooled state); (b) schematic sketch of the small angle pattern together with the Millers indices.

Table 3-3 Scattering vectors of compounds **11/4** - **11/12**.

Comp.	Col _r		SmCP _A
	<i>d</i> ₁ /nm	<i>d</i> ₂ /nm	<i>d</i> /nm
11/4	2.19	1.93	
11/6	2.49	2.10	
11/7	2.64	2.17	
11/8	3.18	2.34	3.70
11/9	3.04	2.32	
11/10			3.72
11/11			3.82
11/12			3.96

Table 3-4 Comparison of the molecular length (*L*), the lattice parameter of the Col_r phase (*a*, *c*) and the layer distance in the SmCP_A phases (*d*).

Comp.	<i>L</i> /nm	Col _r		SmCP _A
		<i>a</i> /nm	<i>c</i> /nm	<i>d</i> /nm
11/4	3.9	2.66	3.86	
11/6	4.3	3.09	4.20	
11/7	4.6	3.33	4.34	
11/8	4.9	4.33	4.68	3.70
11/9	5.1	4.02	4.64	
11/10	5.3			3.72
11/11	5.5			3.82
11/12	5.7			3.96
12/9	5.3	3.46	4.75	
12/11	5.7	6.38	4.78	

Using this bending angle the molecular lengths of compounds **11/n** were calculated according to $L = (L_1^2 + L_2^2 - 2L_1L_2\cos\alpha)^{0.5}$ whereby *L*₁ and *L*₂ correspond to the lengths of the two different half-parts determined using CPK-models and assuming an all-trans conformations of the alkyl chains. In the case of compound **11/4** the calculated length *L*

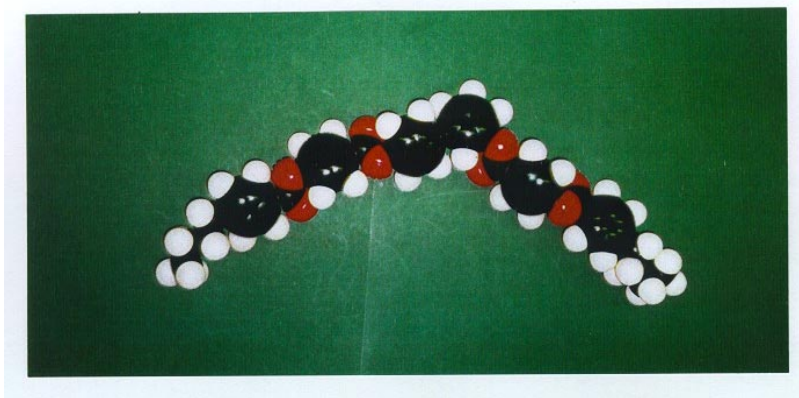


Figure 3-4 CPK-model of compound 11/4.

agrees very well with the periodicity c . Obviously, this long axis is within the a - c plane and is directed parallel to the c -axis, i.e. the molecules are non-tilted. With increasing chain length the difference between L and c increases. The differences to the c parameter can be explained by the deviation of the alkyl chains from the all-trans conformation which becomes more pronounced on elongation of the chains. Thus, this mesophase is a rectangular columnar mesophase (Col_r) built up of ribbons of parallel aligned bent-core molecules. The bending direction of the molecules of neighboring ribbons is antiparallel. In this way the dipoles cancel out from ribbon to ribbon, and the system can escape from a macroscopic polar ordering (figure 3-5a).

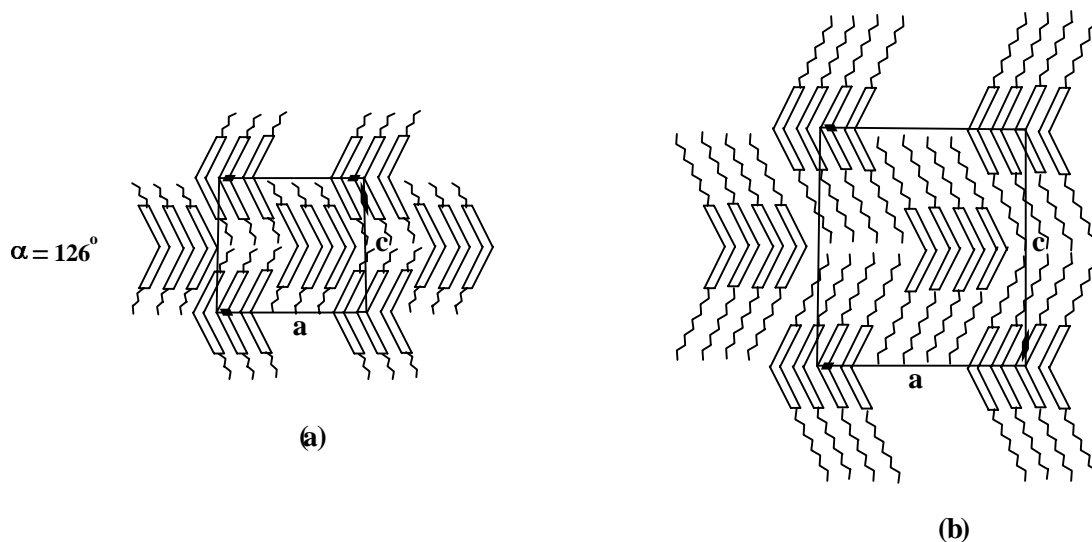


Figure 3-5 Structure model of the Col_r phase: (a) stable Col_r phase of molecules with short chains or with large rigid cores; (b) the same arrangement of molecules with long chains and small bent cores is unstable.

The parameter a is related to the number of molecules arranged side by side in the lateral diameter of each ribbon. Unexpectedly, this parameter increases especially strong on elongation of the alkyl chains which means that the number of molecules also depends on the chain length. It rises from a value between two and three molecules for compound **11/4** to a value of about four molecules in the case of compound **11/8**. Also this observation can be explained on the basis of the ribbon model of this columnar phase. In the bordering regions between the ribbons, the aromatic cores and the aliphatic chains have to overlap (see figure 3-5b). These unfavorable chain-core interactions become increasingly more important with longer terminal alkyl chains. It seems that on increasing the chain length the system tries to reduce the number of these bordering regions by increasing the size of the individual ribbon leading to the increase of the parameter a . On further elongation of the chains, however, the ribbon phase becomes instable. Hence, it is lost or it can only be observed over a small temperature range (compounds **11/8** and **11/10**).

The Values of a and c of compound **11/9** with odd-numbered terminal chains are unusual small in comparison to those of the neighboring homologue **11/8** with shorter but even numbered chains. This should be attributed to an odd-even effect, which can also be observed for the stability of the columnar phase. The fact that compound **11/9**, which exclusively forms the columnar phase, has a reduced diameter of the ribbons in comparison to **11/8** which has only a small existence region of the columnar phase is in line with the explanations given above.

The homologues **11/8** and **11/10** show a rather complicated polymorphism (see table 3-2 and figure 3-1). On cooling from the isotropic liquid state the typical mosaic-texture of the columnar phase occurs, but on further cooling a transition to another phase which has a schlieren texture can be found (figure 3-6).

This mesophase always shows a distinct birefringence and no pseudoisotropic regions can be obtained by shearing which indicates a biaxial mesophase. Furthermore, it has a rather low viscosity, comparable to conventional SmA and SmC phases. These texture features are related with those of the B2 phase of other bent-core molecules. On heating the samples, this mesophase directly turns into the isotropic liquid state without passing the columnar mesophase. The columnar phase is obtained again by cooling. It seems that the 2D-lattice of the columnar phase can only be formed by cooling from the isotropic liquid state.

On further cooling of compound **11/8**, at 86 °C the schlieren texture turns into a mosaic-like texture with a significant increase of the viscosity. This mesophase is designed as SmX.

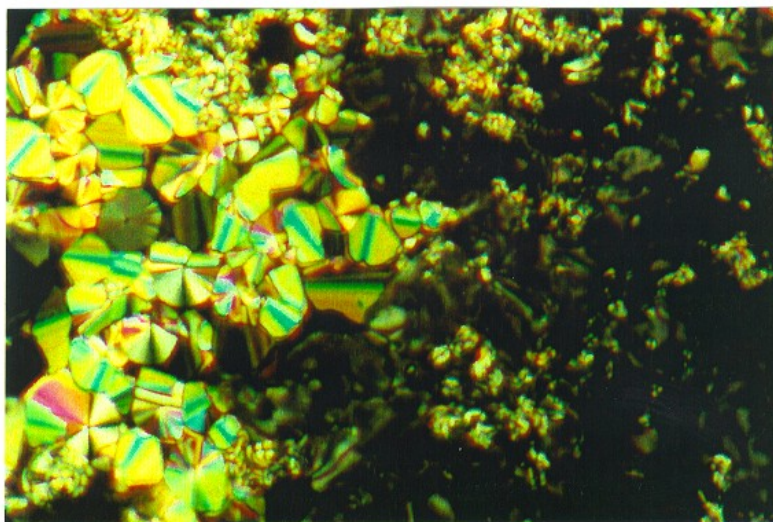


Figure 3-6 Optical photomicrography at the transition of the Col_r phase (mosaic-like texture, left hand side) to the SmCP_A phase (schlieren texture, right hand side) obtained by cooling of compound **11/8** at 147 °C.

Compound **11/8** which forms all three mesophases was investigated in more detailed by X-ray diffraction. Here the changes of the diffraction pattern in dependence on the phase type can be studied. The X-ray diagram (figure 3-7) significantly changes on cooling the sample

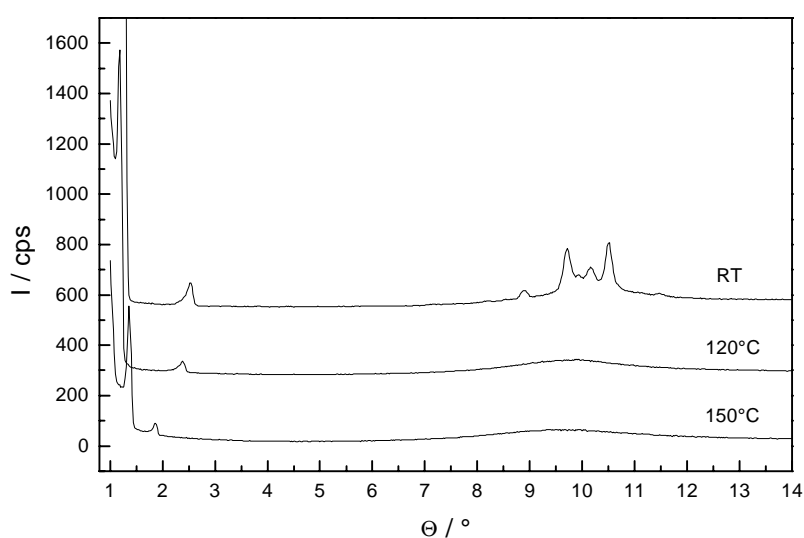


Figure 3-7 Scattering diagrams of a non-oriented sample of compound **11/8** in the Col_r phase (150 °C), in the SmCP_A phase (120 °C) and in the SmX phase (RT = 25 °C).

from the columnar phase. Now the first and second order of a layer reflection can be seen beside the diffuse wide angle scattering which is characteristic for fluid smectic phases. Such pattern is also obtained for the compounds **11/10-11/12**. The layer periods are listed in table 3-4. Compound **11/8** also offers the possibility to compare the molecular length with the periods in both phases. As mentioned above, the c parameter in the columnar phase corresponds with the length of the molecules. The period in the fluid smectic phase however is significantly lower. With both values a tilt of the molecular long axis with respect to the layer normal of 38 degree can be estimated. This means that in this smectic phase the banana-shaped molecules are inclined with respect to the layer normal (see figure 3-8). This structure resembles that one of the B2 phases. As the electrooptical investigations (see chapter IV) reveal an antiferroelectric switching behavior, we assign this fluid smectic phase as SmCP_A phase, a tilted polar smectic phase with an antiferroelectric interlayer correlation, according to the suggestions given by Link et. al..²⁸

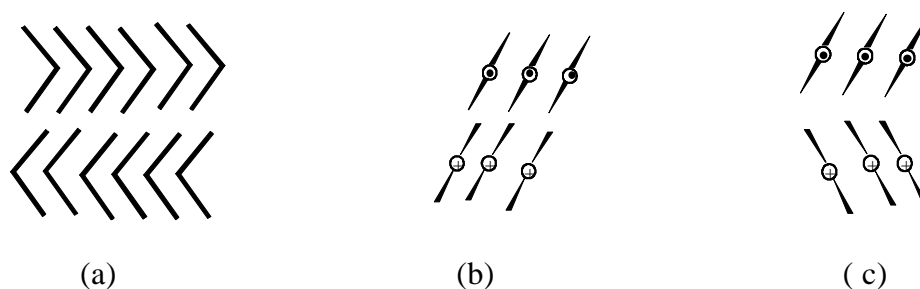


Figure 3-8 Arrangement of the bent-core molecules in the SmCP_A phase (a), and side view of an antiferroelectric arrangement with synclinic interlayer correlation SmC_SP_A (b) and with anticlinic interlayer correlation SmC_AP_A (c).

On cooling down the SmCP_A phases of compounds **11/8** and **11/10 - 11/12** the transition into the SmX takes place. The X-ray pattern of the non-oriented sample is only scarcely changed in the small angle region but the wide angle region several additional reflections occur, which resemble to a highly ordered layer structure, like G or H. This pattern is maintained down to room temperature. Remarkably no crystallization can be observed after the first melting of compounds **11/8** and **11/10 - 11/12** even over prolonged storage at room temperature.

Exclusively the fluid smectic phases and the SmX phases were found for compounds **11/10 - 11/12**. The typical texture of the SmCP_A phase as obtained on cooling the isotropic liquid

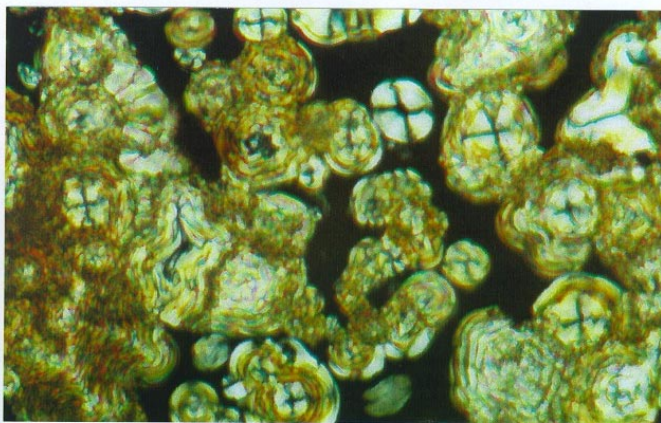


Figure 3-9 Optical photomicrograph of the SmCP_A phase of compound **11/12** as obtained by cooling from the isotropic liquid at 156 °C.

state of **11/12** is shown in figure 3-9. The enthalpies of the transitions from the liquid crystalline to the isotropic liquid phase increase in this homologous series with the chain length, ranging from 11.7 kJ mol⁻¹ for compound **11/4** to 21.6 kJ mol⁻¹ for compound **11/11** (table 3-2). The transition enthalpy between the Col_r and the SmCP_A phase is significantly lower and amounts only 3.4 kJ mol⁻¹ (compound **11/8**). The transition between the SmCP_A phase and the SmX phase is about 6.5 kJ mol⁻¹.

2.2 Mesomorphic properties of bent-core molecules with alkoxy-substituted phenyl-benzoate rigid cores

The transition temperatures of the biphenyl derivatives with alkoxy terminal chains **12/n** are shown in table 3-5. The dependence of the mesomorphic properties on the chain length is shown in figure 3-10.

Again, the homologues with short chains have the columnar phase whereas the homologues with long chains display the SmCP_A phase. However, the length of the alkyl chains which is necessary to obtain the SmCP_A phase ($n = 12$) is significantly larger than in the series of the alkyl-substituted compound **11/n** ($n = 8$). Another interesting difference between these two homologous series is that for the molecules with alkoxy chains the columnar phases suddenly disappear when the terminal chains are longer than C₁₁ whereas in the series of alkyl substituted compounds this occurs over a certain chain length range (C₇-C₁₁) with a

pronounced odd-even effect. Additionally, the alkoxy-substituted compounds do more readily crystallize and no additional low-temperature mesophases could be detected.

Table 3-5 Transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H/\text{kJ mol}^{-1}$ lower lines in italics) of compounds **12/n**.

Comp.	n	Phase transitions
12/8	8	Cr ₁ 97 Cr ₂ 131 Col _r 172 Iso <i>25.7 21.3 21.0</i>
12/9	9	Cr ₁ 89 Cr ₂ 99 Cr ₃ 116 Col _r 169 Iso <i>3.5 25.4 2.9 18.6</i>
12/10	10	Cr 119 Col _r 166 Iso <i>37.7 20.4</i>
12/11	11	Cr 85 Col _r 154 Iso <i>12.4 20.2</i>
12/12	12	Cr ₁ 82 Cr ₂ 106 SmCP _A 159 Iso <i>28.2 19.3 23.2</i>
12/13	13	Cr 86 SmCP _A 161 Iso <i>40.6 24.2</i>
12/14	14	Cr 85 SmCP _A 162 Iso <i>39.4 24.8</i>

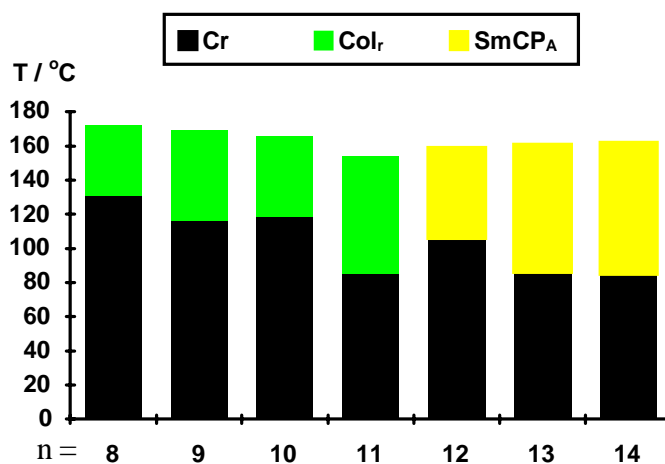


Figure 3-10 Transition temperatures of compounds **12/n** in dependence on the chain length.

X-ray investigation of the columnar mesophase of **12/11** indicate again a centered rectangular cell with the parameter $a = 6.38$ nm and $c = 4.78$ nm. This c -value is in good agreement with the molecular length whereas for the parameter a a significantly larger value in comparison to related alkyl substituted compound **11/n** was observed. It corresponds to approximately six molecules in the diameter of the ribbons. It seems that the critical diameter of the ribbons depends not only on the chain length but also on the precise molecular structure. Obviously, in the case of the alkoxy substituted bent rigid cores an increased stability of the ribbons is provided. This effect of the oxygen atoms could be due to their polarity or to changes of the molecular conformation.⁴⁷ Additionally, the ether oxygen atoms could increase the effective length of the rigid part of the bent core because of the enhanced rotational barrier around the C(ar)-O-bound due to the conjugation of the oxygen lone pairs with the aromatic π - system.

2.3 Mesomorphic properties of bent-core molecules with 2-phenylpyrimidine rigid cores

Because interesting mesophases, specially the antiferroelectrical switchable SmCP_A phases were found in bent-core molecules incorporating the central 3,4'-disubstituted biphenyl system, this central unit was also combined with 2-phenylpyrimidine rigid cores. Surprisingly their mesomorphic behavior is completely different from that one of the compounds with phenylbenzoate rigid cores. The transition temperatures of such compounds are shown in table 3-6.

Compound **13/8** exhibits a well developed fan-shape texture which cannot be homeotropically aligned, but a schlieren texture cannot be detected. This phase has a significantly lower viscosity than the Col_r phases, and it is comparable with those of conventional SmA and SmC phases. The enthalpy of the transition from this mesophase to the isotropic phase is 5.1 kJ mol^{-1} , i.e. it is smaller than the enthalpies of the transition from SmCP_A or Col_r phase to the isotropic phase. As the investigation of other compounds with pyrimidine rigid cores (**17/n**, see next section) which have the same textural features indicated an intercalated phase structure, an intercalated smectic phase ($\text{Sm}_{\text{intercal}}$) can also be assumed for these compounds. On elongation of the length of the terminal chains the molecule do not escape from the intercalated layer structure, instead, this mesophase is strongly destabilized. It seems that the

mesomorphic behavior of such bent-core molecules depends not only on the length of the terminal chains, but also strongly on the type of the rigid cores.

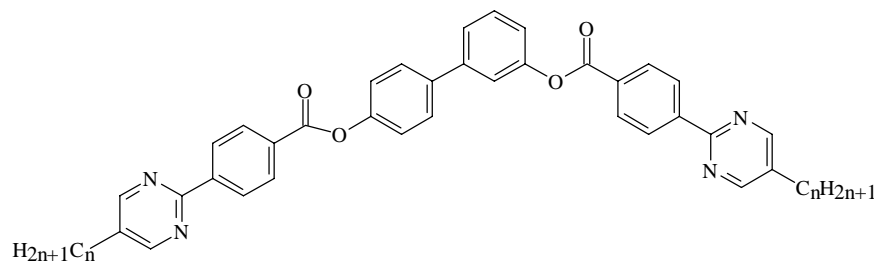


Table 3-6 Transition temperatures ($T/^\circ\text{C}$) and corresponding enthalpy values ($\Delta H/\text{kJ mol}^{-1}$ lower lines in italics) of compounds **13/n**.

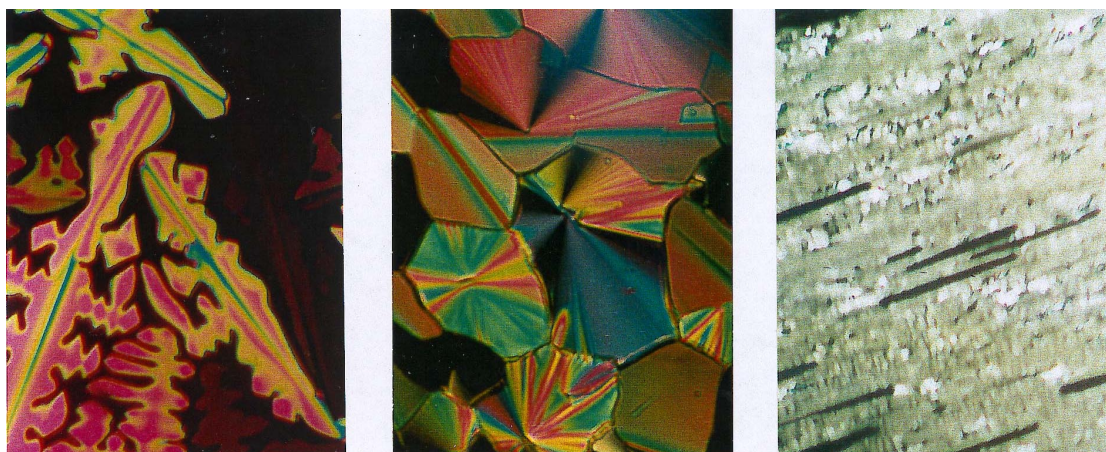
Comp.	n	Phase transitions
13/8	8	Cr 142 <i>Sm_{intercal}</i> 148 Iso <i>34.7</i> <i>5.1</i>
13/12	12	Cr ₁ 93 Cr ₂ (89 <i>Sm_{intercal}</i>) 115 Iso <i>16.4</i> (<i>12.6</i>) <i>44.7</i>

3 m-Terphenyl derivatives

In order to explore the general relationships between the molecular structure of banana-shaped mesogens and their properties, the central unit was further changed. Therefore, in the next step the 4,4''-disubstituted 1,1':3',1''-terphenyl unit was applied as central unit and combined with different rigid cores.

The transition temperatures of the synthesized m-terphenyl derivatives and some structurally related 2,6-diphenylpyridines are summarized in tables 3-7 to 3-10. Mesomorphic properties were found for the compounds with phenylbenzoate and phenylpyrimidine rigid cores (**14/n-18/n**).

The textures of the mesophases of all synthesized m-terphenyl derivatives with phenylbenzoate rigid cores and short terminal chains ($n < 12$) and of the corresponding 2,6-diphenylpyridine derivatives are quite similar. As an example the typical texture of **15/9** is shown in figure 3-11. On cooling from the isotropic liquid state small batonnets are formed which rapidly turn into branched lancets (figure 3-11a) and finally coalesce into a structured mosaic-like texture (figure 3-11b) with some spherulitic domains. This texture is very similar



(a)

(b)

(c)

Figure 3-11 Optical photomicrographs (crossed polarizers) of compound **15/9**:

(a) at the transition from the isotropic liquid state to the Col_r phase at 219 °C.

(b) in the Col_r phase at 210 °C. (c) after shearing the sample at 210 °C.

to that one of the columnar phases of the biphenyl derivatives with short terminal chains (**11/n** $n < 8$, **12/n** $n < 12$). By shearing the samples between glass plates, no pseudo-isotropic regions can be obtained (figure 3-11c).

The mesophase of compound **15/8** which shows the same texture was investigated by means of X-ray scattering. Four small angle reflections could be detected at the Bragg angles $\theta = 1.59^\circ$, $\theta = 1.81^\circ$, $\theta = 2.98^\circ$ and $\theta = 3.57^\circ$ which could be indexed as (101), (002), (103) and (004) reflections, respectively, of a centered rectangular two-dimensional lattice as found for the Col_r phase of compounds **11/n** ($n < 8$) and **12/n** ($n < 12$). The lattice parameters are $a = 3.37$ nm and $c = 4.86$ nm. The molecular length (L), assuming a bow-shape of the molecule with a bending angle between the two half-parts of ca. 120° and all-trans conformation of the alkyl chains is 5.6 nm. Thus the parameter c is again in good agreement with the molecular length and therefore can be related to the thickness of the ribbons. From the parameter a it can be calculated that about four molecules should be arranged side by side in the ribbons forming the 2D lattice. A schlieren texture was found for the mesophases of the compounds **14/12** and **15/14** with very long terminal chains, and an antiferroelectric switching process was observed in the temperature range of these phases (see chapter IV). Hence, they exhibit the SmCP_A phase and their behavior is related to that one of the biphenyl derivatives.

Also for the m-terphenyl derivatives with 2-phenylpyrimidine rigid cores liquid crystalline

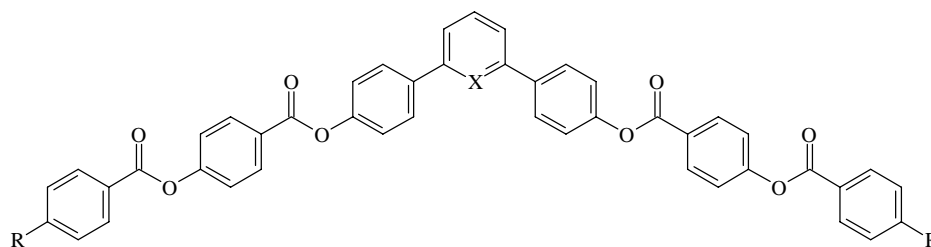


Table 3-7 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **14/n**, **15/n** and **16/9**.

Comp.	R	X	Phase transitions
14/8	C_8H_{17}	CH	Cr ₁ 173 Cr ₂ 180 Col _r 207 Iso <i>11.3 36.9 20.7</i>
14/12	$\text{C}_{12}\text{H}_{25}$	CH	Cr 169 SmCP _A 203 Iso <i>44.5 24.5</i>
15/8	OC_8H_{17}	CH	Cr 160 Col _r 226 Iso <i>20.6 22.8</i>
15/9	OC_9H_{19}	CH	Cr 161 Col _r 219 Iso <i>27.3 25.1</i>
15/12	$\text{OC}_{12}\text{H}_{25}$	CH	Cr 165 Col _r 203 Iso <i>40.8 21.8</i>
15/14	$\text{OC}_{14}\text{H}_{29}$	CH	Cr 155 SmCP _A 199 Iso <i>22.9 23.0</i>
16/9	OC_9H_{19}	N	Cr 179 Col _r 246 Iso <i>25.5 22.9</i>

properties can be found. The transition temperatures of compounds **17/n** and the related 2,6-diphenylpyridine derivatives **18/n** are summarized in table 3-8. However the textures of compounds **17/4-17/8** are different from those of the corresponding phenylbenzoates. On cooling these compounds from the isotropic liquid state the formation of batonets is observed which coalesce to a fan-like texture (see figure 3-13) as typical for SmA and SmC phases. This mesophase has a significantly lower viscosity than the Col_r phase and it is impossible to get pseudoisotropic regions. On shearing the birefringence remains and the texture rapidly turns back into a fan texture. However, the typical SmC schlieren texture could not be observed.

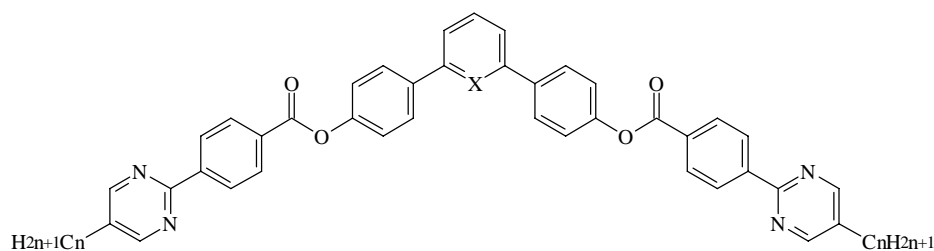


Table 3-8 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in *italics*) of the compounds **17/n** and **18/n**.

Comp.	n	X	Phase transitions
17/4	4	CH	Cr 195 <i>Sm_{intercal}</i> 203 Iso <i>38.6</i> <i>9.8</i>
17/6	6	CH	Cr 209 <i>Sm_{intercal}</i> 222 Iso <i>32.4</i> <i>15.5</i>
17/8	8	CH	Cr ₁ 105 Cr ₂ 178 <i>Sm_{intercal}</i> 206 Iso <i>10.2</i> <i>32.1</i> <i>16.5</i>
17/12	12	CH	Cr 166 Iso <i>39.0</i>
18/6	6	N	Cr 224 Col _r 242 Iso <i>35.5</i> <i>21.1</i>
18/8	8	N	Cr ₁ 131 Cr ₂ 204 Cr ₃ 231 (Col _r 230) Iso <i>12.9</i> <i>47.7</i> <i>29.5</i> (<i>11.9</i>)

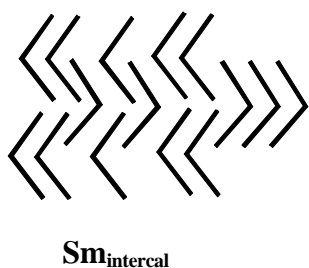


Figure 3-12 Arrangement of the molecules in the $\text{Sm}_{\text{intercal}}$ phase.



Figure 3-13 Optical photomicrograph (crossed polarizers) of the fan texture of **17/6** as obtained by cooling from the liquid state at 194°C .

The X-ray pattern of the mesophase of **17/8** exhibits only the (001) reflection (layer reflection with $d = 2.24$ nm) together with the outer diffuse scattering. Comparison with the molecular length ($L = 5.1$ nm assuming a bending angle of 120°) indicates an intercalated structure of this mesophase (see figure 3-12), because the layer thickness is smaller than one half of the molecular length. The microscopic observation as well as the X-ray data are in agreement with the results obtained for intercalated smectic phases of other banana-shaped molecules, designated as B6.^{27,29} In this mesophase a tilt of the molecules with respect to the layer normal was proven in earlier reports. However, comparison of the obtained d value in the mesophase of **17/8** with the molecular length (bending angle = 120° , all-trans conformation of the alkyl chains) gives a ratio $2d / L = 0.88$, which corresponds to the ratios usually obtained for non-tilted SmA phases. This small difference between molecular length (L) and the observed layer thickness ($2d$) can be explained by the molten liquid state of the alkyl chains and is no indication of a tilted arrangement of the molecules. Furthermore, because of the biaxiality of the molecules no pseudoisotropic regions should be possible between crossed polarizers even if the molecules are non-tilted. Because no oriented samples have been obtained in the X-ray experiments we can not exclude a small tilt ($< 30^\circ$) of the molecules and a SmC structure can not completely be excluded.

Elongation the terminal chains of these compounds lead to the loss of mesomorphic properties. Thus, the behavior of the 2-phenylpyrimidine derivatives is again quite different from that one of the corresponding phenylbenzoates.

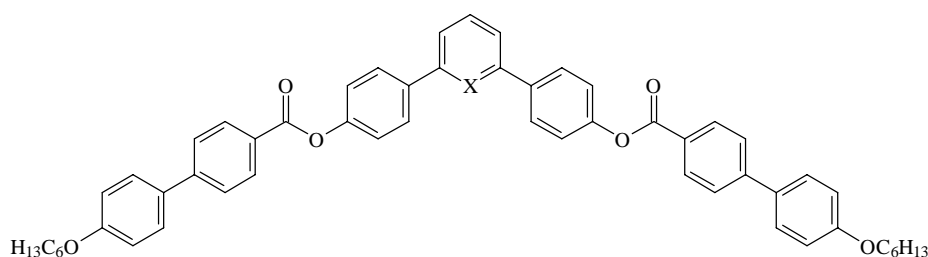
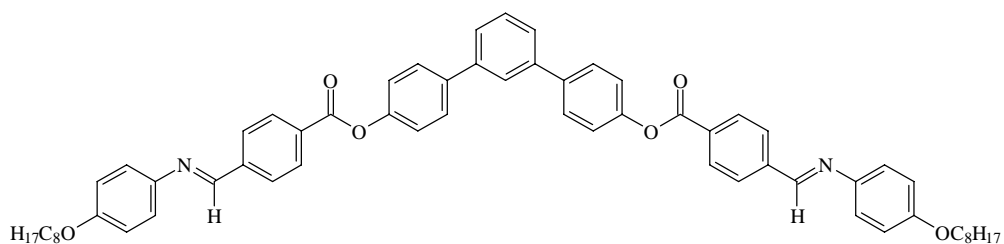


Table 3-9 Transition temperatures ($T / ^\circ\text{C}$) of **19/6** and **20/6**

Comp.	X	Transition temperatures ($T / ^\circ\text{C}$)
19/6	CH	Cr 258 M 268 Iso
20/6	N	Cr 268 Iso



21/8 mp > 270 °C (decomp.)

The m-terphenyl derivative with two biphenyl rigid cores (compound **19/6** in table 3-9) has a high melting temperature and exhibits only a small range of a liquid crystalline phase (M) with a mosaic-like texture pointing to a Col_r phase. The high temperature of the existence range inhibits a more detailed investigation. This mesophase is lost if the m-terphenyl unit is replaced by a 2,6-diphenylpyridine unit (compound **20/6**). The Schiff's base derivative **21/8** is only a high melting solid which decomposes before melting.

Because all of the m-terphenyl derivatives containing seven aromatic ring have rather high melting temperatures, the number of the aromatic rings was reduced. Although the benzoates **22/n** and **23/9** (table 3-10) incorporating only five benzene rings have significantly lower melting points than the seven-ring m-terphenyl derivatives, no mesomorphic properties could be detected, regardless of the chain length. The cyclohexanecarboxylate (**24/8**) has a significantly higher melting point than the corresponding benzoates.

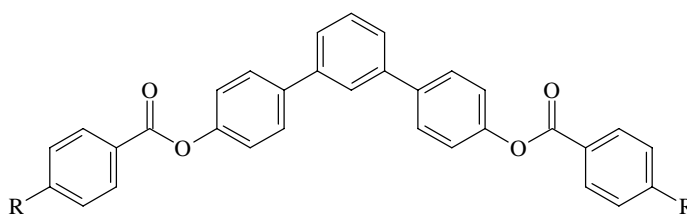
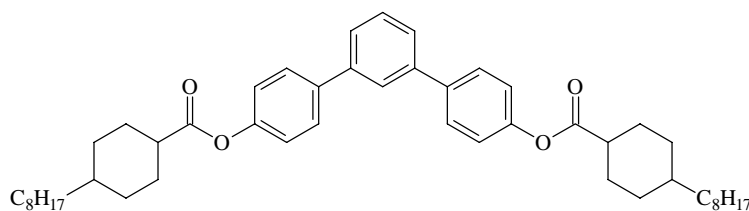


Table 3-10 Melting temperatures of the m-terphenyl-4,4''-diyl bis[4-alkyl(oxy)benzoates] **22/n** and **23/9**.

Comp.	R	mp / °C
22/4	C ₄ H ₉	135
22/6	C ₆ H ₁₃	106
22/12	C ₁₂ H ₂₅	103
23/9	OC ₉ H ₁₉	126



24/8 mp 168 °C

4 1-Phenyl-3-(4-phenylethynyl)benzene derivatives

The less symmetric structure of the banana-shaped molecules containing the 1-phenyl-3-(4-phenylethynyl)benzene unit leads to broader mesomorphic regions in comparing with the more symmetric banana-shaped molecules with 1,3-phenylene and m-terphenyl bent-core units (compounds **1/n**, **14/n** and **15/n**, respectively) due to the lower melting temperatures (about 20K). However, the type of the phases was largely unchanged. The compounds with phenylbenzoate rigid cores exhibit the Col_r phase, whereas the phenypyrimidine derivatives show the intercalated smectic phase.

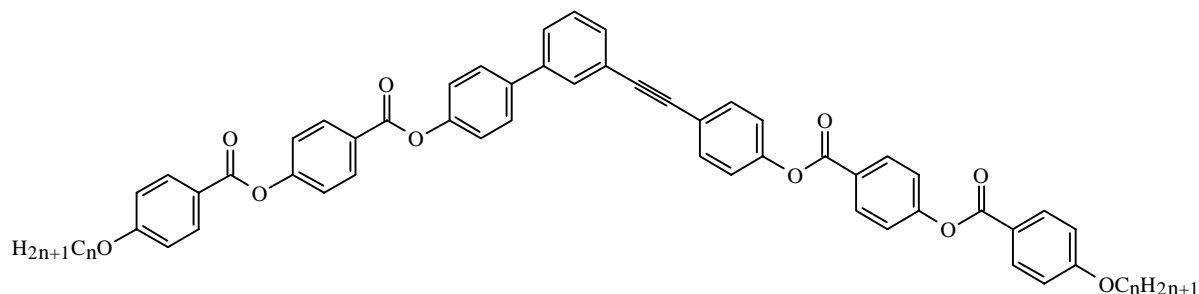
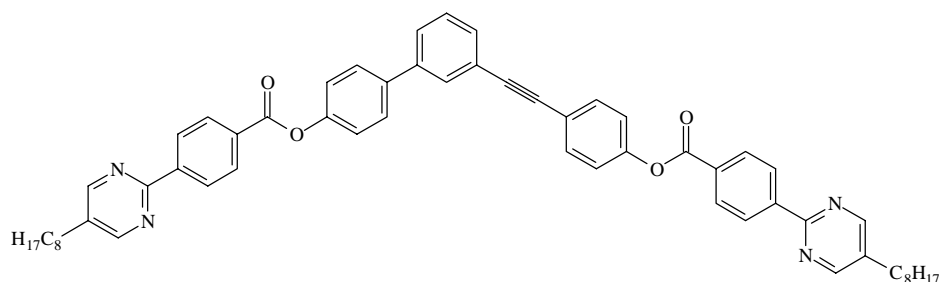


Table 3-11 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **25/9** and **25/14**.

Comp.	n	Phase transitions
25/9	9	Cr ₁ 111 Cr ₂ 142 Col _r 231 Iso <i>2.2 21.5 21.1</i>
25/14	14	Cr 137 Col _r 203 Iso <i>26.3 24.6</i>



26/8 Cr 183 Sm_{intercal} 220 Iso

38.1 20.1

The X-ray pattern of **25/9** supports this conclusion. Two small angle reflections ($d_1 = 2.88$ nm, $d_2 = 2.63$ nm at $T = 165$ °C) prove the existence of a two-dimensional cell. Assuming again a rectangular cell the parameters $c = 5.26$ nm and $a = 3.58$ nm can be calculated, which are a bit larger than those found for the octyloxsubstituted m-terphenyl derivative **15/8**.

5 1,3-Bis(phenylethynyl)benzenes and other diphenylacetylene derivatives

The 1,3-bis(phenylethynyl)benzenes derivatives **27/n** and **28/8**, which have two triple bonds connected to the central 1,3-disubstituted benzene ring, behave similar to the corresponding m-terphenyl derivatives and 1-phenyl-3-(4-phenylethynyl)benzene derivatives: the compound

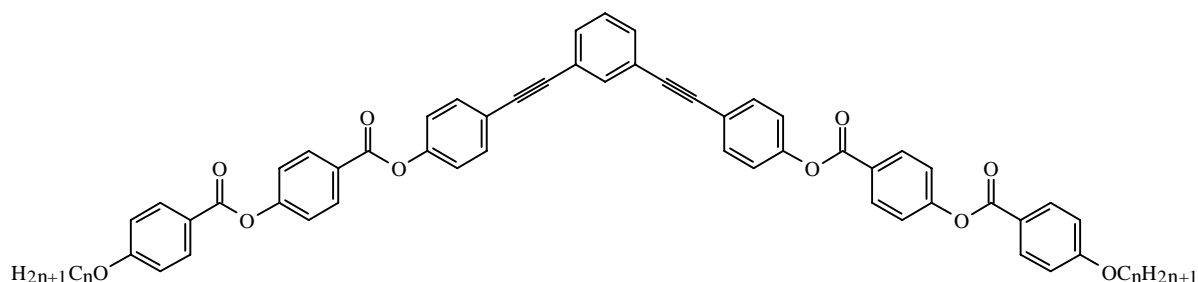


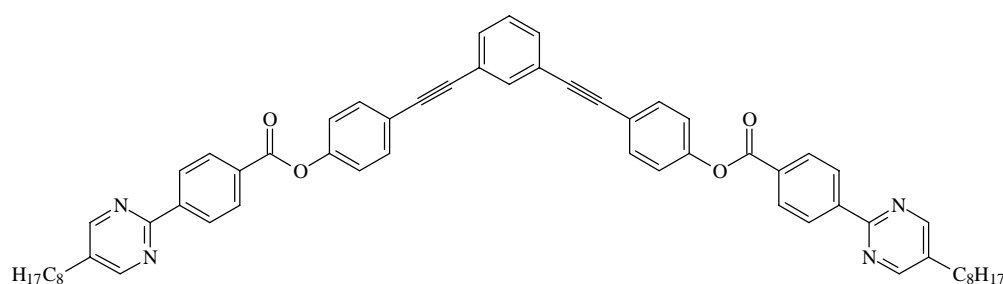
Table 3-12 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **27/n**.

Comp.	n	Phase transitions
27/9	9	Cr ₁ 92 Cr ₂ 159 Col _r 239 Iso <i>6.6 39.0 12.1</i>
27/14	14	Cr ₁ 106 Cr ₂ 136 Col _r 204 Iso <i>17.9 38.8 17.7</i>

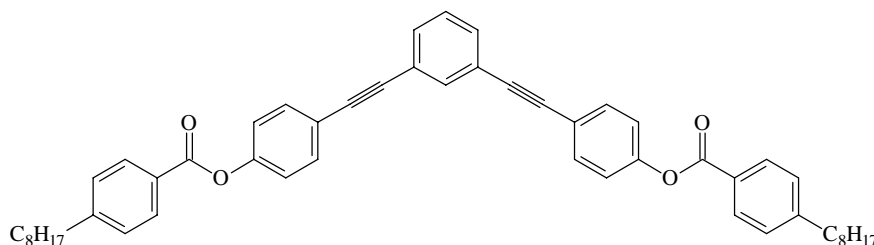
28/8 incorporating the 2-phenylpyrimidine rigid cores shows the typical texture of the intercalated smectic phase and the phenylbenzoates **27/n** displays the typical Col_r texture.

Also in the case of these acetylene derivatives it was not possible to reduced the number of aromatic rings incorporated in the molecules without loss of the mesomorphic properties. Hence, the benzoate **29/8** is a crystalline solid which can be supercooled to 120 °C without formation of a mesophase.

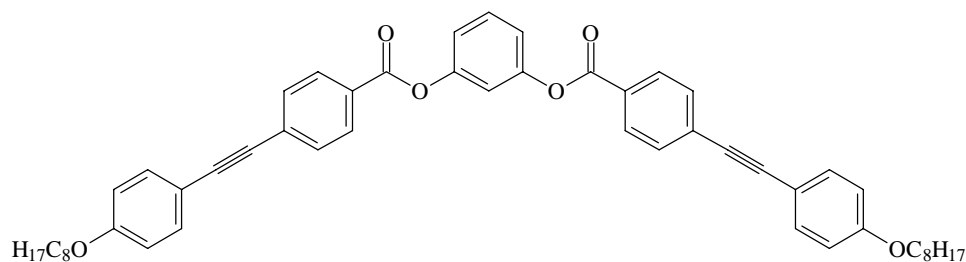
Shifting the position of the acetylenic units from the central part to the rod-like rigid units (see compound **30/8** with the tolane rigid cores) also leads to the loss of the mesomorphic properties.



28/8 Cr₁ 126 Cr₂ 204 Sm_{intercal} 236 Iso
5.9 41.6 25.5



29/8 mp 127 °C



30/8 mp 154 °C

Figure 3-14 Transition temperatures ($T / ^\circ\text{C}$) and transition enthalpies ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of compounds **28/8**, **29/8** and **30/8**.

6 Influence of the core structure on the mesomorphic properties

It was observed that the occurrence of the SmCP_A phases strongly depends on the structure of the rigid calamitic units **B**. In our systems it was only found for molecules incorporating the phenylbenzoates rigid core. If a SmCP_A phase is found, it occurs in the phase sequence of homologues with long terminal chains, whereas the short chain homologues have the Col_r phase. Depending on the central units, the lengths of the terminal chains necessary for the molecules to form SmCP_A phases is different. It seems that there are some relationships between the size of the central unit (A) and the formation of the SmCP_A phase. The transition temperatures of the 4-alkoxybenzoyloxybenzoates **31/n**, **12/n**, **15/n**, **25/14** and **27/14** are summarized in figure 3-15. It can be clearly seen that the stability of the ribbon arrangement is strongly related to the size of the central bent rigid cores and the length of the terminal chains. The alkyl chain length, necessary to replace the columnar phase by the SmCP_A phase increases on enlargement of the bent rigid core. This encouraged us to synthesize new homologues with a 1,3-phenylene central unit. The transition temperatures are shown in table 3-13.

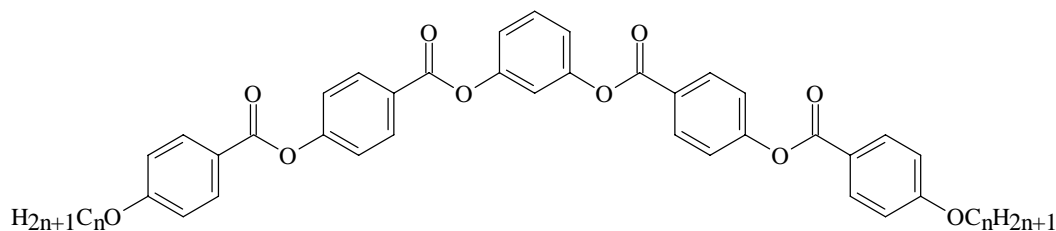


Table 3-13 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in *italics*) of the compounds **31/n**.

Comp.	n	Phase transitions
31/10	10	Cr ₁ 84 Cr ₂ 101 Cr ₃ 110 (SmCP _A 108) Iso <i>13.7 4.8 34.5 (17.1)</i>
31/10^a	10	Iso 108 Col _r 107 SmCP _A 89 Cr
31/12	12	Cr ₁ 70 Cr ₂ 105 SmCP _A 117 Iso <i>6.8 36.2 21.3</i>
31/14	14	Cr ₁ 78 Cr ₂ 105 SmCP _A 119 Iso <i>11.8 44.8 22.2</i>

^a: Phase sequence obtained by cooling (polarizing microscopy).

For these 1,3-phenylene derivatives, the compound with $n = 10$ shows a monotropic SmCP_A phase. For the biphenyl derivatives with alkoxy terminal chains, a chain length of $n = 12$ is needed, and even longer terminal chains are required by the *m*-terphenyl derivatives **15/n** to get the SmCP_A phase. Here only the compound with tetradecyloxy chain ($n = 14$) can form

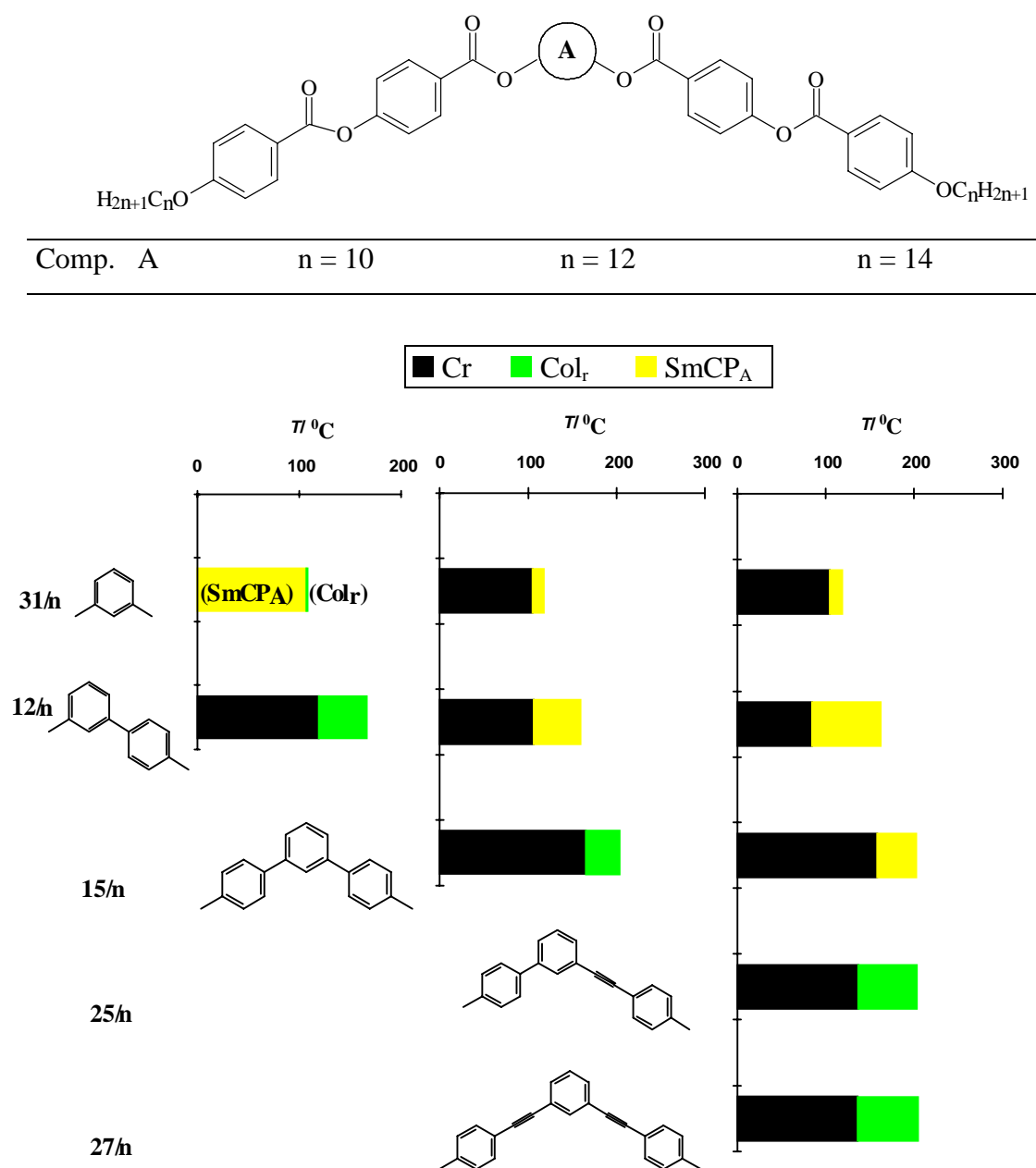


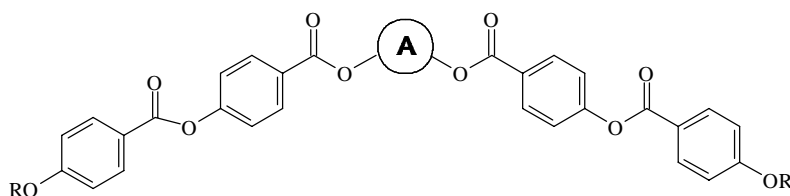
Figure 3-15 The influence of the size of the central units on the liquid crystalline properties of bent-core molecules. The mesophases of compound **31/10** are monotropic, the crystalline phase is not shown for clarity.

the SmCP_A phase. For molecules with a very large central unit [e. g. the 1-phenyl-3-(4-phenylethynyl)benzene derivatives **25/n** and the diphenylacetylene **27/n**], even a tetra-

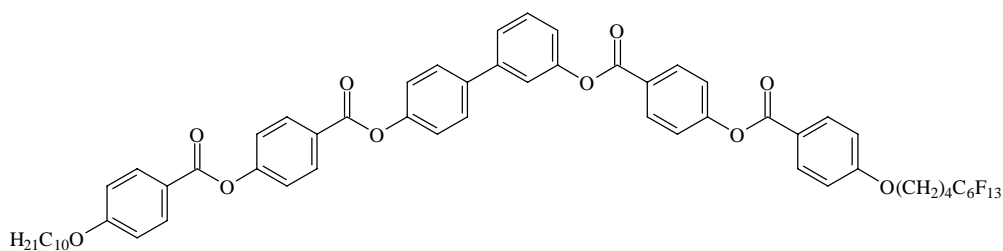
decyloxy chain ($n = 14$) is not sufficient to replace the columnar phase by the SmCP_A phase. Interestingly, the columnar phase disappears if the chain length reaches the length of the rigid aromatic half-parts attached to the central 1,3-disubstituted benzene ring⁴⁸ (respectively the average length for compounds **11/n**, **12/n** and **25/n**). It seems that the columnar phase is only stable if a partial overlap of the aromatic cores of the antiparallel arranged molecules at the ribbon interfaces is possible (see figure 3-5). Hence, the ribbon structure is stabilized by core-core interaction in the borderline regions between neighboring ribbons (see figure 3-5a). These core-core interaction should be especially effective for molecules with extended rigid cores and they can be reduced or lost on increasing the chains length (see figure 3-5b). Therefore, to obtain SmCP_A -phases, sufficiently long and flexible chains must be chosen to suppress the formation of frustrated layer structure, whereby the critical chain length strongly rises with the size of the rigid aromatic molecular part (A+B).

7 Banana-shaped molecules with semifluorinated terminal chains

Table 3-14 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the semifluorinated bent-core molecules.



Comp.	R	Phase transitions
31/6F4	$\text{C}_6\text{H}_{12}\text{C}_4\text{F}_9$	Cr 133 SmCP_A 164 Iso <i>39.8</i> <i>22.4</i>
31/4F6	$\text{C}_4\text{H}_8\text{C}_6\text{F}_{13}$	Cr ₁ 63 Cr ₂ 134 SmCP_A 201 Iso <i>5.9</i> <i>19.9</i> <i>27.0</i>
12/6F4	$\text{C}_6\text{H}_{12}\text{C}_4\text{F}_9$	Cr ₁ 90 Cr ₂ 127 SmCP_A 213 Iso <i>12.7</i> <i>17.1</i> <i>23.5</i>
12/4F6	$\text{C}_4\text{H}_8\text{C}_6\text{F}_{13}$	Cr ₁ 122 Cr ₂ 150 SmCP_A 252 Iso <i>5.5</i> <i>19.0</i> <i>26.9</i>
15/4F6	$\text{C}_4\text{H}_8\text{C}_6\text{F}_{13}$	Cr 211 SmCP_A 309 Iso <i>40.2</i> <i>31.6</i>



32/10 Cr 135 SmCP_A 211 Iso

37.1 25.9

As shown above, the separation of aliphatic and aromatic regions is an important factor determining the mesophase structure of banana-shaped molecules. Therefore, it is possible that by using the fluophobic effect, i.e. the inherent incompatibility of perfluorinated alkyl chains with aliphatic chains, aromatic hydrocarbons and polar groups,⁴⁹ the molecules could have a more pronounced tendency to form layer structures and therefore the SmCP_A phases could be stabilized.

Semifluorinated terminal chains with a different degree of fluorination were combined with different central units. Their melting behavior is shown in table 3-14 and figure 3-16. From this figure it is obvious that the semifluorinated terminal chains can significantly stabilize the SmCP_A phases. Comparison of the hydrocarbon compounds **12/n** and **15/n** with their semifluorinated analogues shows that SmCP_A phases were induced and the clearing temperatures are strongly enhanced for the compounds with semifluorinated terminal chains.

Thus, the regions of the SmCP_A phases are significantly enlarged. The stability of the mesophases rises with increasing degree of fluorination, which can be realized by elongation of the fluorinated segments or by increasing the number of fluorinated chains (compare compounds **12/10** and **32/10**). For example, compound **31/10** has only a monotropic SmCP_A phase, whereas the semifluorinated compound **31/6F4** shows the SmCP_A phase in a temperature region between 133-164°C. Also compound **12/10** does not form a SmCP_A phase, whereas **12/6F4** forms the SmCP_A phase in a region from 127 to 213 °C. Also if only one of the terminal chains is semifluorinated (compound **32/10**), the molecule favors the SmCP_A phase. This means that the semifluorinated chains prevent the molecules strongly from the intercalation of the aliphatic chains between the rigid aromatic cores because of their inherent incompatibility with these aromatic units. As this close contact of aromatic units and terminal chains is required at the boundaries between the ribbons in the Col_r phase

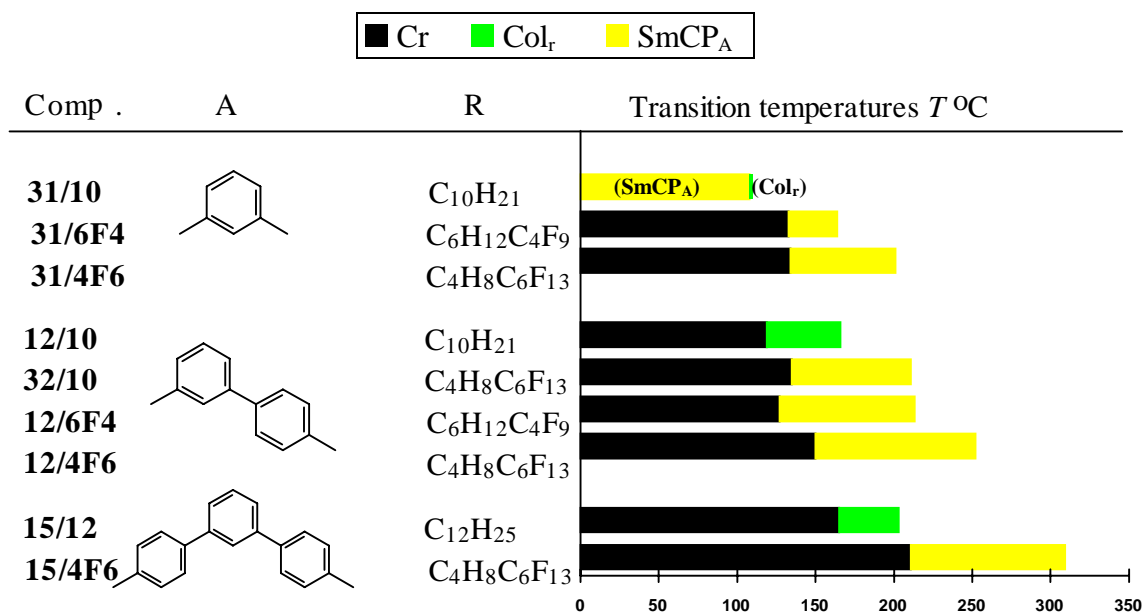


Figure 3-16 Melting behaviors of semifluorinated compounds. The phase sequence of compound **31/10** is obtained by cooling.

(see figure 3-5), the Col_r phase is destabilized. On the other hand it is well known that semifluorination can stabilize smectic liquid crystalline phases. This is mainly due to the increased incompatibility of the semifluorinated chains with the polar central cores and probably also to the larger rigidity of the fluorinated segments. Hence, the SmCP_A phases of bent-core molecules are strongly stabilized by semifluorination of the terminal chains. The mesophase stabilization amounts ca 50 K per C₆F₁₃ segment.

8 Bent-core molecules with a nitro substituent at the central unit

The 2'-nitro-substituted m-terphenyl derivatives **33/n** and **34/n** are especially remarkable, because all of them exhibit an additional nematic phase as high temperature mesophase. The nematic phase was indicated by the typical schlieren texture (figure 3-17) and the low transition enthalpies of the transition to the isotropic liquid.

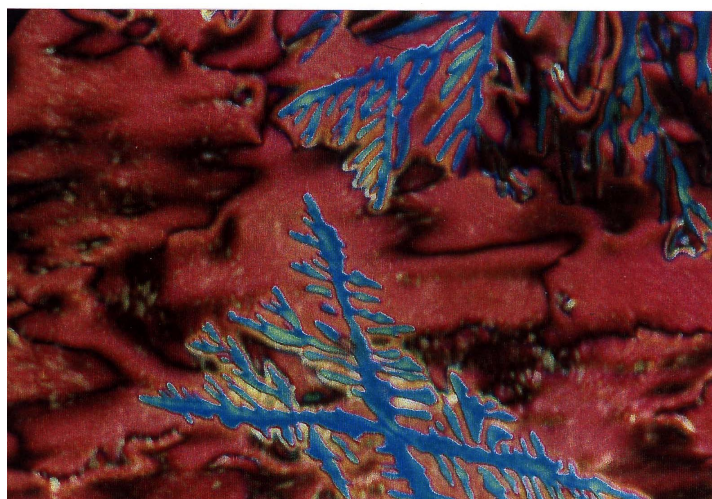


Figure 3-17 Optical photomicrograph (crossed polarizers) of the transition from the nematic phase (orange schlieren texture) to the Col_r phase (blue dendritic domains) of compound **33/9** at 197 °C.

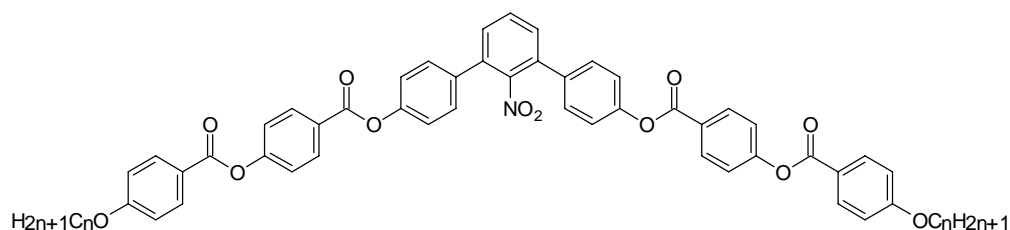


Table 3-15 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in *italics*) of the compounds **33/n**.

Comp.	n	Phase transitions
33/9	9	Cr ₁ 108 Cr ₂ 149 Col _r 197 N 217 Iso <i>4.0 21.2 10.5 0.4</i>
33/12	12	Cr ₁ 100 Cr ₂ 165 SmC _(b) 178 Col _r 183 N 199 Iso <i>28.5 32.2 2.2 10.2 0.3</i>
33/14	14	Cr ₁ 96 Cr ₂ 161 SmC _(b) 186 N ^a 190 Iso <i>39.2 32.2 17.4^b</i>

^a: This nematic phase was detected only by microscopy.

^b: Refers to the transitions SmC_(b) → N → Iso.

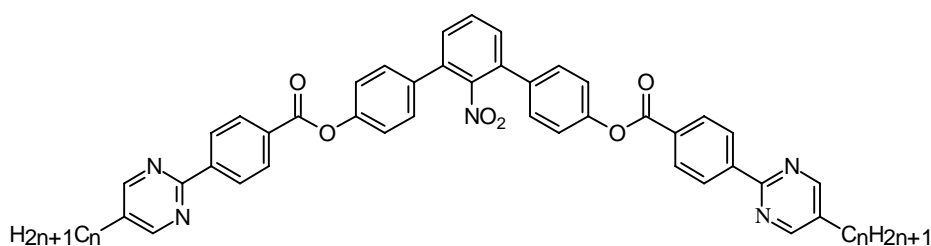


Table 3-16 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **34/n**.

Comp.	n	Phase transitions
34/8	8	Cr 221 (187 <i>Sm_{intercal}</i> 192 N 208) Iso <i>64.7</i>
34/12	12	Cr ₁ 43 Cr ₂ 153 N 164 Iso <i>10.0 40.6 0.3</i>

The transition temperatures of the compounds **33/n** and **34/n** are shown in tables 3-15 and 3-16. For the compounds **33/n** with phenylbenzoate rigid cores, a Col_r phase was detected under the nematic phase which exhibits the typical mosaic like texture (**33/9**). Elongation of the terminal chains ($n=12$) leads to the occurrence of an additional mesophase with schlieren texture below the Col_r phase. This texture is similar to the schlieren textures of the SmCP_A phases. It can not be homeotropically aligned, which indicates that this phase is optically biaxial. However the phase is not switchable. The enthalpy of the transitions between the Col_r phase and this phase (2.16 kJ mol^{-1}) is smaller than the enthalpies of the transitions between the Col_r phase and the SmCP_A phases (3.4 kJ mol^{-1} for compound **11/8**). X-ray investigations show that the mesophase has a layer structure. The layer period of compound **33/12** amounts $d = 4.1 \text{ nm}$ ($d = 4.4 \text{ nm}$ for compound **33/14**) which is only a little bit larger than that one of the SmCP_A phase of the related compounds without the nitro substituents (compound **11/12**: $d = 3.96 \text{ nm}$). Nevertheless, d is significantly smaller than the molecular length ($L = 5.9 \text{ nm}$) which indicates that the molecules should be tilted in the layers.

There are at least three possible structures of optically biaxial smectic phases (see figure 3-18). If the rotational cylinder has an in average circular cross section, a conventional SmC phase is possible. If the cross section of the rotational cylinder is elliptical, then the biaxiality can result from the parallel alignment of the rotational cylinders along the long axis of their ellipses. In this case, both, the tilted (tilted smectic phase, built up by biaxial molecules) and

the nontilted (SmC_M , M refers to McMillan who has described the phase)⁵⁰ arrangement of the molecules in the layers gives rise to optical biaxiality⁵¹. As the layer thickness suggests the presence of a tilt of the molecules, a SmC phase or a SmC_b phase are possible. Because the texture is different from those of conventional SmC phases, a SmC_b structure seems likely. However, further investigations would be necessary to confirm this. Therefore we tentatively assign this phase as $\text{SmC}_{(b)}$ phase.

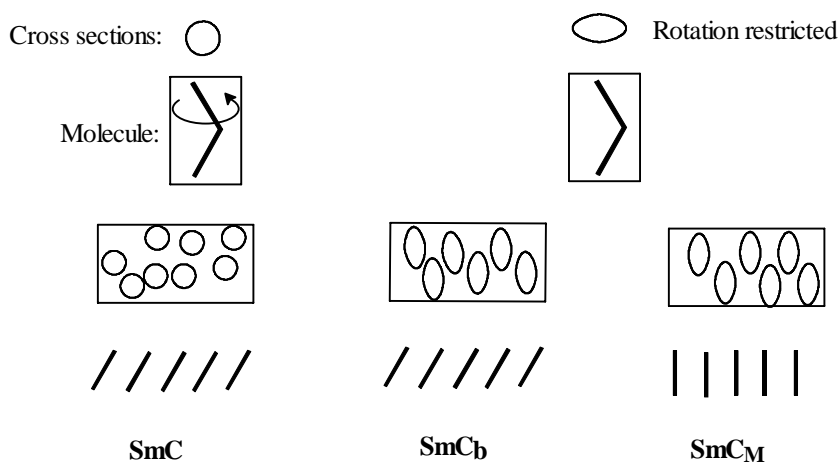


Figure 3-18 Structures of some possible optically biaxial smectic phases of banana-shaped molecules without polar order.

The compound **33/14** with a tetradecyloxy terminal chain has no CoI_r phase and forms only the nematic and the $\text{SmC}_{(b)}$ phase. As found in the series of the corresponding compounds without the nitro substituent at the central unit, the long terminal chains destabilize the CoI_r phase and induce the layer structure. However, the nitro group at the 2'-position at the central unit occupies additional space so that the molecules can not be closely packed and aligned in the direction of bending. It can be assumed that this leads to a loss of polar order within the layers and yields a $\text{SmC}_{(b)}$ phase instead of the SmCP_A phase. Additionally, dipolar interactions can contribute to this effect.

For the compounds with phenylpyrimidine rigid cores, the nitro substituent at the 2'-position obviously reduces the stability of the intercalated smectic phase which is characteristic for the other phenylpyrimidine derivatives. Only the nematic phase was detected in the case of compound **34/12** with the long terminal chains.

9 Miscellaneous bent-core molecules

Comparing the properties of all of the molecules described above, it was found that the compounds with biphenyl central units have the lowest melting points and the broadest SmCP_A regions, some of them did not crystallize again after the first melting. Thus, the biphenyl central unit is a special advantageous central core unit and therefore it was further modified in different ways.

At first, bent-core (banana-shaped) molecules with biphenyl central units, and two different rigid cores were synthesized and investigated. The SmCP_A phase was lost if the length of one of the terminal alkyl chain is significantly reduced (**35/12**, table 3-17). A mesophase with a schlieren texture is found below the columnar phase. As is not switchable, it should be one of the possible optical biaxial smectic phases (Sm_b). However the transition from the columnar phase to the Sm_b phase is very broad and therefore the X-ray investigation show that the two phases are coexistent (figure 3-19). If the short terminal chain is placed at the longer half of the rigid core (compound **36/12**), exclusively the columnar phase was detected.

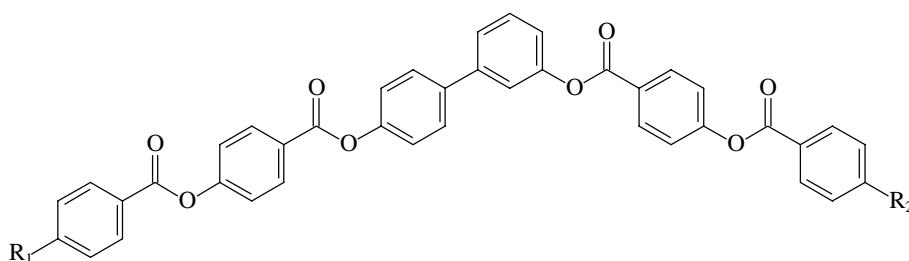
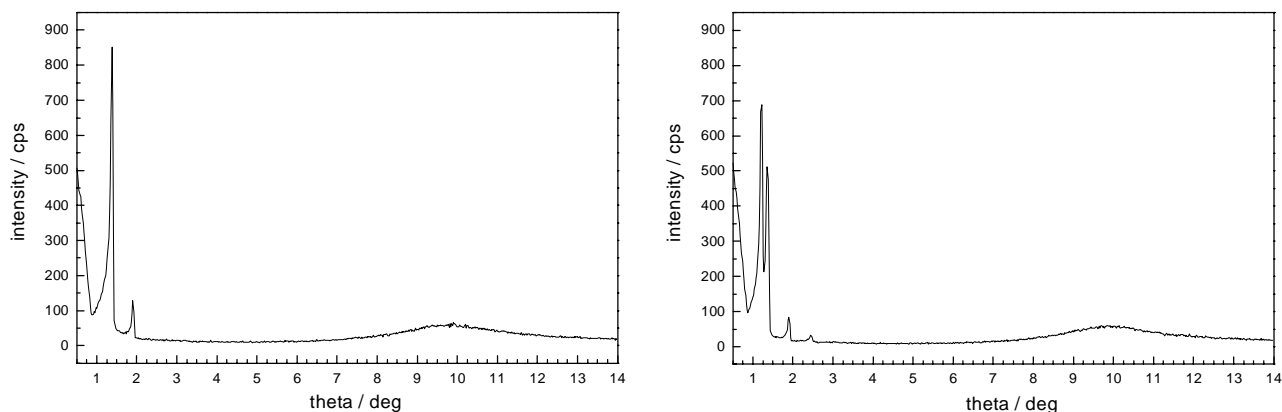


Table 3-17 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **35/12** and **36/6**.

Comp.	R ₁	R ₂	Phase transitions
35/12	C ₁₂ H ₂₅	C ₆ H ₁₃	Cr ₁ 95 Cr ₂ 104 Sm_b / Col 113 ^a Col 143 Iso <i>13.6 4.7 1.8 15.3</i>
36/6	C ₆ H ₁₃	C ₁₂ H ₂₅	Cr ₁ 60 Cr ₂ 98 Col 150 Iso <i>17.9 3.6 17.1</i>

^a: Transition between the Sm_b phase and the columnar phase is very broad and can be supercooled (see figure 3-19 and 3-20).



(a)

(b)

Figure 3-19 Scattering diagrams of a nonoriented sample of compound **35/12**.

(a): in the columnar phase (129 °C).

(b): in the Col / Sm_b coexistence region (100 °C).

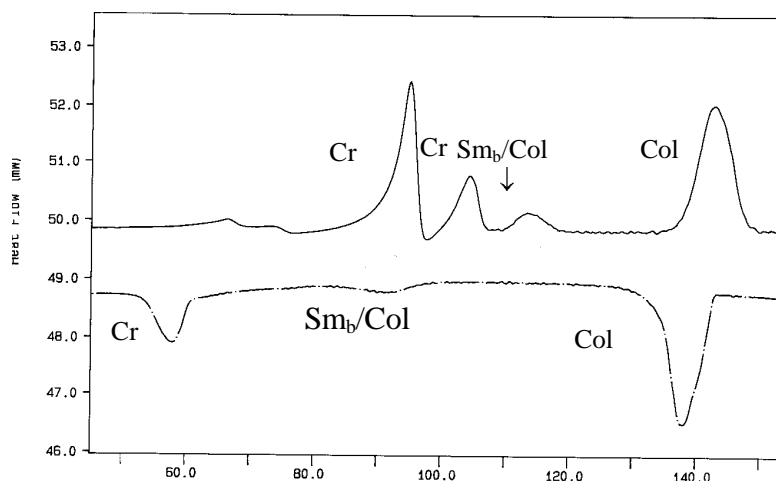
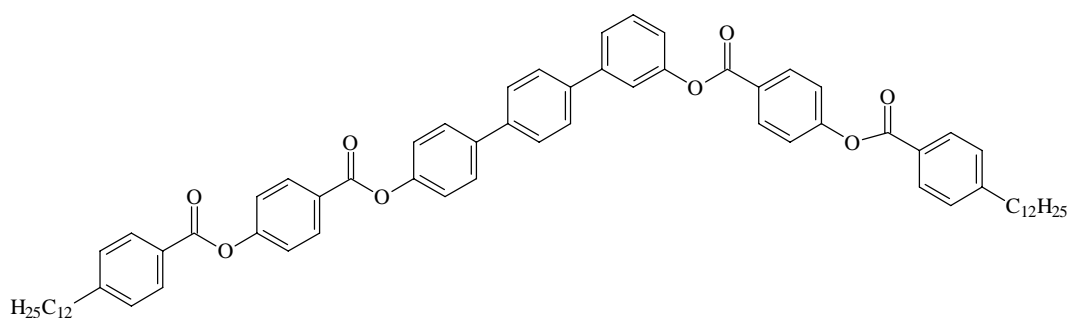


Figure 3-20 DSC thermograms of compound **35/12** (scanning rate 10 °C/min.).

Enlarging the central unit, by replacing the biphenyl unit by an 1,1':4',1''-terphenyl unit (compound **37/12**), with actually is a larger rigid core, leads to the loss of the smectic phases. Even the dodecyl terminal chains are not long enough to form the SmCP_A phase, so only the columnar phase was found.

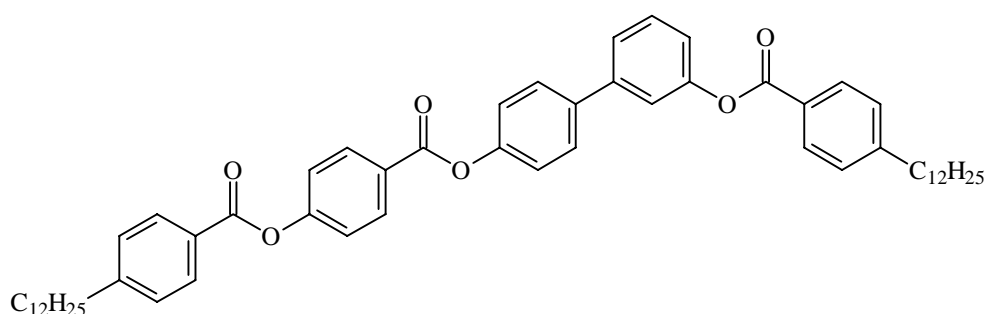
If one of the rigid cores attached to a biphenyl central core represents only a benzoate unit (compound **38/12**), only a monotropic nematic phase was detected. Obviously the molecular bent is not pronounced enough to behave like a typical banana-shaped molecule. The

molecule can be regarded more as a rod shaped molecule with a large lateral substituent.



37/12 Cr₁ 106 Cr₂ 133 Col 202 Iso

12.4 6.3 21.2



38/12 Cr (78 N) 88 Iso

The mesomorphic properties of bent-core molecules depend also on the direction of the ester groups which link the aromatic rings of the rigid cores. If their direction is reversed (compound **39/12** and **40/12**), SmCP_A phases were lost and only columnar phases were found for these compounds, even if they have long terminal chains ($n = 12$).

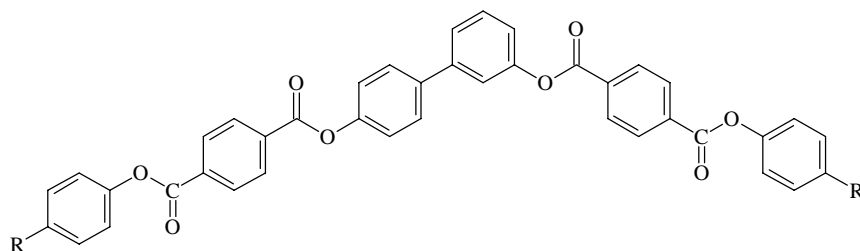
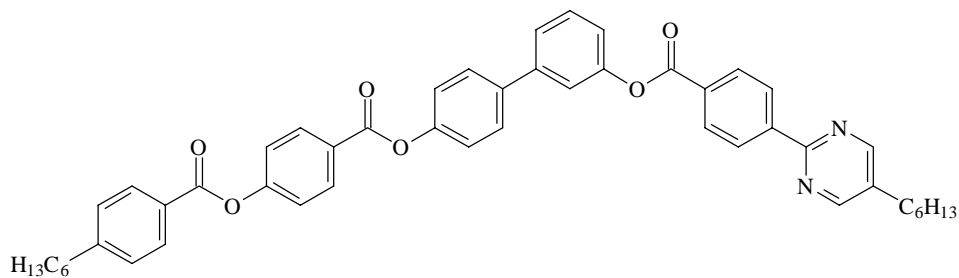


Table 3-18 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **39/12** and **40/12**.

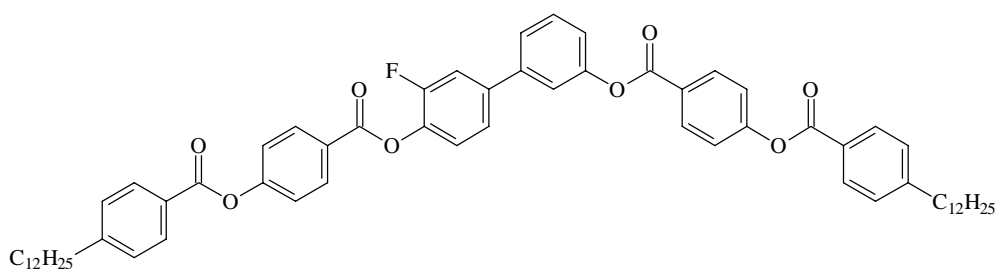
Comp.	R	Phase transitions
39/12	C ₁₂ H ₂₅	Cr ₁ 94 Cr ₂ 150 Col 189 Iso <i>17.0 43.1 21.9</i>
40/12	OC ₁₂ H ₂₅	Cr ₁ 112 Cr ₂ 168 Col 205 Iso <i>7.6 46.4 18.6</i>

If one of the phenylbenzoate rigid cores is replaced by a 2-phenylpyrimidine rigid core, these molecules form a $Sm_{intercal}$ phase and hence behave like the other phenylpyrimidine derivatives (**13/n**, **17/n**, **26/8** and **28/8**). Therefore, it seems that the 2-phenylpyrimidine rigid core has a stronger influence on the type of the mesophases than the phenylbenzoate rigid core. The $Sm_{intercal}$ phase was identified for compound **41/6** by the typical fan texture.



41/6 Cr 135 $Sm_{intercal}$ 142 Iso
34.8 10.9

As shown in section III-7, semifluorinated terminal chains can induce $SmCP_A$ phases or significantly enlarge the $SmCP_A$ phase region for the bent-core molecules. Also fluorine atoms attached to the aromatic cores of liquid crystals can significantly modify the liquid crystalline properties due to their electronegativity and their larger volume compared with hydrogen. Therefore, compounds with one fluoro substituent at the central unit were synthesized and their mesomorphic properties were studied.



42/12 Cr₁ 52 Cr₂ 75 $SmCP_A$ 143 Iso
13.7 10.6 20.6

The compounds **42/12** with a fluoro substituent at the 1,4-disubstituted benzene ring of the central unit has a similar behavior like the corresponding compound **12/12** without this substituent. However, the fluoro substituent at the 2-position of the 1,3-disubstituted benzene ring of the central biphenyl unit reduces the ability to form the $SmCP_A$ phase. On elongation the terminal chains the columnar phase of **43/8** is at first replaced by a Sm_b phase

(Compound **43/10**) which turns into a SmCP_A phase on further elongation of the chains (compound **43/12**).

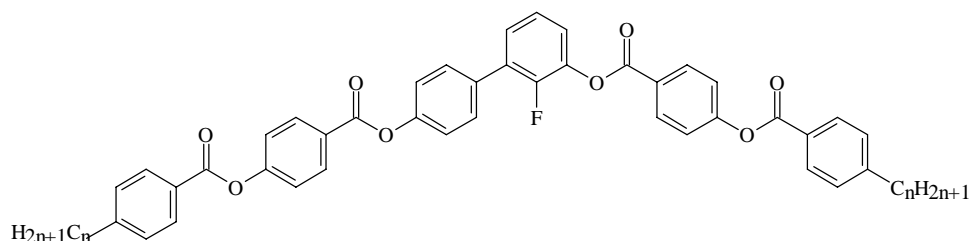


Table 3-19 Phase transition temperatures ($T / ^\circ\text{C}$) and corresponding enthalpy values ($\Delta H / \text{kJ mol}^{-1}$ lower lines in italics) of the compounds **43/n**.

Comp.	n	Phase transitions
43/8	8	Cr ₁ 61 Cr ₂ 136 Col 147 Iso <i>8.0 25.4 16.9</i>
43/10	10	Cr ₁ 45 Cr ₂ 125 Sm _b (Col 137) 141 Iso <i>2.2 5.6 20.1</i>
43/12	12	Cr 62 Mx ^a 122 SmCP _A 149 Iso <i>47.4 5.1 22.8</i>

^a: The phase structure is unclear.

Comparing all molecules with substituents at the angular position at the central unit (compounds **33/n**, **34/n** and **43/n**), reveals that this substituent prevents the molecules from a polar packing within the layers. The space filling and also the changed local and total dipole moments could be responsible for this.

In the case of the fluoro substituted compounds the chain length decides which phase is formed. If the terminal chains are long, the layers are stabilized and allow a dense polar packing of the molecules (**43/12**). When the terminal chains are shorter, the layers are less stable and the molecules can change their bending direction within the layers leading to a loss of the polar order (figure 3-21). The nitro group is larger and more polar than the fluoro atom. Here, even the long terminal tetradecyloxy chains are not long enough to prevent the loss of the polar ordering. So no SmCP_A phase can be found for these compounds, and even nematic phase can be formed.

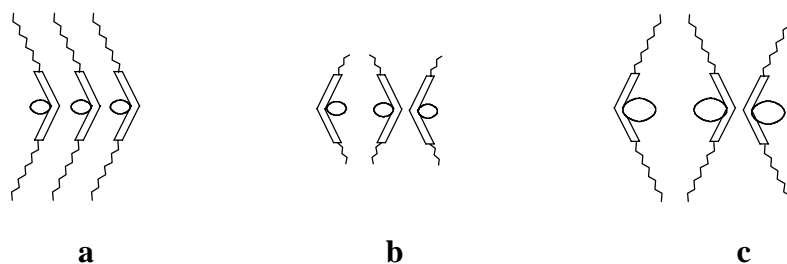


Figure 3-21 Molecular arrangement of the bent core molecules

(a): with small substituents and long terminal chains in the $SmCP_A$ phase.

(b): with small substituents and short terminal chains in the Sm_b phase.

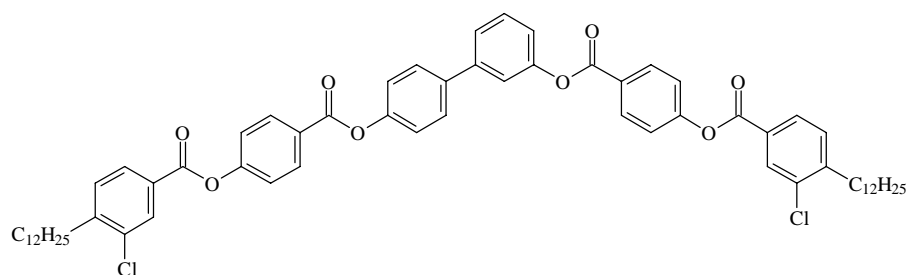
(c): with large substituents and long terminal chains in the Sm_b phase.

(in **a-c** the molecules are tilted in respect to the projection place)

Additionally two compounds with chlorine substituents at the rigid cores have been synthesized, in both compounds the Cl-atoms are directed away from the bent core unit. The compound **44/12** with the chloro substituents at the terminal rings of the phenylbenzoate rigid cores behaves different from the related compound without these chlorine atoms (compound **11/12**). On cooling from the isotropic liquid state, the mesophase occurs nearly without any birefringence, but likes some very small bright spots. This texture remains down to room temperature. X-ray studies show that there is only one sharp reflection in the small angle region and a diffuse scattering in the wide angle region, indicating a fluid smectic layer structure. This reflex remains to room temperature without change. The layer period is calculated to $d = 4.1$ nm, comparable with the period found in the $SmCP_A$ phase of related molecule (**11/12**: $d = 3.96$ nm) without the chloro substituent. DSC investigation reveal 4 phase transitions in the cooling scan. The transition from the isotropic state occurs at 150 °C, then, at 124 °C, 92 °C and 82 °C there are three additional peaks with very small transition enthalpies. Interestingly, by electrooptical investigation in the region between 124°C and 70 °C, some small domains were found with rotating brushes which change their direction of rotation by inverting the applied field similar to the $SmCP_A$ phases (details are described in section IV). Above 124 °C and below 70 °C no switching can be found. It seems that there are different mesophases with a layer structure (SmM_{X_1} - M_{X_3}). However, their precise phase structures are till now unclear.

If the chloro substituents are located at the inner rings of the phenylbenzoate rigid cores (compound **45/12**), only a columnar phases is found with a mosaic like texture, very similar

to that one of the Col_r phases.

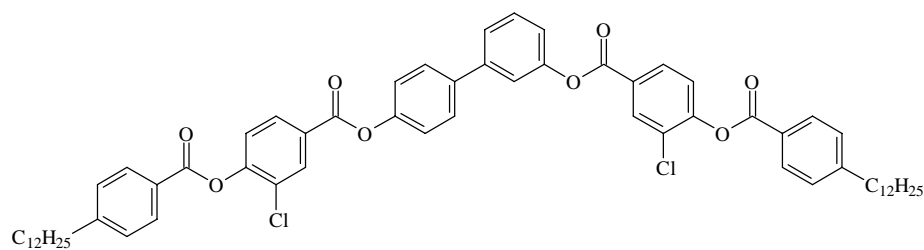


44/12 Cr₁ 100 Cr₂ 144 Mx₁ 155 Iso

1.1 6.1 20.5

Iso 150 Mx₁ 124 Mx₂ 92 Mx₃ 82 Mx₄

22.4 0.2 0.3 0.2



45/12 Cr₁ 74 Cr₂ 85 Col 91 Iso

10.6 28.0^a

^a: Refers to the transitions Cr₂ → Col → Iso.

IV Electrooptical investigations

Electrooptical investigations were performed in 6 or 4 μm thick polyimide-coated ITO cells by applying a triangular voltage. The switching processes were observed between crossed polarizers. All of the SmCP_A and Sm_b phases with exception of those of the compounds **12/4F6** and **14/4F6** were investigated. **12/4F6** and **14/4F6** could not be investigated because of their high clearing points ($>250\text{ }^\circ\text{C}$) which did not allow the filling of the ITO cells without damage. The switching processes and the spontaneous polarizations of the compounds whose clearing points are below $190\text{ }^\circ\text{C}$ were studied by heating to the isotropic phase and then slowly cooling to the SmCP_A phases. Some times an external electric field (30 V) was applied in order to obtain well aligned samples of the SmCP_A phases. Compounds whose clearing points are above $190\text{ }^\circ\text{C}$ were studied only by heating directly to the SmCP_A phase, so the investigations of these compounds is only qualitative (no spontaneous polarization values were obtained).

All the SmCP_A phases which were studied have essentially the same electrooptical properties. The investigation of compound **11/12** will be described in more detail. Two sharp peaks were detected during a half period by applying a triangular voltage, indicating an antiferroelectric switching process. A rather high triangular voltage is necessary because at lower triangular voltage only one sharp peak was recorded, the second peak becomes visible at a certain threshold voltage (for compound **11/12** V_{pp} 87 V) and becomes sharper with increasing V_{pp} (for compound **11/12** at $V_{pp} >150\text{ V}$ two sharp peaks were detected). The spontaneous polarizations P_s are rather high, amounting $400\text{-}700\text{ nC cm}^{-2}$. Some of them are summarized in table 4-1. The switching current response of compound **11/12** is shown in figure 4-1.

Table 4-1 Spontaneous polarizations P_s (nC cm^{-2}) of selected compounds.

Comp.	11/12	12/12	31/12	31/6F4	42/12	43/12
P_s	700	700	530	500	640	490

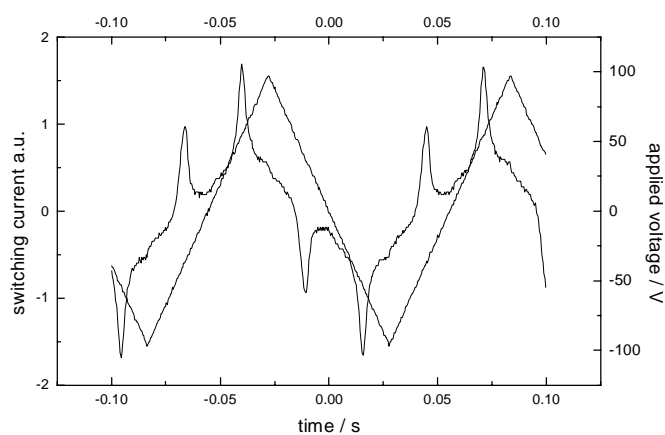


Figure 4-1 Switching current response in the SmCP_A phase of compound **11/12** obtained by applying a triangular voltage ($V_{pp} = 192$ V, $f = 9$ Hz, $T = 100$ °C. cell: $6 \mu\text{m}$ thickness, $1 \times 1 \text{ cm}^2$ area).

The switching processes observed between crossed polarizer is quite complex. If compound **11/12** is heated quickly into the isotropic phase, and then slowly cooled (-0.5 °C/ min.) to SmCP_A phase only the schlieren texture can be seen, which means that the smectic layers are predominately oriented parallel to the surfaces. By very slow cooling (-0.3 °C/ min.) with an applied electric field of 30 V, a focal conic texture with circular stripes is formed. By applying an electric field below 10 V, there is no change of the texture. On increasing the voltage the rotation of the brushes can be seen. They rotate clockwise or anticlockwise with inverting of the electric field. In different domains the brushes can rotate in the same or in opposite directions. Above a saturation voltage (46 V) the texture suddenly becomes significantly brighter and colored, indicating that the birefringence increases. No further changes appear with further increasing voltage. The textures of the two switched state are completely identical, independent of the sign of the applied field (figure 4-2).

The field induced rotation of distinction brushes was first analyzed by Link et al.. The tilt direction of the molecules and the direction of the polar order of the bent-core molecules are two independent symmetry breaking factors which cause the chirality of the smectic layers (see figure 4-3). Changing one of them changes their handedness. Accordingly, there are two possible equilibrium structures which both have an antiferroelectric switching behavior: The racemic state (R), and the homogeneously chiral state (H) (see figure 1-11).



-110 V

0V

+110V

Figure 4-2 Rotation of an extinction cross in the SmCP_A phase of compound **11/12** by applying an electric field.

In the racemic states (R) the tilt of the molecules is uniform (synclinc interlayer correlation), whereas the polar direction alternates in sign from layer to layer (antiferroelectric order). Thus the handedness changes from layer to layer. The texture of the ground state is characterized by parallel stripes. On applying an electric field the stripes disappear and the extinction brushes do not rotate when the direction of the field is reversed.

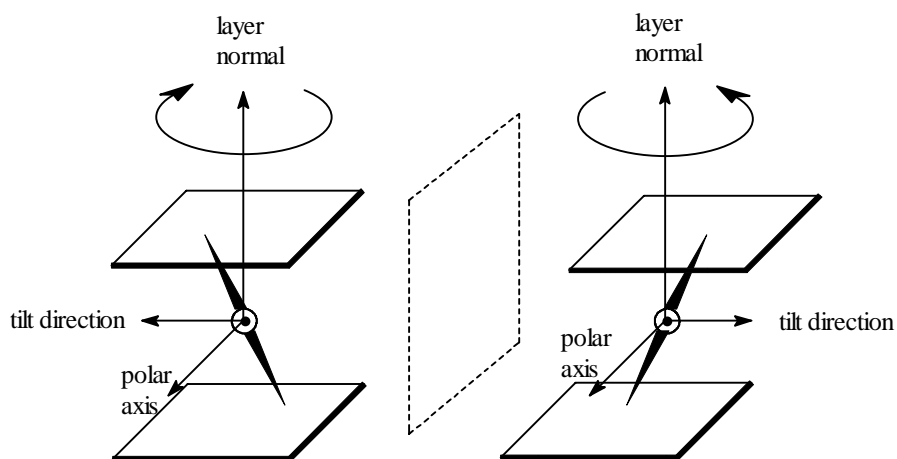


Figure 4-3 Schematic representation of one polar chiral layer consisting of achiral bent-core molecules (only one molecule is shown). In the picture at the left hand side the layer normal, tilt direction, and the polar axis define a right handed coordinate system (+), whereas in the mirror image these vectors define a left handed system (-).

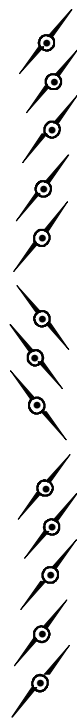
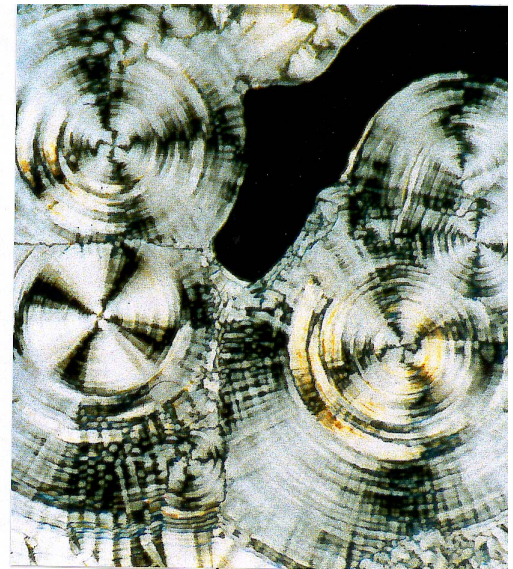
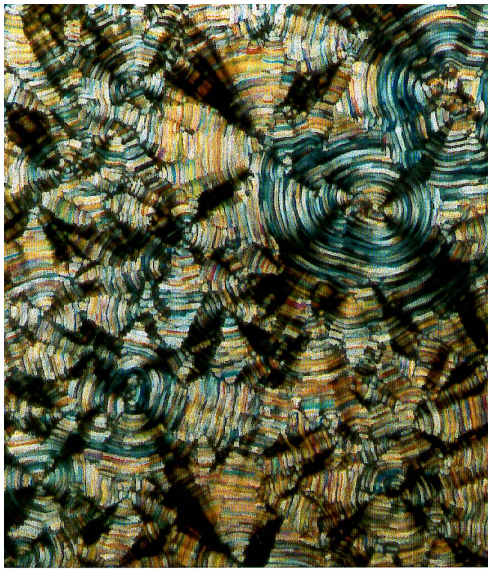
In the homogeneous chiral ground state (H), the tilt direction and also the polar axis alternate from layer to layer (anticlinic and antiferroelectric order). Here the handedness of the layers is uniform. In this case the brushes rotate in opposite directions depending on the polarity of the applied field.

Under our experimental conditions the extinction brushes rotate in different direction on reversing the sign of the field, which points to a predominately homogeneous chiral ground state. As the rotation direction can be different in different domains, separate regions of opposite handedness (H⁺ and H⁻) should coexist in the sample. The angle between the extinction brushes amount to ca. 86 degree. Provided that the smectic layers are arranged perpendicular to the substrate, the average optical axis should be tilted about 43 degree with respect to the layer normal. The increase in birefringence upon field application should be the result of the loss of the tilt alternation at zero field to give uniformly tilted chiral domains (ferroelectric order) with synclinic interlayer correction. Hence, in the predominate ground state the polar axes of the molecules alternate from layer to layer and the interlayer correlation in anticlinic.

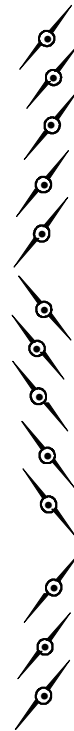
In our systems the homogeneous chiral ground state seems to be dominating, different from many other bent-core molecules with Schiff's-base units, which have a predominating racemic ground state. Another interesting difference is, that most of our compounds exhibit stripe textures after applying a saturation voltage which does not disappear on further increasing the voltage. In contrast, for many Schiff's-base derivatives a fan-like texture without stripes was found above a certain voltage. The stripes in the switched states of some of our compounds are broader. In this case two brushes in neighboring stripes rotating in opposite directions can be observed which means that they have an opposite handedness (figure 4-4). It seems that the predominating homogeneous chiral regions are interrupted by distinct regions with an opposite handedness (see figure 4-4).

Sometimes these regions are very small, so that they can be seen only as a line (figure 4-4a). Sometimes the regions can be larger and two brushes, rotating in opposite directions can be observed (figure 4-4b).

The mesophase of compound **44/12** though it is different from that one of the SmCP_A phase of compound **11/12** also exhibits an antiferroelectric switching behavior. Between crossed polarizers a dark ribbon-like texture can be found which is completely different from the schlieren textures of the SmCP_A phases. Additionally the switching process can only be



a



b

Figure 4-4 The textures of switched states of different compounds and their molecular arrangements.

observed in the temperature region between 124 °C and 70 °C, although the texture and the X-ray investigation show that there is no change between 150 °C and room temperature. On applying an electric field, some brightly colored domains can be seen, and there is a change of the bright and dark states with switching the electric field on and off. Interesting, the

bright domains expand slowly by applying higher electric fields (V_{pp} 150V), and the dark ribbon like texture gradually disappears, if switching is continued. After 30 minutes they have disappeared completely. Some small domains with extinction brushes, rotating with changing the signal of applied field, very similar to those of the $SmCP_A$ phase can be observed. Two sharp peaks were detected during a half period by applying an triangular voltage (figure 4-5) of at least V_{pp} 110 V, indicating an antiferroelectric switching process. The spontaneous polarization P_s is about 500 nC cm^{-2} . However the structure of this mesophase is not really clear.

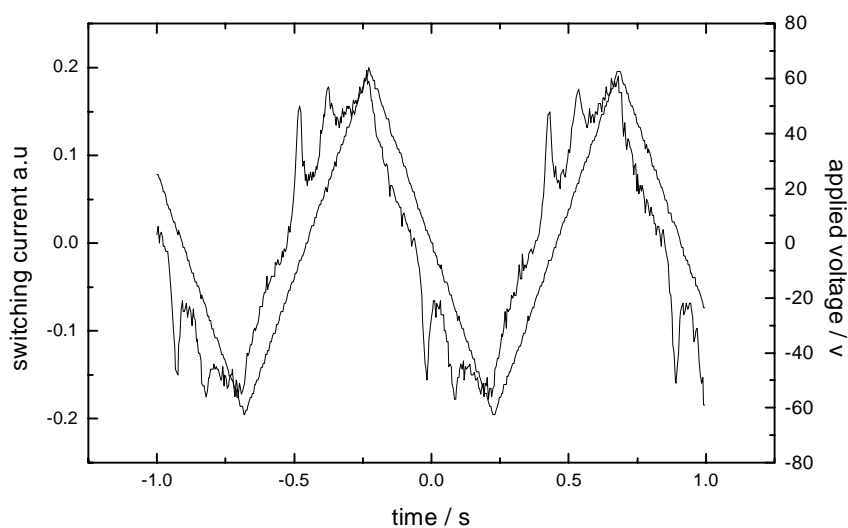


Figure 4-5 Switching current response of compound **44/12** obtained by applying a triangular voltage ($V_{pp} = 126 \text{ V}$, $F = 1.1 \text{ Hz}$, $T = 100 \text{ }^\circ\text{C}$. cell: $4 \text{ }\mu\text{m}$ thickness, $1 \times 1 \text{ cm}^2$ area).

V Summary

A wide variety of novel bent-core (banana-shaped) molecules without the sensitive Schiff's-base unit incorporating different angular units which differ in their size from 1,3-phenylene to 1,3-bis(phenylethynyl)benzene were synthesized in this work. They were combined with phenyl, phenylbenzoate, biphenyl and phenyl pyrimidine rigid cores. Furthermore, compounds with fluorinated terminal chains and molecules having a nitro or a fluoro substituent at the central unit and molecules with two different rigid cores were synthesized.

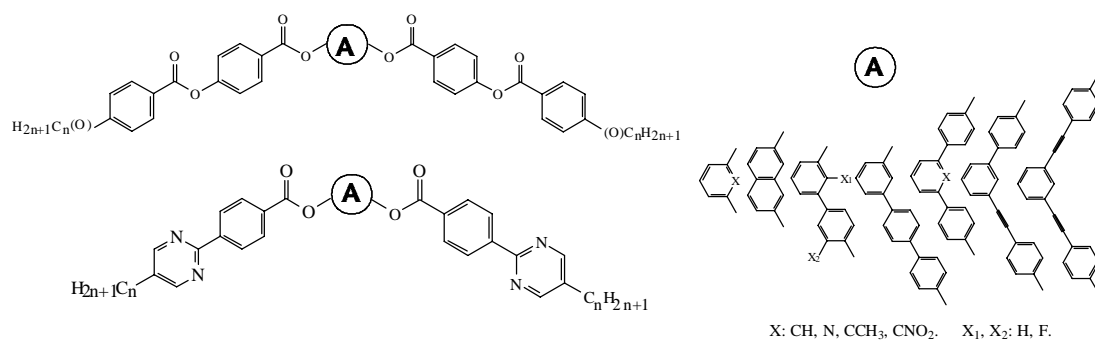


Figure 5-1 Molecular structures of synthesized banana-shaped molecules.

The melting behavior, the phase structure and the electrooptical properties of these molecules were studied. Molecules with 1,3-phenylene, 3,4'-biphenyl, m-terphenyl, 1-phenyl-3-(4-phenylethynyl)benzene and 1,3-bis(phenylethynyl)benzene central units and phenylbenzoates rigid cores (compounds **31/n**, **11/n**, **12/n**, **15/n**, **25/n** and **27/n**) exhibit three different phases, a rectangular columnar phase (Col_r, ribbon phase), an antiferroelectric switchable SmCP_A phase and sometimes a highly ordered smectic phase. The occurrence of the antiferroelectric SmCP_A phase sensitively depends on the length of the terminal chains and the size of the central unit. Compounds with short terminal chains exhibit exclusively the ribbon phase. On elongation of the chains, the SmCP_A phase occurs and for molecules with long terminal chains, only the SmCP_A phase can be found. The length of the terminal chains, necessary for the formation of the SmCP_A phase, depends on the length of the bent rigid unit within the molecules. Molecules with large central units (e.g. m-terphenyl derivatives) must have longer terminal chains than molecules incorporating a smaller rigid unit (e.g. the biphenyl derivatives).

The bent-core (banana-shaped) molecules with phenylpyrimidine rigid cores and short

terminal chains ($n < 8$), exhibit an intercalated smectic phase. Long terminal chains give rise to the loss of their mesomorphic properties.

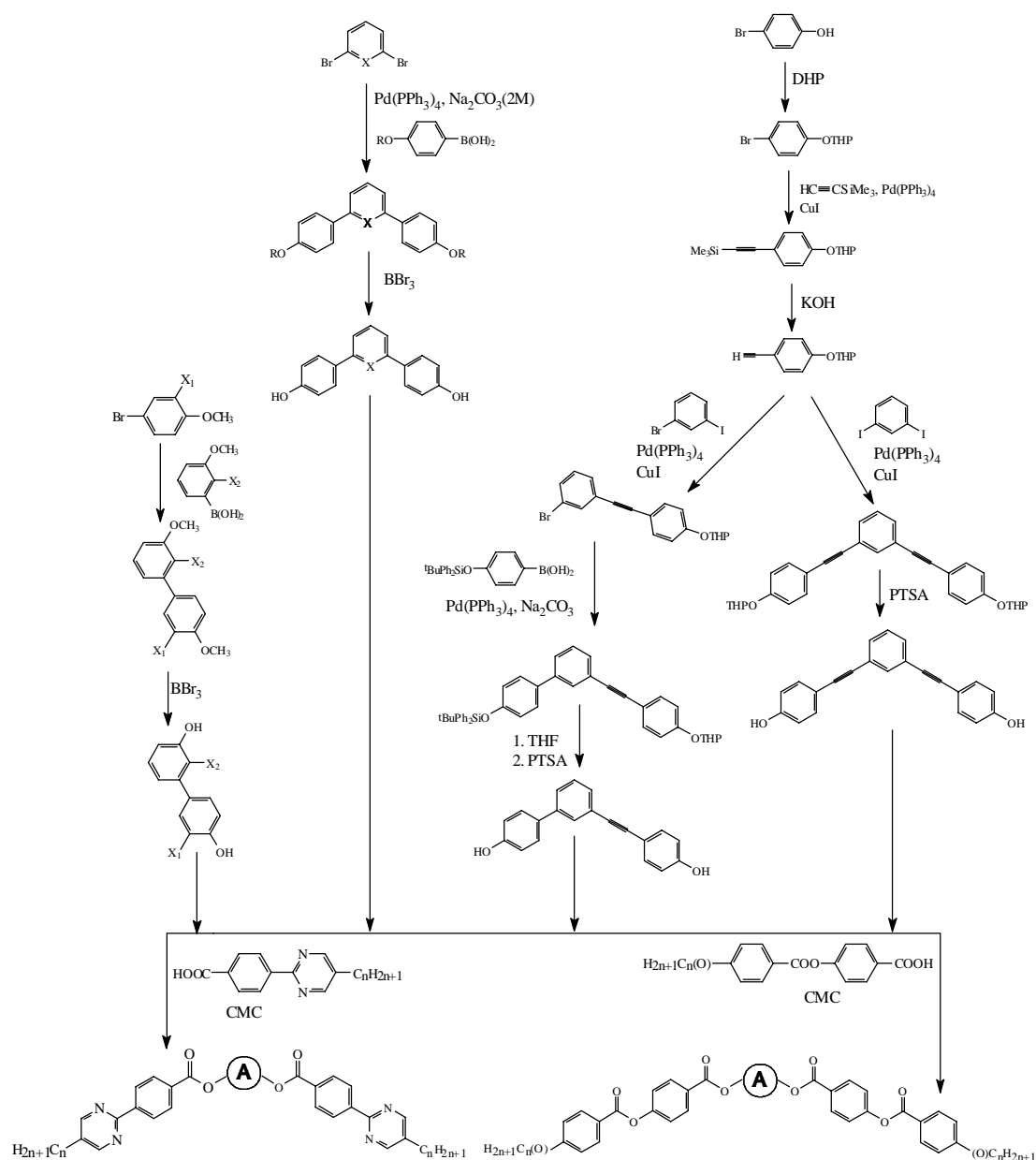


Figure 5-2 Synthesis route to banana-shaped molecules.

The compounds with a 2,6-diphenylpyridine central unit exhibit exclusively Col_r phases with significantly enhanced melting points in comparison with the related m-terphenyl derivatives. Semifluorinated terminal chains favor the formation of the SmCP_A phase. Especially the clearing points are much higher compared with those of the related hydrocarbon derivatives. All 2'-nitro-substituted m-terphenyl compounds have an additional nematic phase.

Substituents (NO₂ or F groups) at the angular position of the central unit give rise to the loss of the polar order, presumably because of the space filling and the changed local and total dipole moments. In the series of compounds with nitro substituents SmCP_A phases were completely lost and only non-polar, optically biaxial smectic phases SmC_(b) were found. Molecules with fluoro substituents exhibit SmCP_A phases if the terminal chains are long, and Sm_b phases if the terminal chains are short.

Molecules with two different calamitic units exhibit different phases depending on the type of the rigid cores. Often the phenylpyrimidine rigid core dominates the mesomorphic behavior, which means that intercalated smectic phases were found.

The compound with chloro substituents at the terminal rings of the phenylbenzoate units has a rather complex mesomorphic behavior. Though the texture is different from the SmCP_A phase, it switches antiferroelectrically in a certain temperature range. Further studies should be done to reveal the phase structure.

All SmCP_A phases show essentially the same electrooptical properties. Two peaks were found during a half period by applying a triangular voltage, indicating an antiferroelectric switching behavior, the P_s is about 400-700 nC/cm².

VI Experimental Section

1 General

The purification and drying of the used solvents was performed according to the methods described in the literature.⁵² The water content was determined using Karl-Fisher-Titration (Mitsubishi Moisturemeter MCI Model CA-02). Thin-layer chromatograph was performed using thin-layer chromatography plates (Silica Gel F₂₅₄, Merck). Silica Gel 60 was used for column chromatography. Confirmation of the structures of the intermediates and products was obtained by ¹H-NMR, ¹³C-NMR and ¹⁹F-NMR spectroscopy (Varian Unity 500, Varian Gemini 200 spectrometer). The numbering of the carbon atom of the molecular formulas shown in the experimental section is only used for the assignments of the NMR signal and is not in accordance with the IUPAC nomenclature rules. Mass spectra were recorded on an AMD 402 mass spectrometer (70 eV). The purity of all compounds was checked by thin-layer chromatography. Microanalysis were performed using a Leco CHNS-932 elemental analyzer. Transition temperatures were determined using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarizing microscope and were confirmed using differential scanning calorimetry (Perkin Elmer DSC-7). X-ray studies were performed by means of a Guinier goniometer (Fa. Huber).

2 Starting materials

Commercial available chemicals:

Alkylbromides (Merck)	2,6-Dibromoaniline (Aldrich)
4-Amidinobenzamide hydrochloride (Aldrich)	2,6-Dibromopyridine (Aldrich)
Bromobenzene (Merck)	1,3-Diiodobenzene (ABCR GmbH & Co)
3-Bromophenol (Lancaster)	4-(Dimethylamino)pyridine (Ferak)
1-Bromo-3-iodobenzene (Aldrich)	4-Hydroxybenzaldehyde (Merck)
Boron tribromide (Aldrich)	Imidazol (Janssen)
n-Butyllithium (Aldrich)	Isophthaloyl chloride (Fluka)
4-Carboxybenzaldehyde (Aldrich)	Methyl 4-formylbenzoate (Fluka)
Chromium(VI)oxide (CrO ₃)	Tetrabutylammonium iodide
Copper(I)iodide	p-Toluene sulfonic acid (Fluka)
	Triethylamine

N-Cyclohexyl-*N'*-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate (Fluka)

The following compounds were available in the working group:

Alkyl(oxy)benzoic acids
Alkyloxyboronic acids
4-(4-Butylbenzoyloxy)benzoic acid
4-(4-Octylbenzoyloxy)benzoic acid
4-(4-Octyloxybenzoyloxy)benzoic acid
4-(5-Alkylpyrimidine-2-yl)phenols
4-(5-Alkyl-1,3,4-thiadiazole-2-yl)phenols
1,1-Dimethoxydecane
4-(5-Heptyl-2,2,2-bicycloctyl)phenol
4-(4-Octyloxybenzoyloxy)phenol

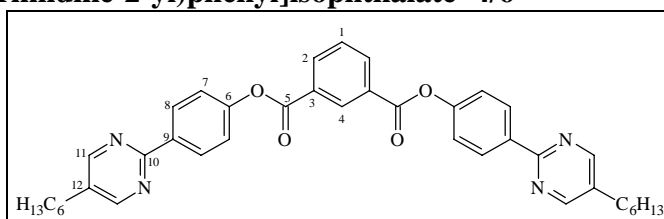
Pd(PPh₃)₄

3 Synthesis of the compounds with two identical calamitic units

3.1 Esterification of isophthaloyl dichloride with phenols

Isophthaloyl dichloride (1.0 mmol), the appropriate phenol (2.0 mmol) and DMAP (0.4 mmol) were dissolved in dry toluene (15 ml) and pyridine (2 ml) was added. The mixture was then heated to reflux for 3h, cooled to room temperature, water (20 ml) was added and then the solution was acidified with concentrated hydrochloride acid (33%) to pH = 2.5. The organic phase was separated. After evaporation of the solvent the product was purified by column chromatography (CHCl₃/MeOH = 10:1.0), and then recrystallized from toluene.

Bis[4-(5-hexylpyrimidine-2-yl)phenyl]isophthalate 4/6



Synthesized from isophthaloyl dichloride (0.20 g, 1.0 mmol) and 4-(5-hexylpyrimidine-2-yl)-phenol (0.5 g, 2.0 mmol).

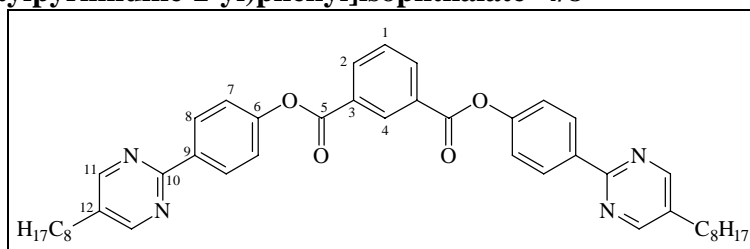
Yield 0.2 g (31.1%); mp 139 °C.

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 9.05 (s, 1H, H-4), 8.61 (s, 4H, H-11), 8.52-8.43 (m, 6H, H-2, 8), 7.70 (t, *J* 7.9, 1H, H-1), 7.37 (d, *J* 9.0, 4H, H-7), 2.62 (t, *J* 7.6, 4H, Pyrimidine-CH₂), 1.65 (m, 4H, CH₂), 1.34-1.24 (m, 12H, CH₂), 0.88 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.2 (2C=O), 162.0 (C-10), 157.2 (C-11), 152.7 (C-6), 135.8 (C-9), 135.1 (C-2), 133.2 (C-12), 131.9 (C-4), 130.4 (C-3), 129.4 (C-8), 129.2 (C-1), 121.7 (C-7), 31.7 (CH₂), 30.6 (CH₂), 30.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): *m/z* (%) 642 (M⁺, 30), 387 (100), 347 (15), 104 (22).

Bis[4-(5-octylpyrimidine-2-yl)phenyl]isophthalate 4/8



Synthesized from isophthaloyl dichloride (0.20 g, 1.0 mmol) and 4-(5-octylpyrimidine-2-yl)-phenol (0.6 g, 2.0 mmol).

Yield 0.4 g (57.3%); mp 142 °C. (Found: C, 76.04; H, 7.20; N, 7.62%; C₄₄H₅₀N₄O₄ requires C, 75.64; H, 7.16; N, 8.02%).

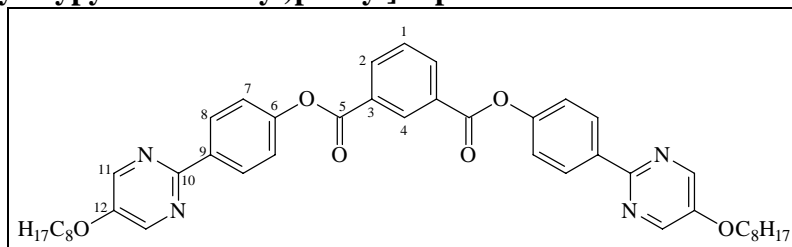
¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 9.07 (s, 1H, H-4), 8.64 (s, 4H, H-11), 8.56-8.48 (m, 6H, H-2, 8), 7.72 (t, *J* 7.9, 1H, H-1), 7.39 (d, *J* 9.0, 4H, H-7), 2.64 (t, *J* 7.6, 4H, Pyrimidine-CH₂), 1.66 (m, 4H, CH₂), 1.33-1.28 (m, 20H, CH₂), 0.89 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.2 (2C=O), 162.0 (C-10), 157.2 (C-11), 152.7 (C-6), 135.8 (C-9), 135.1 (C-2), 133.2 (C-12), 131.9 (C-4), 130.4 (C-3), 129.4 (C-8), 129.2 (C-1),

121.7 (C-7), 31.7 (CH₂), 30.6 (CH₂), 30.1 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): m/z (%) 698 (M⁺, 30), 613 (8), 415 (100), 104 (15).

Bis[4-(5-octyloxypyrimidine-2-yl)phenyl]isophthalate 5/8



Synthesized from isophthaloyl dichloride (0.2 g, 1.0 mmol) and 4-(5-octyloxypyrimidine-2-yl)phenol (0.6 g, 2.0 mmol).

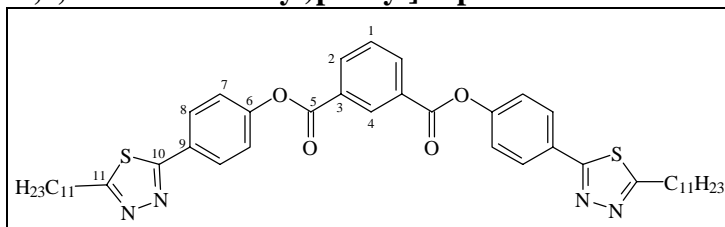
Yield 0.5 g (68.5%); mp 155 °C. (Found: C, 72.74; H, 6.90; N, 7.32%; C₄₄H₅₀N₄O₆ requires C, 72.32; H, 6.85; N, 7.67%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 9.03 (s, 1H, H-4), 8.46-8.41 (m, 10H, H-2, 8, 11), 7.66 (t, *J* 7.8, 1H, H-1), 7.34 (d, *J* 8.8, 4H, H-7), 4.05 (t, *J* 6.5, 4H, OCH₂), 1.80 (m, 4H, CH₂), 1.45 (m, 4H, CH₂), 1.34-1.26 (m, 16H, CH₂), 0.86 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.1 (2C=O), 156.9 (C-10), 152.2 (C-6), 151.7 (C-12), 143.9 (C-11), 135.6 (C-9), 135.0 (C-2), 131.8 (C-4), 130.4 (C-3), 129.2 (C-1), 128.9 (C-8), 121.6 (C-7), 68.9 (OCH₂), 31.6 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 28.9 (CH₂), 25.7 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): m/z (%) 730 (M⁺, 18), 431 (100), 188 (18), 104 (16).

Bis[4-(5-undecyl-1,3,4-thiadiazole-2-yl)phenyl]isophthalate 6/11



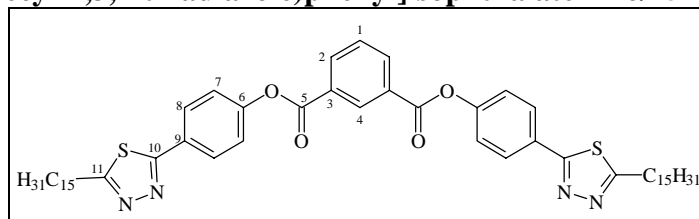
Synthesized from isophthaloyl dichloride (0.2 g, 1.0 mmol) and 4-(5-undecyl-1,3,4-thiadiazole-2-yl)phenol (0.68 g, 2.0 mmol).

Yield 0.1 g (12.5%); mp 179 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 9.02 (s, 1H, H-4), 8.49 (d, *J* 7.8, 2H, H-2), 8.02 (d, *J* 8.8, 4H, H-8), 7.71 (t, *J* 7.8, 1H, H-1), 7.36 (d, *J* 8.8, 4H, H-7), 3.12 (t, *J* 7.9, 4H, CH₂), 1.83 (m, 4H, CH₂), 1.51-1.01 (m, 32H, CH₂), 0.86 (t, *J* 6.8, 6H, CH₃).

MS (70 eV): m/z (%) 794 (M⁺, 10), 667 (18), 463 (100), 447 (30), 205 (35), 192 (62), 104 (48).

Bis[4-(5-pentadecyl-1,3,4-thiadiazole)phenyl]isophthalate 6/15

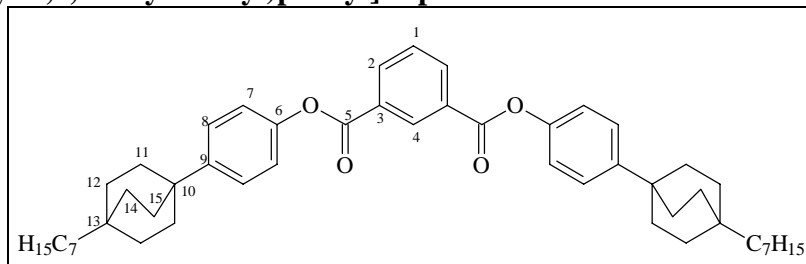


Synthesized from isophthaloyl dichloride (0.2 g, 1.0 mmol) and 4-(5-pentadecyl-1,3,4-thiadiazole-2-yl)phenol (0.77 g, 2.0 mmol).

Yield 0.3 g (33.3%); mp 181 °C. (Found: C, 71.87; H, 8.13; N, 5.72; S, 6.94%; C₅₄H₇₄N₄O₄S₄ requires C, 71.52; H, 8.17; N, 6.18; S, 7.06%).

MS (70 eV): m/z (%) 906 (M⁺, 10), 723 (18), 519 (62), 388 (18), 205 (58), 192 (100), 105 (33).

Bis[4-(4-heptyl-2,2,2-bicyclooctyl)phenyl]isophthalate 7/7



Synthesized from isophthaloyl dichloride (0.2 g, 1.0 mmol) and 4-(4-heptyl-2,2,2-bicyclooct-1-yl)phenol (0.6 g, 2.0 mmol).

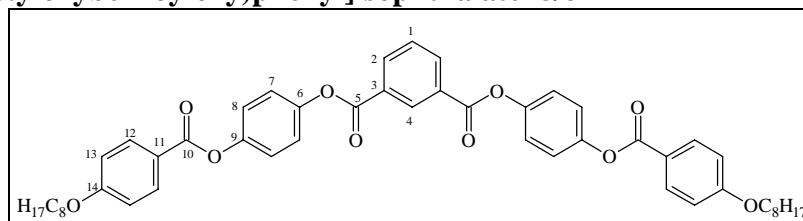
Yield 0.4 g (54.8%); mp 227 °C. (Found: C, 82.31; H, 8.97%; C₅₀H₆₆O₄ requires C, 82.19; H, 9.04%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.97 (s, 1H, H-4), 8.42 (d, *J* 7.8, 2H, H-2), 7.64 (t, *J* 7.8, 1H, H-1), 7.36 (d, *J* 9.0, 4H, H-8), 7.12 (d, *J* 8.8, 4H, H-7), 1.82-1.78 (m, 12H, H-11, 15), 1.52-1.45 (m, 12H, H-12, 14), 1.31-1.09 (m, 24H, CH₂), 0.87 (t, *J* 6.9, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6 (2C=O), 148.5, 148.4 (C-6, 9), 134.9 (C-2), 131.8 (C-4), 130.6 (C-3), 129.1 (C-1), 126.8 (C-8), 120.9 (C-7), 41.7 (C-10), 34.7 (C-13), 32.7 (C-11, 15), 31.8 (CH₂), 31.5 (C-12, 14), 30.6 (CH₂), 30.5 (CH₂), 29.3 (CH₂), 23.6 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

MS (70 eV): m/z (%) 730 (M⁺, 20), 576 (10), 431 (100), 387 (8), 205 (12), 192 (18), 133 (33).

Bis[4-(4-octyloxybenzoyloxy)phenyl]isophthalate 8/8



Synthesized from isophthaloyl dichloride (0.2 g, 1.0 mmol) and 4-(4-octyloxybenzoyloxy)phenol (0.68 g, 2.0 mmol).

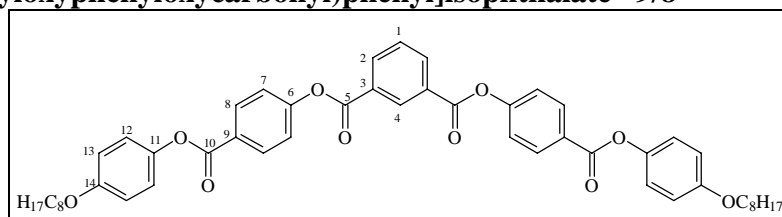
Yield 0.3 g (36.8%); mp 159 °C. (Found: C, 74.30; H, 6.71%; C₅₀H₅₄O₁₀ requires C, 73.71; H, 6.63%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 9.03 (s, 1H, H-4), 8.49 (d, *J* 7.8, 2H, H-2), 8.16 (d, *J* 9.0, 4H, H-12), 7.71 (t, *J* 7.9, 1H, H-1), 7.31 (s, 8H, H-7, 8), 6.98 (d, *J* 9.0, 4H, H-13), 4.06 (t, *J* 6.5, 4H, OCH₂), 1.83 (m, 4H, CH₂), 1.32-1.07 (m, 20H, CH₂), 0.87 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.9, 164.3, 163.8 (4C=O, C-14), 148.9, 148.2 (C-6, 9), 135.1 (C-2), 132.4 (C-12), 131.9 (C-4), 130.4 (C-3), 129.2 (C-1), 122.9, 122.5 (C-7, 8), 121.5 (C-11), 114.4 (C-13), 68.3 (OCH₂), 31.7 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): m/z (%) 814 (M⁺, 3), 730 (17), 574 (23), 233 (100), 121 (43).

Bis[4-(4-octyloxyphenyloxycarbonyl)phenyl]isophthalate 9/8



Synthesized from isophthaloyl dichloride (0.2 g, 1.0 mmol) and 4-(4-octyloxyphenyloxycarbonyl)phenol (0.68 g, 2.0 mmol).

Yield 0.15 g (18.4%); mp 202 °C. (Found: C, 73.86; H, 6.64%; C₅₀H₅₄O₁₀ requires C, 73.71; H, 6.63%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 9.03 (s, 1H, H-4), 8.49 (d, *J* 7.8, 2H, H-2), 8.29 (d, *J* 8.6, 4H, H-8), 7.23 (t, *J* 7.9, 1H, H-1), 7.40 (d, *J* 8.6, 4H, H-7), 7.11 (d, *J* 9.0, 4H, H-12), 6.92 (d, *J* 9.0, 4H, H-13), 3.95 (t, *J* 6.6, 4H, OCH₂), 1.80-1.73 (m, 4H, CH₂), 1.44-1.27 (m, 20H, CH₂), 0.88 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.9, 163.8 (4C=O, C-14), 157.2 (C-6), 154.9 (C-11), 144.3 (C-9), 135.4 (C-2), 132.0 (C-8), 130.1 (C-4), 129.4 (C-3), 127.8 (C-1), 122.4, 122.0 (C-7, 12), 115.3 (C-13), 68.5 (OCH₂), 31.7 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.1 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

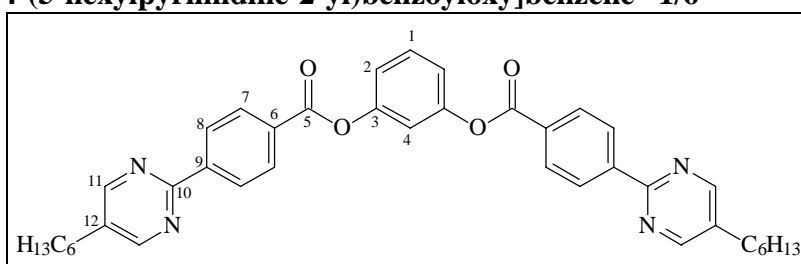
3.2 Esterification of divalent phenols with benzoic acids

The appropriate divalent phenol (0.9 mmol), the substituted benzoic acid (2.0 mmol), CMC (0.9 g, 2.1 mmol) and DMAP (50 mg, 0.4 mmol) were dissolved in dry CH₂Cl₂ (20 ml), the mixture was stirred at room temperature for 12 h - 24 h, then water (20 ml) was added and the organic phase was separated. After evaporation of the solvent the product was purified by column chromatography (CHCl₃/MeOH = 10:0.5), and then recrystallized from ethyl acetate.

3.2.1 Synthesis of the 1,3-dihydroxybenzene derivatives

3.2.1.1 1,3-Bis(4-substituted benzoyloxy)benzenes

1,3-Bis[4-(5-hexylpyrimidine-2-yl)benzoyloxy]benzene 1/6



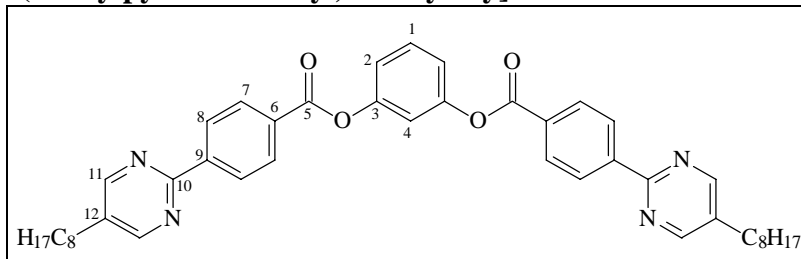
Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and 4-(5-hexylpyrimidine-2-yl)benzoic acid (0.5 g, 1.76 mmol).

Yield 0.18 g (31.0%); mp 160 °C. (Found: C, 74.83; H, 6.76; N, 8.91%; C₄₀H₄₂N₄O₄ requires C, 74.77; H, 6.54; N, 8.72%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.69 (s, 4H, H-11), 8.57 (d, *J* 8.8, 4H, H-8), 8.32 (d, *J* 8.8, 4H, H-7), 7.50 (t, 1H, H-1), 7.26-7.25 (m, 3H, H-2, 4), 2.65 (t, *J* 7.7, 4H, Pyrimidine-CH₂-), 1.8-1.35 (m, 16H, CH₂), 0.9 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8 (2C=O), 161.7 (C-10), 157.3 (C-11), 151.7 (C-3), 142.7 (C-9), 134.0 (C-12), 130.7 (C-6), 130.5 (C-8), 130.0 (C-1), 128.1 (C-7), 119.3 (C-2), 115.9 (C-4), 31.4 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 28.6 (CH₂), 22.4 (CH₂), 13.9 (CH₃).
MS (70 eV): *m/z* (%) 642 (M⁺, 26), 267 (100), 239 (8), 168 (9).

1,3-Bis[4-(5-octylpyrimidine-2-yl)benzoyloxy]benzene 1/8



Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.55 g, 1.76 mmol).

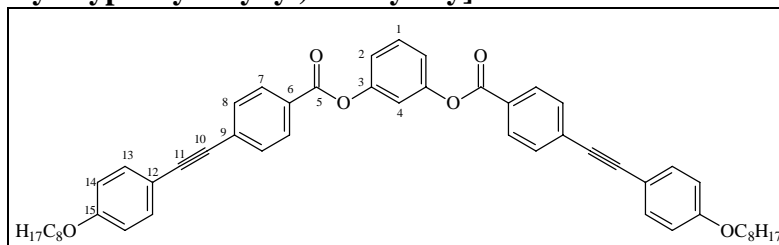
Yield 0.4 g (63.7 %); mp 130 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.7 (s, 4H, H-11), 8.59 (d, *J* 8.4, 4H, H-8), 8.32 (d, *J* 8.4, 4H, H-7), 7.52 (t, *J* 8.2, 1H, H-1), 7.27-7.21 (m, 3H, H-2, 4). 2.67 (t, *J* 7.7, 4H, Pyrimidine-CH₂-), 1.69-1.29 (m, 24H, CH₂), 0.89 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8 (2C=O), 161.7 (C-10), 157.3 (C-11), 151.7 (C-3), 142.7 (C-9), 134.0 (C-12), 130.7 (C-6), 130.5 (C-8), 130.0 (C-1), 128.1 (C-7), 119.3 (C-2), 115.9 (C-4), 31.7 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): *m/z* (%) 698 (M⁺, 45), 295 (100), 267 (5), 168 (5).

1,3-Bis[4-(4-octyloxyphenylethynyl)benzoyloxy]benzene 30/8



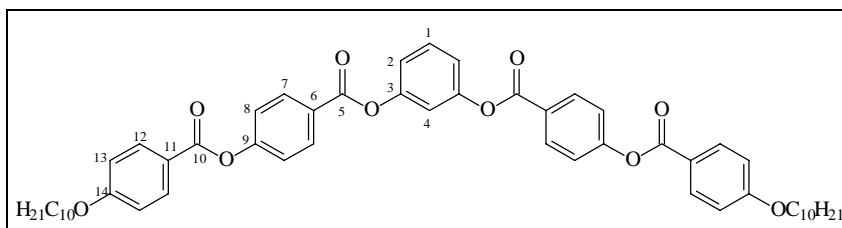
Synthesized from 1,3-dihydroxybenzene (0.07 g, 0.64 mmol) and 4-(4-octyloxyphenylethynyl)benzoic acid (0.48 g, 1.37 mmol).

Yield 0.17g (34.3%); mp 154 °C. (Found: C, 80.40; H, 7.02%; C₅₂H₅₄O₆ requires C, 80.62; H, 6.98%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.16 (d, *J* 8.6, 4H, H-7), 7.62 (d, *J* 8.6, 4H, H-8), 7.51-7.47 (d, 5H, H-1, 13), 7.21-7.17 (m, 3H, H-2, 4), 6.89 (d, *J* 8.8, 4H, H-14), 3.99 (t, *J* 6.5, 4H, OCH₂), 1.80-1.30 (m, 24H, CH₂), 0.90 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.5 (2C=O), 160.9 (C-15), 152.6 (C-3), 134.4 (C-7), 132.6 (C-8), 131.2 (C-13), 131.0 (C-1), 130.5 (C-6), 129.2 (C-9), 120.3 (C-2), 116.8 (C-4), 115.7 (C-14), 115.5 (C-12), 94.4 (C≡), 88.4 (C≡), 69.1 (OCH₂), 32.7 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 30.0 (CH₂), 26.9 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

1,3-Bis[4-(4-decyloxybenzoyloxy)benzoyloxy]benzene 31/10



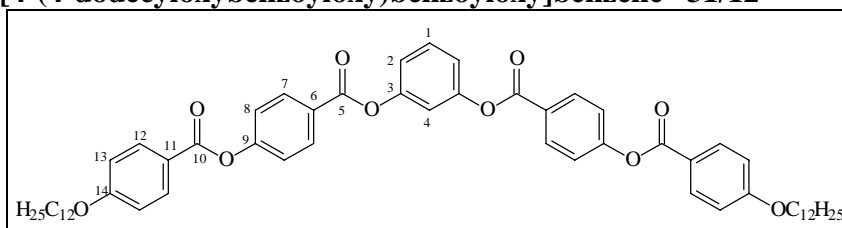
Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and 4-(4-decyloxybenzoyloxy)-benzoic acid (0.80 g, 2.0 mmol).

Yield 0.25 g (32.1%); transition temperatures (°C): Cr₁ 84 Cr₂ 101 Cr₃ 110 (SmCP_A 108) Iso. (Found: C, 74.46; H, 7.00%; C₅₄H₆₂O₁₀ requires C, 74.48; H, 7.13%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-7), 8.13 (d, *J* 8.8, 4H, H-12), 7.48 (t, *J* 7.8, 1H, H-1), 7.36 (d, *J* 8.6, 4H, H-8), 7.19-7.14 (m, 3H, H-2, 4), 6.97 (d, *J* 9.0, 4H, H-13), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.88-1.74 (m, 4H, CH₂), 1.50-1.26 (m, 28H, CH₂), 0.87 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.4, 165.2, 165.0 (4C=O, C-14), 156.7 (C-9), 152.6 (C-3), 133.5 (C-7), 132.9 (C-12), 131.0 (C-1), 127.7 (C-6), 123.2 (C-8), 122.1 (C-11), 120.3 (C-2), 116.9 (C-4), 115.5 (C-13), 69.4 (OCH₂), 32.8 (CH₂), 30.4 (CH₂), 30.2 (CH₂), 30.0 (CH₂), 26.9 (CH₂), 23.6 (CH₂), 15.0 (CH₃).

1,3-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]benzene 31/12



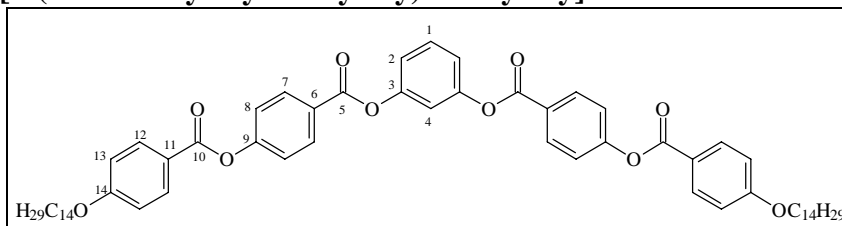
Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and 4-(4-dodecyloxybenzoyloxy)-benzoic acid (0.85 g, 2.0 mmol).

Yield 0.32 g (38.6%); transition temperatures (°C): Cr₁ 70 Cr₂ 105 SmCP_A 117 Iso. (Found: C, 75.31; H, 7.50%; C₅₈H₇₀O₁₀ requires C, 75.16; H, 7.56%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-7), 8.14 (d, *J* 8.8, 4H, H-12), 7.48 (t, *J* 7.8, 1H, H-1), 7.36 (d, *J* 8.8, 4H, H-8), 7.24-7.15 (m, 3H, H-2, 4), 6.97 (d, *J* 8.8, 4H, H-13), 4.04 (t, *J* 6.4, 4H, OCH₂), 1.81 (m, 4H, CH₂), 1.57-1.26 (m, 36H, CH₂), 0.87 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.4, 165.2, 165.0 (4C=O, C-14), 156.7 (C-9), 152.6 (C-3), 133.5 (C-7), 132.9 (C-12), 131.0 (C-1), 127.7 (C-6), 123.2 (C-8), 122.1 (C-11), 120.3 (C-2), 116.9 (C-4), 115.5 (C-13), 69.4 (OCH₂), 32.8 (CH₂), 30.6 (CH₂), 30.5 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.2 (CH₂), 30.0 (CH₂), 26.9 (CH₂), 23.6 (CH₂), 15.0 (CH₃).

1,3-Bis[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]benzene 31/14



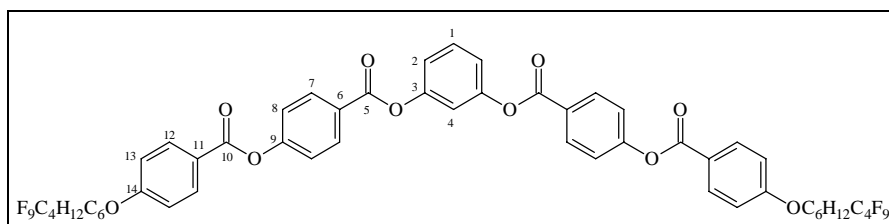
Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and 4-(4-tetradecyloxybenzoyloxy)benzoic acid (0.91 g, 2.0 mmol).

Yield 0.12 g (13.6%); transition temperatures (°C): Cr₁ 78 Cr₂ 105 SmCP_A 119 Iso. (Found: C, 75.83; H, 7.99%; C₅₈H₇₀O₁₀ requires C, 75.76; H, 7.94%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-7), 8.13 (d, *J* 8.8, 4H, H-12), 7.48 (t, *J* 8.0, 1H, H-1), 7.35 (d, *J* 8.8, 4H, H-8), 7.19-7.15 (m, 3H, H-2, 4), 6.97 (d, *J* 9.0, 4H, H-13), 4.03 (t, *J* 6.5, 4H, OCH₂), 1.84-1.77 (m, 4H, CH₂), 1.30-1.20 (m, 44H, CH₂), 0.86 (t, *J* 6.2, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.4, 164.2, 164.0 (4C=O, C-14), 155.7 (C-9), 151.6 (C-3), 132.5 (C-7), 131.9 (C-12), 130.0 (C-1), 126.7 (C-6), 122.2 (C-8), 121.1 (C-11), 119.3 (C-2), 115.9 (C-4), 114.5 (C-13), 68.4 (OCH₂), 31.8 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

1,3-Bis{4-[4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoyloxy]benzoyloxy}benzene 31/6F4



Synthesized from 1,3-dihydroxybenzene (0.1 g, 0.9 mmol) and 4-[4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoyloxy]benzoic acid (1.12 g, 2.0 mmol).

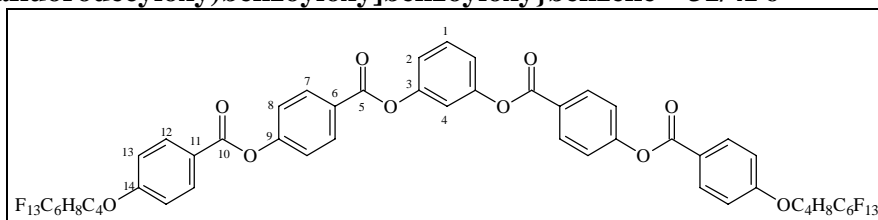
Yield 0.33 g (30.8%); transition temperatures (°C): Cr 133 SmCP_A 164 Iso. (Found: C, 54.13; H, 4.13%, C₅₄H₄₄F₁₈O₁₀ requires C, 54.27; H, 3.69%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-7), 8.14 (d, *J* 9.0, 4H, H-12), 7.48 (t, *J* 8.1, 1H, H-1), 7.36 (d, *J* 9.0, 4H, H-8), 7.20-7.15 (m, 3H, H-2, 4), 6.97 (d, *J* 9.0, 4H, H-13), 4.05 (t, *J* 6.3, 4H, OCH₂), 2.14-2.00 (m, 4H, CF₂CH₂), 1.87-1.80 (m, 4H, OCH₂CH₂), 1.7-1.6 (m, 4H, CF₂CH₂CH₂), 1.6-1.4 (m, 8H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.4, 164.2, 163.9 (4C=O, C-14), 155.6 (C-9), 151.6 (C-3), 132.5 (C-7), 132.0 (C-12), 130.0 (C-1), 126.8 (C-6), 122.2 (C-8), 121.3 (C-11), 119.4 (C-2), 115.9 (C-4), 114.5 (C-13), 68.0 (OCH₂), 30.6 (t, CF₂CH₂), 28.7 (CH₂), 28.7 (CH₂), 25.6 (CH₂), 20.0 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.63 (CF₃), -116.18 (CF₂), -126.07 (CF₂), -127.61 (CF₂).

1,3-Bis{4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]benzoyloxy}benzene 31/4F6



Synthesized from 1,3-dihydroxybenzene (0.05 g, 0.45 mmol) and 4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]benzoic acid (0.63 g, 1.0 mmol).

Yield 0.13 g (21.7%); transition temperatures (°C): Cr₁ 63 Cr₂ 134 SmCP_A 201 Iso. (Found: C, 48.55; H, 3.26%, C₅₄H₃₆F₂₆O₁₀ requires C, 48.43; H, 2.69%).

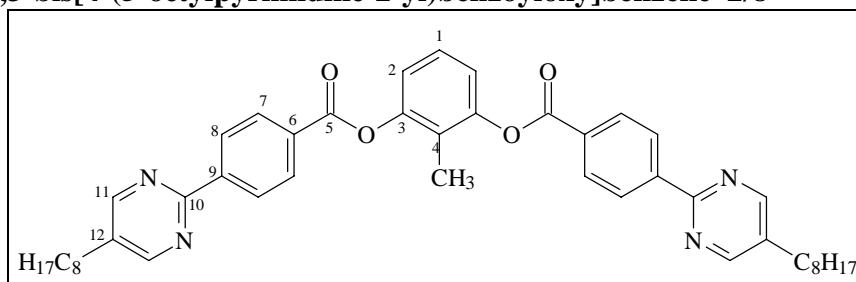
¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-7), 8.15 (d, *J* 8.8, 4H, H-12), 7.48 (t, *J* 8.1, 1H, H-1), 7.36 (d, *J* 8.8, 4H, H-8), 7.20-7.15 (m, 3H, H-2, 4), 6.97 (d, *J* 8.8, 4H, H-13), 4.09 (t, *J* 5.7, 4H, OCH₂), 2.15-2.08 (m, 4H, CF₂CH₂), 2.0-1.7 (m, 8H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.4, 164.2, 163.6 (4C=O, C-14), 155.6 (C-9), 151.6 (C-3), 132.6 (C-7), 132.0 (C-12), 130.0 (C-1), 126.8 (C-6), 122.2 (C-8), 121.5 (C-11), 119.4 (C-2), 115.9 (C-4), 114.5 (C-13), 67.5 (OCH₂), 30.6 (t, CF₂CH₂), 28.5 (CH₂), 17.2 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.4 (CF₃), -116.0 (CF₂), -123.5 (CF₂), -124.5 (CF₂), -125.1 (CF₂), -127.7 (CF₂).

3.2.1.2 2-Methyl-1,3-bis(4-substituted benzoyloxy)benzenes

2-Methyl-1,3-bis[4-(5-octylpyrimidine-2-yl)benzoyloxy]benzene 2/8



Synthesized from 1,3-dihydroxy-2-methylbenzene (0.11 g, 0.9 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.55 g, 1.76 mmol).

Yield 0.3 g (46.8%); mp 166 °C. (Found: C, 75.86; H, 7.12; N, 7.59%; C₄₅H₅₂N₄O₄ requires C, 75.84; H, 7.30; N, 7.87%).

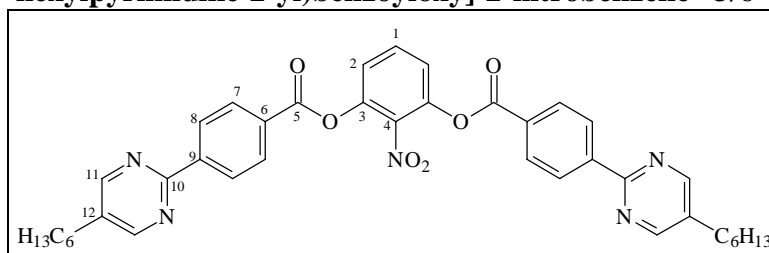
¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.69 (s, 4H, H-11), 8.59 (d, *J* 8.6, 4H, H-8), 8.33 (d, *J* 8.8, 4H, H-7), 7.35 (t, *J* 8.1, 1H, H-1), 7.17 (d, *J* 7.8, 2H, H-2), 2.67 (t, *J* 7.6, 4H, CH₂), 2.17 (s, 3H, Ar-CH₃), 1.72-1.65 (m, 4H, CH₂), 1.52-1.28 (m, 20H, CH₂), 0.89 (t, *J* 6.6, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.6 (2C=O), 162.7 (C-10), 158.3 (C-11), 151.5 (C-3), 143.7 (C-9), 135.0 (C-12), 131.7 (C-6), 131.5 (C-8), 129.2 (C-7), 127.7 (C-1), 125.1 (C-4), 121.0 (C-2), 32.7 (CH₂), 31.6 (CH₂), 31.2 (CH₂), 31.2 (CH₂), 31.0 (CH₂), 30.0 (CH₂), 23.5 (CH₂), 14.9 (CH₃), 11.0 (Ar-CH₃).

MS (70 eV): *m/z* (%) 712 (M⁺, 40), 295 (100), 267 (8), 168 (8).

3.2.1.3 2-Nitro-1,3-bis(4-substituted benzoyloxy)benzenes

1,3-Bis[4-(5-hexylpyrimidine-2-yl)benzoyloxy]-2-nitrobenzene 3/6



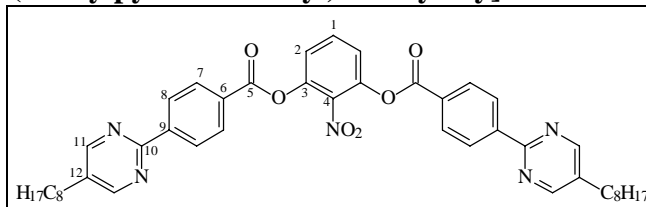
Synthesized from 1,3-dihydroxy-2-nitrobenzene (0.14 g, 0.9 mmol) and 4-(5-hexylpyrimidine-2-yl)benzoic acid (0.5 g, 1.76 mmol).

Yield 0.18 g (29.1%); mp 145 °C. (Found: C, 69.92; H, 5.96; N, 9.93%; C₄₀H₄₁N₅O₆ requires C, 69.87; H, 5.97; N, 10.19%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.69 (s, 4H, H-11), 8.58 (d, *J* 8.8, 4H, H-8), 8.27 (d, *J* 8.8, 4H, H-7), 7.63 (t, 1H, H-1), 7.47 (d, 2H, H-2), 2.67 (t, 4H, Pyrimidine-CH₂-), 1.8-1.2 (m, 16H, CH₂), 0.9 (t, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.7 (2C=O), 162.5 (C-10), 158.3 (C-11), 145.0 (C-3), 144.3 (C-9), 135.1 (C-12), 132.7 (C-6), 131.9 (C-8), 130.3 (C-1), 129.2 (C-7), 122.8 (C-2), 32.4 (CH₂), 31.5 (CH₂), 31.2 (CH₂), 29.6 (CH₂), 23.4 (CH₂), 14.9 (CH₃).
MS (70 eV): *m/z* (%) 687 (M⁺, 25), 267 (100), 239 (7) 168 (8).

2-Nitro-1,3-bis[4-(5-octylpyrimidine-2-yl)benzoyloxy]benzene 3/8



Synthesized from 1,3-dihydroxy-2-nitrobenzene (0.09 g, 0.58 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.35 g, 1.12 mmol).

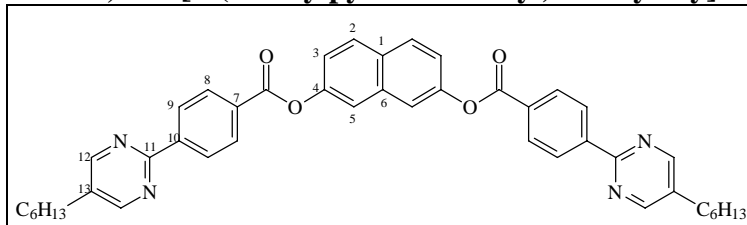
Yield 0.15 g (34.9%); mp 106 °C. (Found: C, 71.01; H, 6.75; N, 9.08%; C₄₄H₄₉N₅O₆ requires C, 70.06; H, 6.59; N, 9.42%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.68 (s, 4H, H-11), 8.58 (d, *J* 8.8, 4H, H-8), 8.26 (d, *J* 8.8, 4H, H-7), 7.70 (t, 1H, H-1), 7.47 (d, 2H, H-2), 2.65 (t, 4H, Pyrimidine-CH₂), 1.8-1.2 (m, 24H, CH₂), 0.89 (t, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 163.7 (2C=O), 161.5 (C-10), 157.3 (C-11), 144.0 (C-3), 143.3 (C-9), 134.1 (C-12), 131.7 (C-6), 130.9 (C-8), 129.3 (C-1), 128.2 (C-7), 121.8 (C-2), 31.7 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): *m/z* (%) 743 (M⁺, 19), 295 (100), 267 (7).

3.2.2 Synthesis of 2,7-bis[4-(5-hexylpyrimidine-2-yl)benzoyloxy]naphthalene 10/6



Synthesized from 2,7-dihydroxynaphthalene (0.15 g, 0.9 mmol) and 4-(5-hexylpyrimidine-2-yl)benzoic acid (0.5 g, 1.76 mmol).

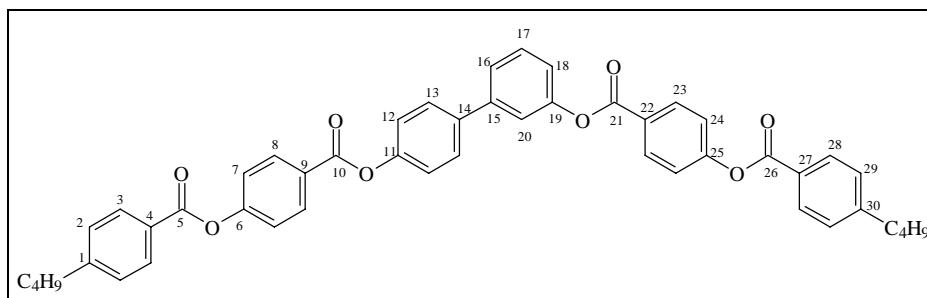
Yield 0.18 g (29.6%); mp 215 °C. (Found: C, 76.21; H, 6.53; N, 8.11%; C₄₄H₄₄N₄O₄ requires C, 76.30; H, 6.36; N, 8.09%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.73 (s, 4H, H-12), 8.63 (d, *J* 8.6, 4H, H-9), 8.37 (d, *J* 8.6, 4H, H-8), 7.94 (d, *J* 9.2, 2H, H-2), 7.72 (d, *J* 2.2, 2H, H-5), 7.39 (d, *J* 9.2, 2H, H-3), 2.68 (t, *J* 7.7, 4H, Pyrimidine-CH₂), 1.68 (t, *J* 7.3, 4H, CH₂), 1.4-1.3 (m, 12H, CH₂), 0.89 (t, *J* 7.0, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.2 (2C=O), 161.7 (C-11), 157.3 (C-12), 149.5 (C-4), 142.7 (C-10), 134.6 (C-6), 134.0 (C-13), 131.0 (C-7), 130.6 (C-9), 129.7 (C-1), 129.5 (C-2), 128.1 (C-8), 121.3 (C-5), 118.7 (C-3), 31.4 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 28.6 (CH₂), 22.4 (CH₂), 13.9 (CH₃).

3.2.3 Synthesis of 3,4'-biphenyl derivatives

3,4'-Bis[4-(4-butylbenzoyloxy)benzoyloxy]biphenyl 11/4



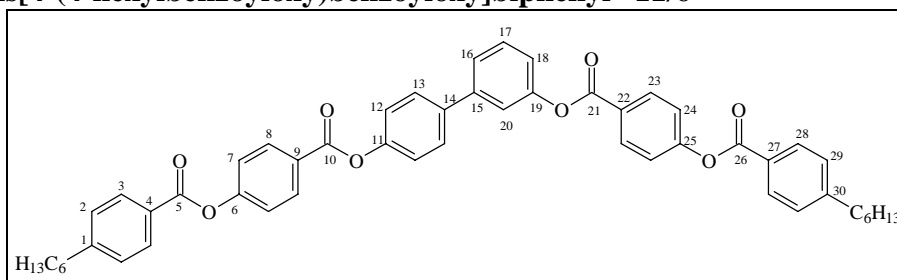
Synthesized from 3,4'-hydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-butylbenzoyloxy)-benzoic acid (0.60 g, 2.0 mmol).

Yield 0.27g (40.3%); transition temperatures (°C): Cr₁ 82 Cr₂ 161 (Col_r 153) Iso. (Found: C, 77.62; H, 5.54%; C₄₈H₄₂O₈ requires C, 77.21; H, 5.63%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.31 (m, 4H, H-8, 23), 8.13 (d, *J* 8.2, 4H, H-3, 28), 7.67 (d, *J* 8.6, 2H, H-13), 7.52 (d, *J* 5.1, 2H, H-16, 18), 7.47 (s, 1H, H-20), 7.42-7.31 (m, 10H, Ar-H), 7.23 (m, 1H, H-17), 2.72 (t, *J* 7.7, 4H, CH₂), 1.66 (m, 4H, CH₂), 1.39 (m, 4H, CH₂), 0.96 (t, *J* 7.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.6, 164.5 (4C=O), 156.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.1 (C-14), 132.9 (C-8, 23), 131.4 (C-3, 28), 129.9 (C-17), 129.4 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 123.1 (C-7, 24, 12), 120.7 (C-18), 120.5 (C-20), 36.7 (CH₂), 34.1 (CH₂), 23.2 (CH₂), 14.7 (CH₃).

3,4'-Bis[4-(4-hexylbenzoyloxy)benzoyloxy]biphenyl 11/6



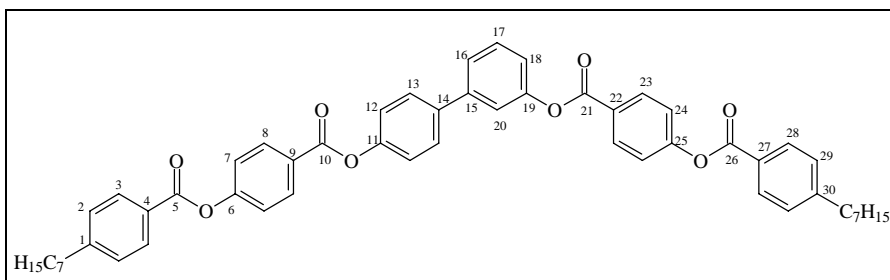
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-hexylbenzoyloxy)-benzoic acid (0.65 g, 2.0 mmol).

Yield 0.3 g (41.7%); transition temperatures (°C): Cr 119 Col_r 158 Iso. (Found: C, 77.79; H, 6.35%; C₅₂H₅₀O₈ requires C, 77.81; H, 6.23%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.31 (d, *J* 8.6, 4H, H-8, 23), 8.13 (d, *J* 8.2, 4H, H-3, 28), 7.68 (d, *J* 8.8, 2H, H-13), 7.52 (d, *J* 5.3, 2H, H-16, 18), 7.47 (d, *J* 1.4, 1H, H-20), 7.41-7.31 (m, 10H, Ar-H), 7.24 (m, 1H, H-17), 2.72 (t, *J* 7.6, 4H, CH₂), 1.68-1.27 (m, 16H, CH₂), 0.90 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.6, 164.5 (4C=O), 156.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.1 (C-14), 133.0 (C-8, 23), 131.5 (C-3, 28), 130.0 (C-17), 129.9 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 123.1 (C-7, 24, 12), 120.7 (C-18), 120.5 (C-20), 37.0 (CH₂), 32.6 (CH₂), 32.0 (CH₂), 29.8 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

3,4'-Bis[4-(4-heptylbenzoyloxy)benzoyloxy]biphenyl 11/7



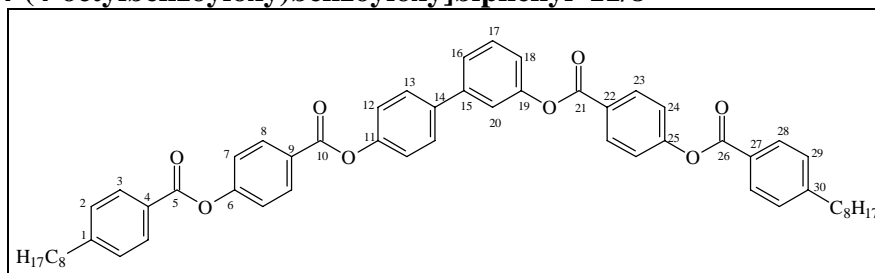
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-heptylbenzoyloxy)-benzoic acid (0.68 g, 2.0 mmol).

Yield 0.19 g (25.4%); transition temperatures (°C): Cr₁ 89 Cr₂ 129 Col_r 167 Iso. (Found: C, 78.38; H, 6.64%; C₅₄H₅₄O₈ requires C, 78.07; H, 6.51%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, *J* 8.6, 4H, H-8, 23), 8.11 (d, *J* 8.2, 4H, H-3, 28), 7.66 (d, *J* 8.6, 2H, H-13), 7.50 (d, *J* 5.1, 2H, H-16, 18), 7.45 (s, 1H, H-20), 7.40-7.28 (m, 10H, Ar-H), 7.21 (m, 1H, H-17), 2.70 (t, *J* 7.6, 4H, CH₂), 1.68 (m, 4H, CH₂), 1.32-1.27 (m, 16H, CH₂), 0.87 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.6 (4C=O), 155.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.1 (C-14), 132.0 (C-8, 23), 130.4 (C-3, 28), 130.0 (C-17), 128.9 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 122.2 (C-7, 24, 12), 120.7, 120.5 (C-20, 18), 36.0 (CH₂), 31.7 (CH₂), 31.0 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

3,4'-Bis[4-(4-octylbenzoyloxy)benzoyloxy]biphenyl 11/8



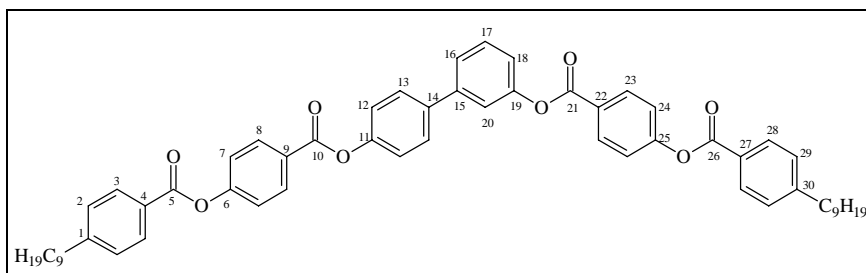
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-octylbenzoyloxy)-benzoic acid (0.71 g, 2.0 mmol).

Yield 0.33 g (42.9%); transition temperatures (°C): Cr₁ 68 Cr₂ 85 SmX 86 SmCP_A 152 (SmCP_A 147 Col_r 152) Iso. (Found: C, 78.23; H, 7.15%; C₅₆H₅₈O₈ requires C, 78.32; H, 6.82%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.33 (d, *J* 8.6, 4H, H-8, 23), 8.14 (d, *J* 8.2, 4H, H-3, 28), 7.68 (d, *J* 8.6, 2H, H-13), 7.53 (d, *J* 4.9, 2H, H-16, 18), 7.47 (s, 1H, H-20), 7.42-7.26 (m, 11H, Ar-H), 2.72 (t, *J* 7.6, 4H, CH₂), 1.67 (m, 4H, CH₂), 1.32-1.27 (m, 20H, CH₂), 0.89 (2t, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 50 MHz): 164.8, 164.6 (4C=O), 155.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.1 (C-14), 131.9 (C-8, 23), 130.4 (C-3, 28), 130.0 (C-17), 128.8 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 122.1 (C-7, 24, 12), 120.5 (C-20, 18), 36.1 (CH₂), 31.9 (CH₂), 31.1 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-nonylbenzoyloxy)benzoyloxy]biphenyl 11/9



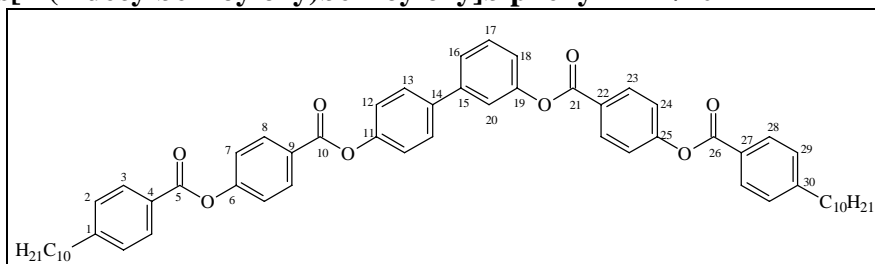
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-nonylbenzoyloxy)-benzoic acid (0.74 g, 2.0 mmol).

Yield 0.36 g (45.1%); transition temperatures (°C): Cr 99 Col_r 158 Iso. (Found: C, 78.80; H, 7.24%; C₅₈H₆₂O₈ requires C, 78.56; H, 7.00%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.30 (m, 4H, H-8, 23), 8.11 (d, *J* 8.2, 4H, H-3, 28), 7.66 (d, *J* 8.8, 2H, H-13), 7.50 (d, *J* 4.9, 2H, H-16, 18), 7.45 (s, 1H, H-20), 7.39-7.29 (m, 10H, Ar-H), 7.22 (m, 1H, H-17), 2.69 (t, *J* 7.7, 4H, CH₂), 1.65 (t, *J* 7.3, 4H, CH₂), 1.31-1.29 (m, 24H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.6 (4C=O), 155.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.1 (C-14), 132.0 (C-8, 23), 130.5 (C-3, 28), 130.0 (C-17), 128.9 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 122.2 (C-7, 24, 12), 120.5 (C-20, 18), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-decylbenzoyloxy)benzoyloxy]biphenyl 11/10



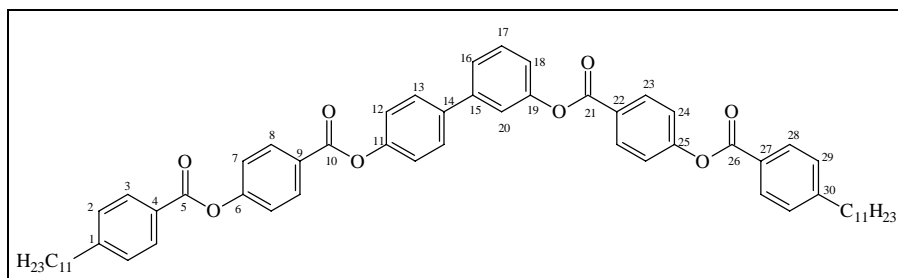
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-decylbenzoyloxy)-benzoic acid (0.76 g, 2.0 mmol).

Yield 0.25 g (30.4%); transition temperatures (°C): SmX 79 SmCP_A 148 (SmCP_A 147 Col_r 148) Iso. (Found: C, 78.17; H, 7.53%; C₆₀H₆₆O₈ requires C, 78.77; H, 7.22%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.32 (m, 4H, H-8, 23), 8.13 (d, *J* 8.2, 4H, H-3, 28), 7.67 (d, *J* 8.6, 2H, H-13), 7.52 (d, *J* 5.1, 2H, H-16, 18), 7.47 (t, *J* 1.2, 1H, H-20), 7.44-7.31 (m, 10H, Ar-H), 7.23 (m, 1H, H-17), 2.71 (t, *J* 7.7, 4H, CH₂), 1.66 (m, 4H, CH₂), 1.33-1.31 (m, 28H, CH₂), 0.89 (t, *J* 6.9, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.8, 165.6 (4C=O), 156.5 (C-6, 25), 152.5 (C-19), 151.8 (C-11), 151.0 (C-1, 30), 143.2 (C-15), 139.1 (C-14), 132.9 (C-8, 23), 131.4 (C-3, 28), 131.0 (C-17), 129.8 (C-2, 29), 129.4 (C-13), 128.0 (C-9, 22), 127.6 (C-4, 27), 125.8 (C-16), 123.1 (C-7, 24, 12), 121.5 (C-18, 20), 37.0 (CH₂), 32.8 (CH₂), 32.0 (CH₂), 30.5 (CH₂), 30.5 (CH₂), 30.3 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 23.5 (CH₂), 15.0 (CH₃).

3,4'-Bis[4-(4-undecylbenzoyloxy)benzoyloxy]biphenyl 11/11



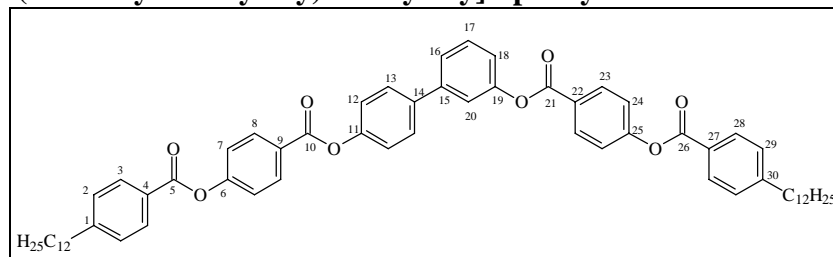
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-undecylbenzoyloxy)-benzoic acid (0.79 g, 2.0 mmol).

Yield 0.19 g (22.4%); transition temperatures ($^{\circ}\text{C}$): Cr₁ 67 Cr₂ 88 SmCP_A 157 Iso. (Found: C, 78.80; H, 7.42%; C₆₂H₇₀O₈ requires C, 78.98; H, 7.43%).

¹H-NMR: δ_{H} (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, *J* 8.6, 4H, H-8, 23), 8.11 (d, *J* 8.2, 4H, H-3, 28); 7.66 (d, *J* 8.8, 2H, H-13), 7.50 (d, *J* 4.9, 2H, H-16, 18), 7.45 (s, 1H, H-20), 7.40-7.27 (m, 10H, Ar-H), 7.20 (m, 1H, H-20), 2.70 (t, *J* 7.5, 4H, CH₂), 1.65-1.29 (m, 36H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 164.8, 164.6, 164.5 (4C=O), 155.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.2 (C-14), 132.0 (C-8, 23), 130.4 (C-3, 28), 130.0 (C-17), 128.9 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 122.2 (C-7, 24, 12), 120.7 (C-18), 120.5 (C-20), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-dodecylbenzoyloxy)benzoyloxy]biphenyl 11/12



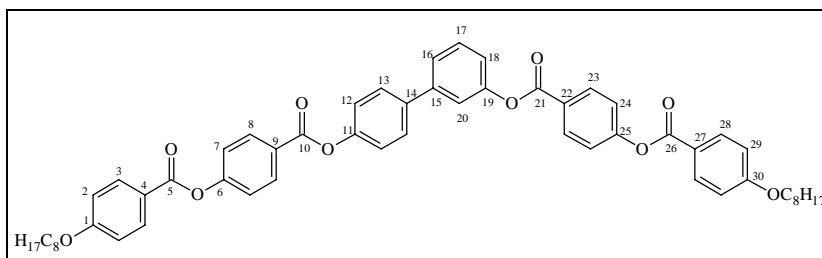
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-dodecylbenzoyloxy)-benzoic acid (1.10 g, 2.0 mmol).

Yield 0.35 g (40.2%); transition temperatures ($^{\circ}\text{C}$): SmX 78 SmCP_A 156 Iso. (Found: C, 78.87; H, 7.57%; C₆₄H₇₄O₈ requires C, 79.18; H, 7.63%).

¹H-NMR: δ_{H} (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, *J* 8.6, 4H, H-8, 23), 8.11 (d, *J* 8.2, 4H, H-3, 28), 7.65 (d, *J* 8.6, 2H, H-13), 7.51 (d, *J* 5.1, 2H, H-16, 18), 7.44 (s, 1H, H-20), 7.39-7.27 (m, 10H, Ar-H), 7.20 (m, 1H, H-17), 2.70 (t, *J* 7.6, 4H, CH₂), 1.68-1.29 (m, 40H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 164.8, 164.6, 164.5 (4C=O), 155.5 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 150.0 (C-1, 30), 142.2 (C-15), 138.1 (C-14), 131.9 (C-8, 23), 130.4 (C-3, 28), 130.0 (C-17), 128.8 (C-2, 29), 128.4 (C-13), 127.1 (C-9, 22), 126.6 (C-4, 27), 124.8 (C-16), 122.1 (C-7, 24, 12), 120.7 (C-18), 120.5 (C-20), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-octyloxybenzoyloxy)benzoyloxy]biphenyl 12/8



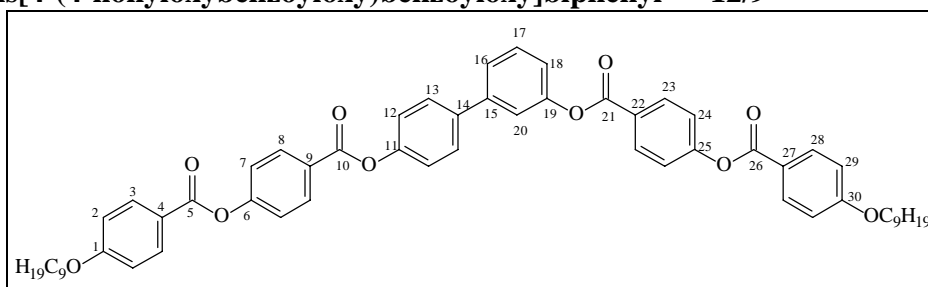
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-octyloxybenzoyloxy)benzoic acid (0.72 g, 2.0 mmol).

Yield 0.40 g (50.0%); transition temperatures ($^{\circ}\text{C}$): Cr₁ 97 Cr₂ 131 Col_r 172 Iso. (Found: C, 75.80; H, 6.22%; C₅₆H₅₈O₁₀ requires C, 75.50; H, 6.52%).

¹H-NMR: δ_{H} (CDCl₃; 400 MHz; *J*/Hz): 8.31 (d, *J* 8.8, 4H, H-8, 23), 8.16 (d, *J* 8.6, 4H, H-3, 28), 7.67 (d, *J* 8.8, 2H, H-13), 7.53-7.21 (m, 10H, Ar-H), 7.00 (d, *J* 8.8, 4H, H-2, 29), 4.06 (t, *J* 6.6, 4H, OCH₂), 1.84 (m, 4H, CH₂), 1.52-1.31 (m, 20H, CH₂), 0.90 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 165.6, 165.5, 165.0 (4C=O, C-1, 30), 156.6 (C-6, 25), 152.5 (C-19), 151.8 (C-11), 143.2 (C-15), 139.1 (C-14), 133.5 (C-8, 23), 132.9 (C-3, 28), 131.0 (C-17), 129.4 (C-13), 128.0 (C-9, 22), 125.8 (C-16), 123.2 (C-7, 24), 123.1 (C-12), 122.1 (C-4, 27), 121.7 (C-18), 121.5 (C-20), 115.5 (C-2, 29), 69.4 (OCH₂), 32.7 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 30.0 (CH₂), 26.9 (CH₂), 23.5 (CH₂), 15.0 (CH₃).

3,4'-Bis[4-(4-nonyloxybenzoyloxy)benzoyloxy]biphenyl 12/9



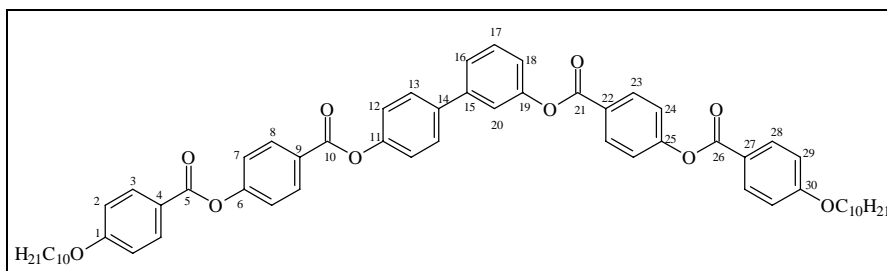
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol).

Yield 0.39 g (47.0%); transition temperatures ($^{\circ}\text{C}$): Cr₁ 89 Cr₂ 99 Cr₃ 116 Col_r 169 Iso. (Found: C, 76.21; H, 7.08%; C₅₈H₆₂O₁₀ requires C, 75.82; H, 6.75%).

¹H-NMR: δ_{H} (CDCl₃; 400 MHz; *J*/Hz): 8.29 (d, *J* 8.8, 4H, H-8, H-23), 8.14 (d, *J* 8.8, 4H, H-3, 28), 7.65 (d, *J* 8.6, 2H, H-13), 7.51-7.21 (m, 10H, Ar-H), 7.00 (d, *J* 9.0, 4H, H-2, 29), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.83 (m, 4H, CH₂), 1.52-1.31 (m, 24H, CH₂), 0.87 (t, *J* 6.7, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 164.6, 164.5, 164.0 (4C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.1 (C-14), 132.5 (C-8, 23), 131.9 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.1 (C-12), 121.1 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.5 (C-2, 29), 68.4 (OCH₂), 31.7 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-decyloxybenzoyloxy)benzoyloxy]biphenyl 12/10



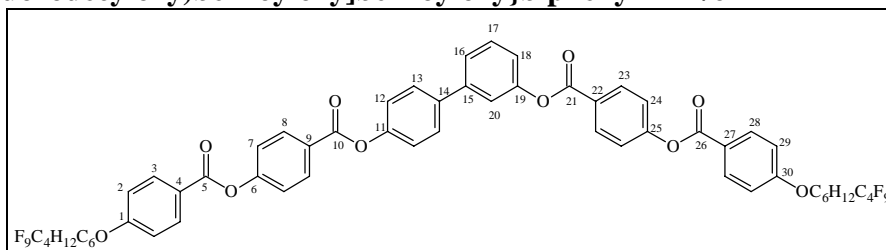
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-decyloxybenzoyloxy)benzoic acid (0.80 g, 2.0 mmol).

Yield 0.34 g (50.0%); transition temperatures (°C): Cr 119 Col_r 166 Iso. (Found C, 75.68; H, 7.15%; C₆₀H₆₆O₁₀ requires C, 76.11; H, 6.98%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.29 (m, 4H, H-8, 23), 8.14 (d, *J* 8.6, 4H, H-3, 28), 7.66 (d, *J* 8.8, 2H, H-13), 7.50 (d, 2H, H-16, 18), 7.44-7.20 (m, 8H, Ar-H), 6.97 (d, *J* 9.0, 4H, H-2, 29), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.85-1.77 (m, 4H, CH₂), 1.49-1.26 (m, 28H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, 164.0 (4C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.1 (C-14), 132.5 (C-8, 23), 131.9 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.1 (C-12), 121.1 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.5 (C-2, 29), 68.4 (OCH₂), 31.8 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-[4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoyloxy]benzoyloxy]biphenyl 12/6F4



Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-[4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoyloxy]benzoic acid (1.12 g, 2.0 mmol).

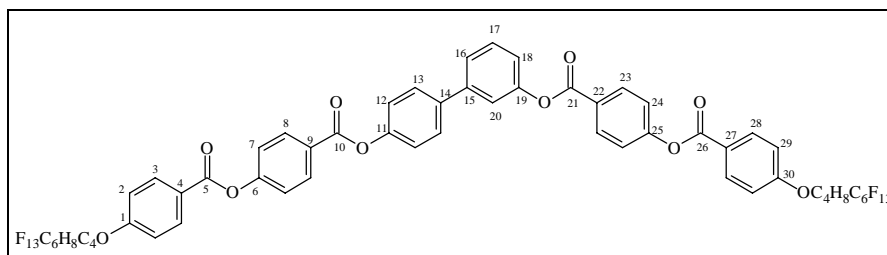
Yield 0.25 g (21.9%); transition temperatures (°C): Cr₁ 90 Cr₂ 127 SmCP_A 213 Iso. (Found C, 56.54; H, 4.30%; C₆₀H₄₈F₁₈O₁₀ requires C, 56.69; H, 3.78%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 2H, H-8), 8.28 (d, *J* 8.8, 2H, H-23), 8.15 (d, *J* 8.6, 4H, H-3, 28), 7.66 (d, *J* 8.6, 2H, H-13), 7.50 (d, *J* 4.88, 2H, H-16, 18), 7.45 (m, 1H, H-20), 7.37 (d, *J* 8.8, 2H, H-7), 7.36 (d, *J* 8.8, 2H, H-24), 7.30 (d, *J* 8.8, 2H, H-12), 7.20 (m, 1H, H-17), 6.97 (d, *J* 9.0, 4H, H-2, 29), 4.05 (t, *J* 6.3, 4H, OCH₂), 2.15-2.0 (m, 4H, CF₂CH₂), 1.90-1.80 (m, 4H, CH₂), 1.70-1.60 (m, 4H, CH₂), 1.6-1.4 (m, 8H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.4, 163.8 (4C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.2 (C-14), 132.6 (C-8, 23), 131.9 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.2 (C-12), 121.3 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.5 (C-2, 29), 68.0 (OCH₂), 30.6 (t, CF₂CH₂), 28.8 (CH₂), 28.7 (CH₂), 25.6 (CH₂), 20.0 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.63 (CF₃), -116.20 (CF₂), -126.08 (CF₂), -127.66 (CF₂).

3,4'-Bis[4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]benzoyloxy]biphenyl 12/4F6



Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-[4-(5,5,6,6,7,7,8,8,9,9,-10,10,10-tridecafluorodecyloxy)benzoyloxy]benzoic acid (1.26 g, 2.0 mmol).

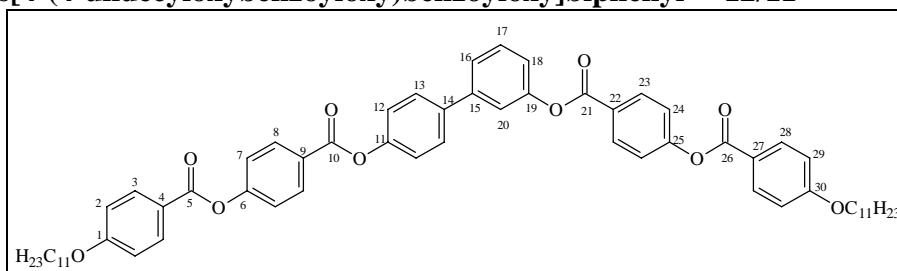
Yield 0.47 g (37.0%); transition temperatures (°C): Cr₁ 122 Cr₂ 150 SmCP_A 252 Iso. (Found: C, 50.82; H, 2.97%; C₆₀H₄₀F₂₆O₁₀ requires: C, 50.92; H, 2.83%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 4H, H-8, 23), 8.15 (d, *J* 9.0, 4H, H-3, 28), 7.66 (d, *J* 8.6, 2H, H-13), 7.50 (d, *J* 4.88, 2H, H-16, 18), 7.44 (m, 1H, H-20), 7.39-7.21 (m, 7H, Ar-H), 7.00 (d, *J* 9.0, 4H, H-2, 29), 4.09 (t, *J* 5.5, 4H, OCH₂), 2.17 (m, 4H, CH₂), 1.90-1.83 (m, 8H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6 (C=O), 164.6 (C=O), 164.4, 163.6 (C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.2 (C-14), 132.6 (C-8, 23), 132.0 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.2 (C-12), 121.5 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.5 (C-2, 29), 67.5 (OCH₂), 30.6 (t, CF₂CH₂), 28.5 (CH₂), 17.2 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.4 (CF₃), -116.0 (CF₂), -123.5 (CF₂), -124.5 (CF₂), -125.1 (CF₂), -127.7 (CF₂).

3,4'-Bis[4-(4-undecyloxybenzoyloxy)benzoyloxy]biphenyl 12/11



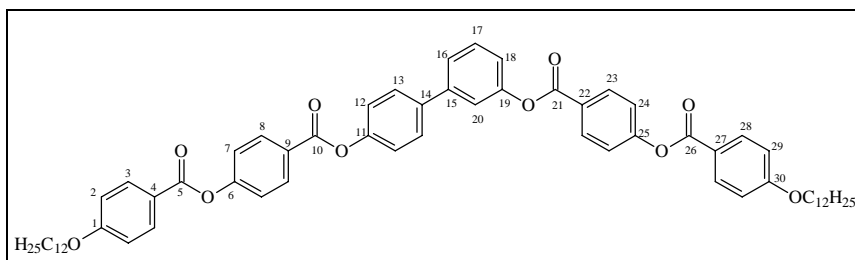
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-undecyloxybenzoyloxy)benzoic acid (0.82 g, 2.0 mmol).

Yield 0.12 g (13.6%); transition temperatures (°C): Cr 85 Col_r 154 Iso. (Found: C, 76.42; H, 7.31%; C₆₂H₇₀O₁₀ requires C, 76.39; H, 7.19%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.29 (2t, 4H, H-8, 23), 8.14 (d, *J* 8.4, 4H, H-3, 28), 7.65 (d, *J* 8.8, 2H, H-13), 7.50 (d, 2H, H-16, 18), 7.44-7.21 (m, 8H, Ar-H), 6.97 (d, *J* 8.8, 4H, H-2, 29), 4.04 (t, *J* 6.6, 4H, OCH₂), 1.80 (m, 4H, CH₂), 1.49-1.26 (m, 32H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, 164.0 (4C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.2 (C-14), 132.5 (C-8, 23), 131.9 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.1 (C-12), 121.1 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.5 (C-2, 29), 68.4 (OCH₂), 31.8 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]biphenyl 12/12



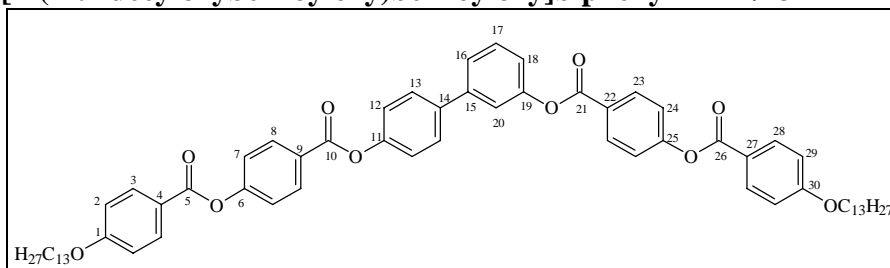
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-dodecyloxybenzoyloxy)benzoic acid (0.85 g, 2.0 mmol).

Yield 0.38 g (42.2%); transition temperatures (°C): Cr₁ 82 Cr₂ 106 SmCP_A 159 Iso. (Found: C, 76.58; H, 7.10%; C₆₄H₇₄O₁₀ requires C, 76.65; H, 7.38%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.29 (m, 4H, H-8, 23), 8.14 (d, *J* 8.8, 4H, H-3, 28), 7.65 (d, *J* 8.6, 2H, H-13), 7.49 (d, 2H, H-16, 18), 7.44-7.20 (m, 8H, Ar-H), 6.97 (d, *J* 9.0, 4H, H-2, 29), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.81 (m, 4H, CH₂), 1.52-1.25 (m, 36H, CH₂), 0.87 (t, *J* 6.7, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, 164.0 (4C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.1 (C-14), 132.5 (C-8, 23), 131.9 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.1 (C-12), 121.1 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.4 (C-2, 29), 68.4 (OCH₂), 31.8 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

3,4'-Bis[4-(4-tridecyloxybenzoyloxy)benzoyloxy]biphenyl 12/13



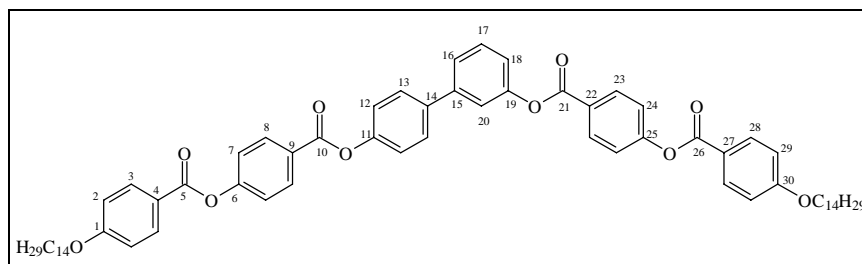
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-tridecyloxybenzoyloxy)benzoic acid (0.88 g, 2.0 mmol).

Yield 0.18 g (19.4%); transition temperatures (°C): Cr 86 SmCP_A 161 Iso. (Found: C, 76.74; H, 7.41%; C₆₆H₇₈O₁₀ requires C, 76.89; H, 7.57%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, *J* 8.8, 4H, H-8, 23), 8.14 (d, *J* 8.8, 4H, H-3, 28), 7.66 (d, *J* 8.8, 2H, H-13), 7.51-7.20 (m, 10H, Ar-H), 7.0 (d, *J* 8.8, 4H, H-2, 29), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.85-1.74 (m, 4H, CH₂), 1.51-1.42 (m, 40H, CH₂), 0.87 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.6, 165.5, 165.0 (4C=O, C-1, 30), 156.6 (C-6, 25), 152.5 (C-19), 151.8 (C-11), 143.2 (C-15), 139.2 (C-14), 133.5 (C-8, 23), 132.9 (C-3, 28), 131.0 (C-17), 129.4 (C-13), 128.0 (C-9, 22), 125.8 (C-16), 123.2 (C-7, 24), 123.1 (C-12), 122.1 (C-4, 27), 121.7 (C-18), 121.5 (C-20), 115.5 (C-2, 29), 69.4 (OCH₂), 32.8 (CH₂), 30.5 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.4 (CH₂), 30.3 (CH₂), 26.9 (CH₂), 23.5 (CH₂), 15.0 (CH₃).

3,4'-Bis[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]biphenyl 12/14



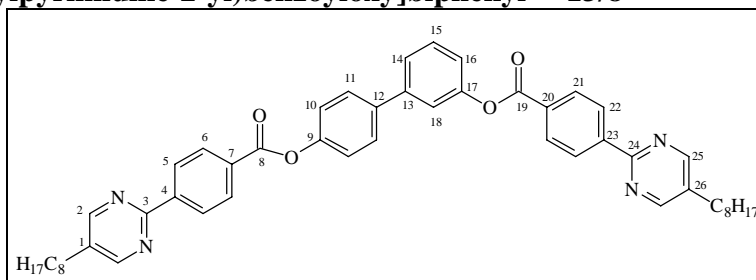
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-tetradecyloxybenzoyloxy)benzoic acid (0.91 g, 2.0 mmol).

Yield 0.23 g (24.9%); transition temperatures (°C): Cr 85 SmCP_A 162 Iso. (Found: C, 77.47; H, 7.95%; C₆₈H₈₂O₁₀ requires C, 77.13; H, 7.75%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.29 (d, *J* 8.8, 4H, H-8, 23), 8.14 (d, *J* 8.8, 4H, H-3, 28), 7.66 (d, *J* 8.8, 2H, H-13), 7.51-7.20 (m, 10H, Ar-H), 7.0 (d, *J* 9.0, 4H, H-2, 29), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.85-1.74 (m, 4H, CH₂), 1.53-1.42 (m, 44H, CH₂), 0.86 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 50 MHz): 164.6, 164.5, 163.8 (4C=O, C-1, 30), 155.6 (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.1 (C-14), 132.4 (C-8, 23), 131.8 (C-3, 28), 130.0 (C-17), 128.3 (C-13), 127.8 (C-9, 22), 124.8 (C-16), 122.1 (C-7, 24), 122.1 (C-12), 121.1 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.4 (C-2, 29), 68.4 (OCH₂), 31.9 (CH₂), 29.6 (CH₂), 29.4 (CH₂), 29.1 (CH₂), 25.9 (CH₂), 22.7 (CH₂), 14.1 (CH₃).

3,4'-Bis[4-(5-octylpyrimidine-2-yl)benzoyloxy]biphenyl 13/8



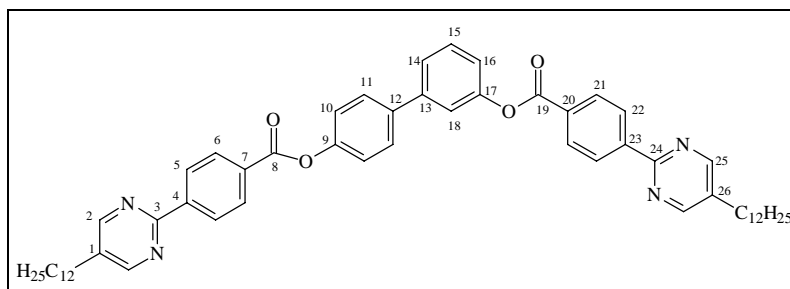
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.62 g, 2.0 mmol).

Yield 0.22 g (31.4%); transition temperatures (°C): Cr 142 Sm_{intercal} 148 Iso. (Found C, 77.84; H, 7.19; N, 7.18 %; C₅₀H₅₄N₄O₄ requires C, 77.52; H, 6.98; N, 7.23%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; J/Hz): 8.67 (s, 4H, H-2, 25), 8.56 (d, *J* 8.8, 4H, H-5, 22), 8.31 (m, 4H, H-6, 21), 7.66 (d, *J* 8.6, 2H, H-11), 7.52-7.47 (m, 3H, H-14, 16, 18), 7.32 (d, *J* 8.8, 2H, H-10), 7.25 (m, 1H, H-15), 2.65 (t, *J* 7.6, 4H, CH₂), 1.66 (m, 4H, CH₂), 1.33-1.26 (m, 20H, CH₂), 0.86 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.2, 166.1 (2C=O), 162.7 (C-3, 24), 158.3 (C-2, 25), 152.6 (C-17), 151.9 (C-9), 143.6 (C-4, 23), 143.2 (C-13), 139.1 (C-12), 135.0 (C-1, 26), 132.0 (C-7, 20), 131.5 (C-5, 22), 130.9 (C-15), 129.4 (C-11), 129.1 (C-6, 21), 125.7 (C-14), 123.2 (C-10), 121.7 (C-16), 121.5 (C-18), 32.7 (CH₂), 31.6 (CH₂), 31.2 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 30.0 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

3,4'-Bis[4-(5-dodecylpyrimidine-2-yl)benzoyloxy]biphenyl 13/12



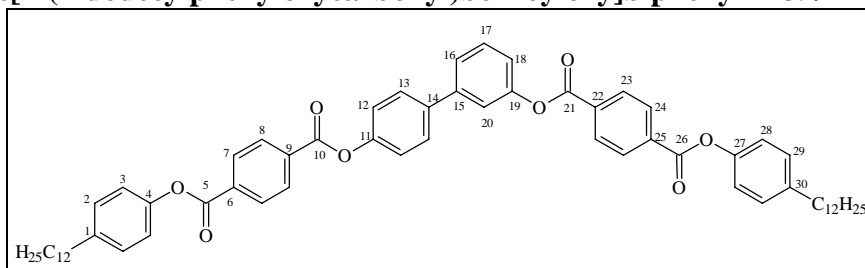
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(5-dodecylpyrimidine-2-yl)benzoic acid (0.74 g, 2.0 mmol).

Yield 0.25 g (31.2%); transition temperatures (°C): Cr₁ 93 Cr₂ (89 Sm_{intercal}) 115 Iso. (Found C, 78.86; H, 8.26; N, 6.29 %; C₅₈H₇₀N₄O₄ requires C, 78.55; H, 7.90; N, 6.32%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.67 (s, 4H, H-2, 25), 8.56 (d, *J* 8.4, 4H, H-5, 22), 8.32 (m, 4H, H-6, 21), 7.67 (d, *J* 8.6, 2H, H-11), 7.52-7.47 (m, 3H, H-14, 16, 18), 7.35-7.25 (m, 3H, H-10, 15), 2.64 (t, *J* 7.5, 4H, CH₂), 1.66 (m, 4H, CH₂), 1.40-1.24 (m, 36H, CH₂), 0.86 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.2, 166.1 (2C=O), 162.7 (C-3, 24), 158.3 (C-2, 25), 152.6 (C-17), 151.9 (C-9), 143.6 (C-4, 23), 143.2 (C-13), 139.1 (C-12), 135.0 (C-1, 26), 132.0 (C-7, 20), 131.5 (C-5, 22), 130.9 (C-15), 129.4 (C-11), 129.1 (C-6, 21), 125.7 (C-14), 123.2 (C-10), 121.7 (C-16), 121.5 (C-18), 32.8 (CH₂), 31.6 (CH₂), 31.2 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.2 (CH₂), 30.0 (CH₃), 23.5 (CH₂), 15.0 (CH₃).

3,4'-Bis[4-(4-dodecylphenoxy)carbonyl]benzoyloxy]biphenyl 39/12



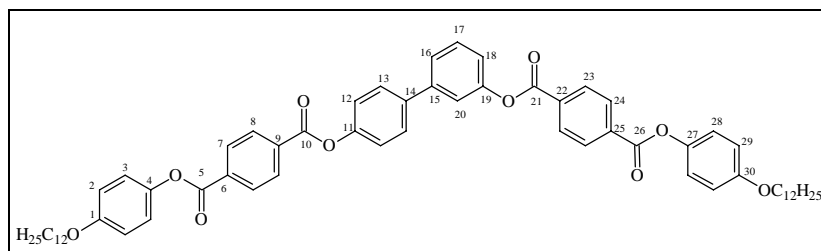
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(4-dodecylphenoxy)carbonyl)benzoic acid (1.1 g, 2.0 mmol).

Yield 0.32 g (36.8%); transition temperatures (°C): Cr₁ 94 Cr₂ 150 Col 189 Iso. (Found C, 78.84; H, 7.87%; C₆₄H₇₄O₈ requires C, 79.18; H, 7.63 %).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.33 (s, 8H, H-7, 8, 23, 24), 7.68 (d, *J* 8.8, 2H, H-13), 7.52 (d, *J* 5.08, 2H, H-16, 18), 7.48 (s, 1H, H-20), 7.33 (d, *J* 8.6, 2H, H-12), 7.27-7.15 (m, 8H, Ar-H), 7.11 (m, 1H, H-17), 2.62 (t, *J* 7.6, 4H, CH₂), 1.62 (m, 4H, CH₂), 1.4-1.25 (m, 36H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.3 (4C=O), 151.5 (C-19), 150.8 (C-11), 148.6 (C-4, 27), 142.1 (C-15), 140.9 (C-1, 30), 138.1 (C-14), 134.2 (C-9, 22), 133.8 (C-6, 25), 130.3 (C-7, 8, 23, 24), 130.0 (C-17), 129.4 (C-2, 29), 128.4 (C-13), 124.8 (C-16), 122.0 (C-12), 121.1 (C-3, 28), 120.7 (C-18), 120.5 (C-20), 35.4 (CH₂), 31.9 (CH₂), 31.5 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 22.7 (CH₂), 14.1 (CH₃).

3,4'-Bis[4-(4-dodecylphenoxy)carbonyl]benzoyloxy]biphenyl 40/12



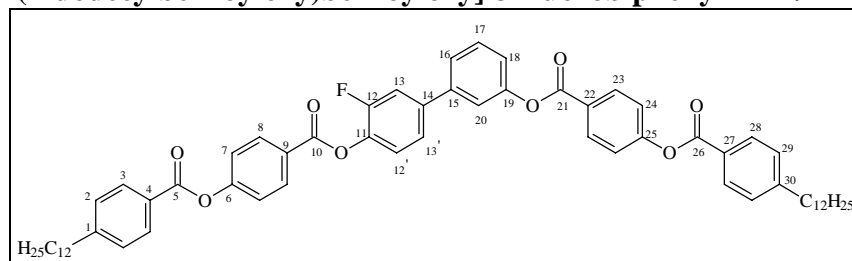
Synthesized from 3,4'-dihydroxybiphenyl (0.056 g, 0.3 mmol) and 4-(4-dodecyloxyphenyl-carbonyl)benzoic acid (0.28 g, 0.66 mmol).

Yield 0.02 g (6.7%); transition temperatures (°C): Cr₁ 112 Cr₂ 168 Col 205 Iso. (Found: C, 76.31; H, 7.25%; C₆₄H₇₄O₁₀ requires C, 76.65; H, 7.38%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; J/Hz): 8.33 (s, 8H, H-7, 8, 23, 24), 7.68 (d, *J* 8.6, 2H, H-13), 7.53 (d, *J* 5.1, 2H, H-16, 18), 7.48 (s, 1H, H-20), 7.33 (d, *J* 8.6, 2H, H-12), 7.27-7.22 (m, 1H, H-17), 7.13 (d, *J* 9.0, 4H, H-3, 28), 6.93 (d, *J* 9.0, 4H, H-2, 29), 3.95 (t, *J* 6.5, 4H, OCH₂), 1.78 (m, 4H, CH₂), 1.48-1.25 (m, 36H, CH₂), 0.86 (t, *J* 6.9, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.5, 164.4 (4C=O), 157.3 (C-1, 30), 151.4 (C-19), 150.7 (C-11), 144.2 (C-4, 27), 142.2 (C-15), 138.3 (C-14), 134.3 (C-9, 22), 133.9 (C-6, 25), 130.4 (C-7, 8, 23, 24), 130.1 (C-17), 128.5 (C-13), 125.0 (C-16), 122.3 (C-3, 28), 122.1 (C-12), 120.6 (C-18), 120.4 (C-20), 115.3 (C-2, 29), 68.5 (OCH₂), 31.8 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

3',4-Bis[4-(4-dodecylbenzoyloxy)benzoyloxy]-3-fluorobiphenyl 42/12



Synthesized from 3-fluoro-3',4-dihydroxybiphenyl (0.19 g, 0.9 mmol) and 4-(4-decylbenzoyloxy)benzoic acid (0.82 g, 2.0 mmol).

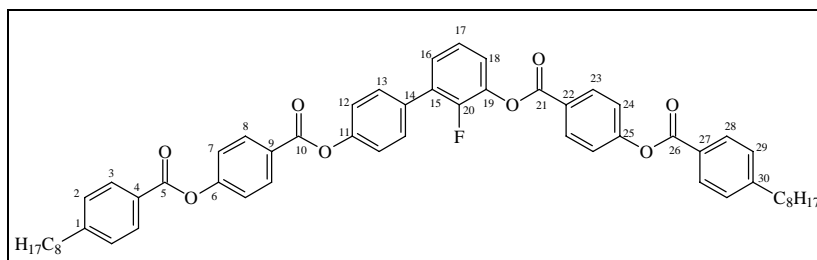
Yield 0.06 g (6.7%); transition temperatures (°C): Cr₁ 52 Cr₂ 75 SmCP_A 143 Iso. (Found: C, 77.42; H, 7.72 %; C₆₄H₇₃FO₈ requires C, 77.73; H, 7.39%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; J/Hz): 8.30 (d, *J* 8.6, 4H, H-8, 23), 8.11 (d, *J* 8.0, 4H, H-3, 28), 7.54-7.20 (m, 15H, Ar-H), 2.70 (t, *J* 7.7, 4H, CH₂), 1.68-1.61 (m, 4H, CH₂), 1.31-1.19 (m, 36H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.6 (4C=O), 163.6 (C-12), 155.7, 155.6 (C-6, 25), 151.6 (C-19), 150.0 (C-1, 30), 141.1 (C-15), 139.9 (C-14), 132.2, 132.0 (C-8, 23), 130.5 (C-3, 28), 130.1 (C-17), 128.9 (C-2, 29), 127.0 (C-4, 27), 126.5, 126.2 (C-9, 22), 124.7 (C-16), 124.3 (C-13'), 123.2 (C-12'), 122.2 (C-7, 24), 121.3 (C-18), 120.5 (C-20), 115.7, 115.5 (C-11, 13), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -129.1 (F).

3,4'-Bis[4-(4-octylbenzoyloxy)benzoyloxy]-2-fluorobiphenyl 43/8



Synthesized from 2-fluoro-3,4'-dihydroxybiphenyl (0.19 g, 0.9 mmol) and 4-(4-octylbenzoyloxy)benzoic acid (0.71 g, 2.0 mmol).

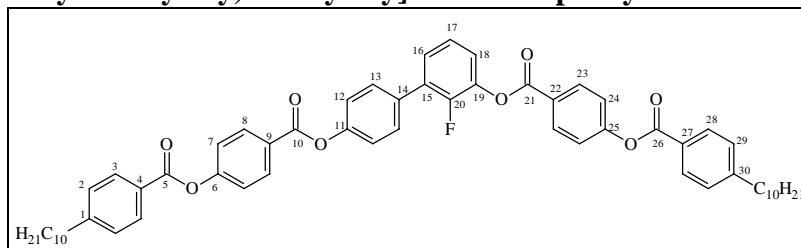
Yield 0.12 g (15.2%); transition temperatures (°C): Cr₁ 61 Cr₂ 136 Col 147 Iso. (Found: C, 76.74; H, 7.34%; C₅₆H₆₇FO₈ requires C, 76.71; H, 6.51%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.31 (d, *J* 8.6, 4H, H-8, 23), 8.10 (d, *J* 8.4, 4H, H-3, 28), 7.63 (d, *J* 7.4, 2H, H-13), 7.4-7.25 (m, 13H, Ar-H), 2.70 (t, *J* 7.7, 4H, CH₂), 1.66-1.61 (m, 4H, CH₂), 1.4-1.25 (m, 20H, CH₂), 0.87 (t, *J* 6.9, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.7, 164.5 (4C=O), 163.7 (C-20), 155.7, 155.6 (C-6,25), 150.0 (C-1, 11, 30), 132.9 (C-14, 19), 132.2 (C-13), 132.0 (C-8, 23), 130.5 (C-16, 17), 130.3 (C-3, 28), 128.9 (C-2,29), 127.0 (C-9,22), 126.5 (C-4,27), 122.2 (C-7,24), 122.2, 121.9 (C-15, 12, 18), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -135.2 (F).

3,4'-Bis[4-(4-decylbenzoyloxy)benzoyloxy]-2-fluorobiphenyl 43/10



Synthesized from 2-fluoro-3,4'-dihydroxybiphenyl (0.19 g, 0.9 mmol) and 4-(4-decylbenzoyloxy)benzoic acid (0.76 g, 2.0 mmol).

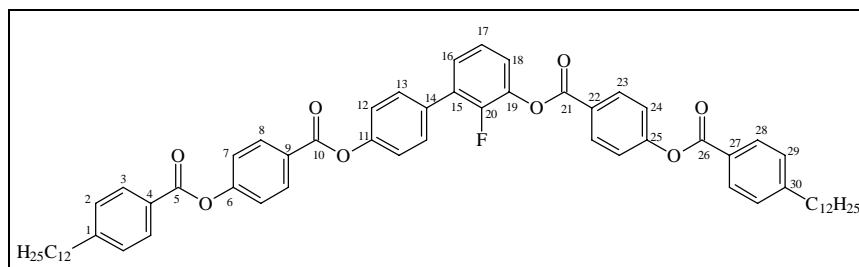
Yield 0.17 g (20.2%); transition temperatures (°C): Cr₁ 45 Cr₂ 125 Sm_b 141 Iso.

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 4H, H-8, 23), 8.11 (d, *J* 8.4, 4H, H-3, 28), 7.63 (d, *J* 7.4, 2H, H-13), 7.4-7.25 (m, 13H, Ar-H), 2.69 (t, *J* 7.7, 4H, CH₂), 1.68-1.61 (m, 4H, CH₂), 1.4-1.25 (m, 28H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.7, 164.5 (4C=O), 163.7 (C-20), 155.7, 155.6 (C-6,25), 150.0 (C-1, 11, 30), 132.9 (C-14, 19), 132.2 (C-13), 132.0 (C-8, 23), 130.5 (C-16, 17), 130.3 (C-3, 28), 128.9 (C-2, 29), 127.0 (C-9, 22), 126.5 (C-4, 27), 122.2 (C-7, 24), 122.2, 121.9 (C-15, 12, 18), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -135.2 (F).

3,4'-Bis[4-(4-dodecylbenzoyloxy)benzoyloxy]-2-fluorobiphenyl 43/12



Synthesized from 2-fluoro-3,4'-dihydroxybiphenyl (0.19 g, 0.9 mmol) and 4-(4-dodecylbenzoyloxy)benzoic acid (0.82 g, 2.0 mmol).

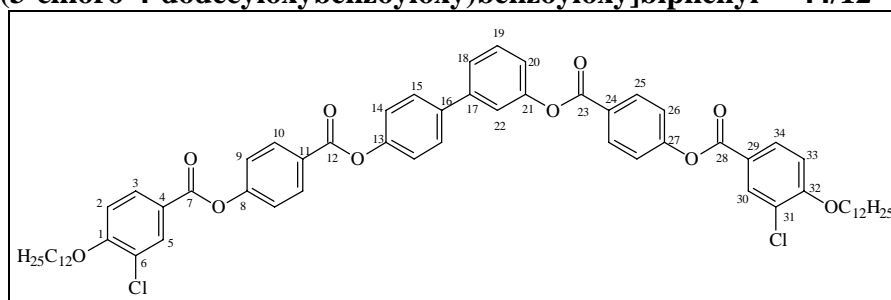
Yield 0.38 g (42.7%); transition temperatures (°C): Cr 62 M_x 122 SmCP_A 149 Iso. (Found: C, 77.71; H, 7.70 %; C₆₄H₇₃FO₈ requires C, 77.73; H, 7.39%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.30 (m, 4H, H-8, 23), 8.11 (d, *J* 8.4, 4H, H-3, 28), 7.63 (d, *J* 7.2, 2H, H-13), 7.4-7.26 (m, 13H, Ar-H), 2.70 (t, *J* 7.6, 4H, CH₂), 1.68-1.61 (m, 4H, CH₂), 1.4-1.2 (m, 36H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.7, 164.5 (4C=O), 163.7 (C-20), 155.7, 155.6 (C-6, 25), 150.0 (C-1, 11, 30), 132.9 (C-14, 19), 132.2 (C-13), 132.0 (C-8, 23), 130.5 (C-16, 17), 130.4 (C-3, 28), 128.9 (C-2, 29), 127.0 (C-9, 22), 126.5 (C-4, 27), 122.2 (C-7, 24), 122.2, 122.0 (C-15, 12, 18), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -135.2 (F).

3,4'-Bis[4-(3-chloro-4-dodecyloxybenzoyloxy)benzoyloxy]biphenyl 44/12



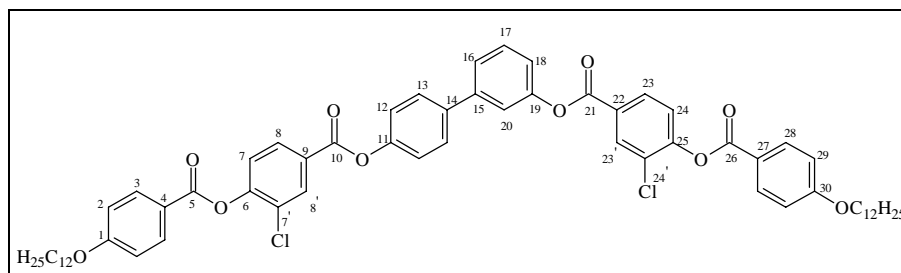
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 4-(3-chloro-4-dodecyloxybenzoyloxy)benzoic acid (0.92 g, 2.0 mmol).

Yield 0.29 g (30.2%); transition temperatures (°C): Cr₁ 100 Cr₂ 144 M_{x1} 155 Iso. (Found: C, 71.18; H, 7.05%; C₆₄H₇₂Cl₂O₁₀ requires C, 71.7; H, 6.72%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, *J* 8.6, 4H, H-10, 25), 8.21 (d, *J* 2.0, 2H, H-5, 30), 8.07 (d, *J* 8.6, 2H, H-3, 34), 7.65 (d, *J* 8.6, 2H, H-15), 7.51-7.19 (m, 10H, Ar-H), 6.97 (d, *J* 8.8, 2H, H-2, 33), 4.12 (t, *J* 6.4, 4H, OCH₂), 1.88 (m, 4H, CH₂), 1.53-1.24 (m, 36H, CH₂), 0.87 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.4, 163.4 (4C=O), 159.2 (C-1, 32), 155.2 (C-8, 27), 151.3 (C-21), 150.6 (C-13), 142.1 (C-17), 138.0 (C-16), 132.3 (C-10, 25), 131.9 (C-3, 5, 30, 34), 130.6 (C-6, 31), 129.9 (C-19), 128.3 (C-15), 127.1 (C-11, 24), 123.2 (C-18), 122.0 (C-9, 14, 26), 121.6 (C-4, 29), 120.4 (C-20, 22), 120.5 (C-20), 112.3 (C-2, 33), 69.5 (OCH₂), 31.8 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 28.9 (CH₂), 25.9 (CH₂), 22.7 (CH₂), 14.1 (CH₃).

3,4'-Bis[3-chloro-4-(4-dodecylbenzoyloxy)benzoyloxy]biphenyl 45/12



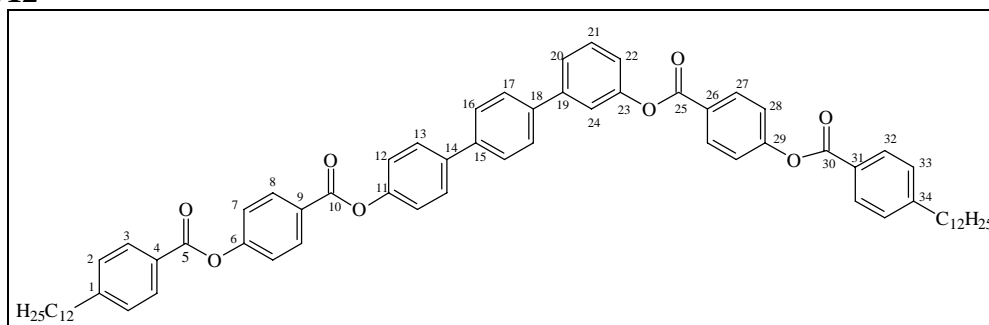
Synthesized from 3,4'-dihydroxybiphenyl (0.17 g, 0.9 mmol) and 3-chloro-4-(4-dodecyloxybenzoyloxy)benzoic acid (0.92 g, 2.0 mmol).

Yield 0.10 g (10.4%); transition temperatures ($^{\circ}\text{C}$): Cr₁ 74 Cr₂ 85 Col 91 Iso.

¹H-NMR: δ_{H} (CDCl₃; 400 MHz; *J*/Hz): 8.35-8.34 (m, 2H, H-8, 23), 8.20-8.16 (m, 6H, H-3, 8', 23', 28), 7.67 (d, *J* 8.8, 2H, H-13), 7.51 (d, 2H, H-16,18), 7.48-7.44 (m, 3H, H-7, 20, 24), 7.30 (d, *J* 8.6, 2H, H-12), 7.23-7.19 (m, 1H, H-17), 6.99 (d, *J* 8.8, 4H, H-2, 29), 4.04 (t, *J* 6.6, 4H, OCH₂), 1.81 (m, 4H, CH₂), 1.50-1.26 (m, 36H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 164.2, 163.7, 163.6 (4C=O, C-1, 30), 161.2 (C-6, 25), 151.9 (C-19), 151.3 (C-11), 142.2 (C-15), 138.3 (C-14), 132.8 (C-3, 28), 132.4 (C-8, 23), 130.0 (C-17), 129.9 (C-8', 23'), 128.4 (C-13), 127.9 (C-7', 24'), 125.0 (C-9, 22), 124.3 (C-16), 122.1 (C-12), 122.0 (C-4, 27), 122.0 (C-7, 24, 20), 120.4 (C-18), 114.6 (C-2, 29), 68.4 (OCH₂), 31.8 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

3.2.4 Synthesis of 3,4''-bis[4-(4-dodecylbenzoyloxy)benzoyloxy]-1,1':4'1''-terphenyl 37/12



Synthesized from 3,4''-dihydroxy-1,1':4'1''-terphenyl (0.23 g, 0.9 mmol) and 4-(4-decylbenzoyloxy)benzoic acid (0.82 g, 2.0 mmol).

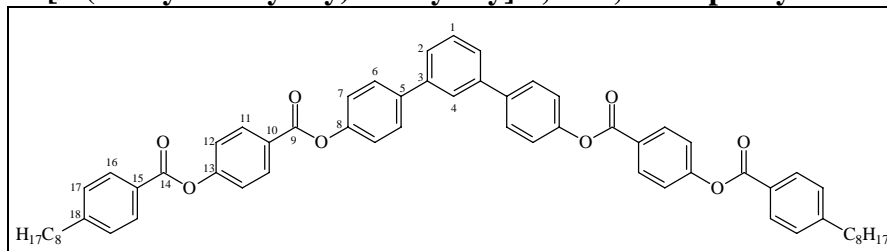
Yield 0.52 g (55.2%); transition temperatures ($^{\circ}\text{C}$): Cr₁ 106 Cr₂ 133 Col 202 Iso. (Found: C, 80.24; H, 7.58 %; C₇₀H₇₈O₈ requires C, 80.31; H, 7.46 %).

¹H-NMR: δ_{H} (CDCl₃; 400 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 4H, H-8, 27), 8.11 (d, *J* 8.2, 4H, H-3, 32), 7.71-7.66 (m, 6H, H-13, 16, 17), 7.57-7.49 (m, 3H, H-20, 22, 24), 7.40-7.30 (m, 10H, Ar-H), 7.20 (m, 1H, H-21), 2.70 (t, *J* 7.7, 4H, CH₂), 1.65 (m, 4H, CH₂), 1.31-1.89 (m, 36H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 164.8, 164.6 (4C=O), 155.5 (C-6, 29), 151.6 (C-23), 150.8 (C-11), 150.0 (C-1, 34), 142.5 (C-19), 139.9, 139.3, 138.6 (C-14, 15, 18), 132.0 (C-8, 27), 130.5 (C-3, 32), 130.0 (C-21), 129.0 (C-2, 33), 128.3 (C-13), 127.7, 127.6 (C-16, 17), 127.1 (C-9, 26), 126.6 (C-4, 31), 124.7 (C-20), 122.2, 122.1 (C-7, 12, 28), 120.7 (C-22), 120.4 (C-24), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

3.2.5 Synthesis of the 1,1':3',1''-terphenyl derivatives

4,4''-Bis[4-(4-octylbenzoyloxy)benzoyloxy]-1,1':3',1''-terphenyl 14/8



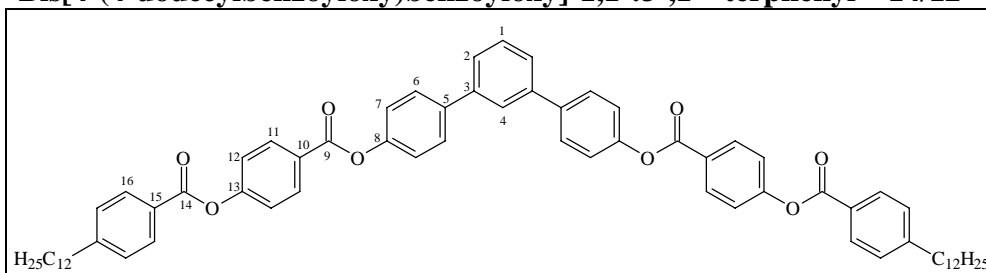
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-(4-octylbenzoyloxy)benzoic acid (0.71 g, 2.0 mmol).

Yield 0.25 g (29.8%); transition temperatures (°C): Cr₁ 173 Cr₂ 180 Col_r 207 Iso. (Found: C, 80.02; H, 7.12%; C₆₂H₆₂O₈ requires C, 79.66; H, 6.64%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.3 (d, *J* 8.6, 4H, H-11), 8.10 (d, *J* 8.6, 4H, H-16), 7.8 (s, 1H, H-4), 7.70 (d, *J* 8.6, 4H, H-6), 7.6-7.53 (m, 3H, H-1, 2), 7.4-7.3 (m, 12H, Ar-H), 2.70 (t, *J* 7.6, 4H, Ar-CH₂), 1.65-1.26 (m, 24H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8, 164.7, (4C=O), 155.5 (C-13), 150.7 (C-8), 150.0 (C-18), 141.2 (C-3), 139.1 (C-5), 132.0 (C-11), 130.5 (C-16), 129.4 (C-1), 128.9 (C-17), 128.5 (C-6), 127.1 (C-10), 126.6 (C-2), 126.3, 126.2 (C-15, 4), 122.2, 122.1 (C-7, 12), 36.0 (CH₂), 31.8 (CH₂), 31.0 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

4,4''-Bis[4-(4-dodecylbenzoyloxy)benzoyloxy]-1,1':3',1''-terphenyl 14/12



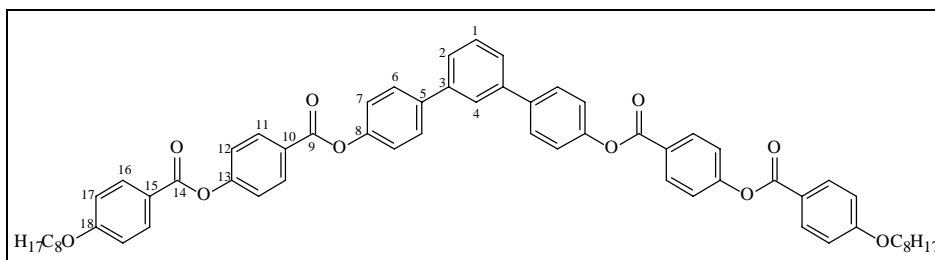
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-(4-dodecylbenzoyloxy)benzoic acid (0.82 g, 2.0 mmol).

Yield 0.28 g (29.8%); transition temperatures (°C): Cr 169 SmCP_A 203 Iso. (Found: C, 80.21; H, 7.50%; C₇₀H₇₈O₈ requires C, 80.31; H, 7.46%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.31 (d, *J* 8.6, 4H, H-11), 8.12 (d, *J* 8.2, 4H, H-16), 7.8 (s, 1H, H-4), 7.70 (d, *J* 8.6, 4H, H-6), 7.6-7.48 (m, 3H, H-1, 2), 7.4-7.3 (m, 12H, Ar-H), 2.70 (t, *J* 7.5, 4H, Ar-CH₂), 1.66 (m, 4H, CH₂), 1.30-1.26 (m, 36H, CH₂), 0.88 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, (4C=O), 155.4 (C-13), 150.5 (C-8), 149.8 (C-18), 141.0 (C-3), 138.9 (C-5), 131.9 (C-11), 130.3 (C-16), 129.9 (C-1), 128.8 (C-17), 128.3 (C-6), 127.0 (C-10), 126.4 (C-2, 15), 126.2 (C-4), 122.1 (C-7, 12), 36.1 (CH₂), 31.9 (CH₂), 31.1 (CH₂), 29.6 (CH₂), 22.7 (CH₂), 14.0 (CH₃).

4,4''-Bis[4-(4-octyloxybenzoyloxy)benzoyloxy]-1,1':3',1''-terphenyl 15/8



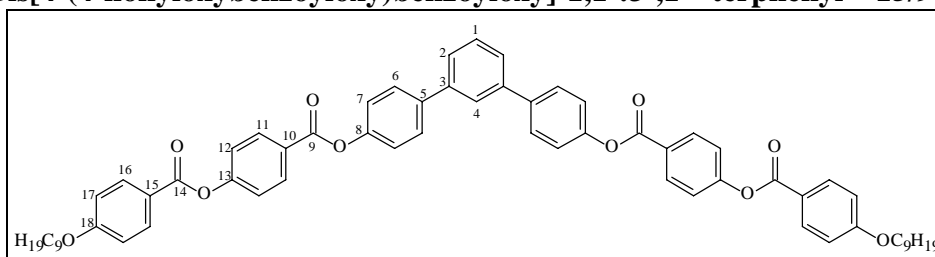
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.15 g, 0.56 mmol) 4-(4-octyloxybenzoyloxy)benzoic acid (0.39 g, 1.1 mmol).

Yield 0.12 g (21.8%); transition temperatures (°C): Cr 160 Col_r 226 Iso. (Found: C, 77.22; H, 6.65%; C₆₂H₆₂O₁₀ requires C, 77.02; H, 6.42%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, *J* 8.6, 4H, H-11), 8.14 (d, *J* 9.0, 4H, H-16), 7.80 (s, 1H, H-4), 7.70 (d, *J* 8.6, 4H, H-6), 7.56-7.54 (m, 3H, H-1, 2), 7.4-7.3 (m, 8H, H-7, 12), 6.97 (d, *J* 9.0, 4H, H-17), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.85-1.29 (m, 24H, CH₂), 0.88 (t, *J* 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.7, 164.5, 164.0 (4C=O, C-18), 155.6 (C-13), 150.7 (C-8), 141.2 (C-3), 139.1 (C-5), 132.5 (C-11), 131.9 (C-16), 129.4 (C-1), 128.4 (C-6), 127.0 (C-10), 126.3 (C-2), 126.2 (C-4), 122.2 (C-12), 122.1 (C-7), 121.1 (C-15), 114.5 (C-17), 68.4 (OCH₂), 31.7 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 14.0 (CH₃).

4,4''-Bis[4-(4-nonyloxybenzoyloxy)benzoyloxy]-1,1':3',1''-terphenyl 15/9



Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) 4-(4-nonyloxybenzoyloxy)benzoic acid, (0.77 g, 2.0 mmol).

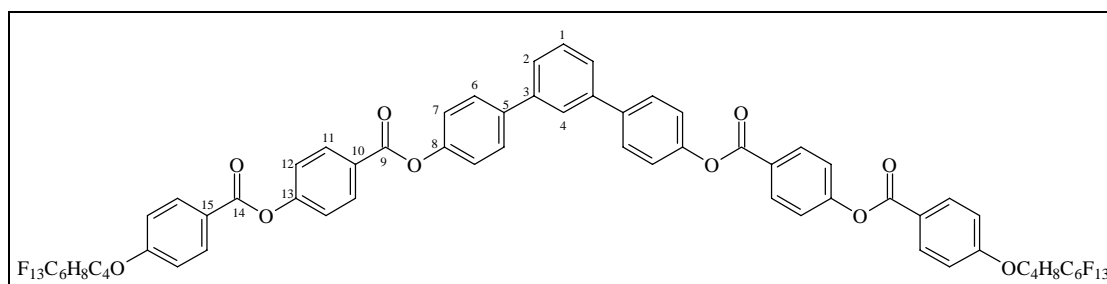
Yield 0.38 g (42.5%); transition temperatures (°C): Cr 161 Col_r 219 Iso. (Found: C, 77.18; H, 6.94%; C₆₄H₆₆O₁₀ requires C, 77.24; H, 6.68%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.32 (d, *J* 8.8, 4H, H-11), 8.17 (d, *J* 8.9, 4H, H-16), 7.82 (s, 1H, H-4), 7.72 (d, *J* 8.8, 4H, H-6), 7.62-7.43 (m, 3H, H-1, 2), 7.42-7.27 (m, 8H, H-7, 12), 7.01 (d, *J* 8.9, 4H, H-17), 4.07 (t, *J* 6.5, 4H, OCH₂), 1.87-1.25 (m, 28H, CH₂), 0.9 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.7, 164.5, 164.0 (4C=O, C-18), 155.6 (C-13), 150.7 (C-8), 141.2 (C-3), 139.1 (C-5), 132.5 (C-11), 131.9 (C-16), 129.4 (C-1), 128.4 (C-6), 127.0 (C-10), 126.3 (C-2), 126.2 (C-4), 122.2 (C-12), 122.1 (C-7), 121.1 (C-15), 114.5 (C-17), 68.4 (OCH₂), 31.8 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): *m/z* (%) 994 (M⁺, 8), 367 (4), 247 (100), 121 (76).

4,4''-Bis{4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]benzoyloxy}-1,1':3',1''-terphenyl 15/4F6

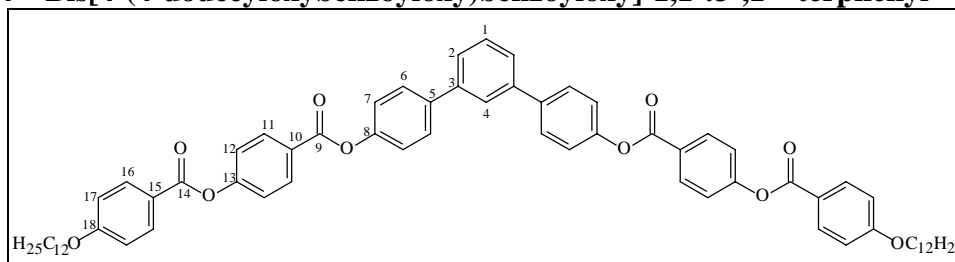


Synthesized from 4,4''-dihydroxy-1,1':3,1''-terphenyl (0.24 g, 0.9 mmol) and 4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]benzoic acid (1.26 g, 0.2 mmol).

Yield 0.29 g (21.6%); transition temperatures (°C): Cr 211 SmCP_A 309 Iso. (Found: C, 53.33; H, 3.50% C₆₆H₄₄F₂₆O₁₀ requires C, 53.15; H, 2.95%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 4H, H-11), 8.16 (d, *J* 8.8, 4H, H-16), 7.80 (s, 1H, H-4), 7.70 (d, *J* 8.6, 4H, H-6), 7.57-7.55 (m, 3H, H-1, 2), 7.40-7.30 (m, 8H, H-7, 12), 6.99 (d, *J* 8.8, 4H, H-17), 4.10 (t, *J* 5.6, 4H, OCH₂), 2.1-2.2 (m, 4H, CF₂CH₂), 2.0-1.7 (m, 8H, CH₂).

4,4''-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-1,1':3,1''-terphenyl 15/12



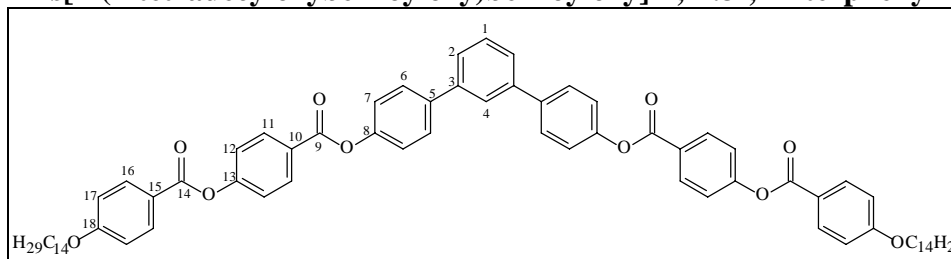
Synthesized from 4,4''-dihydroxy-1,1':3,1''-terphenyl (0.24 g, 0.9 mmol) and 4-(4-dodecyloxybenzoyloxy)benzoic acid, (0.85 g, 2.0 mmol).

Yield 0.4 g (41.2%); transition temperatures (°C): Cr 165 Col_r 203 Iso. (Found: C, 78.03; H, 7.27%; C₇₀H₇₈O₁₀ requires C, 77.92; H, 7.24%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.32 (d, *J* 8.6, 4H, H-11), 8.17 (d, *J* 8.8, 4H, H-16), 7.82 (s, 1H, H-4), 7.72 (d, *J* 8.6, 4H, H-6), 7.59-7.55 (m, 3H, H-1, 2), 7.42-7.32 (m, 8H, H-7, 12), 7.01 (d, *J* 9.0, 4H, H-17), 4.06 (t, *J* 6.5, 4H, OCH₂), 1.84 (m, 4H, OCH₂CH₂), 1.5-1.2 (m, 36H, CH₂), 0.89 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, 164.0 (4C=O, C-18), 155.6 (C-13), 150.7 (C-8), 141.2 (C-3), 139.0 (C-5), 132.5 (C-11), 131.9 (C-16), 129.4 (C-1), 128.4 (C-6), 127.0 (C-10), 126.3 (C-2), 126.2 (C-4), 122.2 (C-12), 122.1 (C-7), 121.1 (C-15), 114.5 (C-17), 68.4 (OCH₂), 31.8 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

4,4''-Bis[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]-1,1':3,1''-terphenyl 15/14



Synthesized from 4,4''-dihydroxy-1,1':3,1''-terphenyl (0.24 g, 0.9 mmol) and 4-(4-tetra-

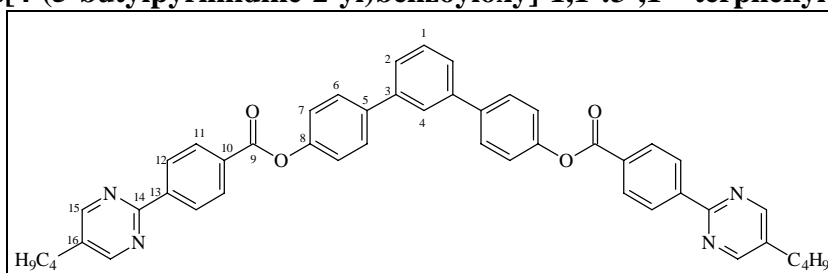
decyloxybenzoyloxy)benzoic acid, (0.91 g, 2.0 mmol).

Yield 0.17 g (16.7%); transition temperatures (°C): Cr 155 SmCP_A 199 Iso. (Found: C, 78.21; H, 7.44%; C₇₄H₈₆O₁₀ requires C, 78.31; H, 7.58%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.32 (d, *J* 8.6, 4H, H-11), 8.17 (d, *J* 8.8, 4H, H-16), 7.82 (s, 1H, H-4), 7.72 (d, *J* 8.6, 4H, H-6), 7.59-7.55 (m, 3H, H-1, 2), 7.42-7.32 (m, 8H, H-7, 12), 7.01 (d, *J* 9.0, 4H, H-17), 4.06 (t, *J* 6.5, 4H, OCH₂), 1.84 (m, 4H, OCH₂CH₂), 1.5-1.2 (m, 44H, CH₂), 0.89 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, 164.0 (4C=O, C-18), 155.6 (C-13), 150.7 (C-8), 141.2 (C-3), 139.0 (C-5), 132.5 (C-11), 131.9 (C-16), 129.4 (C-1), 128.4 (C-6), 127.0 (C-10), 126.3 (C-2), 126.2 (C-4), 122.2 (C-12), 122.1 (C-7), 121.1 (C-15), 114.5 (C-17), 68.4 (OCH₂), 31.8 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

4,4''-Bis[4-(5-butylpyrimidine-2-yl)benzoyloxy]-1,1':3',1''-terphenyl 17/4



Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-(5-butylpyrimidine-2-yl)benzoic acid (0.51 g, 2.0 mmol).

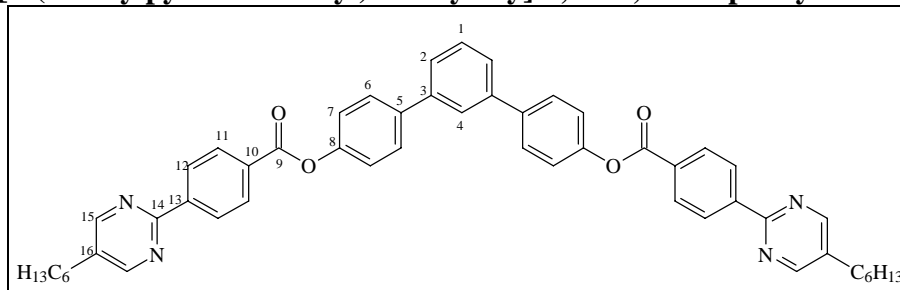
Yield 0.2 g (30.1%); transition temperatures (°C): Cr 195 Sm_{intercal} 203 Iso. (Found: C, 78.16; H, 5.78; N, 7.73%; C₄₈H₄₂N₄O₄ requires C, 78.03; H, 5.73; N, 7.58%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.68 (s, 4H, H-15), 8.57 (d, *J* 8.6, 4H, H-12), 8.32 (d, *J* 8.6, 4H, H-11), 7.81 (s, 1H, H-4), 7.70 (d, *J* 8.6, 4H, H-6), 7.60-7.5 (m, 3H, H-1, 2), 7.34 (d, *J* 8.6, 4H, H-7), 2.66 (t, *J* 7.5, 4H, Pyrimidine-CH₂-), 1.70-1.19 (m, 8H, CH₂), 0.95 (t, *J* 7.2, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.2 (2C=O), 161.7 (C-14), 157.3 (C-15), 150.7 (C-8), 142.6 (C-13), 141.2 (C-3), 139.0 (C-5), 134.0 (C-16), 131.0 (C-10), 130.5 (C-12), 129.4 (C-1), 128.4 (C-6), 128.1 (C-11), 126.3 (C-2), 126.2 (C-4), 122.1 (C-7), 32.7 (CH₂), 29.8 (CH₂), 22.0 (CH₂), 13.6 (CH₃).

MS (70 ev): *m/z* (%) 738 (M⁺, 56), 239 (100), 211 (10).

4,4''-Bis[4-(5-hexylpyrimidine-2-yl)benzoyloxy]-1,1':3',1''-terphenyl 17/6



Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-(5-hexylpyrimidine-2-yl)benzoic acid (0.5 g, 1.76 mmol).

Yield 0.23 g (32.2%); transition temperatures (°C): Cr 209 Sm_{intercal} 222 Iso. (Found: C, 78.29; H, 6.50; N, 6.93%; C₅₂H₅₀N₄O₄ requires C, 78.56; H, 6.34; N, 7.05%).

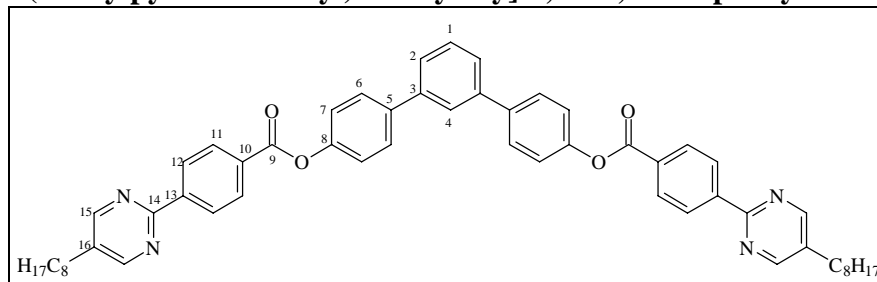
¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.67 (s, 4H, H-15), 8.57 (d, *J* 8.4, 4H, H-12), 8.32

(d, J 8.4, 4H, H-11), 7.81 (s, 1H, H-4), 7.70 (d, J 8.4, 4H, H-6), 7.57-7.55 (m, 3H, H-1, 2), 7.34 (d, J 8.4, 4H, H-7), 2.65 (t, J 7.8, 4H, Pyrimidine-CH₂), 1.67-1.33 (m, 16H, CH₂), 0.89 (t, J 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.2 (2C=O), 161.7 (C-14), 157.3 (C-15), 150.7 (C-8), 142.6 (C-13), 141.2 (C-3), 139.0 (C-5), 134.0 (C-16), 131.0 (C-10), 130.5 (C-12), 129.4 (C-1), 128.4 (C-6), 128.1 (C-11), 126.3 (C-2), 126.2 (C-4), 122.1 (C-7), 31.4 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 28.6 (CH₂), 22.4 (CH₂), 13.9 (CH₃).

MS (70 eV): m/z (%) 794 (M⁺, 82), 267 (100), 239 (7).

4,4''-Bis[4-(5-octylpyrimidine-2-yl)benzoyloxy]-1,1':3',1''-terphenyl 17/8



Synthesized from 4-(5-octylpyrimidine-2-yl)benzoic acid (0.62 g, 2.0 mmol) and 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol).

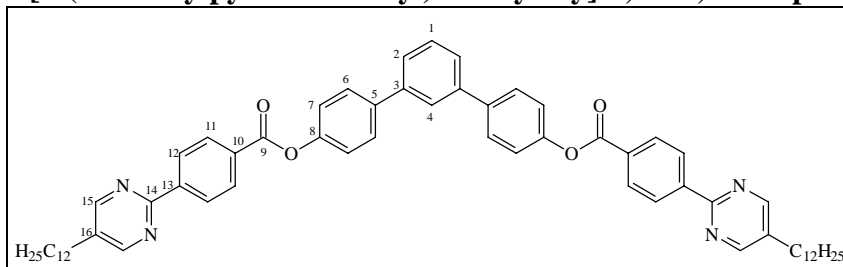
Yield 0.26 g (47.1%); transition temperatures (°C): Cr₁ 105 Cr₂ 178 Sm_{intercal} 206 Iso. (Found: C, 80.14; H, 6.64; N, 6.75%; C₅₆H₅₈N₄O₄ requires C, 79.03; H, 6.87; N, 6.58%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J /Hz): 8.7 (s, 4H, H-15), 8.59 (d, J 8.6, 4H, H-12), 8.34 (d, J 8.6, 4H, H-11), 7.83 (s, 1H, H-4), 7.73 (d, J 8.6, 4H, H-6), 7.65-7.55 (m, 3H, H-1, 2), 7.36 (d, J 8.6, 4H, H-7), 2.68 (d, J 7.6, 4H, Pyrimidine-CH₂-), 1.69-1.28 (m, 24H, CH₂), 0.89 (t, J 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.2 (2C=O), 161.7 (C-14), 157.3 (C-15), 150.7 (C-8), 142.6 (C-13), 141.2 (C-3), 139.0 (C-5), 134.0 (C-16), 131.0 (C-10), 130.5 (C-12), 129.4 (C-1), 128.4 (C-6), 128.1 (C-11), 126.3 (C-2), 126.2 (C-4), 122.1 (C-7), 31.7 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): m/z (%) 858 (M⁺, 38), 295 (100), 267 (7), 239 (43).

4,4''-Bis[4-(5-dodecylpyrimidine-2-yl)benzoyloxy]-1,1':3',1''-terphenyl 17/12



Synthesized from 4-(5-dodecylpyrimidine-2-yl)benzoic acid (0.74 g, 2.0 mmol) and 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol).

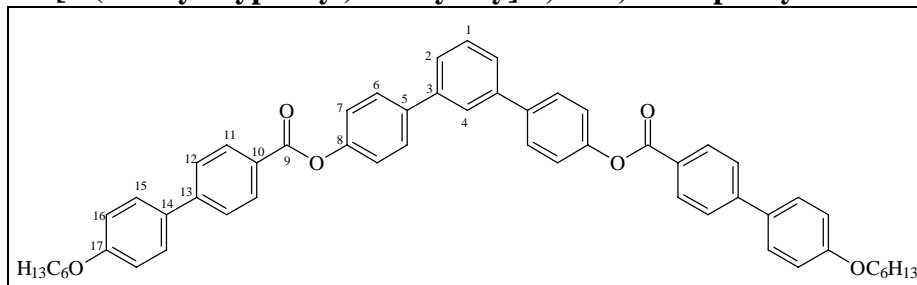
Yield 0.33 g (38.4%); transition temperatures (°C): Cr 166 Iso. (Found: C, 79.99; H, 7.80; N, 5.64%; C₆₄H₇₄N₄O₄ requires C, 79.83; H, 7.69; N, 5.82%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J /Hz): 8.67 (s, 4H, H-15), 8.57 (d, J 8.8, 4H, H-12), 8.32 (d, J 8.8, 4H, H-11), 7.81 (s, 1H, H-4), 7.70 (d, J 8.6, 4H, H-6), 7.60-7.53 (m, 3H, H-1, 2), 7.34 (d, J 8.6, 4H, H-7), 2.65 (d, J 7.5, 4H, Pyrimidine-CH₂-), 1.67 (m, 4H, CH₂), 1.49-1.32 (m, 36H, CH₂), 0.86 (t, J 6.5, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.2 (2C=O), 162.7 (C-14), 158.3 (C-15), 151.7 (C-8),

143.6 (C-13), 142.2 (C-3), 140.0 (C-5), 135.0 (C-16), 132.0 (C-10), 131.5 (C-12), 130.4 (C-1), 129.4 (C-6), 129.1 (C-11), 127.3 (C-2), 127.2 (C-4), 123.1 (C-7), 32.8 (CH₂), 31.6 (CH₂), 31.2 (CH₂), 30.5 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.2 (CH₂), 30.0 (CH₂), 23.5 (CH₂), 15.0 (CH₃).

4,4''-Bis[4-(4-hexyloxyphenyl)benzoyloxy]-1,1':3',1''-terphenyl 19/6



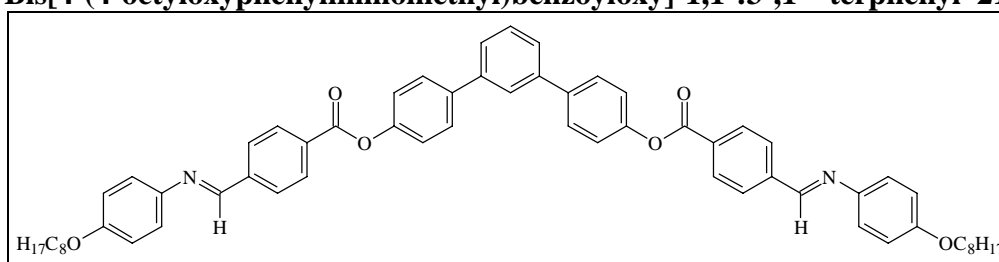
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-(4-hexyloxyphenyl)benzoic acid (0.6 g, 2.0 mmol).

Yield 10 mg (1.4%); transition temperatures (°C): Cr 258 M 268 Iso.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.28 (d, 4H, *J* 8.6, H-11), 7.8 (s, 1H, H-4), 7.72 (d, *J* 7.6, 8H, H-6, 12); 7.64-7.59 (m, 7H, H-1, 2, 15), 7.35 (d, *J* 8.6, 4H, H-7), 7.0 (d, 4H, *J* 9.0, H-16), 4.03 (t, 4H, OCH₂), 1.81 (t, 4H, CH₂), 1.39-1.26 (m, 12H, CH₂), 0.93 (t, 6H, CH₃).

MS (70 eV): *m/z* (%) 281(100), 197(15), 169(10), 141(5).

4,4''-Bis[4-(4-octyloxyphenyliminomethyl)benzoyloxy]-1,1':3',1''-terphenyl 21/8

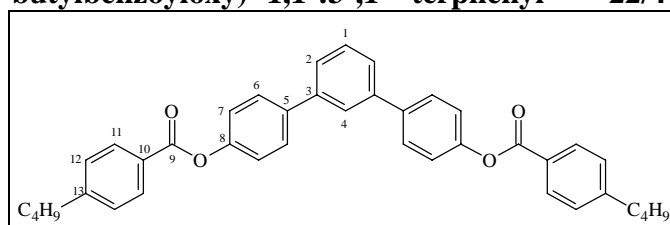


Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-(4-octyloxyphenyliminomethyl)benzoic acid (0.71 g, 2.0 mmol).

Yield 0.09 g (10.8%); mp >270 °C. (Found: C, 79.66; H, 6.77; N, 3.31%; C₆₂H₆₄N₂O₆ requires C, 79.83; H, 6.87; N, 3.00%).

MS (70 eV): *m/z* (%) 932 (M⁺, 4), 597(2), 484(2), 352(3), 336(100), 241(6), 224(6), 195(13).

4,4''-Bis(4-butylbenzoyloxy)-1,1':3',1''-terphenyl 22/4



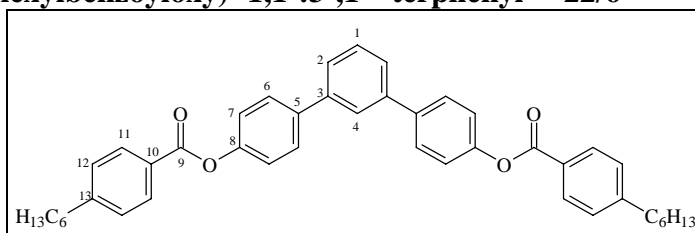
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-butylbenzoic acid (0.36 g, 2.0 mmol).

Yield 0.17 g (32.5%); mp 135 °C. (Found: C, 82.71; H, 6.59%; C₄₀H₃₈O₄ requires C, 82.47; H, 6.53%).

¹H-NMR: δ_{H} (CDCl₃; 400 MHz; *J*/Hz): 8.14 (2d, *J* 8.2, 4H, H-11), 7.8 (d, *J* 1.75, 1H, H-4), 7.7 (2d, *J* 8.6, 4H, H-6), 7.6-7.5 (m, 3H, H-1, 2), 7.35-7.30 (m, 8H, H-7, 12), 2.72 (t, *J* 7.7, 4H, CH₂), 1.69-1.36 (m, 8H, CH₂), 0.95 (t, *J* 7.4, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 166.4, (2C=O), 151.8 (C-8), 150.6 (C-13), 142.2 (C-3), 139.9 (C-5), 131.4 (C-11), 130.4 (C-1), 129.8 (C-12), 129.4 (C-6), 128.1 (C-10), 127.3 (C-2), 127.2 (C-4), 123.2 (C-7), 36.7 (CH₂), 34.2 (CH₂), 23.2 (CH₂), 14.7 (CH₃).

4,4''-Bis(4-hexylbenzoyloxy)-1,1':3',1''-terphenyl 22/6



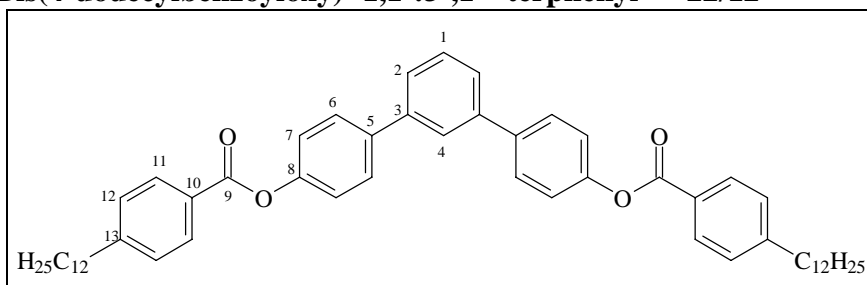
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-hexylbenzoic acid (0.41 g, 2.0 mmol).

Yield 0.19 g (33.1%); mp 106 °C. (Found: C, 82.76; H, 7.32%; C₄₄H₄₆O₄ requires C, 82.76; H, 7.21%).

¹H-NMR: δ_{H} (CDCl₃; 200 MHz; *J*/Hz): 8.12 (d, *J* 8.2, 4H, H-11), 7.78 (d, *J* 1.4, 1H, H-4), 7.67 (2d, *J* 8.6, 4H, H-6), 7.58-7.51 (m, 3H, H-1, 2), 7.33-7.27 (m, 8H, H-7, 12), 2.69 (t, *J* 7.8, 4H, CH₂), 1.65-1.61 (m, 4H, CH₂), 1.32-1.24 (m, 12H, CH₂), 0.88 (t, *J* 6.6, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 166.4 (2C=O), 151.8 (C-8), 150.6 (C-13), 142.2 (C-3), 139.9 (C-5), 131.4 (C-11), 130.4 (C-1), 129.8 (C-12), 129.4 (C-6), 128.1 (C-10), 127.3 (C-2), 127.2 (C-4), 123.2 (C-7), 37.0 (CH₂), 32.6 (CH₂), 32.0 (CH₂), 29.8 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

4,4''-Bis(4-dodecylbenzoyloxy)-1,1':3',1''-terphenyl 22/12



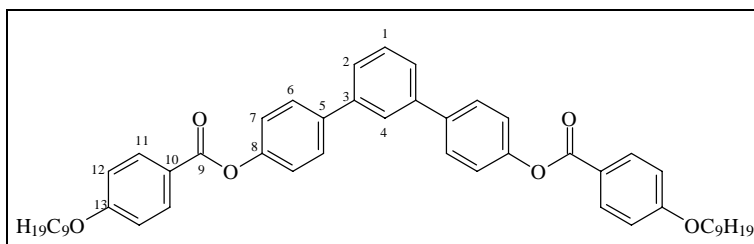
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-dodecylbenzoic acid (0.58 g, 2.0 mmol).

Yield 0.18 g (24.8%); mp 103 °C. (Found: C, 83.47; H, 8.60%; C₅₆H₇₀O₄ requires C, 83.37; H, 8.68%).

¹H-NMR: δ_{H} (CDCl₃; 200 MHz; *J*/Hz): 8.15 (d, *J* 8.2, 4H, H-11), 7.81(s, 1H, H-4), 7.70 (d, *J* 8.8, 4H, H-6), 7.61-7.54 (m, 3H, H-1, 2), 7.36-7.30 (m, 8H, H-7, 12), 2.72 (t, *J* 7.6, 4H, CH₂), 1.67-1.32 (m, 40H, CH₂), 0.89 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 166.4 (2C=O), 151.8 (C-8), 150.6 (C-13), 142.2 (C-3), 139.9 (C-5), 131.4 (C-11), 130.4 (C-1), 129.8 (C-12), 129.4 (C-6), 128.1 (C-10), 127.3 (C-2), 127.2 (C-4), 123.2 (C-7), 37.0 (CH₂), 32.8 (CH₂), 32.0 (CH₂), 30.6 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 23.6 (CH₂), 15.0 (CH₃).

4,4''-Bis(4-nonyloxybenzoyloxy)-1,1':3',1''-terphenyl 23/9



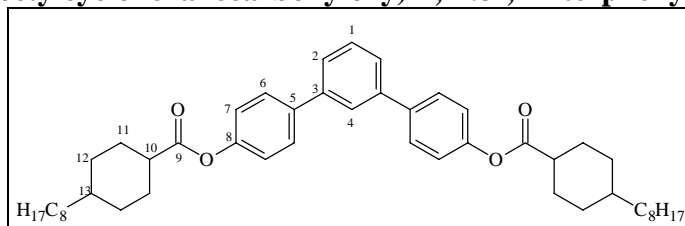
Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and 4-nonyloxybenzoic acid (0.53 g, 2.0 mmol).

Yield 0.19 g (28.0%); mp 126 °C. (Found: C, 79.59; H, 7.70%; C₅₀H₅₈O₆ requires C, 79.58; H, 7.69%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.18 (d, *J* 9.0, 4H, H-11), 7.81 (s, 1H, H-4), 7.70 (d, *J* 8.8, 4H, H-6), 7.6-7.53 (m, 3H, H-1, 2), 7.32 (d, *J* 8.8, 4H, H-7), 7.00 (d, *J* 9.0, 4H, H-12), 4.06(t, *J* 6.5, 4H, OCH₂), 1.87-1.77 (m, 4H, CH₂), 1.29-1.26 (m, 24H, CH₂), 0.90 (t, *J* 6.6, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.1 (2C=O), 164.8 (C-13), 151.8 (C-8), 142.2 (C-3), 139.8 (C-5), 133.4 (C-11), 130.4 (C-1), 129.4 (C-6), 127.3 (C-2), 127.2 (C-4), 123.2 (C-7), 122.6 (C-10), 115.4 (C-12), 69.3 (OCH₂), 32.8 (CH₂), 30.4 (CH₂), 30.3 (CH₂), 30.1 (CH₂), 30.0 (CH₂), 26.9 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

4,4''-Bis(*trans*-4-octylcyclohexanecarbonyloxy)-1,1':3',1''-terphenyl 24/8



Synthesized from 4,4''-dihydroxy-1,1':3',1''-terphenyl (0.24 g, 0.9 mmol) and *trans*-4-octylcyclohexanecarboxylic acid (0.48 g, 2.0 mmol).

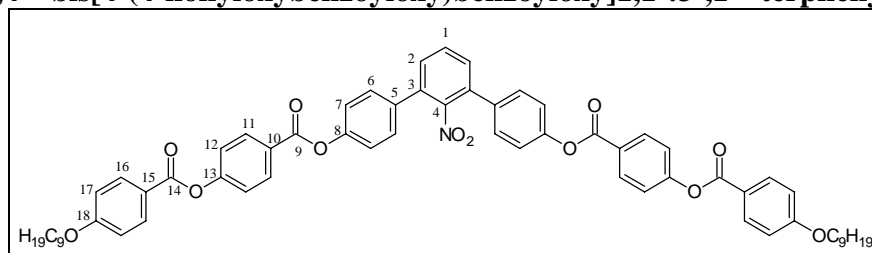
Yield 0.89 g (76.5%); mp 168 °C. (Found: C, 81.77; H, 9.01%; C₄₈H₆₆O₄ requires C, 81.59; H, 9.35%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 7.73 (s, 1H, H-4), 7.62 (d, *J* 8.6, 4H, H-6), 7.55-7.51 m. 3H, H-1, 2), 7.16 (d, *J* 8.6, 4H, H-7), 2.5 (m, 2H, H-10), 2.17-2.14 (m, 4H, H-11), 1.9-1.87 (m, 4H, H-12), 1.6-1.55 (m, 20H, CH₂), 1.26-0.95 (m, 18H, CH₂), 0.89 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 174.9 (2C=O), 150.7 (C-8), 141.2 (C-3), 138.7 (C-5), 129.3 (C-1), 128.3 (C-6), 126.2, 126.1 (C-2, 4), 122.0 (C-7), 43.7(C-10), 37.1(C-13), 36.9 (CH₂), 32.22 (C-12), 31.8 (CH₂), 29.8 (CH₂), 29.5 (CH₂), 29.2 (CH₂), 29.0 (C-11), 26.8 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

3.2.6 Synthesis of the 2'-nitro-4,4''-bis(4-substituted benzoyloxy)-1,1':3',1''-terphenyls

2'-Nitro-4,4''-bis[4-(4-nonyloxybenzoyloxy)benzoyloxy]1,1':3',1''-terphenyl 33/9



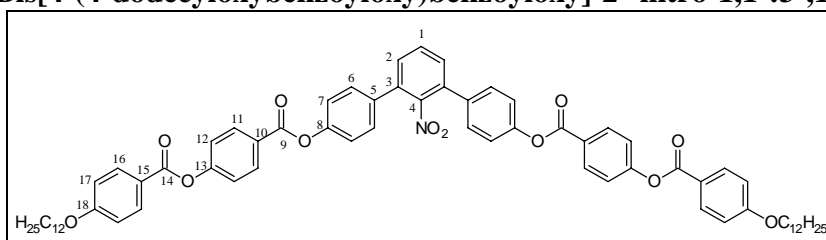
Synthesized from 4,4''-dihydroxy-2'-nitro-1,1':3',1''-terphenyl (0.28 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol).

Yield 35 mg (3.7%); transition temperatures (°C): Cr₁ 108 Cr₂ 149 Col_r 197 N 217 Iso. (Found: C, 74.20; H, 6.49; N, 1.26%; C₆₄H₆₅NO₁₂ requires C, 73.92; H, 6.26; N, 1.35%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.29 (d, 4H, *J* 8.8, H-11), 8.16 (d, *J* 8.8, 4H, H-16), 7.56 (m, 1H, H-1), 7.48-7.28 (m, 14H, Ar-H), 7.0 (d, *J* 9.0, 4H, H-17), 4.07 (t, *J* 6.5, 4H, OCH₂), 1.82 (m, 4H, CH₂), 1.3 (m, 24H, CH₂), 0.9 (t, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.5, 164.4, 164.0 (4C=O, C-18), 155.7 (C-13), 151.4 (C-8), 150.0 (C-4), 134.1 (C-3), 133.8 (C-5), 132.5 (C-11), 132.0 (C-16), 130.5 (C-2), 130.2 (C-1), 129.6 (C-6), 126.8 (C-10), 122.2, 122.1 (C-7, 12), 121.1 (C-15), 114.5 (C-17), 68.4 (OCH₂), 31.8 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

4,4''-Bis[4-(4-dodecyloxybenzoyloxy)benzoyloxy]-2'-nitro-1,1':3',1''-terphenyl 33/12



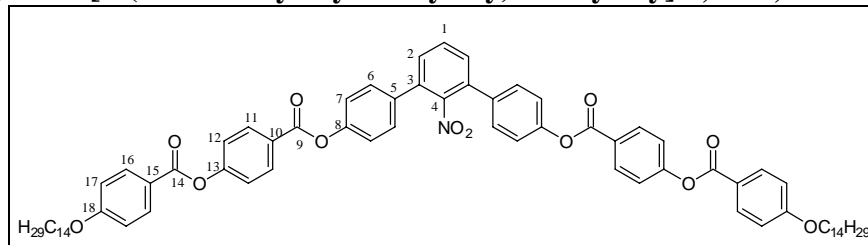
Synthesized from 4,4''-dihydroxy-2'-nitro-1,1':3',1''-terphenyl (0.28 g, 0.9 mmol) and 4-(4-dodecyloxybenzoyloxy)benzoic acid (0.85 g, 2.0 mmol).

Yield 0.37 g (36.6%); transition temperatures (°C): Cr₁ 100 Cr₂ 165 SmC_(b) 178 Col_r 183 N 199 Iso (Found: C, 74.82; H, 6.77; N, 1.17%; C₇₀H₇₇NO₁₂ requires C, 74.80; H, 6.86; N, 1.25 %);

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.27 (d, *J* 8.8, 4H, H-11), 8.14 (d, *J* 8.8, 4H, H-16), 7.56 (m, 1H, H-1), 7.49-7.27 (m, 14H, Ar-H), 6.97 (d, *J* 8.8, 4H, H-17), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.82-1.78 (m, 4H, CH₂), 1.49-1.26 (m, 36H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.3 (4C=O), 163.8 (C-18), 155.5 (C-13), 151.2 (C-8), 150.0 (C-4), 134.0 (C-3), 133.7 (C-5), 132.4 (C-11), 131.9 (C-16), 130.5 (C-2), 130.2 (C-1), 129.4 (C-6), 126.6 (C-10), 122.2 (C-7, 12), 120.9 (C-15), 114.4 (C-17), 68.4 (OCH₂), 31.9 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.7 (CH₂), 14.1 (CH₃).

2'-Nitro-4,4''-bis[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]-1,1':3',1''-terphenyl 33/14



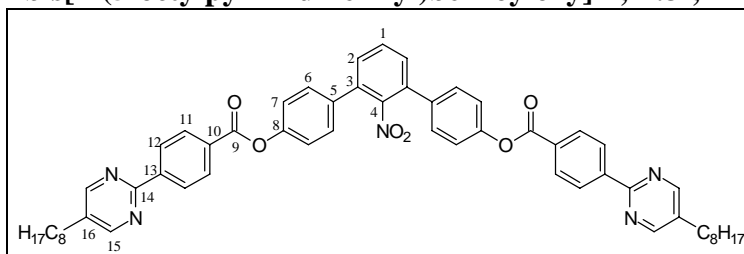
Synthesized from 4,4''-dihydroxy-2'-nitro-1,1':3',1''-terphenyl (0.28 g, 0.9 mmol) and 4-(4-tetradecyloxybenzoyloxy)benzoic acid (0.91 g, 2.0 mmol).

Yield 0.26 g (24.5%); transition temperatures (°C): Cr₁ 96 Cr₂ 161 SmC_(b) 186 N 190 Iso. (Found C, 75.20; H, 7.38; N, 1.13%; C₇₄H₈₅O₁₂N requires C, 75.32; H, 7.21; N, 1.19%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.27 (d, *J* 8.8, 4H, H-11), 8.14 (d, *J* 8.8, 4H, H-16), 7.56 (m, 1H, H-1), 7.49-7.27 (m, 14H, Ar-H), 6.97 (d, *J* 8.8, 4H, H-17), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.82-1.78 (m, 4H, CH₂), 1.48-1.25 (m, 44H, CH₂), 0.86 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.5, 164.4 (4C=O), 164.0 (C-18), 155.7 (C-13), 151.4 (C-8), 150.0 (C-4), 134.1 (C-3), 133.8 (C-5), 132.5 (C-11), 132.0 (C-16), 130.5 (C-2), 130.2 (C-1), 129.6 (C-6), 126.8 (C-10), 122.2 (C-7, 12), 121.0 (C-15), 114.5 (C-17), 68.4 (OCH₂), 31.8 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

2'-Nitro-4,4''-bis[4-(5-octylpyrimidine-2-yl)benzoyloxy]-1,1':3',1''-terphenyl 34/8



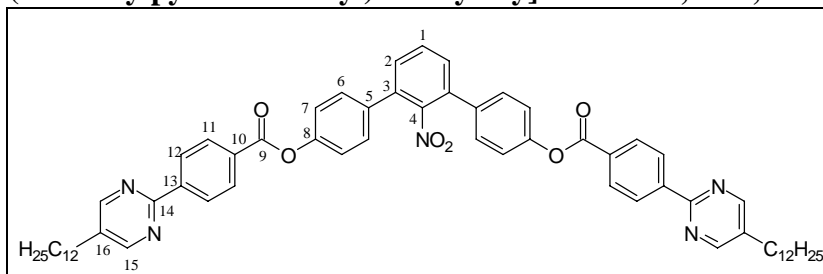
Synthesized from 4,4''-dihydroxy-2'-nitro-1,1':3',1''-terphenyl (0.28 g, 0.9 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.62 g, 2.0 mmol).

Yield 0.23 g (29.1%); transition temperatures (°C): Cr 221 (187 Sm_{intercal} 192 N 208) Iso.

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.67 (s, 4H, H-15), 8.56 (d, *J* 8.8, 4H, H-12), 8.30 (d, *J* 8.8, 4H, H-11), 7.62-7.58 (m, 1H, H-1), 7.49-7.46 (m, 6H, H-2, 6), 7.32 (d, *J* 8.8, 4H, H-7), 2.64 (t, *J* 7.7, 4H, CH₂), 1.70-1.63 (m, 4H, CH₂), 1.34-1.22 (m, 20H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.0 (2C=O), 161.7 (C-14), 157.3 (C-15), 151.5 (C-8), 150.0 (C-4), 142.7 (C-13), 134.1, 134.0 (C-3, 16), 133.9 (C-5), 131.6 (C-10), 130.8 (C-2), 130.6 (C-12), 130.2 (C-1), 129.6 (C-6), 128.1 (C-11), 122.2 (C-7), 31.7 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

4,4''-Bis[4-(5-dodecylpyrimidine-2-yl)benzoyloxy]-2'-nitro-1,1':3',1''-terphenyl 34/12



Synthesized from 2'-nitro-4,4''-dihydroxy-1,1':3',1''-terphenyl (0.28 g, 0.9 mmol) and 4-(5-dodecylpyrimidine-2-yl)benzoic acid (0.74 g, 2.0 mmol).

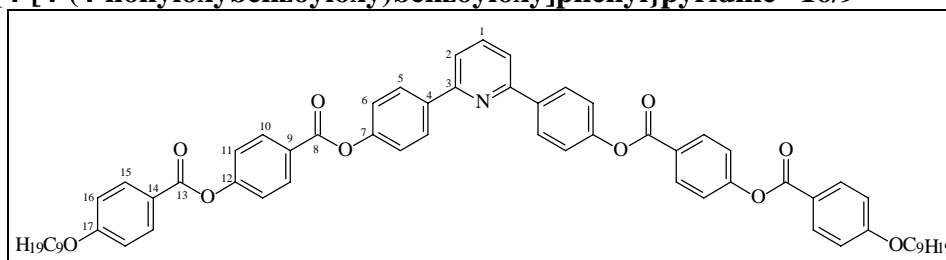
Yield 0.19 g (20.9%); transition temperatures (°C): Cr₁ 43 Cr₂ 153 N 164 Iso. (Found: C, 76.00; H, 7.41; N, 6.74%; C₆₄H₇₃N₅O₆ requires C, 76.27; H, 7.25; N, 6.95%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.6 (s, 4H, H-15), 8.56 (d, *J* 8.6, 4H, H-12), 8.30 (d, *J* 8.8, 4H, H-11), 7.62-7.58 (m, 1H, H-1), 7.49-7.46 (m, 6H, H-2, 6), 7.34-7.30 (m, 4H, H-7), 2.64 (t, *J* 7.6, 4H, CH₂), 1.66 (m, 4H, CH₂), 1.4-1.24 (m, 36H, CH₂), 0.86 (t, *J* 6.9, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.0 (2C=O), 161.7 (C-14), 157.3 (C-15), 151.5 (C-8), 150.0 (C-4), 142.7 (C-13), 134.1, 134.0 (C-3, 16), 133.9 (C-5), 131.6 (C-10), 130.8 (C-2), 130.6 (C-12), 130.2 (C-1), 129.6 (C-6), 128.1 (C-11), 122.2 (C-7), 31.8 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

3.2.7 Synthesis of the 2,6-diphenylpyridine derivatives

2,6-Bis{4-[4-(4-nonyloxybenzoyloxy)benzoyloxy]phenyl}pyridine 16/9



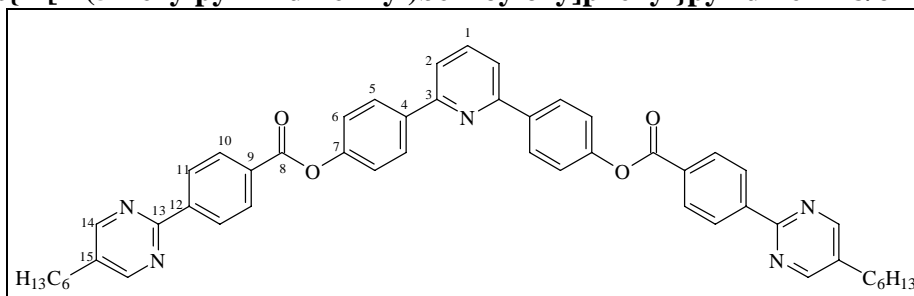
Synthesized from 2,6-bis(4-hydroxyphenyl)pyridine (0.24 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol).

Yield 0.35 g (39.1%); transition temperatures (°C): Cr 179 Col_r 246 Iso. (Found: C, 76.13; H, 6.76; N, 1.28%; C₆₃H₆₅NO₁₀ requires C, 75.96; H, 6.58; N, 1.41%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.32 (d, *J* 8.8, 4H, H-10), 8.24 (d, *J* 8.4, 4H, H-5), 8.17 (d, *J* 8.8, 4H, H-15), 7.74 (m, 3H, H-1, 2), 7.39 (d, *J* 8.8, 4H, H-11), 7.38 (d, *J* 8.6, 4H, H-6), 7.0 (d, *J* 9.0, 4H, H-16), 4.07 (t, 4H, *J* 6.4, OCH₂), 1.82 (m, 4H, CH₂), 1.3 (m, 24H, CH₂), 0.87 (t, *J* 6.6, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.5, 164.5, 164.0 (4C=O, C-17), 156.2 (C-3), 155.6 (C-12), 151.9 (C-7), 137.8 (C-1), 137.3 (C-4), 132.5 (C-10), 131.9 (C-15), 128.3 (C-5), 127.0 (C-9), 122.2 (C-11), 122.0 (C-6), 121.1 (C-14), 118.6 (C-2), 114.5 (C-16), 68.4 (OCH₂), 31.8 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

2,6-Bis{4-[4-(5-hexylpyrimidine-2-yl)benzoyloxy]phenyl}pyridine 18/6



Synthesized from 2,6-bis(4-hydroxyphenyl)pyridine (0.24 g, 0.9 mmol) and 4-(5-hexylpyrimidine-2-yl)benzoic acid (0.5 g, 1.76 mmol).

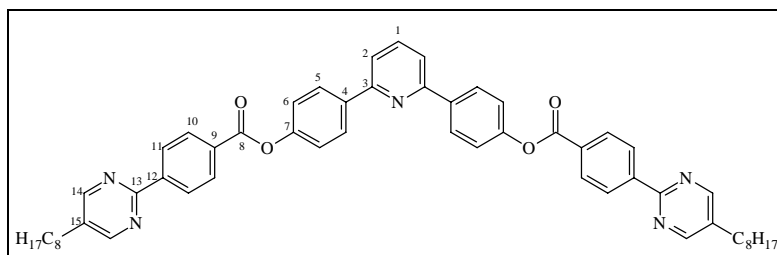
Yield 0.3 g (41.9%), transition temperatures (°C): Cr 224 Col_r 242 Iso. (Found: C, 77.12; H, 6.53; N, 8.63%; C₅₁H₄₉N₅O₄ requires C, 76.96; H, 6.21; N, 8.80%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.68 (s, 4H, H-14), 8.58 (d, *J* 8.6, 4H, H-11), 8.33 (d, *J* 8.6, 4H, H-10), 8.23 (d, *J* 8.6, 4H, H-5), 7.88-7.69 (m, 3H, H-1, 2), 7.38 (d, *J* 8.6, 4H, H-6), 2.65 (t, *J* 7.5, 4H, Pyrimidine-CH₂-), 1.67-1.24 (m, 16H, CH₂), 0.89 (t, *J* 6.6, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.1 (2C=O), 161.7 (C-13), 157.3 (C-14), 156.2 (C-3), 152.0 (C-7), 142.6 (C-12), 137.7 (C-1), 137.3 (C-4), 134.0 (C-15), 131.0 (C-9), 130.5 (C-11), 128.3 (C-5), 128.1 (C-10), 122.0 (C-6), 118.6 (C-2), 31.4 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 28.6 (CH₂), 22.4 (CH₂), 13.9 (CH₃).

MS (70 ev): *m/z* (%) 795 (M⁺, 88), 267 (100), 239 (8).

2,6-Bis{4-[4-(5-octylpyrimidine-2-yl)benzoyloxy]phenyl}pyridine 18/8



Synthesized from 2,6-bis(4-hydroxyphenyl)pyridine (0.24 g, 0.9 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.62 g, 2.0 mmol).

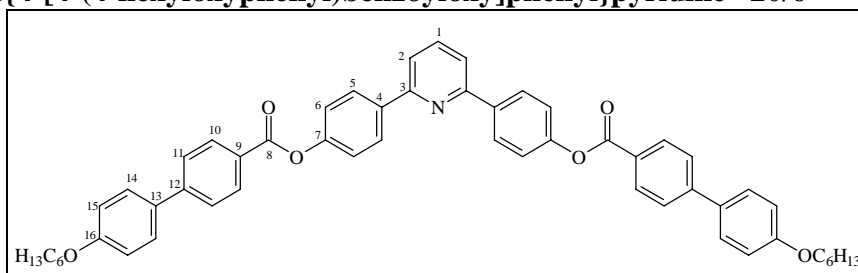
Yield 0.37 g (48.4%); transition temperatures (°C): Cr₁ 131 Cr₂ 204 Cr₃ 231 (Col_r 230) Iso. (Found: C, 77.01; H, 6.75; N, 7.89%; C₅₅H₅₇N₅O₄ requires C, 77.53; H, 6.74; N, 8.22%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.68 (s, 4H, H-14), 8.58 (d, *J* 8.6, 4H, H-11), 8.33 (d, *J* 8.6, 4H, H-10), 8.23 (d, *J* 8.6, 4H, H-5), 7.88-7.69 (m, 3H, H-1, 2), 7.38 (d, *J* 8.6 4H, H-6), 2.65 (t, *J* 7.5, 4H, Pyrimidine-CH₂-), 1.66-1.27 (m, 24H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.1 (2C=O), 162.7 (C-13), 158.3 (C-14), 157.2 (C-3), 153.0 (C-7), 143.6 (C-12), 138.7 (C-1), 138.3 (C-4), 135.0 (C-15), 132.0 (C-9), 131.5 (C-11), 129.3 (C-5), 129.1 (C-10), 123.0 (C-6), 119.6 (C-2), 32.7 (CH₂), 31.6 (CH₂), 31.2 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 30.0 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

MS (70 ev): *m/z* (%) 851 (M⁺, 85), 295 (100), 267 (10).

4,4''-Bis{4-[4-(4-hexyloxyphenyl)benzoyloxy]phenyl}pyridine 20/6



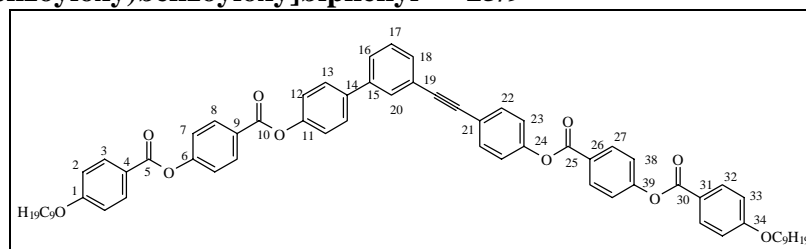
Synthesized from 2,6-bis(4-hydroxyphenyl)pyridine (0.24 g, 0.9 mmol) and 4-(4-hexyloxyphenyl)benzoic acid (0.60 g, 2.0 mmol).

Yield 5 mg (0.68%); mp 268 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.28-8.20 (t, 6H, Ar-H), 7.71-7.35 (m, 17H, Ar-H), 7.0 (d, *J* 8.8, 4H, H-15), 4.01 (t, *J* 6.4, 4H, OCH₂), 1.81 (m, 4H, CH₂), 1.34-1.24 (m, 12H, CH₂), 0.9 (t, 6H, CH₃).

3.2.8 Synthesis of 1-phenyl-3-(4-phenylethynyl)benzene derivatives

3-[4-[4-(4-Nonyloxybenzoyloxy)benzoyloxy]phenylethynyl]-4'-[4-(4-nonyloxybenzoyloxy)benzoyloxy]biphenyl 25/9



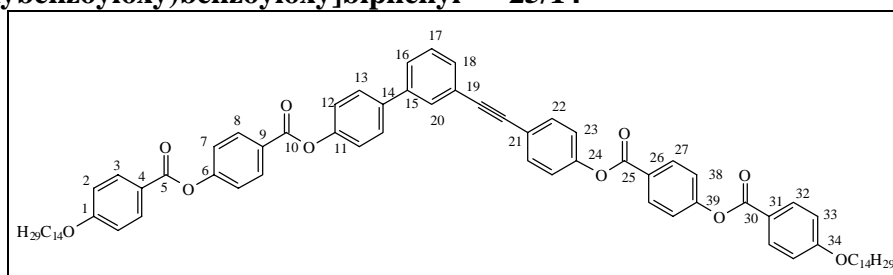
Synthesized from 4'-hydroxy-3-(4-hydroxyphenylethynyl)biphenyl (0.26 g, 0.9 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol).

Yield 0.20 g (21.8%); transition temperatures (°C): Cr₁ 111 Cr₂ 142 Col_r 231 Iso. (Found: C, 77.61; H, 6.67%; C₆₆H₆₆O₁₀ requires C, 77.77; H, 6.53%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.32-8.24 (m, 4H, H-8, 27), 8.14 (d, *J* 9.0, 4H, H-3, 32), 7.77 (s, 1H, H-20), 7.68-7.21 (m, 15H, Ar-H), 6.97 (d, *J* 8.8, 4H, H-2, 33), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.85-1.24 (m, 28H, CH₂), 0.87 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.5, 164.5, 164.3 (4C=O), 164.0 (C-34), 155.7 (C-29), 155.6 (C-6), 151.0 (C-11), 150.8 (C-24), 140.8 (C-15), 138.3 (C-14), 133.0 (C-22), 132.5 (C-8, 27), 131.9 (C-3, 32), 130.6 (C-18), 130.4 (C-20), 129.0 (C-17), 128.3 (C-13), 127.3 (C-16, 19), 127.0 (C-9), 126.8 (C-26), 123.8 (C-21), 122.2 (C-7, 28), 122.2 (C-12), 122.0 (C-23), 121.1 (C-4, 31), 114.5 (C-2, 33), 89.4 (C≡), 88.9 (C≡), 68.4 (OCH₂), 31.8 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

3-[4-[4-(4-Tetradecyloxybenzoyloxy)benzoyloxy]phenylethynyl]-4'-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]biphenyl 25/14



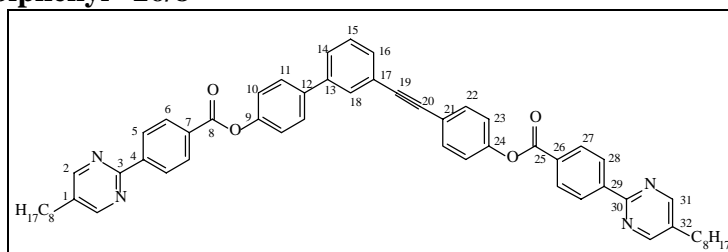
Synthesized from 4'-hydroxy-3-(4-hydroxyphenylethynyl)biphenyl (0.26 g, 0.9 mmol) and 4-(4-tetradecyloxybenzoyloxy)benzoic acid (0.91 g, 2.0 mmol).

Yield 0.09 g (9.0%); transition temperatures (°C): Cr 137 Col_r 203 Iso. (Found: C, 78.87; H, 7.69%; C₇₆H₈₆O₁₀ requires C, 78.76; H, 7.43%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.27 (m, 4H, H-8, 27), 8.14 (d, *J* 8.8, 4H, H-3, 32), 7.77 (s, 1H, H-20), 7.66 (d, *J* 9.0, 2H, H-13), 7.59-7.29 (m, 9H, Ar-H), 7.23 (d, *J* 8.6, 4H, H-7, 28), 6.97 (d, *J* 9.0, 4H, H-2, 33), 4.04 (t, *J* 6.4, 4H, OCH₂), 1.81 (m, 4H, CH₂), 1.25 (m, 44H, CH₂), 0.87 (t, *J* 6.4, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.6, 164.3, 164.5 (4C=O), 164.0 (C-34), 155.7 (C-29), 155.6 (C-6), 151.0 (C-11), 150.8 (C-24), 140.8 (C-15), 138.3 (C-14), 133.0 (C-22), 132.5 (C-8, 27), 131.9 (C-3, 32), 130.6 (C-18), 130.4 (C-20), 129.0 (C-17), 128.3 (C-13), 127.3 (C-16), 127.3 (C-19), 127.0 (C-9), 126.8 (C-26), 123.8 (C-21), 122.2 (C-7, 28), 122.2 (C-12), 122.0 (C-23), 121.1 (C-4, 31), 114.5 (C-2, 33), 89.4 (C≡), 88.9 (C≡), 68.4 (OCH₂), 31.8 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

3-[4-[4-(5-Octylpyrimidine-2-yl)benzoyloxy]phenylethynyl]-4'-[4-(5-octylpyrimidine-2-yl)benzoyloxy]biphenyl 26/8



Synthesized from 4'-hydroxy-3-(4-hydroxyphenylethynyl)biphenyl (0.26 g, 0.9 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.62 g, 2.0 mmol).

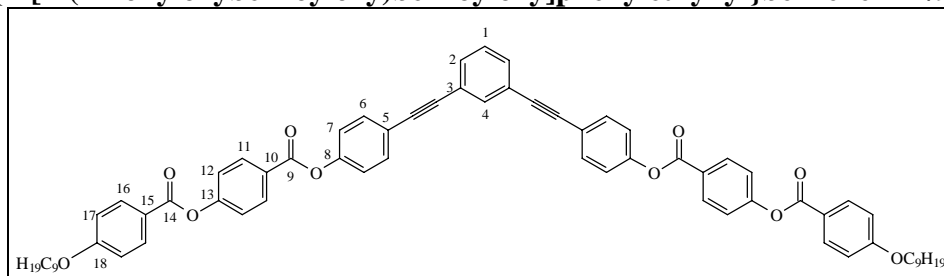
Yield 0.30 g (38.1%); transition temperatures (°C): Cr 183 Sm_{intercal} 220 Iso. (Found: C, 79.79; H, 6.70; N, 6.23%; C₅₈H₅₈N₄O₄ requires C, 79.60; H, 6.68; N, 6.40%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.67 (d, *J* 1.4, 4H, H-2, 31), 8.56 (2t, 4H, H-5, 28), 8.31 (m, 4H, H-6, 27), 7.78 (s, 1H, H-18), 7.67-7.25 (m, 11H, Ar-H), 2.64 (t, *J* 7.6, 4H, CH₂), 1.7-1.63 (m, 4H, CH₂), 1.50-1.26 (m, 20H, CH₂), 0.86 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.2, 164.9 (2C=O), 161.7 (C-3, 29), 157.3 (C-2, 31), 151.0, 150.9 (C-9, 24), 142.7, 142.6 (C-4, 29), 140.8 (C-13), 138.3 (C-12), 134.1 (C-1, 32), 133.0 (C-22), 130.8 (C-16), 130.6 (C-5, 28), 130.4 (C-18), 129.0 (C-15), 128.3 (C-11), 128.1 (C-6, 27), 127.3 (C-17, 14), 123.8 (C-21), 122.2 (C-10), 122.0 (C-23), 121.1 (C-7, 26), 89.4 (C≡), 88.9 (C≡), 31.7 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

3.2.9 Synthesis of 1,3-bis(phenylethynyl)benzene derivatives

1,3-Bis{4-[4-(4-nonyloxybenzoyloxy)benzoyloxy]phenylethynyl}benzene 27/9



Synthesized from 1,3-bis(4-hydroxyphenylethynyl)benzene (0.31 g, 1.0 mmol) and 4-(4-nonyloxybenzoyloxy)benzoic acid (0.77 g, 2.0 mmol).

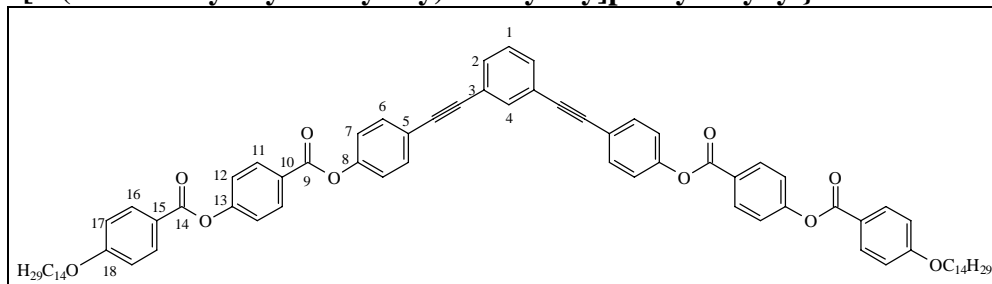
Yield 0.38 g (36.5%); transition temperatures (°C): Cr₁ 92 Cr₂ 159 Col_r 239 Iso. (Found: C, 78.00; H, 6.58%; C₆₈H₆₆O₁₀ requires C, 78.29; H, 6.38%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-11), 8.14 (d, *J* 9.0, 4H, H-16), 7.72 (s, 1H, H-4), 7.59 (d, *J* 8.8, 4H, H-6), 7.59 (d, *J* 8.6, 2H, H-2), 7.39-7.27 (m, 5H, H-1, 12), 7.23 (d, *J* 8.6, 4H, H-7), 6.97 (d, *J* 9.0, 4H, H-17), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.81 (t, *J* 6.9, 4H, CH₂), 1.27-1.24 (m, 24 H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.5, 164.3, 164.0 (4C=O, C-18), 155.7 (C-13), 151.0 (C-8), 134.8 (C-4), 133.0 (C-6), 132.5 (C-11), 131.9 (C-16), 131.5 (C-2), 128.6 (C-1), 126.8 (C-10), 123.7 (C-3), 122.2 (C-12), 122.0 (C-7), 121.1 (C-15), 120.9 (C-5), 114.5 (C-17), 89.3 (C≡), 88.7 (C≡), 68.4 (OCH₂), 31.8 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): *m/z* (%) 1042 (M⁺, 5), 367 (9), 247 (100), 121 (51).

1,3-Bis{4-[4-(4-tetradecyloxybenzoyloxy)benzoyloxy]phenylethynyl}benzene 27/14



Synthesized from 1,3-bis(4-hydroxyphenylethynyl)benzene (0.22 g, 0.9 mmol) and 4-(4-tetradecyloxybenzoyloxy)benzoic acid (0.9 mmol).

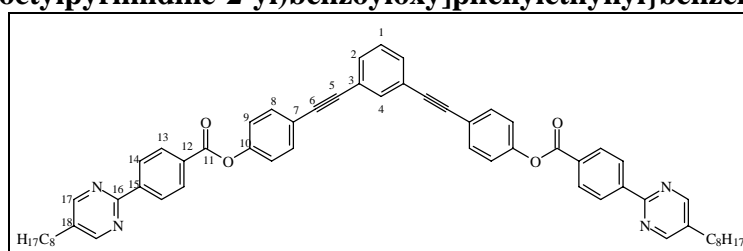
tetradecyloxybenzoyloxy)benzoic acid (0.71 g, 2.0 mmol).

Yield 0.05 g (5.0%); transition temperatures (°C): Cr₁ 106 Cr₂ 136 Col_r 204 Iso. (Found: C, 79.10; H, 7.47%; C₇₈H₈₆O₁₀ requires C, 79.19; H, 7.28%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.26 (d, *J* 8.8, 4H, H-11), 8.13 (d, *J* 8.8, 4H, H-16), 7.72 (s, 1H, H-4), 7.59 (d, *J* 8.8, 4H, H-6), 7.49 (d, *J* 8.6, 2H, H-2), 7.38-7.34 (m, 5H, H-1, 12), 7.23 (d, *J* 8.8, 4H, H-7), 6.97 (d, *J* 9.0, 4H, H-17), 4.04 (t, *J* 6.5, 4H, OCH₂), 1.85-1.77 (t, *J* 6.9, 4H, OCH₂CH₂), 1.45-1.25 (m, 44H, CH₂), 0.86 (t, *J* 6.3, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.5, 164.3, 164.0 (4C=O, C-18), 155.7 (C-13), 151.0 (C-8), 134.8 (C-4), 133.0 (C-6), 132.5 (C-11), 132.0 (C-16), 131.5 (C-2), 128.6 (C-1), 126.8 (C-10), 123.7 (C-3), 122.2 (C-12), 122.0 (C-7), 121.1 (C-15), 120.9 (C-5), 114.5 (C-17), 89.5 (C≡), 88.9 (C≡), 68.4 (OCH₂), 31.8 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃).

1,3-Bis{4-[4-(5-octylpyrimidine-2-yl)benzoyloxy]phenylethynyl}benzene 28/8



Synthesized from 1,3-bis(4-hydroxyphenylethynyl)benzene (0.31 g, 1.0 mmol) and 4-(5-octylpyrimidine-2-yl)benzoic acid (0.62 g, 2.0 mmol).

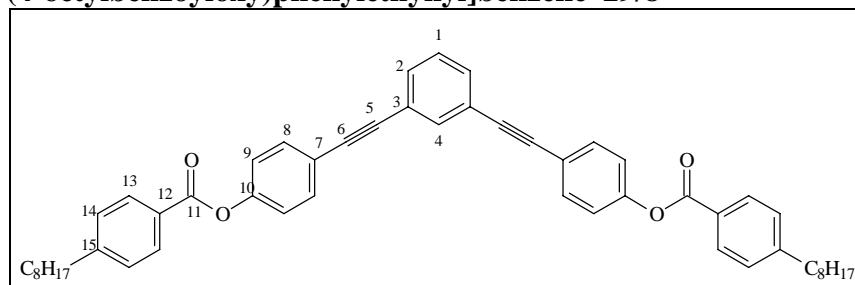
Yield 0.27 g (30.1%); transition temperatures (°C): Cr₁ 126 Cr₂ 204 Sm_{intercal} 236 Iso. (Found: C, 80.01; H, 6.60; N, 6.01%; C₆₀H₅₈N₄O₄ requires C, 80.15; H, 6.50; N, 6.23%).

¹H-NMR: δ_H (CDCl₃; 200MHz; *J*/Hz): 8.69 (s, 4H, H-17), 8.59 (d, *J* 8.4, 4H, H-14), 8.32 (d, *J* 8.4, 4H, H-13), 7.72 (s, 1H, H-4), 7.6 (d, *J* 8.6, 4H, H-8), 7.5 (d, *J* 7.4, 2H, H-2), 7.38-7.21 (m, 5H, H-1, 9), 2.65 (t, *J* 7.6, 4H, CH₂), 1.66-1.26 (m, 24H, CH₂), 0.87 (t, *J* 6.6, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 164.8 (2C=O), 161.7 (C-16), 157.3 (C-17), 151.1 (C-10), 142.7 (C-15), 134.7 (C-4), 134.1 (C-18), 133.0 (C-8), 131.5 (C-2), 130.8 (C-12), 130.5 (C-14), 128.6 (C-1), 128.1 (C-13), 123.7 (C-3), 122.0 (C-9), 120.9 (C-7), 89.3 (C≡), 88.7 (C≡), 31.7 (CH₂), 30.6 (CH₂), 30.2 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 eV): *m/z* (%) 898 (M⁺, 42), 295 (100).

1,3-Bis[4-(4-octylbenzoyloxy)phenylethynyl]benzene 29/8



Synthesized from 1,3-bis(4-hydroxyphenylethynyl)benzene (0.31 g, 1.0 mmol), 4-octylbenzoic acid (0.47 g, 2.0 mmol).

Yield 0.25 g (37.4%); mp 127. (Found: C, 84.52; H, 7.42%; C₅₂H₅₄O₄ requires C, 84.06; H, 7.33%).

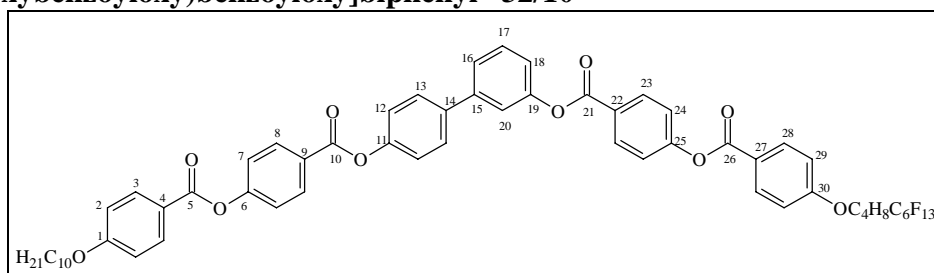
¹H-NMR: δ_{H} (CDCl₃; 400 MHz; *J*/Hz): 8.09 (2d, *J* 8.4, 4H, H-13), 7.71 (s, 1H, H-4), 7.57 (2d, *J* 8.8, 4H, H-8), 7.5-7.47 (m, 2H, H-2), 7.39-7.35 (m, 5H, H-1, 14), 7.22-7.18 (m, 4H, H-9), 2.68 (t, *J* 7.7, 4H, CH₂), 1.64 (t, *J* 7.0, 4H, CH₂), 1.3-1.26 (m, 20H, CH₂), 0.87 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 165.1 (2C=O), 151.2 (C-10), 149.7 (C-15), 134.7 (C-4), 133.0 (C-8), 131.4 (C-2), 130.4 (C-13), 128.8 (C-14), 128.6 (C-1), 126.8 (C-12), 123.7 (C-3), 122.0 (C-9), 120.7 (C-7), 89.3 (C \equiv), 88.6 (C \equiv), 36.0 (CH₂), 31.7 (CH₂), 31.0 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 22.5 (CH₂), 13.9 (CH₃).

MS (70 ev): *m/z* (%) 742 (M⁺, 2), 217 (100), 91 (14).

4 Synthesis of the compounds with two different calamitic units

3-[4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyloxy)benzoyloxy]benzoyloxy}-4'-[4-(4-decyloxybenzoyloxy)benzoyloxy]biphenyl 32/10



Synthesized from 4'-[4-(4-decyloxybenzoyloxy)benzoyloxy]-3-hydroxybiphenyl (0.43 g, 0.76 mmol) and 4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]-benzoic acid (0.51 g, 0.8 mmol).

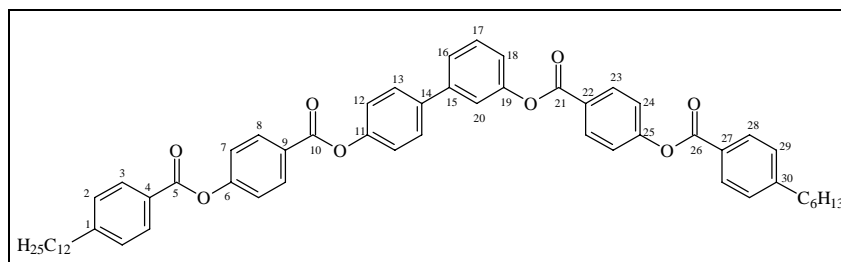
Yield 0.27 g (30.0%); transition temperatures (°C): Cr 135 SmCP_A 211 Iso. (Found: C, 60.87; H, 5.19% C₆₀H₅₃F₁₃O₁₀ requires C, 61.00; H, 4.53%).

¹H-NMR: δ_{H} (CDCl₃; 200 MHz; *J*/Hz): 8.31 (d, *J* 8.8, 2H, H-23), 8.29 (d, *J* 8.8, 2H, H-8), 8.17 (d, *J* 9.0, 2H, H-28), 8.15 (d, *J* 9.0, 2H, H-3), 7.65 (d, *J* 8.4, 2H, H-13), 7.51-7.27 (m, 10H, Ar-H), 6.97 (d, *J* 7.8, 4H, H-2, 29), 4.09 (t, *J* 5.5, 2H, OCH₂), 4.04 (t, *J* 5.5, 2H, OCH₂), 2.15-2.25 (m, 2H, CF₂CH₂), 2.05-1.80 (m, 6H, CH₂), 1.5-1.2 (m, 14H, CH₂), 0.87 (t, *J* 7.2, 3H, CH₃).

¹³C-NMR: δ_{C} (CDCl₃; 100 MHz): 164.6 (2C=O), 164.5, 164.4, 164.0, 163.6 (2C=O, C-1, 30), 155.6, 155.5, (C-6, 25), 151.5 (C-19), 150.8 (C-11), 142.2 (C-15), 138.1 (C-14), 132.6, 132.5 (C-8, 23), 131.9 (C-3, 28), 130.0 (C-17), 128.4 (C-13), 127.0, 126.9 (C-9, 22), 124.8 (C-16), 122.2 (C-7, 24), 122.2 (C-12), 121.5, 121.1 (C-4, 27), 120.7 (C-18), 120.5 (C-20), 114.5, 114.4 (C-2, 29), 68.4 (OCH₂), 67.5 (OCH₂), 31.8 (CH₂), 30.6 (t, CF₂CH₂), 29.4 (CH₂), 29.2 (CH₂), 29.2 (CH₂), 29.0 (CH₂), 28.4 (CH₂), 25.9 (CH₂), 22.5 (CH₂), 17.2 (CH₂), 13.9 (CH₃).

¹⁹F-NMR: δ_{F} (CDCl₃; 188 MHz): -82.4 (CF₃), -116.0 (CF₂), -123.5 (CF₂), -124.5 (CF₂), -125.1 (CF₂), -127.7 (CF₂).

4'-[4-(4-Dodecylbenzoyloxy)benzoyloxy]-3-[4-(4-hexylbenzoyloxy)benzoyloxy]biphenyl 35/12



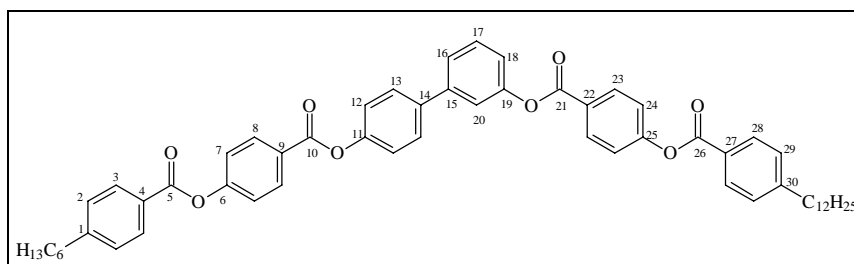
Synthesized from 4'-[4-(4-dodecylbenzoyloxy)benzoyloxy]-3-hydroxybiphenyl (0.57 g, 1.0 mmol) and 4-(4-hexylbenzoyloxy)benzoic acid (0.36 g, 1.1 mmol).

Yield 0.4 g (45.1%), transition temperatures (°C): Cr₁ 95 Cr₂ 104 Sm_b/ Col 113 Col 143 Iso. (Found C, 78.70; H, 6.88% C₅₈H₆₂O₈ requires C, 78.55; H, 7.00%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 4H, H-8, 23), 8.11 (d, *J* 8.0, 4H, H-3, 28), 7.66 (d, *J* 8.8, 2H, H-13), 7.50 (d, *J* 5.1, 2H, H-16, 18), 7.45 (s, 1H, H-20), 7.40-7.27 (m, 10H, Ar-H), 7.20 (m, 1H, H-17), 2.70 (t, *J* 7.6, 4H, CH₂), 1.65 (m, 4H, CH₂), 1.32-1.25 (m, 24H, CH₂), 0.87 (m, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.8, 165.6, 165.5 (4C=O), 156.5 (C-6, 25), 152.5 (C-19), 151.8 (C-11), 151.0 (C-1, 30), 143.2 (C-15), 139.2 (C-14), 133.0 (C-8, 23), 131.5 (C-3, 28), 131.0 (C-17), 129.9 (C-2, 29), 129.4 (C-13), 128.1 (C-9, 22), 127.6 (C-4, 27), 125.8 (C-16), 123.1 (C-7, 24, 2), 121.7 (C-18), 121.5 (C-20), 37.0 (CH₂), 32.8 (CH₂), 32.6 (CH₂), 32.0 (CH₂), 30.6 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.3 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 29.8 (CH₂), 23.5 (CH₂), 23.4 (CH₂), 15.0 (CH₃), 14.9 (CH₃).

3-[4-[4-Dodecylbenzoyloxy]benzoyloxy]-4'-[4-(4-hexylbenzoyloxy)benzoyloxy]biphenyl 36/6



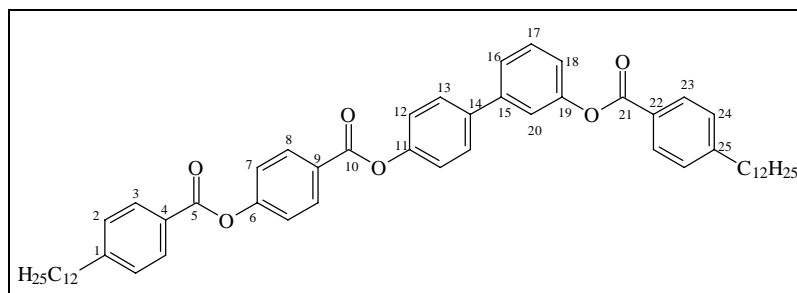
Synthesized from 4'-[4-(4-hexylbenzoyloxy)benzoyloxy]-3-hydroxybiphenyl (0.44 g, 0.9 mmol) and 4-(4-dodecylbenzoyloxy)benzoic acid (0.41 g, 1.0 mmol).

Yield 0.27 g (33.7%), transition temperatures (°C): Cr₁ 60 Cr₂ 98 Col 150 Iso. (Found C, 78.67; H, 7.07% C₅₈H₆₂O₈ requires C, 78.55; H, 7.00%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.30 (d, *J* 8.8, 4H, H-8, 23), 8.11 (d, *J* 8.4, 4H, H-3, 28), 7.66 (d, *J* 8.8, 2H, H-13), 7.50 (d, *J* 5.1, 2H, H-16, 18), 7.45 (s, 1H, H-20), 7.40-7.27 (m, 10H, Ar-H), 7.20 (m, 1H, H-17), 2.70 (t, *J* 7.5, 4H, CH₂), 1.65 (m, 4H, CH₂), 1.32-1.25 (m, 24H, CH₂), 0.87 (m, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 165.8, 165.6, 165.6 (4C=O), 156.5 (C-6, 25), 152.5 (C-19), 151.8 (C-11), 151.0 (C-1, 30), 143.2 (C-15), 139.2 (C-14), 133.0 (C-8, 23), 131.5 (C-3, 28), 131.0 (C-17), 129.9 (C-2, 29), 129.4 (C-13), 128.1 (C-9, 22), 127.6 (C-4, 27), 125.8 (C-16), 123.2 (C-7, 24, 12), 121.7 (C-18), 121.5 (C-20), 37.0 (CH₂), 32.8 (CH₂), 32.6 (CH₂), 32.0 (CH₂), 30.6 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.3 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 29.8 (CH₂), 23.5 (CH₂), 23.4 (CH₂), 15.0 (CH₃), 14.9 (CH₃).

3-(4-Dodecylbenzoyloxy)-4'-[4-(4-dodecylbenzoyloxy)benzoyloxy]biphenyl 38/12



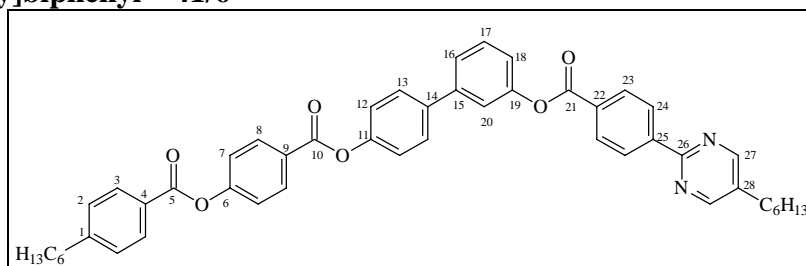
Synthesized from 3-hydroxy-4'-[4-(4-dodecylbenzoyloxy)benzoyloxy]biphenyl (0.37 g, 0.64 mmol) and 4-dodecylbenzoic acid (0.20 g, 0.7 mmol).

Yield 0.08 g (14.7%); transition temperatures (°C): Cr (78 N) 88 Iso. (Found: C, 80.73; H, 8.31% C₅₇H₇₀O₆ requires C, 80.47; H, 8.23%).

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 8.29 (d, *J* 8.8, 2H, H-8), 8.12 (m, 4H, H-3, 23), 7.64 (d, *J* 8.8, 2H, H-13), 7.48 (d, *J* 5.3, 2H, H-16, 18), 7.42 (s, 1H, H-20), 7.36 (d, *J* 8.8, 2H, H-12), 7.33-7.28 (m, 6H, Ar-H), 7.20 (m, 1H, H-17), 2.69 (t, *J* 7.5, 4H, CH₂), 1.65 (m, 4H, CH₂), 1.31-1.20 (m, 36H, CH₂), 0.86 (t, *J* 6.8, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.4, 165.8, 165.6 (3C=O), 156.5 (C-6), 152.7 (C-19), 151.8 (C-11), 151.0, 150.6 (C-1, 25), 143.1 (C-15), 139.2 (C-14), 133.0 (C-8), 131.5, 131.4 (C-3, 23), 130.9 (C-17), 129.9 (C-2, 24), 129.4 (C-13), 128.1 (C-4, 22), 127.6 (C-9), 125.6 (C-16), 123.2 (C-7, 12), 121.8 (C-18), 121.6 (C-20), 37.0 (CH₂), 32.8 (CH₂), 32.0 (CH₂), 30.6 (CH₂), 30.5 (CH₂), 30.4 (CH₂), 30.3 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 23.5 (CH₂), 15.0 (CH₃).

4'-[4-(4-Hexylbenzoyloxy)benzoyloxy]-3-[4-(5-hexylpyrimidine-2-yl)benzoyloxy]biphenyl 41/6



Synthesized from 4'-[4-(4-hexylbenzoyloxy)benzoyloxy]-3-hydroxybiphenyl (0.44 g, 0.9 mmol) and 4-(5-hexylpyrimidine-2-yl)benzoic acid (0.28 g, 1.0 mmol).

Yield 0.18 g (26.5%), transition temperatures (°C): Cr 135 Sm_{intercal} 142 Iso. (Found C, 77.47; H, 6.43; N, 3.66% C₄₉H₄₈N₂O₆ requires C, 77.37; H, 6.32; N, 3.68%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 8.70 (s, 2H, H-27), 8.60 (d, *J* 8.4, 2H, H-24), 8.37-8.29 (m, 4H, H-8, 23), 8.14 (d, *J* 8.4, 2H, H-3), 7.69 (d, *J* 8.6, 2H, H-13), 7.50 (d, *J* 5.1, 2H, H-16, 18), 7.45 (s, 1H, H-20), 7.37-7.30 (m, 7H, Ar-H), 2.67 (m, 4H, CH₂), 1.70 (m, 4H, CH₂), 1.53-1.31 (m, 12H, CH₂), 0.90 (t, 6H, CH₃).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.2, 165.8, 165.6 (4C=O), 162.7 (C-26), 158.3 (C-27), 156.5 (C-6), 152.6 (C-19), 151.8 (C-11), 151.0 (C-1), 143.6 (C-25), 143.2 (C-15), 139.2 (C-14), 135.0 (C-28), 133.0 (C-8), 132.0 (C-22), 131.5 (C-3, 24), 131.0 (C-17), 129.9 (C-2), 129.4 (C-13), 129.1 (C-23), 128.1 (C-9), 127.6 (C-4), 125.8 (C-16), 123.2 (C-7, 12), 121.7 (C-18), 121.5 (C-20), 37.0 (CH₂), 32.5 (CH₂), 32.4 (CH₂), 32.0 (CH₂), 31.6 (CH₂), 31.2 (CH₂), 29.8 (CH₂), 29.6 (CH₂), 23.5 (CH₂), 14.9 (CH₃).

VII References

1. P. J. Collings, *Liquid Crystals*, Adam Hilger, Bristol, **1990**.
2. A. M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem.*, **1991**, 103, 370; F. D. Saeva, *Liquid Crystals-the Fourth State of Matter*, Marcell Dekker Inc., New York Basel, **1979**.
3. S. Chandrasekhar, *Liq. Cryst.*, **1993**, 14, 3.
4. R. B. Meyer, *Mol. Cryst. Liq. Cryst.* **1976**, 40, 74; J. W. Goodby, *J. Mater. Chem.* **1991**, 1, 307.
5. M. Eich, *Ber. Bunsenges. Phys. Chem.*, **1993**, 97, 1261.
6. B. Bahadur, *Liquid Crystals, Applications and uses*, Vol. 1, World Scientific, **1990**.
7. A. S. Sonin, B. A. Strukom, *Einführung in die Ferroelektrizität*, Akademie-Verlag, Berlin, **1974**.
8. R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. Phys.*, **1975**, 36, L-69.
9. J. W. Goodby, I. Nishiyama, A. J. Slaney, C. J. Booth, K. J. Toyne, *Liq. Cryst.*, **1993**, 14, 37.
10. L. A. Beresnev, L. M. Blinov, V. A. Baikalov, E. P. Pozhidayev, G. V. Purvanetskas, A. I. Pavlyuchenko, *Mol. Cryst. Liq. Cryst.* **1982**, 89, 327.
11. A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe, *J. Mater. Chem.* **1994**, 4, 997.
12. J. S. Patel, J. W. Goodby, *Optical Engineering* 26 (5), **1987**.
13. R. H. Tredgold, *J. Phys. D: Appl. Phys.* **1990**, 23, 119; H. R. Brand, P. E. Cladis, H. Pleiner, *Macromolecules*, **1992**, 25, 7223.
14. A. G. Vanakaras, D. J. Photinos, *Physical Review E*, **1998**, 57(5), 4875.
15. F. Tournihac, L. M. Blinov, J. Simon, S. V. Yablonsky, *Nature*, **1992**, 359, 621.
16. L. Lei, *Mol. Cryst. Liq. Cryst.* , **1983**, 91, 77; T. M. Swager, A. G. Serrette, D. B. Knawby, H. Zeng, *15th International Liquid Crystal Conference, Budapest, abstract*, **1994**, 2, 771.
17. E. Schröter, *Thesis, Halle(Saale)*. **1925**. *D. Vorländer, Ber, Dtsch. Chem. Ges.*, **1929**, 65, 2831.
18. D. Vorländer, A. Apel, *Ber*, **1932**, 65, 1101.

19. T. Akutagawa, Y. Matsunaga, K. Yasuhara, *Liquid Crystals*, **1994**, 17(5), 659.
20. T. Niori, F. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.
21. T. Sekine, Y. Takanishi, T. Niori, J. Watanabe, H. Takezoe, *Jpn. J. Appl. Phys.* **1997**, 36, L1201. J; Watanabe, T. Niori, T. Sekine, H. Takezoe, *Jpn. J. Appl. Phys.* **1998**, 37, L139.
22. T. Sekine, T. Niori, M. Sone, J. Watanabe, S. Choi, Y. Takanishi, H. Takezoe. *Jpn. J. Appl. Phys.* **1997**, 36, 6455.
23. G. Heppke, D. Krüerke, C. Löhning, D. Löttsch, S. Rauch, N. K. Sharma, *Freiburger Arbeitstagung Flüssige Kristalle 1997*, Freiburg, P70.
24. The nomenclature of the mesophases of the banana-shaped molecules as B1, B2, etc. was recommended at the Workshop“Banana-shaped Liquid Crystals: Chirality by Achiral Molecules“, Dec. 1997, Berlin.
25. W. Weissflog, C. Lischka, I. Benne, T. Scharf, G. Pelzl, S. Diele, H. Kruth, *Friburge Arbeitstagung*, **1997**, P84.
26. G. Heppke, D. Moro, *Science*, **1998**, 279, 1872.
27. G. Pelzl, S. Diele, W. Weissflog, *Advanced Materials*, **1999**, 11, 707.
28. D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Körblova and D. M. Walba, *Science*, **1997**, 278, 1924.
29. W. Weissflog, C. Lischka, I. Benne, T. Scharf, G. Pelzl, S. Diele, H. Kruth, *Proc. SPIE: Int. Soc. Opt. Eng.* **1998**, 3319, 14.
30. S. Diele, S. Grande, H. Kruth, C. Lischka, G. Pelzl, W. Weissflog, I. Wirth, *Ferroelectrics*, **1998**, 212, 169.
31. G. Pelzl, S. Diele, A. Jakli, C. Lischka, I. Wirth, W. Weissflog, *Liq. Cryst.* **1999**, 26, 135.
32. C. K. Lee, L. C. Chien, *Liquid Crystals*, **1999**, 26, 609.
33. G. Heppke, D. D. Parghi, H. Sawade, *ECLC 99*, 25-30. April, **1999**, Crete, Greece, P3-038
34. K. K. Semmler, T. Dingemans, E. Samulski, *Liquid Crystals*, **1998**, 24(6), 799.
35. S. W. Choi, M. Zennyoji, Y. Takanishi, H. Takezoe, T. Niori, J. Watanabe, *Jpn. J. Appl. Phy.* **1998**, 37, L401.
36. F. Kentischer, R. Macdonald, G. Heppke, *Liq. Cryst.* **1998**, 25, 341; F. Araoka, B.

- Park, Y. Kinoshita, K. Ishikawa, H. Takezoe, J. Thisayukta, J. Watanabe, *Jpn. J. Appl. Phys.* **1999**, 38, 3526.
37. N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.*, 1981, 11, 513.; M. Hird, G. W. Gray, K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **1991**, 206, 187.
 38. J. F. W. McOmie, D. E. West, *Org. Synth.*, **1973**, Coll. Vol. V, 412.
 39. According to the IUPAC rules 3,4'-biphenol (respective 1,1'-biphenol-4,4'-diol) and 1,1': 3',1''-terphenyl-4,4''-diol are recommended for **2** and **12**, respectively, however for uniformity with the nomenclature of the other compounds (**13**, **20** and **22** etc.), this nomenclature is used throughout.
 40. L. DiNunno, S. Florio, P. E. Todesco, *J. Chem. Soc. C*, **1970**, 1433; R. Kuhn, W. Klaveren, *Ber.*, **1938**, 71, 779.
 41. W. A. Austin, N. Bilow, W. J. Kelleghana, K. S. Y. Lan, *J. Org. Chem.*, **1981**, 46, 2280; L. Brandsma, S. F. Vasilevsky, H. D. Verkruijsse, *Application of Transition Metal Catalysts in Organic Synthesis*, Springer-Verlag, Berlin, Heidelberg, **1998**, 179; M. Hird, K. J. Toyne, G. W. Gray, *Liq. Cryst.* , **1993**, 14, 741.
 42. E. J. Corey, A. Venkateswarln, *J. Am. Chem. Soc.*, **1972**, 94, 6190.
 43. S. M. Kelly, A. Villiger, *Liq. Cryst.*, **1983**, 3, 1173.
 44. C. Tschierske, H. Zschke, *J. Prakt. Chem.*, **1988**, 330, 1.
 45. V. Perces, G. Johansson, G. Ungar, J. Zhou, *J. Am. Chem. Soc.* **1996**, 118, 9855.
 46. A. Bouchta, H. T. Nguyen, M. F. Achard, F. Hardouin, C. Destrade, R. J. Twieg, A. Maaroufi. N. Isaert, *Liq. Cryst.* , **1992**, 12, 575.
 47. E. Kleinpeter, H. Köhler, A. Lunow, C. Tschierske, H. Zschke. *Tetrahedron*, **1988**, 44, 1609.
 48. The aromatic half parts consist of the rigid calamitic cores (B) and the rigid parts of the bent central unit (A) which are connected to the central 1,3-phenylene unit.
 49. B. E. Smart, *Organofluorine Chemistry-Principles and Commercial Applications*; R. E. Banks, B. E. Smart, J. C. Tatlow, Eds., Plenum Press, New York, 1994, 57; C. Viney, R. J. Twig, T. P. Russell, L. E. Depero, *Liq. Cryst.* **1989**, 5, 1783; T. Doi, Y. Sakurai, A. Tamatani, S. Tanenaka, S. Kusabashi, Y. Nishihata, H. Terauchi, *J. Mater. Chem.* **1991**, 1, 169; S. V. Arehart, C. Pugh, *J. Am. Chem. Soc.*, **1997**, 119, 3027; A. Pegenau, X. H. Cheng, C. Tschierske, P. Göring, S. Diele, *New J. Chem.* **1999**, 23, 465; X. H. Cheng, S. Diele, C. Tschierske, *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 592;

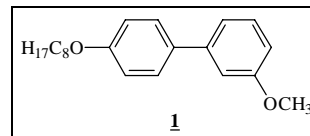
- V. Percec, D. Schlueter, Y. K. Kwon, J. Blackwell, M. Möller, P. J. Slangen, *Macromolecules* **1995**, 28, 8807; H. T. Nguyen, G. Sigaud, M. F. Achard, F. Hardouin, R. J. Twieg, K. Betterton, *Liq. Cryst.* **1991**, 10, 389.
50. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford: Clarendon Press), **1974**, 279.
51. H. R. Brand, P. E. Cladis, H. Pleiner, *Eur. J. Phys. (B)*, **1998**, 6, 347.
52. B. S. Furniss, A. J. Hannaford, P. W. G. Smoth, A. R. Tatchel, **1989**, *Vogel's Textbook of Practical Organic Chemistry, 5th Edn.*; Longman Scientific & Technical Essex **1989**; *Organikum*, VEB Deutscher Verlag der Wissenschaften Berlin, 18. Aufl., **1990**.

Supplement

Synthesis of the intermediates

1 Synthesis of the divalent phenols

3-Methoxy-4'-octyloxybiphenyl **1**

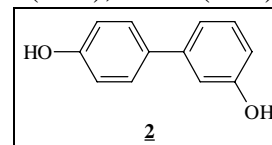


4-Octyloxyphenylboronic acid (2.25 g, 9.0 mmol) was added to a solution of 3-bromoanisole (1.40g, 7.5 mmol) in a mixture of benzene (19 ml) and aqueous sodium carbonate (2M, 19 ml) at room temperature under an argon atmosphere. Pd(PPh₃)₄ (0.2 g, 0.2 mmol, 5mol%) was then added to the mixture. The mixture was heated under reflux with stirring for 4 hours. Afterwards the solution was extracted with CH₂Cl₂ (2×150 ml) and dried with Na₂SO₄. The solvent was removed and the product was purified by column chromatography (CHCl₃), and then recrystallized from n-hexane.

Yield 1.9 g (81.2%); mp 27 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 7.52 (d, *J* 8.8, 2H, Ar-H), 7.38-7.31 (m, 1H, Ar-H), 7.18-7.10 (m, 2H, Ar-H), 6.97 (d, *J* 8.8, 2H, Ar-H), 6.90-6.84 (m, 1H, Ar-H), 4.01 (t, *J* 6.5, 2H, OCH₂), 3.88 (s, 3H, OCH₃), 1.83 (m, 2H, CH₂), 1.57-1.32 (m, 10H, CH₂), 0.91 (t, *J* 6.5, 3H, CH₃).

¹³C-NMR: δ_c (CDCl₃; 100Hz): 160.1 (Cq), 159.0 (Cq), 142.6 (Cq), 133.5 (Cq), 129.8 (Cq), 128.2 (Cq), 119.4 (Cq), 114.9 (2C-H), 119.4 (C-H), 114.9 (2C-H), 112.6 (C-H), 112.1 (C-H), 68.1 (OCH₂), 55.2 (OCH₃), 31.7 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 26.0 (CH₂), 22.5 (CH₂), 14.0 (CH₃).



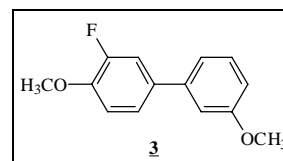
3,4'-Dihydroxybiphenyl **2**

3-Methoxy-4'-octyloxybiphenyl (1.9 g, 6.0 mmol) was dissolved in dry benzene (400 ml) and then BBr₃ (5 ml) was carefully added at room temperature with stirring to the solution, the solution was refluxed for 2 h and then cooled to room temperature. Water (163 ml) was slowly added and the white crystals were collected. The product was recrystallized from MeOH.

Yield 0.7 g (62.7%); mp 182 °C.

¹H-NMR: δ_H (DMSO-D₆; 400 MHz; J/Hz): 9.47 (s, 1H, OH), 9.37 (s, 1H, OH), 7.38 (d, *J* 8.6, 2H, Ar-H), 7.17 (t, 1H, Ar-H), 6.96-6.90 (m, 2H, Ar-H), 6.80 (d, *J* 8.6, 2H, Ar-H), 6.67-6.64 (m, 1H, Ar-H).

¹³C-NMR: δ_c (DMSO-D₆; 100 MHz): 157.9 (Cq), 157.2 (Cq), 141.8 (Cq), 131.2 (Cq), 129.8 (C-H), 127.7 (2C-H), 116.9 (C-H), 115.7 (2C-H), 113.3 (C-H), 112.9 (C-H).



3-Fluoro-4,3'-dimethoxybiphenyl **3**

Synthesized as described for the preparation of the compound **1**. Quantities: 3-methoxyphenylboronic acid (4.5 g, 30.0 mmol), 4-bromo-2-fluoroanisole (5.1 g, 24.9 mmol).

Yield 3.88 g (67.2%); oil.

¹H-NMR: δ_{H} (CDCl₃; 200 MHz; *J*/Hz): 7.36-7.26 (m, 3H, Ar-H), 7.13-7.00 (m, 3H, Ar-H), 6.96-6.83 (m, 1H, Ar-H), 3.91 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃).

3-Fluoro-4,3'-dihydroxybiphenyl 4

Synthesized as described for the preparation of compound 2. Quantities: 3-fluoro-4,3'-dimethoxybiphenyl (3.77 g, 16.25 mmol), benzene (350 ml), BBr₃ (10 ml).

Yield 2.72 g (82.0%); mp 108 °C.

¹H-NMR: δ_{H} (DMSO-D₆; 200 MHz; *J*/Hz): 9.92 (s, 1H, OH), 9.44 (s, 1H, OH), 7.39-7.15 (m, 3H, Ar-H), 7.04-6.93 (m, 3H, Ar-H), 6.73-6.67 (m, 1H, Ar-H).

¹⁹F-NMR: δ_{F} (DMSO-D₆; 188 MHz): -132.9.

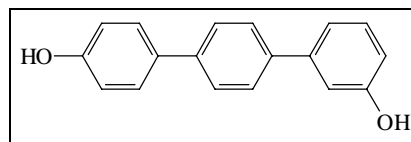
2-Fluoro-3,4'-dihydroxybiphenyl 5

Synthesized as described for the preparation of compound 2. Quantities: 2-fluoro-3-methoxyphenylboronic acid (2.5 g, 14.7 mmol), 4-Bromoanisole (2.78g, 20.0 mmol).

Yield 1.6 g (53.3%); mp 123 °C.

¹H-NMR: δ_{H} (DMSO-D₆; 200 MHz; *J*/Hz): 9.76 (s, 1H, OH), 9.57 (s, 1H, OH), 7.34-7.30 (m, 2H, Ar-H), 7.03-6.75 (m, 5H, Ar-H).

¹⁹F-NMR: δ_{F} (DMSO-D₆; 188 MHz): -139.8.

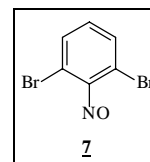


3,4''-Dihydroxy-1,1':4',1''-terphenyl 6

Synthesized as described for the preparation of compound 2. Quantities: 3-methoxy-4''-butoxy-1,1':4',1''-terphenyl (4.05 g, 12.2 mmol), benzene (300 ml), BBr₃ (7.6 ml).

Yield 2.35 g (74.0%); mp > 260 °C.

¹H-NMR: δ_{H} (DMSO-D₆; 200 MHz; *J*/Hz): 9.54 (s, 1H, OH), 9.50 (s, 1H, OH), 7.63 (s, 4H, Ar-H), 7.53 (d, *J* 8.6, 2H, Ar-H), 7.25 (t, *J* 7.7, 1H, Ar-H), 7.11-7.04 (m, 2H, Ar-H), 6.88-6.74 (m, 3H, Ar-H).



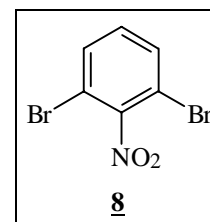
2,6-Dibromonitrosobenzene 7

2,6-Dibromoaniline (1.26 g, 5.0 mmol) and 3-chloroperoxybenzoic acid (3.85 g, 22.3 mmol) were dissolved in CH₂Cl₂ (35 ml). The solution was heated under reflux for 2 hours, then cooled to room temperature. The precipitate (3-chlorobenzoic acid) was filtered off and the liquid phase was washed with NaOH (1 M, 3×55 ml) and dried with MgSO₄. The solvent was removed, and the 2,6-dibromonitrosobenzene was obtained by recrystallization from n-hexane.

Yield 1.10 g (83.0%); mp 132-133 °C (lit., 134-135 °C, L. Dinunno, S. Florio and P.E. Todesco, *J. Chem. Soc. C*, 1970, 1433.).

IR (KBr): 1548, 1423, 1274, 804.

MS (70 ev): *m/z* (%) 265 (M⁺, 100), 235 (85), 154 (25).



2,6-Dibromonitrobenzene 8

2,6-Dibromonitrosobenzene 7 (1.23 g, 4.64 mmol) was dissolved in glacial acetic acid (25 ml), a solution of H₂O₂ (a mixture of 12.5 ml of a 33% solution in water and 12.5 ml glacial acetic acid) was added at room temperature. Then concentrated HNO₃ (0.83 ml) was added. The mixture was heated in a water bath to 90 °C, till the color of the solution has turned to orange (1h). Water

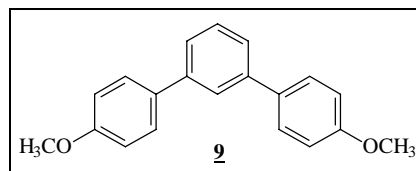
(52 ml) was added, and the formed solid was separated. The product obtained was recrystallized from n-hexane.

Yield 1.13 g (86.9%); mp 78-79 °C (lit., 82 °C, R. Kuhn and W. van Klaveren, *Ber.*, 1938, 71, 779.).

IR (KBr): 1548, 1523, 1400, 780.

MS (70 ev): m/z (%) 280 (M-1⁺, 45), 251(37), 234(28), 223 (37), 156 (30), 75 (100).

4,4''-Dimethoxy-1,1':3'1''-terphenyl 9



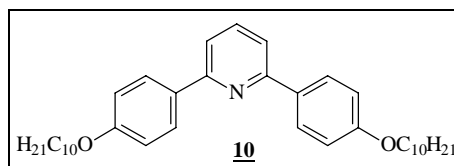
4-Methoxyphenylboronic acid (0.8 g, 5.3 mmol)

was added to a solution of 1,3-dibromobenzene (0.52 g, 2.2 mmol) in a mixture of benzene (12 ml) and aqueous sodium carbonate (2M, 12 ml) at room temperature under an argon atmosphere, Pd(PPh₃)₄ (0.1 g, 0.1 mmol, 5mol%) was then added to the mixture. The mixture was heated under reflux with stirring for 4 hours. Afterwards the solution was extracted with CH₂Cl₂ (2×150 ml) and dried with Na₂SO₄. The solvent was removed and the product was purified by column chromatography (CHCl₃), and then recrystallized from n-hexane.

Yield 0.55 g (86.2%); mp 198-200 °C (lit., 197-198 °C, C. C. Price and G. P. Mueller, *J. Am. Chem. Soc.*, 1944, 66, 628.).

¹H-NMR: δ_H (CDCl₃; 400 MHz; J/Hz): 7.72 (d, J 1.45, 1H, Ar-H), 7.58 (d, J 8.9, 4H, Ar-H), 7.51-7.44 (m, 3H, Ar-H), 7.0 (d, J 8.9, 4H, Ar-H), 3.86 (s, 6H, OCH₃).

2,6-Bis(4-decyloxyphenyl)pyridine 10



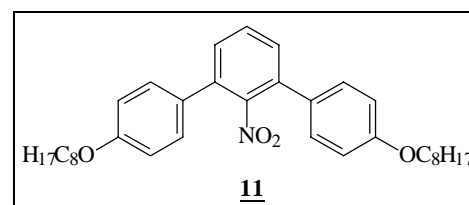
Synthesized as described for the

preparation of compound 9. Quantities: 4-decyloxyphenylboronic acid (1.46 g, 5.3 mmol), 2,6-dibromopyridine (0.52 g, 2.2 mmol), Pd(PPh₃)₄ (0.11 g, 0.11 mmol, 5mol%), benzene (11 ml), Na₂CO₃ (2M, 11 ml).

Yield 0.9 g (75.6%); mp 132-133 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.08 (d, J 9.0, 4H, Ar-H), 7.78 (t, 1H, Ar-H), 7.58 (d, J 8.0, 2H, Ar-H), 7.02 (d, J 9.0, 4H, Ar-H), 4.03 (t, J 6.5, 4H, OCH₂), 1.85-1.75 (m, 4H, OCH₂-CH₂), 1.52-1.44 (m, 28H, CH₂), 0.89 (t, J 6.5, 6H, CH₃).

2'-Nitro-4,4''-dioctyloxy-1,1':3'1''-terphenyl 11

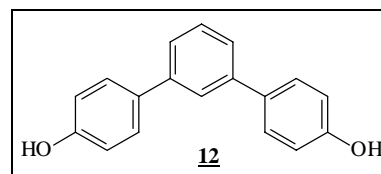


Synthesized as described for the preparation of compound 9. Quantities: 2,6-dibromonitrobenzene 8 (1.06 g, 3.77 mmol), 4-octyloxyphenylboronic acid (2.26 g, 9.05 mmol), benzene (19 ml), Na₂CO₃ (2M, 19 ml), Pd(PPh₃)₄ (0.2 g, 0.2 mmol, 5mol%), purified by column chromatography (CHCl₃).

Yield 1.48 g (74.0%); light yellow oil.

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 7.65-7.25 (m, 6H, Ar-H), 7.00-6.90 (m, 5H, Ar-H), 3.96 (t, 4H, OCH₂), 1.8-1.3 (m, 24H, CH₂), 0.9 (t, J 6.3, 6H, CH₃).

4,4''-Dihydroxy-1,1':3',1''-terphenyl 12



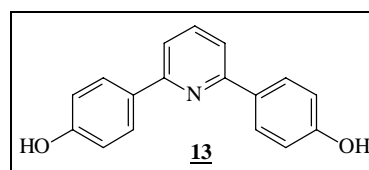
4,4''-Dimethoxy-1,1':3',1''-terphenyl 9 (0.55 g, 1.9 mmol) was dissolved in dry benzene (158 ml) and then BBr_3

(1 ml) was carefully added at room temperature with stirring to the solution, the solution was refluxed for 2 h and then cooled to room temperature. Water (50 ml) was slowly added and the white crystals were collected. The product was recrystallized from MeOH.

Yield 0.35 g (70.0%); mp 182-183 °C (lit., 182-183 °C, C. C. Price and G. P. Mueller, *J. Am. Chem. Soc.*, 1944, 66, 628.).

$^1\text{H-NMR}$: δ_{H} (DMSO- D_6 ; 200 MHz; J/Hz): 9.53 (s, 2H, OH), 7.70 (s, 1H, Ar-H), 7.57-7.43 (m, 7H, Ar-H), 6.85 (d, J 8.6, 4H, Ar-H).

2,6-Bis(4-hydroxyphenyl)pyridine 13



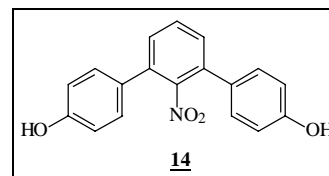
Synthesized as described for the preparation of

compound 12. Quantities: 2,6-bis(4-decyloxyphenyl)pyridine 10 (0.5 g, 0.92 mmol), benzene (70 ml), BBr_3 (0.5 ml).

Yield 0.18 g (75.0%); mp 265 °C.

$^1\text{H-NMR}$: δ_{H} (DMSO- D_6 ; 200MHz; J/Hz): 8.00 (d, J 8.8, 4H, Ar-H), 7.76 (d, 2H, J 7.6, Ar-H), 7.20 (t, 1H, J 7.6, Ar-H), 6.9 (d, J 8.8, 4H, Ar-H).

4,4''-Dihydroxy-2'-nitro-1,1':3',1''-terphenyl 14



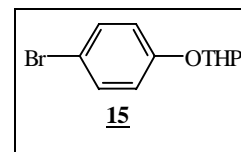
Synthesized as described for the preparation of

compound 12. Quantities: 2'-Nitro-4,4''-dioctyloxy-1,1':3',1''-terphenyl 11 (2.38 g, 4.48 mmol), benzene (237 ml), BBr_3 (2 ml).

Yield 1.10 g (80.0%); mp >265 °C.

$^1\text{H-NMR}$: δ_{H} (DMSO- D_6 ; 400 MHz; J/Hz): 9.72 (s, 2H, OH), 7.62 (t, J 7.6, 1H, Ar-H), 7.42 (d, J 7.6, 2H, Ar-H), 7.14 (d, J 8.8, 4H, Ar-H), 6.81 (d, J 8.8, 4H, Ar-H).

4-Tetrahydropyranyloxybromobenzene 15



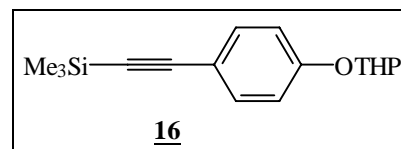
To a stirred solution of 4-bromophenol (10.0 g, 57.8 mmol)

in CH_2Cl_2 (35 ml), cooled with an ice bath, dihydropyrane (6.03 g, 0.07 mol) was added dropwise over 10 min at 0-5 °C. After the solution became clear, p-toluenesulphonic acid (10 mg) were added. The solution was stirred at 20°C for 15 min.. Then it was quenched by addition of NaHCO_3 (0.7 g) and 3 drops of water, after stirring for 5 min. at 20°C, the solvent was removed in vacuo and the product obtained was purified by column chromatography (CHCl_3).

Yield 14.0 g (94.2%); mp 54-55 °C (lit., 55-56 °C, W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.*, 1948, 70, 4187.).

$^1\text{H-NMR}$: δ_{H} (CDCl_3 ; 200 MHz; J/Hz): 7.35 (d, J 9.0, 2H, Ar-H), 6.92 (d, J 9.0, 2H, Ar-H), 5.35 (t, J 3.0, 1H, O-CH-O), 3.85 (m, 1H, THP), 3.61 (m, 1H, THP), 2.1-1.5 (m, 6H, THP).

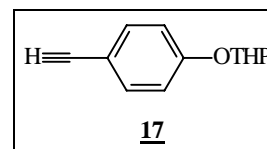
4-Tetrahydropyranyloxy(trimethylsilylethynyl)-benzene 16



A stirred mixture of 4-tetrahydropyranyloxybromobenzene 15 (5.65 g, 22.0 mmol), trimethylsilylacetylene (2.24 g, 22.9 mmol), copper(I)-iodide (0.22 g, 1.15 mmol), and tetrakis(triphenylphosphine)-palladium(0) (1.26 g, 1.26 mmol) in dry triethylamine (70 ml) was heated under reflux under an argon atmosphere for 19 h. Afterwards ether (100 ml) and water (100 ml) were added to the cooled reaction mixture and the aqueous layer was washed with ether (2×100 ml). The combined ethereal extracts were washed with brine and dried with MgSO₄. The solvent was removed in vacuo and the residue was purified by column chromatography (n-hexane: acetate = 9:1) to give a yellow-brown oil.

Yield 4.47 g (74.2%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 7.37 (d, J 9.0, 2H, Ar-H), 6.95 (d, J 9.0, 2H, Ar-H), 5.35 (t, 1H, O-CH-O), 3.85 (m, 1H, THP), 3.61 (m, 1H, THP), 2.0-1.5 (m, 6H, THP), 0.22 (s, 9H, CH₃).

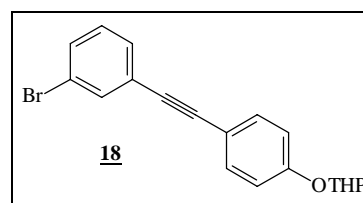


4-Tetrahydropyranyloxyphenylacetylene 17

An aqueous solution of potassium hydroxide (1.0M, 21.0 ml) was added dropwise to a stirred solution of 4-tetrahydropyranyloxy(trimethylsilylethynyl)benzene 16 (4.47 g, 16.3 mmol) in MeOH (175 ml) at room temperature. The solution was stirred at this temperature for 1.5 h. Water (100 ml) was added, the aqueous phase was separated and washed with ether (2×150 ml), the combined ethereal extracts were washed with brine (100 ml) and dried with MgSO₄, the solvent was removed in vacuo to yield a yellow solid.

Yield 2.9 g (88.0%); mp 64-65.0 °C (lit., 65.5 °C, A. Bouchta, H. T. Nguyen, M. F. Achard, F. Hardouin, C. Destrade, R. J. Twieg, A. Maaroufi and N. Isaert, *Liq. Cryst.*, 1992, 12, 575.).

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 7.42 (d, J 9.0, 2H, Ar-H), 6.98 (d, J 9.0, 2H, Ar-H), 5.43 (t, 1H, O-CH-O), 3.88 (m, 1H, THP), 3.64 (m, 1H, THP), 2.99 (s, 1H, C=CH), 1.9-1.5 (m, 6H, THP).



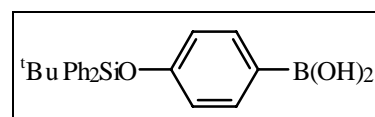
3-(4-Tetrahydropyranyloxyphenylethynyl)bromobenzene 18

Synthesized as described for the preparation of compound 16. Quantities: 1-bromo-3-iodobenzene (3.54 g, 12.5 mmol) and 4-tetrahydropyranyloxyphenylacetylene 17 (2.53 g, 12.5 mmol), CuI (0.19 g, 1.0 mmol), Pd(PPh₃)₄ (0.54 g, 0.54 mmol), triethylamine (58 ml), 10 h.

Yield 3.4 g (76.3%); mp 42-43 °C.

¹H-NMR: δ_H (CDCl₃; 500 MHz; J/Hz): 7.64 (s, 1H, Ar-H), 7.44-7.38 (m, 4H, Ar-H), 7.18 (t, J 7.9, 1H, Ar-H), 7.01 (d, J 8.8, 2H, Ar-H), 5.43 (t, J 3.1 1H, O-CH-O), 3.87 (m, 1H THP), 3.61 (m, 1H, THP), 2.0-1.5 (m, 6H, THP).

4-(tert-Butyldiphenylsilyloxy)phenylboronic acid



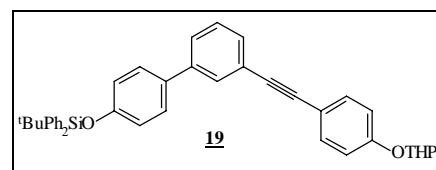
4-Bromophenol (8.65 g, 50 mmol) was dissolved in dry DMF (70 ml). Under an argon atmosphere imidazol (13.6 g, 200 mmol) was then added with stirring. The mixture was cooled with an ice bath while tert-butyldiphenylsilylchloride (16.5 g, 60 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for additional 12 h. Then H₂O (20 ml) and diethyl ether (125 ml) were added and the organic phase was separated. The aqueous phase was extracted 3 times with diethyl ether (3×100 ml), the combined organic phases were washed with H₂O (3 ×40 ml), brine (40 ml) and dried with Na₂SO₄. Then the solvent was removed and the 4-(tert-butyldiphenylsilyloxy)bromobenzene was purified by column chromatography (petroleum ether 80-110 °C : ethyl acetate = 9:1). Yield 20.87 g, mp 46-48 °C.

A solution of 4-(tert-butyldiphenylsilyloxy)bromobenzene (10.52 g, 25.6 mmol) in dry THF (200 ml) was cooled with violent stirring to -78 °C. BuLi (22 ml of a 1.6 mol dm⁻³ solution in hexane, 35.2 mmol) was added dropwise. The suspension was stirred at -78 °C for additional 3 h and then trimethylborate (5.4 g, 51.9 mmol) was added *via* a syringe. The temperature was kept below -70 °C during the addition. The reaction mixture was stirred overnight and was allowed to warm up to room temperature during this time. After the addition of hydrochloric acid (120 ml, 3 mol dm⁻³), the mixture was stirred for an additional hour at 20 °C. Afterwards it was extracted with diethyl ether (2×200 ml). The combined organic phases were washed with water (100 ml) and dried with Na₂SO₄. After evaporation of the solvent the residue was recrystallized from petroleum ether.

Yield 8.9 g (92.7%); mp 164-170 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 7.86 (d, *J* 8.4, 2H, Ar-H), 7.71 (m, 4H, Ar-H), 7.49-7.34 (m, 6H, Ar-H), 6.81-6.75 (m, 2H, Ar-H), 1.1 (s, 9H, CH₃).

4'-(tert-Butyldiphenylsilyloxy)-3-(4-tetrahydropyranyloxyphenylethynyl)biphenyl 19

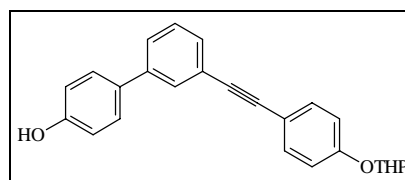


Synthesized as described for the preparation of compound 9. Quantities: 3-(4-tetrahydropyranyloxyphenylethynyl)bromobenzene 18 (2.0 g, 5.62 mmol), 4-(tert-butyldiphenylsilyloxy)phenylboronic acid (2.53 g, 6.73 mmol), Pd(PPh₃)₄ (0.3 g), benzene (30 ml), Na₂CO₃ (2M, 30 ml).

Yield 1.93 g (56.5%); mp 142-143 °C.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 7.75-7.00 (2d, 4H, Ar-H), 7.62 (s, 1H, Ar-H), 7.45-7.30 (m, 13H, Ar-H), 7.02-6.78 (2d, 4H, Ar-H), 5.42 (t, *J* 3.1, 1H, O-CH-O), 3.84 (m, 1H, THP), 3.59 (m, 1H, THP), 2.0-1.5 (m, 6H, THP), 1.1 (s, 9H, CH₃).

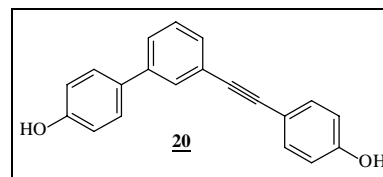
4'-Hydroxy-3-(4-tetrahydropyranyloxyphenylethynyl)biphenyl



4'-(tert-Butyldiphenylsilyloxy)-3-(4-tetrahydropyranyloxyphenylethynyl)biphenyl 19 (1.45 g, 2.5 mmol) was dissolved in dry THF (45 ml), Bu₄NF (5.0 ml, 1 M THF) was added and the mixture was stirred at room temperature for 10 h. Afterwards the solvent was removed and CHCl₃ (60 ml) and H₂O (40 ml) were added. The organic phase was washed with water (20 ml) and dried with Na₂SO₄. The product was purified by column chromatography (petroleum ether:ethyl acetate = 10:4).

Yield 0.5 g (56.8%); mp 82-87 °C.

$^1\text{H-NMR}$: δ_{H} (CDCl_3 ; 200 MHz; J/Hz): 7.68 (d, J 1.6, 1H, Ar-H), 7.49-7.31 (m, 7H, Ar-H), 7.01 (d, J 8.8, 2H, Ar-H), 6.89 (d, J 8.6, 2H, Ar-H), 5.43 (t, J 2.8, 1H, O-CH-O), 3.88 (m, 1H, THP), 3.63 (m, 1H, THP), 2.03-1.25 (m, 6H, THP).



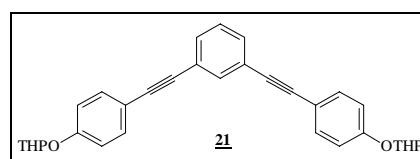
4'-Hydroxy-3-(4-hydroxyphenylethynyl)biphenyl 20

Synthesized as described for the preparation of compound 22. Quantities: 4'-hydroxy-3-(4-tetrahydropyranyloxyphenylethynyl)biphenyl (0.5 g, 1.35 mmol), CH_2Cl_2 (16 ml), MeOH (10 ml), PTSA (0.03 g).

Yield 0.2 g (51.7%); mp 158-160 °C.

$^1\text{H-NMR}$: δ_{H} (CDCl_3 ; 200 MHz; J/Hz): 9.90 (s, 1H, OH), 9.58 (s, 1H, OH), 7.70-7.36 (m, 8H, Ar-H), 6.89-6.76 (m, 4H, Ar-H).

1,3-Bis(4-tetrahydropyranyloxyphenylethynyl)benzene 21

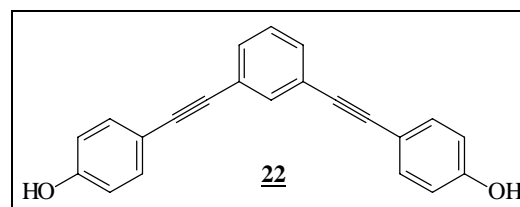


Synthesized in analogy to the preparation of compound 16, but the reaction mixture was stirred at room temperature for 3 h. Quantities: 1,3-diiodobenzene (1.79 g, 5.42 mmol) and 4-tetrahydropyranyloxyphenylacetylene 17 (2.18 g, 10.79 mmol), CuI (0.22 g, 1.15 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.64 g, 0.64 mmol), Et_3N (68 ml).

Yield 1.4 g (54.3%); mp 136-137 °C.

$^1\text{H-NMR}$: δ_{H} (CDCl_3 ; 200 MHz; J/Hz): 7.67 (s, 1H, Ar-H), 7.48-7.34 (m, 7H, Ar-H), 7.02 (d, J 9.0, 4H, Ar-H), 5.46 (m, 2H, THP), 4.1-3.6 (m, 4H, THP), 1.91-1.64 (m, 12H, THP).

1,3-Bis(4-hydroxyphenylethynyl)benzene 22



1,3-Bis(4-tetrahydropyranyloxyphenylethynyl)benzene 21 (1.4 g, 2.9 mmol) was dissolved in a mixture of CH_2Cl_2 (38 ml) and MeOH (27 ml). To this solution p-toluenesulphonic acid (0.07 g) was added, and the mixture was stirred at room temperature for 1 h. The solvent was evaporated and the pure compound was obtained by column chromatography ($\text{CHCl}_3:\text{MeOH} = 10:1$), followed by recrystallization from CH_2Cl_2 .

Yield 0.75 g (83.4%). mp 207-208 °C.

$^1\text{H-NMR}$: δ_{H} (CDCl_3 ; 200 MHz; J/Hz): 10.0 (s, 2H, OH), 7.62 (s, 1H, Ar-H), 7.49-7.43 (m, 7H, Ar-H), 6.82 (d, J 8.6, 4H, Ar-H).

2 Synthesis of the 4-substituted benzoic acids

2.1 Synthesis of the 4-(5-alkylpyrimidine-2-yl)benzoic acids

1,1-Dimethoxyoctane

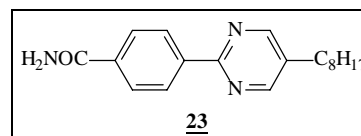
Octanal (15.26 g, 0.12 mol) was added to dry methanol (82 ml), with stirring concentrated sulfuric acid (98%, 0.6 ml) was dropwise added. The solution was heated under reflux for 3

h, then cooled to room temperature and was stored at this temperature for 4 days. Then the solution was basified with NaOH (30%) to $p_H = 9-10$. After the methanol was removed, water (100 ml) was added, the organic phase was separated, and the product was obtained by vacuum distillation (80 °C/10 Torr).

Yield 17.46 g; (83.6%).

$^1\text{H-NMR}$: δ_H (CDCl_3 ; 200 MHz; J/Hz): 4.33 (m, 1H, CH), 3.28 (s, 6H, OCH_3), 1.55 (m, 2H, CH_2), 1.35-1.25 (m, 10H, CH_2), 0.86 (t, J 6.5, 3H, CH_3).

4-(5-Octylpyrimidine-2-yl)benzamide 23

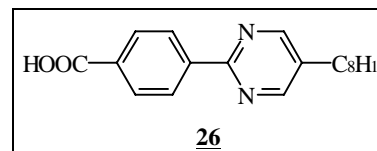


POCl_3 (3.4 ml, 37.1 mmol) was added dropwise to DMF (3.4 g, 46.2 mmol) with stirring at 0-5 °C (ice bath), the mixture was then allowed to warm up to 20°C and was stirred at this temperature for 15 min.. A solution of 1,1-dimethoxydecane (5.05 g 25.0 mmol) in DMF (12.5 ml) was added at room temperature. The mixture was stirred at 20°C for additional 3 hours. 4-Amidinobenzamide hydrochloride (5.0 g, 26.7 mmol) was added and the resulting suspension was stirred at 20°C for 1 hour. Triethylamine (27.5 ml, 0.2 mmol) followed by DMF (17.5 ml) were slowly added at 20-25°C. After that the solvent Et_3N was distilled off. The residue was cooled to room temperature and poured into ice water (150 ml). The yellow solid was filtered off, and purified by column chromatography (CHCl_3 : MeOH = 10:1). The 4-(5-octylpyrimidine-2-yl)benzamide obtained was recrystallized from MeOH.

Yield 0.67 g (8.6%); m.p. 118-120 °C.

$^1\text{H-NMR}$: δ_H (CDCl_3 ; 200 MHz; J/Hz): 8.64 (s, 2H, Pyrimidine-H), 8.52 (d, J 8.6, 2H, Ar-H), 7.74 (d, J 8.6, 2H, Ar-H), 2.63 (t, J 7.6, 2H Pyrimidine- CH_2 -), 1.68-1.59 (m, 4H, CH_2), 1.33-1.25 (m, 8H, CH_2), 0.86 (t, J 6.4, 3H, CH_3).

4-(5-Octylpyrimidine-2-yl)benzoic acid 26



4-(5-Octylpyrimidine-2-yl)benzamide (0.67 g, 2.15 mmol) was suspended in H_2O (3 ml), glacial acetic acid (10 ml) and H_2SO_4 (3 ml) were added. The solution was refluxed for 12 h, cooled to room temperature, and then poured into ice-water (100 ml). The precipitate obtained was recrystallized from a MeOH / H_2O mixture (95:5).

Yield 0.55 g (82.1%); mp 218-221 °C.

$^1\text{H-NMR}$: δ_H (CDCl_3 ; 200MHz; J/Hz): 8.67 (s, 2H, Pyrimidine-H), 8.52 (d, J 8.6, 2H, Ar-H), 8.20 (d, J 8.6, 2H, Ar-H), 2.64 (t, J 7.6, 2H, Pyrimidine- CH_2), 1.66-1.19 (m, 12H, CH_2), 0.86 (t, J 6.5, 3H, CH_3).

4-(5-Butylpyrimidine-2-yl)benzoic acid 24

Synthesized as described for the preparation of compounds 1,1-dimethyloctane, 23 and 26. Quantities: Hexanal (12.0 g, 0.12 mol); 4-amidinobenzamide hydrochloride (21.0 g, 112.1 mmol)

Yield 10.52 g (34.3%); mp 229-230 °C.

$^1\text{H-NMR}$: δ_H (DMSO-D_6 ; 400 MHz; J/Hz): 8.80 (s, 2H, pyrimidine-H), 8.45 (d, J 8.6, 2H, Ar-H), 8.05 (d, J 8.6, 2H, Ar-H), 2.62 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 0.90 (t, J 7.3, 3H, CH_3).

4-(5-Hexylpyrimidine-2-yl)benzoic acid 25

Synthesized as described for the preparation of compounds **23** and **26**. Quantities: 1,1-dimethoxyoctane (8.7 g, 50.0 mmol), 4-amidinobenzamide hydrochloride (10.0 g, 53.4 mmol).

Yield 2.24 g (15.8%); mp 224-226 °C.

¹H-NMR: δ_H (DMSO-D₆; 400 MHz; *J*/Hz): 8.80 (s, 2H, Pyrimidine-H), 8.45 (d, *J* 8.6, 2H, Ar-H), 8.05 (d, *J* 8.6, 2H, Ar-H), 2.63 (t, *J* 7.7, 2H, Pyrimidine-CH₂-), 1.63-1.57 (m, 2H, CH₂), 1.28-1.26 (m, 6H, CH₂), 0.84 (t, *J* 6.9, 3H, CH₃).

4-(5-Dodecylpyrimidine-2-yl)benzoic acid 27

Synthesized as described for the preparation of compounds **23** and **26**. Quantities: tetradecanal (23.5 g, 118.6 mmol), 4-amidinobenzamide hydrochloride (10.0 g, 53.4 mmol).

Yield 5.76 g (26.80%); mp 198-200 °C.

¹H-NMR: δ_H (DMSO-D₆; 200MHz; *J*/Hz): 8.8 (s, 2H, Pyrimidine-H), 8.46 (d, *J* 8.4, 2H, Ar-H), 8.06 (d, *J* 8.4, 2H, Ar-H), 2.63 (t, *J* 7.4, 2H, Pyrimidine-CH₂), 1.61 (m, 2H, CH₂), 1.28-1.21 (m, 18H, CH₂), 0.83 (t, *J* 6.4, 3H, CH₃).

2.2 Synthesis of the 4-(benzoyloxy)benzoic acids.

5-Iodo-7,7,8,8,9,9,10,10,10-nonafluorodecanol 28

5-Hexen-1-ol (10.7 g, 107 mmol) was added to dry hexane (100 ml), Dissolved oxygen was removed by irradiation with ultrasonic waves under a stream of Argon at 0-5 °C (ice bath) for 1h. Then Pd(PPh₃)₄ (5.6 g, 4.0 mol%) was added, and the mixture was stirred at room temperature for 3 days. Then Pd(PPh₃)₄ was filtered off, the product was obtained by removing of the solvent and used for the next reaction without further purification.

Yield 48.65 g (crude product); oil.

¹H-NMR: δ_H (CDCl₃; 500 MHz; *J*/Hz): 4.35-4.29 (m, 1H, CHI), 3.66 (t, *J* 6.0, 2H, CH₂OH), 3.00-2.72 (m, 2H, CF₂CH₂), 1.90-1.77 (m, 2H, CH₂), 1.66-1.59 (m, 4H, CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.65 (CF₃), -115.79 (CF₂), -126.17 (CF₂), -127.49 (CF₂).

7,7,8,8,9,9,10,10,10-Nonafluorodecanol 29

LiAlH₄ (4 g) was added to dry ether (150 ml), the mixture was heated under reflux, and 5-iodo-7,7,8,8,9,9,10,10,10-nonafluorodecanol (48.65 g, dissolved in 80 ml dry ether) was dropwise added, the mixture was refluxed for 2 h, then cooled to room temperature, water (4 ml) and sulfuric acid (20%) were carefully added respectively till all of the solid was dissolved, the aqueous phase was separated and extracted with ether (3 × 200 ml), the combined organic phase was washed with Na₂S₂O₃ (10 %, 3× 150 ml), dried with Na₂SO₄, solvent was removed and the product was obtained by vacuum fractional distillation (107 °C/ 14 Torr).

Yield 17.43 g (50.0%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 3.63 (t, *J* 6.4, 2H, CH₂), 2.17-1.91 (m, 2H, CH₂), 1.60-1.38 (m, 4H, CH₂).

1-Bromo-7,7,8,8,9,9,10,10,10-nonafluorodecane 30

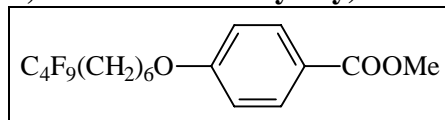
7,7,8,8,9,9,10,10,10-Nonafluorodecanol **29** (17.43 g, 54.3 mmol), HBr (48%, 34.5 ml), H₂SO₄ (96%, 5.6 ml), Bu₄NBr (1.13 g) were carefully added. The mixture was refluxed for 5 days, cooled down and then extracted with diethyl ether (3× 100 ml), washed with water and dried with Na₂SO₄, after the solvent was removed, the product was obtained by vacuum

fractional distillation (96 °C/ 11 Torr).

Yield 17.79 g (85.5%).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 3.39 (t, 2H, CH₂Br), 2.18-1.79 (m, 4H, CH₂), 1.69-1.35 (m, 6H, CH₂).

Methyl 4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoate **31**

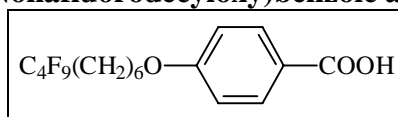


Methyl 4-hydroxybenzoate (5.7 g, 37.4 mmol) and K₂CO₃ (31.1 g) were added to dry DMF (400 ml), the mixture was heated to 65 °C, 1-bromo-7,7,8,8,9,9,10,10,10-nonafluorodecane **30** (15.55 g, 40.6 mmol) was added, the mixture was stirred at 65 °C for 5 h, then cooled to room temperature, ice-water (500 ml) was added, and the solution was acidified with HCl (37%) to pH = 2-3, extracted with ether, washed with water and dried with Na₂SO₄, the solvent was removed and the product was used for next reaction without further purification. Yield 18.5 g (crude product).

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 7.96 (d, *J* 9.0, 2H, Ar-H), 6.87 (d, *J* 8.8, 2H, Ar-H), 3.99 (t, *J* 6.3, 2H, OCH₂), 3.86 (s, 3H, CH₃), 2.18-1.47 (m, 10H, CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.67 (CF₃), -116.22 (CF₂), -126.11 (CF₂), -127.68 (CF₂).

4-(7,7,8,8,9,9,10,10,10-Nonafluorodecyloxy)benzoic acid **32**



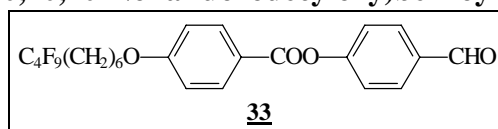
Methyl 4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoate **31** (18.5 g, 40.7 mmol) was dissolved in ethanol (95%, 260 ml), KOH (10N, 26 ml) was added, the solution was heated under reflux for 2 h, then cooled to room temperature, THF (50 ml) was added, and then acidified with HCl (37%) to pH = 1-2, the solid was collected, and was recrystallized from ethanol.

Yield 13.9 g (77.6%); transition temperatures (°C): 142 SmC 165 Iso.

¹H-NMR: δ_H (DMSO-D₆; 200 MHz; *J*/Hz): 7.86 (d, *J* 8.8, 2H, Ar-H), 7.00 (d, *J* 8.8, 2H, Ar-H), 4.02 (t, *J* 6.4, 2H, OCH₂), 2.31-2.07 (m, 2H, CH₂), 1.75-1.43 (m, 8H, CH₂).

¹⁹F-NMR: δ_F (DMSO-D₆; 188 MHz): -77.46 (CF₃), -110.43 (CF₂), -120.84 (CF₂), -122.61 (CF₂).

4-[4-(7,7,8,8,9,9,10,10,10-Nonafluorodecyloxy)benzoyloxy]benzaldehyde. **33**



A mixture of 4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoic acid (12.4 g, 28.2 mmol) and thionyl chloride (50 ml) was refluxed for 3 hours. Excess SOCl₂ was carefully distilled off, first at atmospheric pressure and finally in vacuo. The residue [4-(7,7,8,8,9,9,10,10,10-nonafluorodecyloxy)benzoyl chloride] was added to a stirred solution of 4-hydroxybenzaldehyde (3.44 g, 28.2 mmol) in dry pyridine (60 ml) at room temperature. The mixture was heated to 90 °C with stirring for 5 hours. After cooling to room temperature the solution was poured onto ice (100g) and hydrochloric acid (50 ml, 33%). The precipitate was filtered

off and crystallized from ethanol.

Yield 12.2 g (79.5%); transition temperatures (°C): Cr 63 SmA 121 Iso.

¹H-NMR: δ_H (CDCl₃; 200 MHz; *J*/Hz): 10.00 (s, 1H, CHO), 8.13 (d, *J* 9.0, 2H, Ar-H), 7.95 (d, *J* 8.8, 2H, Ar-H), 7.38 (d, *J* 8.6, 2H, Ar-H), 6.96 (d, *J* 9.0, 2H, Ar-H), 4.05 (t, *J* 6.3, 2H, OCH₂), 2.1-1.4 (m, 10H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 191.1 (CHO), 164.4, 163.9 (COO, Cq), 156.1 (Cq), 134.1 (Cq), 132.6 (2C-H), 131.3 (2C-H), 122.7 (2C-H), 121.2 (Cq), 114.5 (2C-H), 68.1 (OCH₂), 30.7 (t, CF₂CH₂), 28.8 (CH₂), 28.7 (CH₂), 25.6 (CH₂), 20.0 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.63 (CF₃), -116.18 (CF₂), -126.09 (CF₂), -127.6 (CF₂).

4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyloxy)benzoyloxy]benzaldehyde **34**

Synthesized as described for the preparation of compound **33** from 4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoic acid (9.7 g, 18.2 mmol), and 4-hydroxybenzaldehyde (2.22 g, 18.2 mmol).

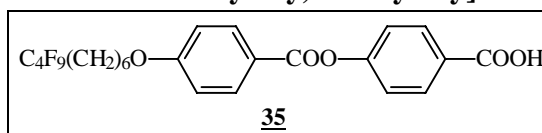
Yield 6.6 g (59%); transition temperatures (°C): Cr 86 SmA 154 Iso.

¹H-NMR: δ_H (CDCl₃; 400 MHz; *J*/Hz): 10.00 (s, 1H, CHO), 8.13 (d, *J* 8.8, 2H, Ar-H), 7.95 (d, *J* 8.8, 2H, Ar-H), 7.38 (d, *J* 8.6, 2H, Ar-H), 6.96 (d, *J* 9.0, 2H, Ar-H), 4.08 (t, *J* 6.4, 2H, OCH₂), 2.3-2.1 (m, 2H, CF₂CH₂), 2.0-1.8 (m, 4H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 191.1 (CHO), 164.3, 163.6 (COO, Cq), 156.0 (Cq), 134.1 (Cq), 132.6 (2C-H), 131.3 (2C-H), 122.7 (2C-H), 121.4 (Cq), 114.5 (2C-H), 67.5 (OCH₂), 30.6 (t, CF₂CH₂), 28.5 (CH₂), 17.2 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.38 (CF₃), -116.02 (CF₂), -123.52 (CF₂), -124.49 (CF₂), -125.14 (CF₂), -127.7 (CF₂).

4-[4-(7,7,8,8,9,9,10,10,10-Nonafluorodecyloxy)benzoyloxy]benzoic acid **35**



4-[4-(7,7,8,8,9,9,10,10,10-Nonafluorodecyloxy)benzoyloxy]benzaldehyde (12.20 g, 22.4 mmol) was dissolved in acetic acid (90%, 45 ml) and a solution of CrO₃ (4.5 g) in acetic acid (60%, 45 ml) was added. The resulting solution was refluxed with stirring for 5 hours. Afterwards water (20 ml) was added and the solution was allowed to cool to room temperature and was stored overnight in a refrigerator (0-4 °C). The precipitate formed was filtered off, washed with water (2 x 100 ml), and recrystallized from ethanol.

Yield 7.3 g (58.0%); transition temperatures (°C): Cr 158 SmC 250 Iso.

¹H-NMR: δ_H (DMSO-D₆; 400 MHz; *J*/Hz): 13.02 (br. 1H, COOH), 8.07 (d, *J* 8.8, 2H, Ar-H), 8.02 (d, *J* 8.8, 2H, Ar-H), 7.38 (d, *J* 8.8, 2H, Ar-H), 7.10 (d, *J* 8.8, 2H, Ar-H), 4.09 (t, *J* 6.4, 2H, OCH₂), 2.15-2.32 (m, 2H, CH₂CF₂), 1.8-1.7 (m, 2H, CH₂), 1.6-1.5 (m, 6H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.8, 164.0, 163.5 (2C=O, Cq), 154.4 (Cq), 132.2 (2C-H), 131.0 (2C-H), 128.5 (Cq), 122.3 (2C-H), 120.6 (Cq), 114.8 (2C-H), 67.9 (OCH₂), 29.5 (t, CF₂CH₂), 28.1 (CH₂), 27.7 (CH₂), 24.9 (CH₂), 19.5 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -82.63 (CF₃), -116.18 (CF₂), -126.07 (CF₂), -127.6 (CF₂CH₂).

4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyloxy)benzoyloxy]benzoic acid **36**

Synthesized as described for the preparation of the compound **35** from 4-[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyloxy)benzoyloxy]benzaldehyde (6.16 g, 10 mmol).

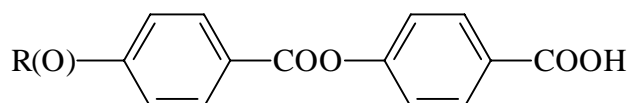
Yield 4.4 g (70.0%); transition temperatures (°C): Cr 186 SmC 267 Iso.

¹H-NMR: δ_H (DMSO-D₆); 400 MHz; *J*/Hz): 13.01 (br. 1H, COOH), 8.07 (d, *J* 8.8, 2H, Ar-H), 8.02 (d, *J* 8.8, 2H, Ar-H), 7.38 (d, *J* 8.8, 2H, Ar-H), 7.10 (d, *J* 8.8, 2H, Ar-H), 4.14 (t, *J* 6.4, 2H, OCH₂), 2.15-2.32 (m, 2H, CF₂CH₂), 1.87 (m, 2H, OCH₂CH₂), 1.71 (m, 2H, CH₂).

¹³C-NMR: δ_C (CDCl₃; 100 MHz): 166.8, 164.0, 163.4 (2C=O, Cq), 154.4 (Cq), 132.2 (2C-H), 131.0 (2C-H), 128.5 (Cq), 122.3 (2C-H), 120.7 (Cq), 114.8 (2C-H), 67.5 (OCH₂), 29.4 (t, CF₂CH₂), 27.5 (CH₂), 16.5 (CH₂).

¹⁹F-NMR: δ_F (CDCl₃; 188 MHz): -77.1 (CF₃), -110.3 (CF₂), -118.6 (CF₂), -119.6 (CF₂), -120.0 (CF₂), -122.7 (CF₂).

All synthesized 4-(4-alkylbenzoyloxy)benzoic acids and 4-(4-alkoxybenzoyloxy)-benzoic acids were obtained in analogy to the preparation of compound **35**. They are summarized in the following table. The ¹H-NMR spectra of 4-(4-dodecylbenzoyloxy)benzoic acid and 4-(4-tetradecyloxybenzoyloxy)benzoic acid are given as typical examples.



R(O)	Yield %	Formula (M)	Transition temperatures (°C)
C ₆ H ₁₃	34.1	C ₂₀ H ₂₂ O ₄ (326.42)	Cr 171 N 247 Iso
C ₇ H ₁₅	40.5	C ₂₁ H ₂₄ O ₄ (340.45)	Cr 150 N 230 Iso
C ₉ H ₁₉	41.5	C ₂₃ H ₂₈ O ₄ (368.51)	Cr 159 N 233 Iso
C ₁₀ H ₂₁	39.7	C ₂₄ H ₃₀ O ₄ (382.54)	Cr 143 N 230 Iso
C ₁₁ H ₂₃	37.6	C ₂₅ H ₃₂ O ₄ (396.57)	Cr 134 N 221 Iso
C ₁₂ H ₂₅	72.7	C ₂₆ H ₃₄ O ₄ (410.60)	Cr 144 N 226 Iso
OC ₉ H ₁₉	36.4	C ₂₃ H ₂₈ O ₅ (384.51)	Cr 131 N 237 Iso
OC ₁₀ H ₂₁	66.7	C ₂₄ H ₃₀ O ₅ (398.54)	Cr 125 N 234 Iso
OC ₁₁ H ₂₃	34.5	C ₂₅ H ₃₂ O ₅ (412.57)	Cr 124 N 226 Iso
OC ₁₂ H ₂₅	48.7	C ₂₆ H ₃₄ O ₅ (426.60)	Cr 127 N 233 Iso
OC ₁₃ H ₂₇	54.1	C ₂₇ H ₃₆ O ₅ (440.63)	Cr 126 N 230 Iso
OC ₁₄ H ₂₉	62.2	C ₂₈ H ₃₈ O ₅ (454.66)	Cr 126 N 231 Iso

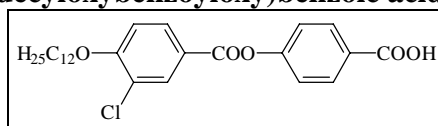
4-(4-Dodecylbenzoyloxy)benzoic acid

¹H-NMR: δ_H (DMSO-D₆; 200 MHz; *J*/Hz): 8.06-8.01 (m, 4H, Ar-H), 7.44-7.38 (m, 4H, Ar-H), 2.68 (t, *J* 7.5, 2H, CH₂), 1.60 (m, 2H, CH₂), 1.23 (m, 18H, CH₂), 0.84 (t, *J* 6.5, 3H, CH₃).

4-(4-Tetradecyloxybenzoyloxy)benzoic acid

¹H-NMR: δ_H (DMSO-D₆; 200 MHz; *J*/Hz): 8.09-8.00 (t, 4H, Ar-H), 7.38 (d, *J* 8.6, 2H, Ar-H), 7.11 (d, *J* 8.8, 2H, Ar-H), 4.08 (t, 2H, OCH₂), 1.74 (m, 2H, CH₂), 1.23 (m, 22H, CH₂), 0.84 (t, 3H, CH₃).

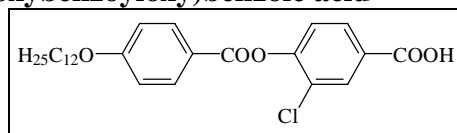
4-(3-Chloro-4-dodecyloxybenzoyloxy)benzoic acid



Synthesized as described for the preparation of compounds **34** and **35** from 3-chloro-4-dodecyloxybenzoic acid (18.8 g, 55.2 mmol) and 4-hydroxybenzaldehyde (6.7g, 55.2 mmol). Yield 16.0 g (63.1%); transition temperatures (°C): Cr 143 N 204 Iso.

¹H-NMR: δ_{H} (DMSO- D_6 ; 200 MHz; J/Hz): 13.09 (br. 1H, COOH), 8.10-8.00 (t, 4H, Ar-H), 7.42-7.31 (m, 3H, Ar-H), 4.18 (t, J 6.3, 2H, OCH_2), 1.80-1.73 (m, 2H, CH_2), 1.42-1.23 (m, 18H, CH_2), 0.84 (t, J 5.9, 3H, CH_3).

3-Chloro-4-(4-dodecyloxybenzoyloxy)benzoic acid

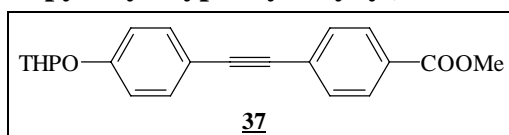


Synthesized as described for the preparation of compounds **34** and **35** from 4-dodecyloxybenzoic acid (15.0 g, 49.0 mmol) and 3-chloro-4-hydroxybenzaldehyde (7.67 g, 49.0 mmol). Yield 12.53 g (55.8%); transition temperatures ($^{\circ}\text{C}$): Cr 100 N 180 Iso

¹H-NMR: δ_{H} (DMSO- D_6 ; 200 MHz; J/Hz): 8.11-7.95 (m, 4H, Ar-H), 7.58 (d, J 8.4, 1H, Ar-H), 7.12 (d, J 8.8, 2H, Ar-H), 4.08 (t, J 6.4, 2H, OCH_2), 1.73 (m, 2H, CH_2), 1.23 (m, 18H, CH_2), 0.84 (t, J 6.3, 3H, CH_3).

2.3 Synthesis of 4-(4-octyloxyphenylethynyl)benzoic acid **39**

Methyl 4-(4-tetrahydropyranyloxyphenylethynyl)benzoate **37**

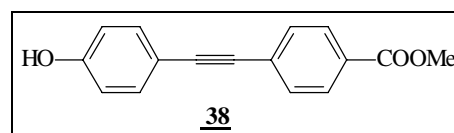


Synthesized as described for the preparation of compound **16**. Quantities: 4-tetrahydropyranyloxyphenylacetylene **17** (2.02 g, 10.6 mmol), methyl 4-bromobenzoate (2.15 g, 10.6 mmol).

Yield 1.5 g (42.1%); mp 120 $^{\circ}\text{C}$.

¹H-NMR: δ_{H} (CDCl_3 ; 200 MHz; J/Hz): 7.98 (d, J 8.6, 2H, Ar-H), 7.54 (d, J 8.6, 2H, Ar-H), 7.45 (d, J 8.8, 2H, Ar-H), 7.02 (d, J 8.8, 2H, Ar-H), 5.43 (t, J 3.12, 1H, THP), 3.92-3.87 (m, 4H, CH_3 , THP), 3.63 (m, 1H, THP), 1.6-2.1 (m, 6H, THP).

Methyl 4-(4-hydroxyphenylethynyl)benzoate **38**

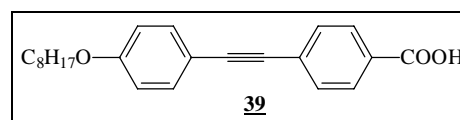


Synthesized as described for the preparation of compound **22** from methyl 4-(4-tetrahydropyranyloxyphenylethynyl)benzoate **37** (1.08 g, 3.2 mmol).

Yield, 0.75 g (92.6%); mp 210 $^{\circ}\text{C}$.

¹H-NMR: δ_{H} (CDCl_3 ; 400 MHz; J/Hz): 7.99 (d, J 8.6, 2H, Ar-H), 7.53 (d, J 8.6, 2H, Ar-H), 7.41 (d, J 8.8, 2H, Ar-H), 6.81 (d, J 8.8, 2H, Ar-H), 3.91 (s, 3H, CH_3).

4-(4-Octyloxyphenylethynyl)benzoic acid **39**



Methyl 4-(4-hydroxyphenylethynyl)benzoate **38**

(0.65 g, 2.5 mmol) was added to a solution of KOH (0.15 g, 2.75 mmol) in H_2O (1.25 ml) and ethanol (7.5 ml). The mixture was stirred at 50 $^{\circ}\text{C}$ until the methyl 4-(4-hydroxyphenylethynyl)benzoate has completely dissolved. Then 1-bromooctane (0.53 g, 2.75 mmol) was dropwise added and the solution was refluxed for 4 h. A solution of KOH in water (10%, 1.6 ml) was cautiously added to the mixture and the resulting solution was refluxed for 2 h. After cooling to room temperature, ethanol was evaporated. Cold water (0 $^{\circ}\text{C}$, 30

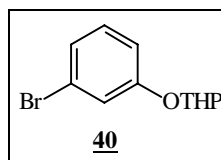
ml) and concentrated hydrochloric (0.5 ml) were added. The solid was filtered off and recrystallized from acetic acid.

Yield 0.7 g (77.7%); mp > 250 °C.

¹H-NMR: δ_H (DMSO-D₆; 500 MHz; J/Hz): 7.92 (d, *J* 8.3, 2H, Ar-H), 7.58 (d, *J* 8.3, 2H, Ar-H), 7.49 (d, *J* 8.8, 2H, Ar-H), 6.97 (d, *J* 8.8, 2H, Ar-H), 4.00 (t, *J* 6.5, 2H, OCH₂), 1.71 (m, 2H, CH₂), 1.41-1.25 (m, 10H, CH₂), 0.85 (t, *J* 6.8, 3H, CH₃).

3 Synthesis of the 4'-[4-(decyloxybenzoyloxy)benzoyloxy]-3-hydroxy-biphenyl 44

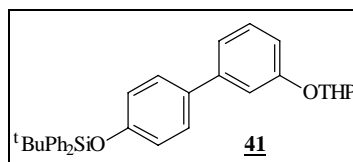
3-Tetrahydropyranyloxybromobenzene 40



Synthesized as described for the preparation of compound 15. Quantities: 3-bromophenol (20.0 g, 0.116 mol), DHP (12.05 g). Yield 13.46 g (45.1%); oil.

¹H-NMR: δ_H (CDCl₃; 500 MHz; J/Hz): 7.22 (m, 1H, Ar-H), 7.12-7.08 (m, 2H, Ar-H), 6.97-6.95 (m, 1H, Ar-H), 5.38 (t, *J* 3.1, 1H, THP), 3.88-3.83 (m, 1H, THP), 3.62-3.57 (m, 1H, THP), 2.00-1.51 (m, 6H, THP).

4'-(tert-Butyldiphenylsilyloxy)-3-tetrahydropyranyloxybiphenyl 41

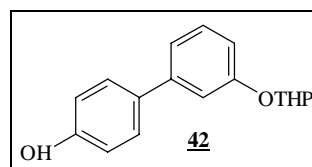


Synthesized as described for the preparation of compound 9. Quantities: 3-tetrahydropyranyloxybromobenzene 40 (3.6 g, 14.05 mmol), 4-(tert-butyl-diphenylsilyloxy)phenylboronic acid (6.33 g, 16.83 mmol).

Yield 5.46 g (81.0%); oil.

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 7.73 (m, 4H, Ar-H), 7.46-7.08 (m, 11H, Ar-H), 6.99-6.83 (m, 1H, Ar-H), 6.79 (d, *J* 8.8, 2H, Ar-H), 5.43 (m, 1H, THP), 3.91 (m, 1H, THP), 3.61 (m, 1H, THP), 2.04-1.60 (m, 6H, THP), 1.1 (3, 9H, CH₃).

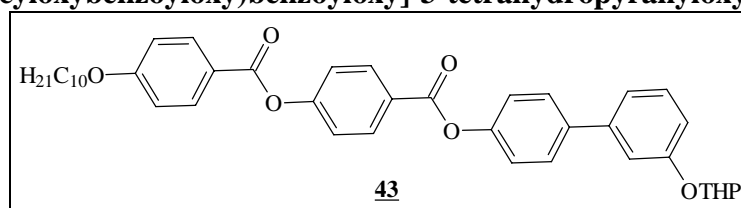
4'-Hydroxy-3-tetrahydropyranyloxybiphenyl 42



Synthesized as described for the preparation of compound 4'-Hydroxy-3-(4-tetrahydropyranyloxyphenylethynyl)biphenyl. Quantities: 4'-(tert-butyl-diphenylsilyloxy)-3-tetrahydropyranyloxybiphenyl 41 (5.27 g, 10.98 mmol). Yield 1.14 g (38.5%); mp 120 °C.

¹H-NMR: δ_H (DMSO-D₆; 200 MHz; J/Hz): 9.51 (br. 1H, OH), 7.45 (d, *J* 8.6, 2H, Ar-H), 7.30 (m, 1H, Ar-H), 7.18-7.14 (m, 2H, Ar-H), 6.97-6.90 (m, 1H, Ar-H), 6.82 (d, *J* 8.6, 2H, Ar-H), 5.3 (t, *J* 3.13, 1H, THP), 3.84-3.73 (m, 1H, THP), 3.60-3.52 (m, 1H, THP), 1.98-1.53 (m, 6H, THP).

4'-[4-(4-Decyloxybenzoyloxy)benzoyloxy]-3-tetrahydropyranyloxybiphenyl 43

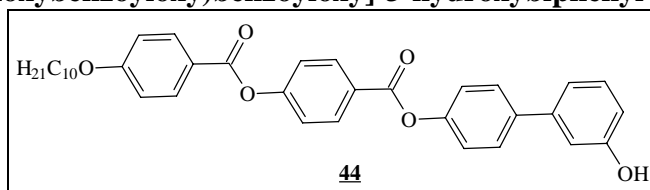


4'-Hydroxy-3-tetrahydropyranyloxybiphenyl **42** (0.36 g, 1.33 mmol), 4-(4-decyloxybenzoyloxy)benzoic acid (0.58 g, 1.46 mmol), CMC (0.5 g, 1.17 mmol), 4-(dimethylamino)pyridine (0.02 g), were dissolved in dry CH₂Cl₂ (15) ml. The solution was stirred at room temperature for 12 h. Then water 15 ml was added and the organic phase was separated. After evaporation of the solvent the product was purified by column chromatography (CHCl₃/MeOH = 10: 0.5).

Yield 0.76 g (90.1%); transition temperatures (°C): Cr 119 N 136 Iso.

¹H-NMR: δ_H (CDCl₃; 200 MHz; J/Hz): 8.28 (d, *J* 8.8, 2H, Ar-H), 8.14 (d, *J* 8.8, 2H, Ar-H), 7.63 (d, *J* 8.8, 2H, Ar-H), 7.39-7.22 (m, 7H, Ar-H), 7.18-7.02 (m, 1H, Ar-H), 6.97 (d, *J* 8.8, 2H, Ar-H), 5.48 (t, *J* 3.0, 1H, THP), 4.04 (t, *J* 6.5, 2H, OCH₂), 3.94-3.88 (m, 1H, THP), 3.59 (m, 1H, THP), 1.89-1.26 (m, 22H, CH₂), 0.87 (t, *J* 6.3, 3H, CH₃).

4'-[4-(4-Decyloxybenzoyloxy)benzoyloxy]-3-hydroxybiphenyl **44**



4'-[4-(4-Decyloxybenzoyloxy)benzoyloxy]-3-tetrahydropyranyloxybiphenyl **43** (0.7 g, 1.1 mmol) was dissolved in CH₂Cl₂ (80 ml), HCl (33%, 1 ml) was added, the solution was stirred at room temperature for 12 h, NaHCO₃ (3.0 g), H₂O (10 ml) were added, the solid was filtered off, and H₂O (20 ml) was added, the organic phase was separated. The solvent was removed and the product was purified by column chromatography (CHCl₃:MeOH) = 10:0.5.

Yield 0.52 g (83.9%); transition temperatures: Cr 143 N 225 Iso.

¹H-NMR: δ_H (CDCl₃, 200 MHz; J/Hz): 8.28 (d, *J* 8.8, 2H, Ar-H), 8.14 (d, *J* 8.8, 2H, Ar-H), 7.60 (d, *J* 8.6, 2H, Ar-H), 7.39-7.25 (m, 5H, Ar-H), 7.15 (d, *J* 8.2, 1H, Ar-H), 7.05-6.95 (m, 3H, Ar-H), 6.82 (d, *J* 8.0, 1H, Ar-H), 4.80 (s, 1H, OH), 4.04 (t, *J* 6.5, 2H, OCH₂), 1.85-1.78 (m, 2H, CH₂), 1.49-1.27 (m, 14H, CH₂), 0.87 (t, *J* 6.8, 3H, CH₃).

Zusammenfassung

Im Rahmen dieser Arbeit wurden verschiedene Serien neuer gewinkelter (bananenförmiger) Moleküle ohne die chemisch und photochemisch empfindlichen Schiff-Base Einheiten synthetisiert. Diese Moleküle enthalten verschiedene nichtlineare Strukturelemente, deren Größe von 1,3-Phenylene bis 1,3-Bis(phenylethynyl)benzol verändert wurde und die mit rigiden Phenyl-, Phenylbenzoat-, Biphenyl- und Phenylpyrimidinstrukturelementen verknüpft wurden. Weiterhin wurden Moleküle mit perfluorierten Alkylketten und solche mit einer Nitrogruppe oder einem Fluorsubstituenten an der Zentraleinheit, sowie Moleküle mit zwei verschiedenen rigiden Strukturelementen synthetisiert.

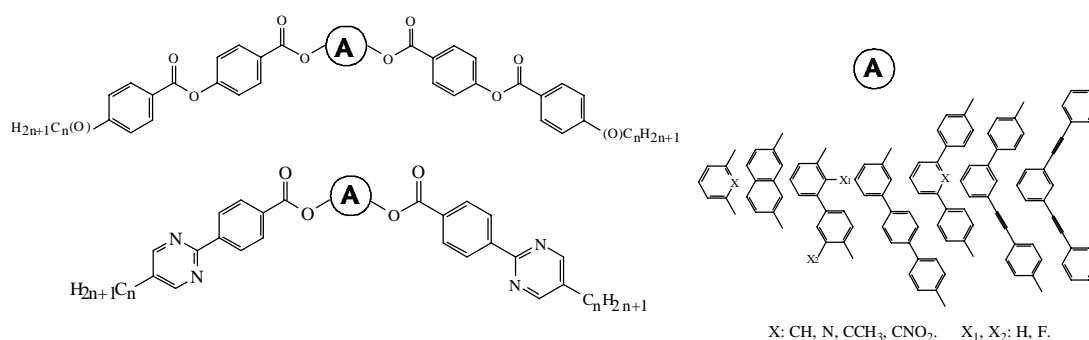


Abb. 5-1 Molekulare Struktur der synthetisierten bananenförmigen Moleküle.

Das flüssigkristalline Verhalten, die Phasenstrukturen und die elektrooptischen Eigenschaften dieser Moleküle wurden untersucht. Moleküle, in denen 1,3-Phenylene-, 3,4'-Biphenyl-, m-Terphenyl-, 1-Phenyl-3-(4-phenylethynyl)benzol- oder 1,3-Bis(phenylethynyl)benzol-zentraleinheiten mit rigiden Phenylbenzoateinheiten verknüpft sind (Verbindungen **31/n**, **11/n**, **12/n**, **15/n**, **25/n** und **27/n**) zeigen drei verschiedene Phasen, eine rechtwinklig columnare Phase (Col_r), eine antiferroelektrisch schaltbare SmCP_A Phase und manchmal zusätzlich eine hoch geordnete smektische Phase. Das Auftreten der antiferroelektrischen SmCP_A Phase ist stark abhängig von der Länge der Alkylketten und der Größe der Zentraleinheiten. Moleküle mit kurzen Alkylketten zeigen nur die columnaren Phasen. Die SmCP_A Phasen wurden durch Verlängerung der Alkylketten induziert. Bei Molekülen mit langen Alkylketten konnte nur die SmCP_A Phase beobachtet werden. Die Kettenlänge, die notwendig ist, damit die Moleküle die SmCP_A Phasen ausbilden können ist stark abhängig von der Größe der starren gewinkelten Strukturelemente in den Molekülen. So müssen

Moleküle mit großen Zentraleinheiten (z. B. m-Terphenyl-derivate) mit längeren Alkylketten ausgestattet werden als Moleküle mit kleineren Zentralelementen (z. B. die Biphenyl-derivate).

Die Moleküle mit rigiden Phenylpyrimidinstrukturelementen und kurzen Alkylketten ($n < 8$) besitzen eine interkalierte smektische Phase. Lange Alkylketten führen hier zum Verlust der mesogenen Eigenschaften.

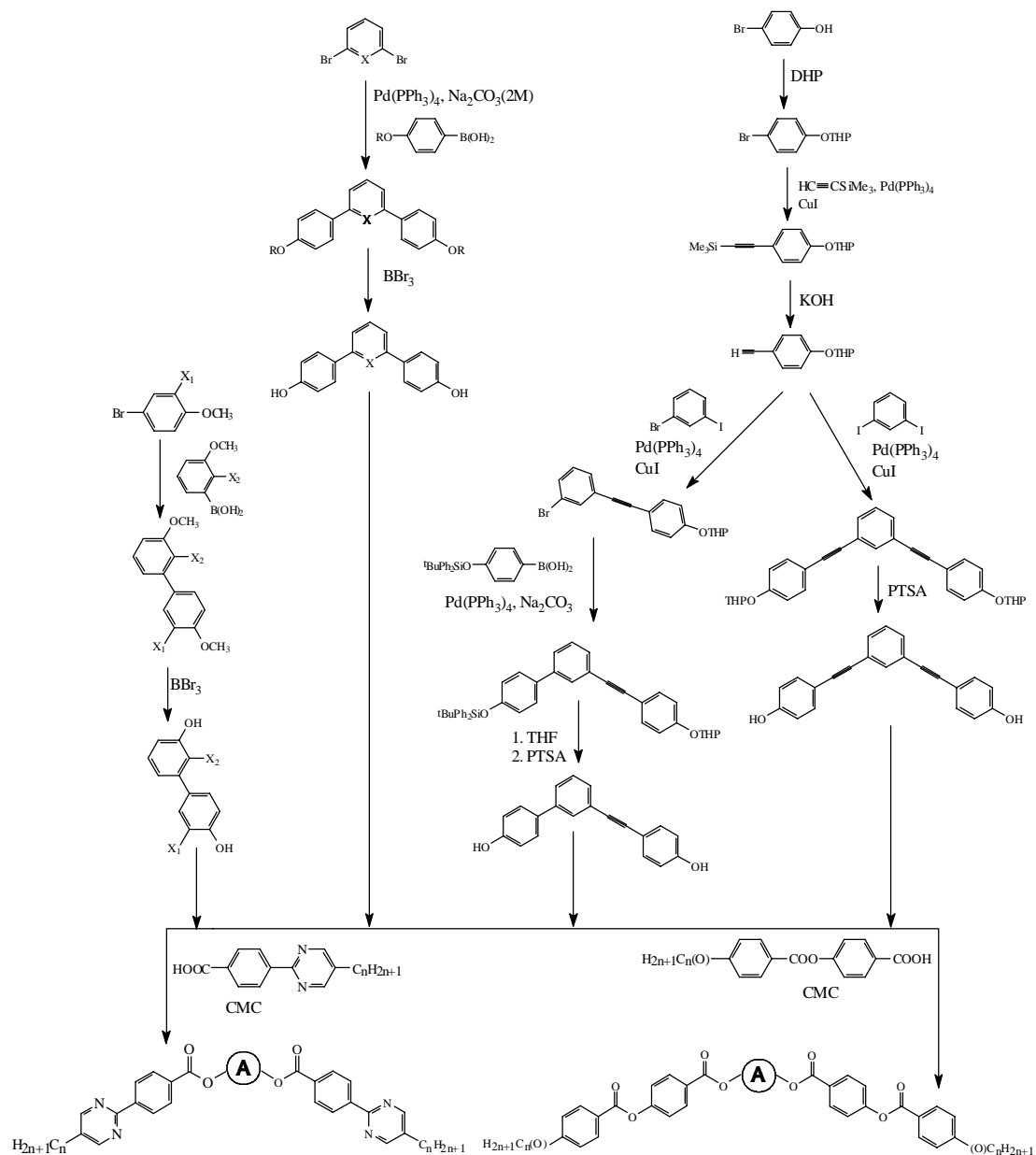


Abb. 5-2 Synthesewege zu den bananenförmigen Molekülen.

Die Moleküle mit einer 2,6-Diphenylpyridinzentraleinheit besitzen ausschließlich Col_r Phasen, wobei aber die Schmelzpunkte im Vergleich zu den verwandten m-Terphenylderivaten erheblich höher sind.

Perfluoralkylketten können die $SmCP_A$ Phasen deutlich stabilisieren, bzw. diese induzieren. Die erhöhten Klärpunkte bewirken eine Vergrößerung des Mesophasenexistenzgebietes der $SmCP_A$ Phasen.

Alle 2'-nitrosubstituierten m-Terphenylderivate zeigen eine zusätzliche nematische Phase. Aufgrund des größeren Raumbedarfes und der Veränderung der lokalen Dipolmomente sowie des Gesamtdipolmomentes der Moleküle bewirken polare Substituten (NO_2 oder F) an der Zentraleinheit den Verlust der polaren Ordnung in der Mesophase. So geht bei den Molekülen mit einer NO_2 Gruppe die $SmCP_A$ Phase vollständig verloren und es werden nur noch unpolare, optisch biaxiale smektische Phasen $SmC_{(b)}$ gefunden. Bei den fluorsubstituierten Molekülen konnte nur bei den Homologen mit langen Alkylketten die $SmCP_A$ Phasen gefunden werden. Die kurzkettingen Homologen besitzen nur noch eine Sm_b Phase.

Für Phenylpyrimidinderivate sind interkalierte smektische Phasen ($Sm_{intercal}$) typisch.

Moleküle, in denen verschiedene rigide Strukturelemente verknüpft sind zeigen verschiedene Mesophasen; ist eine der rigiden Einheiten eine Phenylpyrimidineinheit, so dominiert die interkalierte smektische Phase.

Ein kompliziertes Mesophasenverhalten weisen Moleküle mit einem Chlorsubstituenten am terminalen Phenylring der Phenylbenzoateinheit auf. Deren Textur unterscheidet sich von der $SmCP_A$ Phase, jedoch wurde in einem bestimmten Temperaturbereich ein antiferroelektrischer Schaltprozess beobachtet. Die Phasenstruktur ist bisher jedoch noch nicht aufgeklärt.

Alle $SmCP_A$ Phasen haben im wesentlichen die gleichen elektrooptischen Eigenschaften, die dadurch charakterisiert sind, daß beim Anlegen einer Dreiecksspannung zwei Spannungspeaks pro Halbperiode beobachtet werden, was auf einen antiferroelektrischen Schaltprozess hinweist. Die spontane Polarisierung beträgt ca. $400-700 \text{ nC/cm}^2$.

Curriculum Vitae

Name	Dong Shen
Family status	Married, one child.
7. 11. 1965	Born in Shanghai, People's Republic of China
1. 1972-7. 1977	Yuangjiazhuang elementary school, Shanghai
8. 1977- 7. 1980	Fengxi middle school, Shanghai
8. 1980-7. 1982	Shongjiang second high school, Shanghai
8. 1982-7. 1986	Study at department of fine chemical technology, East China University of Chemical Technology (renamed in 1992 as East China University of Science and Technology), Shanghai, Bachelor degree.
8. 1986-7. 1989	Study at the department of fine chemical technology, East China University of Science and Technology, Shanghai, Master degree. Masterwork: A Study on Mechanism of Light Fading of Magenta Azomethine Dye
8. 1989-7. 1993	Work in chemical physic laboratory, East China University of Science and Technology, research assistant.
7. 1993-3. 1997	Work in Liquid crystal laboratory, East China University of Science and Technology, research assistant.
(9. 1995-3. 1997	Learning German at Tongji University).
4. 1997-9. 2000	Ph.D. student at the institute of organic chemistry, Martin-Luther University Halle-Wittenberg.

Publications

Parts of this work have been published:

1. D. Shen, S. Diele, I. Wirth and C. Tschierske, *Chem. Commun.*, **1998**, 2573.
2. D. Shen, S. Diele, G. Pelzl, I. Wirth and C. Tschierske, *J. Mater. Chem.*, **1999**, 9, 661.
3. H. Schmalfuss, D. Shen, C. Tschierske and H. Kresse, *Liq. Cryst.*, **1999**, 26, 1767.
4. D. Shen, A. Pegenau, S. Diele, I. Wirth and C. Tschierske, *J. Am. Chem. Soc.*, **2000**, 122, 1593.

Hiermit erkläre ich an Eides statt, daß ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Quellen und Hilfsmittel angefertigt habe.

Diese Arbeit wurde bisher an keiner anderen Hochschule oder Universität vorgelegt.

Dong Shen

Halle(Saale), Deutschland, September 2000