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Synthesis and thermotropic liquid crystalline properties of calamitic molecules with laterally attached hydrophilic groups: Y-shaped three-block molecules which can form smectic and columnar mesophases

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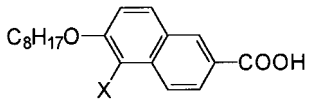
The synthesis and the thermotropic liquid crystalline properties of calamitic mesogens (*p*-terphenyl derivatives, a biphenyl and a *p*-quintaphenyl derivative) with a laterally attached hydrophilic group (1,2-diol groups, primary and secondary amides, polyether chains, crown ether units, carbohydrate units, a hydrazide, a quaternary ammonium salt, a carboxylic acid and a sodium carboxylate) are reported. The compounds were investigated by means of polarizing microscopy and calorimetry. The influence of the type of the polar group, of the length of the rigid core and the position of the connection of the hydrophilic group with the rod-like rigid core have been investigated. Many of these amphiphilic molecules can form monolayer S_A phases. If a sufficient amount of hydrogen bonding is available their mesophase stability can be higher than that of related compounds with other lateral substituents. Rectangular columnar mesophases can be found for compounds with rather large and flexible polar lateral substituents (polyether chains) fixed to the center of the rigid terphenyl unit. These columnar phases should represent ribbon phases resulting from the collapse of the smectic layers (modulated smectic phases). The proposed model is also related to that suggested for supermolecular structures of triblock copolymers. Thus, these molecules can be regarded as low molecular weight block compounds consisting of three different and incompatible molecular parts.

1. Introduction

Liquid crystalline materials are of great interest for material science as well as for life science. Their properties can be tuned by appropriate molecular design. Thus, it is well known that the mesomorphic properties of calamitic liquid crystals can largely be influenced by lateral substituents, like halogens,[1–3] alkyl or alkoxy groups.[4,5] This can influence the melting points, the mesophase types, the dielectric properties, *etc*. In most cases, however, a significant mesophase destabilization is connected with this structural variation. Especially large lateral groups suppress smectic phases and therefore nearly all calamitic mesogens with long lateral alkyl chains show exclusively nematic phases.[5] However, in rare cases lateral substituents can have a mesophase stabilizing effect. The earliest example was provided by the laterally substituted 5-alkoxy-



X = H: K 161.5 N 190 Iso

X = Cl: K 169 S_C 183 N 199 Iso

naphthoic acids.[6] The smectic tendency of the chloro substituted naphthoic acid is remarkably high, whereas the naphthoic acid without the lateral chloro substituent is only a nematic liquid crystal. It seems that a significant mesophase stabilizing effect is provided by the polar chloro substituent which can override its steric disturbance.

Likewise suitable molecular design, especially the introduction of electron withdrawing substituents like cyano or nitro in laterally attached aromatic rings, can produce strongly branched calamitic mesogens with unexpectedly high mesophase stabilities.[5,7]

We have synthesized a novel class of liquid crystals in which hydrophilic functional groups such as diol groups, polyether chains, carbohydrate units or ionic groups were laterally attached to a rigid rod-like oligo-*p*-phenylene rigid core. These molecules are of special interest, because two different organizing forces of liquid crystalline phases are perpendicularly directed to each other in these compounds (Fig. 1). Firstly, the tendency of the rigid calamitic units is to adopt an orientational long range order which is characteristic for thermotropic liquid crystals and provides nematic and smectic mesophases. Secondly, there is the tendency of amphiphilic molecules to segregate their incompatible (*e.g.* hydrophilic and hydrophobic) parts into segregated regions, giving rise to large aggregates which themselves are the basis of lamellar, columnar or cubic thermotropic and lyotropic mesophases.[8] In the compounds described here, the parallel arrangement of the rigid units should be disturbed by the segregation of hydrophilic and hydrophobic parts of the molecules and, conversely, the aggregation of the amphiphilic molecules should be disturbed because of the unfavorable size and shape of their lipophilic parts. Indeed, these unusual molecules represent a new class of amphiphiles with an unique organization in Langmuir films at the air–water interface,[9] but their liquid crystalline behavior is also remarkable. They represent novel amphotropic compounds[10] which can form thermotropic as well as lyotropic liquid crystalline phases.[11,12] The lyotropic phase behavior will be reported in detail in a separate paper.[13]

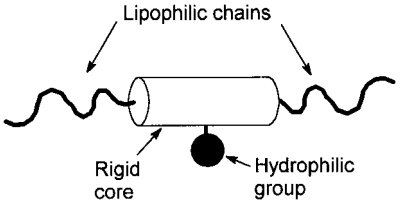
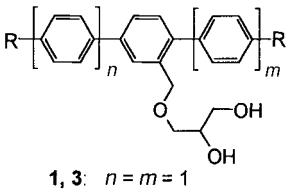
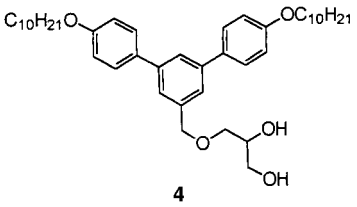


Fig. 1 Structure of the amphiphilic molecules under investigation.

Herein we describe the synthesis and summarize the results obtained during investigation of their thermotropic liquid crystalline properties.



1, 3: $n = m = 1$
5: $n = m = 2$
6: $n = 1; m = 0$
7: $n = m = 0$
11: $n = 0; m = 2$
13: $n = 2; m = 0$



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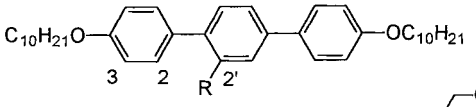
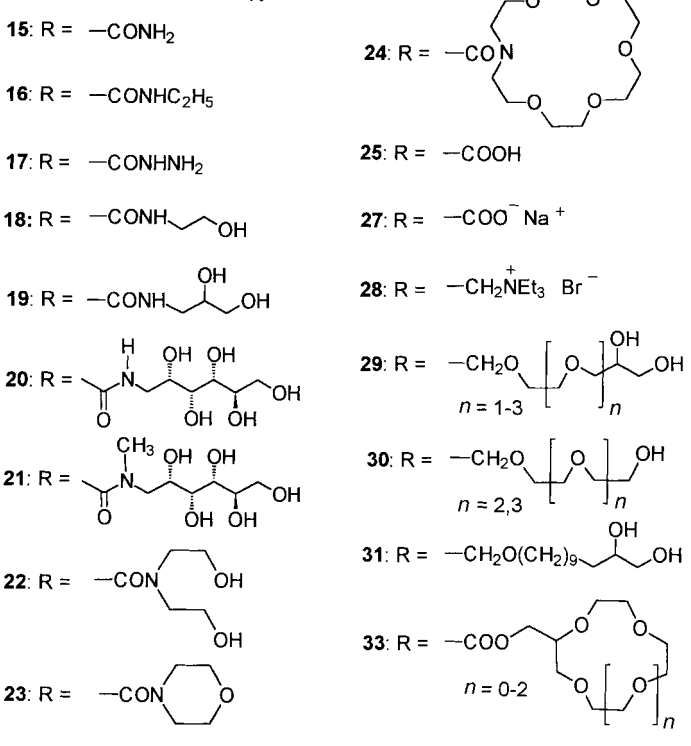
First the *p*-terphenyl derivatives **1** and **3** (**1**: R = alkoxy; **3**: R = alkyl, $n = m = 1$) both carrying a lateral 4,5-dihydroxy-2-oxapentyl group were synthesized and the influence of changes of the terminal substituents R was investigated. Afterwards we changed the structure of the rigid core. Besides *m*-terphenyl derivative **4**, a biphenyl derivative **6**, a molecule without a rigid unit **7** and a quinquaphenyl derivative **5** were synthesized. In the next step the position of the lateral hydrophilic group was shifted along the *p*-terphenyl unit (compounds **11** and **13**). Finally, a wide variation of the structure of the lateral hydrophilic group was carried out in the series of 4,4″-didecyloxy-*p*-terphenyl derivatives by appending amido groups (compounds **15**–**24**), ionic groups (compounds **27** and **28**), polyether chains (compounds **29**, **30** and **34**) or crown ethers (compounds **33**) to the 2′-position and in some cases to the 3-position of the *p*-terphenyl unit.

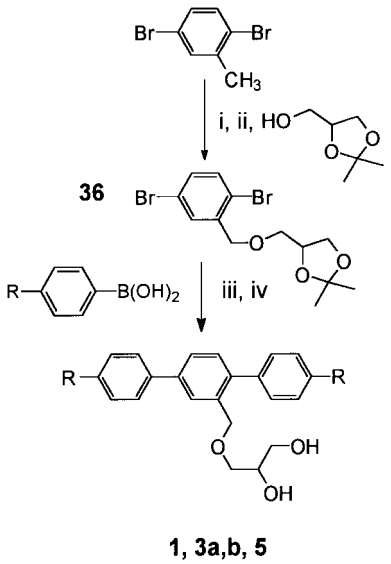
2. Syntheses

Pd^0-catalyzed cross-coupling reactions between aryl halides and arylboronic acids (Suzuki coupling)[14] represent the key steps of all syntheses which are outlined in Schemes 1–5. There are three different approaches to the compounds **1**–**3** and **29**–**31** all carrying a lateral group connected *via* an ether linkage to the 2′-position of the *p*-terphenyl rigid core. Compounds **1** and **3**, which all have the 4,5-dihydroxy-2-oxapentyl group but differ in the type of the terminal substituents, have been synthesized starting with 4-(2,5-dibromobenzyloxymethyl)-2,2-dimethyl-1,3-dioxolane **36** (Scheme 1). After cross-coupling of **36** with the appropriate 4-substituted phenylboronic acids, the 1,2-*O*-isopropylidene protecting groups were cleaved by acidolysis. In an analogous manner the quinquaphenyl derivative **5** was obtained by cross coupling of **36** with 4-(4-decyloxyphenyl)phenylboronic acid (Scheme 1).

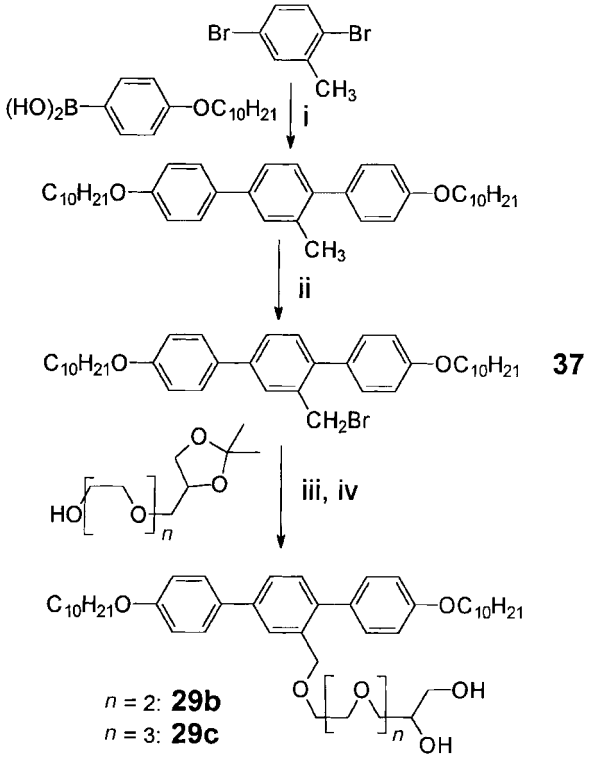
The terphenyl derivatives **29**–**31**, which differ in the structure of the lateral group in the 2′-position, and the optically active compound (*S*)-**1e** were synthesized using another strategy shown in Scheme 2 for the syntheses of compounds **29b** and **29c**. Here, the *p*-terphenyl rigid core was built up first and the lateral groups were introduced in a second step. This allowed a broad variation of the lateral hydrophilic groups. 2,5-Bis(4-decyloxyphenyl)toluene was obtained by cross coupling of two equivalents of 4-decyloxyphenylboronic acid with 2,5-dibromotoluene.[15] The methyl group was brominated using NBS.[15] The 2,5-bis(4-decyloxyphenyl)benzyl bromide **37**[15] obtained was afterwards etherified with different functionalized alcohols, followed by deprotection, if necessary. The best yields in the etherification step were obtained using phase transfer conditions. The optically active compound (*S*)-**1e** was obtained by etherification of **37** with enantiomerically pure (*R*)-(−)-4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane.







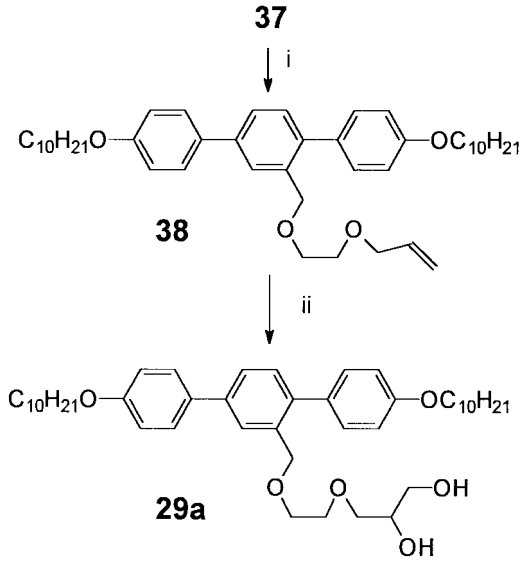
Scheme 1 *Reagents and conditions*: i, NBS, AIBN, *hv*, CCl_4, reflux, 2 h; ii, NaOH, H_2O, Bu_4NHSO_4, 60 °C, 15 h; iii, cat. $Pd(PPh_3)_4$, Na_2CO_3, H_2O, benzene–EtOH, reflux, 4 h; iv, HCl, H_2O–EtOH, reflux 2 h.



Scheme 2 *Reagents and conditions*: i, cat. $Pd(PPh_3)_4$, Na_2CO_3, H_2O, benzene–EtOH, reflux, 4 h; ii, NBS, AIBN, *hv*, CCl_4, reflux, 2 h; iii, NaOH, Bu_4NHSO_4, H_2O, reflux, 15 h; iv, HCl, H_2O–EtOH, reflux, 2 h.

Only compound **29a** carrying the 7,8-dihydroxy-2,5-dioxaoctyl group was prepared in a slightly different way, as shown in Scheme 3. The benzyl bromide **37** was at first etherified with 2-allyloxyethanol.[16] The resulting allyl ether **38** was dihydroxylated using catalytic amounts of OsO_4 in the presence of the oxidant *N*-methylmorpholine *N*-oxide.[17]

The amphiphiles **11**, **13** (Scheme 4), **34** and **35** (see Fig. 15) carrying their lateral substituents in the 2-position (compound **11**) or in the 3-position (compounds **13**, **34** and **35**) at the *p*-terphenyl rigid core were obtained in an analogous manner to the corresponding 2′-substituted materials, starting with the



Scheme 3 *Reagents and conditions*: i, $HOCH_2CH_2OCH_2CH{=}CH_2$, NaOH, Bu_4NHSO_4, H_2O, 60 °C, 12 h; ii, cat. OsO_4, NMMNO, acetone–H_2O, 25 °C, 24 h.

benzyl bromides **39** and **40**, respectively.[18] The benzyl bromides **39** and **40** were synthesized as outlined in Scheme 4.[18]

Also compound **7**, the biphenyl derivative **6** and the *m*-terphenyl derivative **4** were prepared in an analogous procedure to that given in Scheme 2 starting with 2,5-didecyloxybenzyl bromide,[18] 5-decyloxy-2-(4-decyloxyphenyl)benzyl bromide[19] and 3,5-bis(4-decyloxyphenyl)benzyl bromide,[20] respectively.

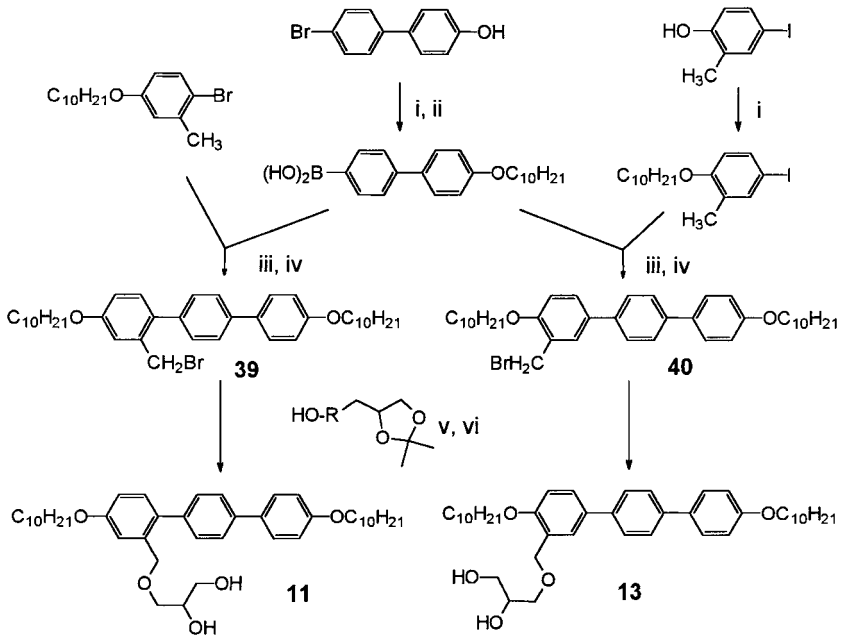
All 2,5-bis(4-decyloxyphenyl)benzoyl derivatives **15**–**24** were synthesized according to Scheme 5. Cross-coupling of methyl 2,5-dibromobenzoate is possible with $NaHCO_3$ as base in a water–glyme solvent system without saponification during the reaction (which would lead to a failure of the reaction).[15] The 2,5-bis(4-decyloxyphenyl)benzoic acid **25** which is obtained after saponification is treated with oxalyl chloride[21] to yield the acid chloride **26**. The use of oxalyl chloride at low temperatures is crucial, because other conditions (*e.g.* $SOCl_2$) would lead to an intramolecular Friedel–Crafts acylation with formation of 7-decyloxy-2-(4-decyloxyphenyl)fluoren-9-one. The acid chloride **26** was aminolyzed to give the amides **15**–**24**. The crown compounds **33** were obtained by esterification of **25** with 2-hydroxymethyl substituted crown ethers. The detailed procedure and the analytical data for the crown compounds **33** are reported in a separate paper concerning their monolayer behavior.[22]

Additionally, two ionic amphiphiles were synthesized. The ammonium salt **28** was obtained by quaternization of triethylamine with **37**.[23] The sodium carboxylate **27** was isolated after saponification of the methyl carboxylate **14**.

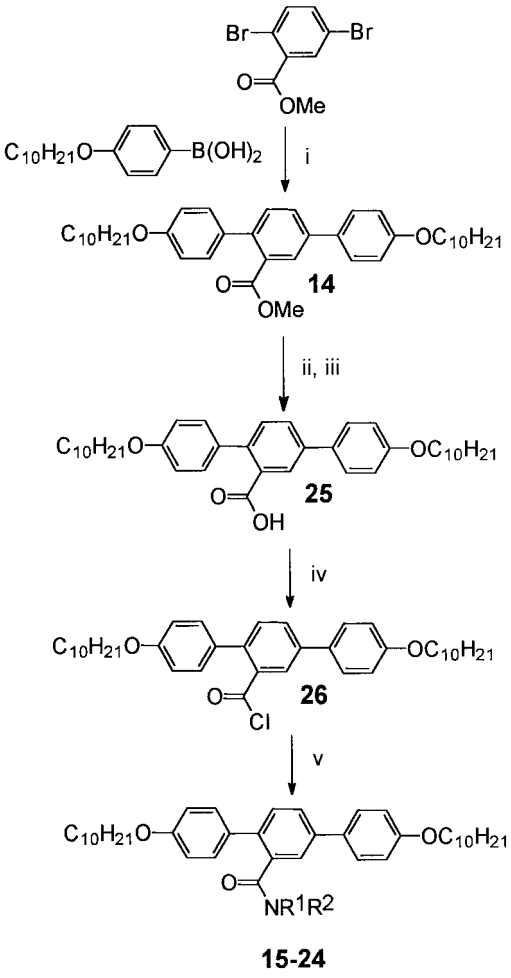
3. Experimental

3.1. General

Confirmation of the structures of intermediates and products was obtained by ^1H and ^{13}C NMR spectroscopy (Varian Unity 500 and Varian Gemini 200 spectrometers) and by mass spectrometry (Intectra GmbH, AMD 402, electron impact, 70 eV). All materials were purified by chromatography and/or recrystallization until constant transition temperatures were obtained. The purity was checked by thin layer chromatography (TLC, aluminum sheets, silica gel 60 F254 from Merck) and elemental analysis. Some compounds take up moisture during sample preparation which causes a deviation of the microanalysis from the calculated values. In these cases the



Scheme 4 *Reagents and conditions*: i, $C_{10}H_{21}Br$, K_2CO_3, CH_3CN, reflux, 17 h; ii, BuLi, THF, −78 °C, then $B(OMe)_3$, −70 °C, then HCl, H_2O; iii, cat. $Pd(PPh_3)_4$, Na_2CO_3, H_2O–EtOH, reflux, 4 h; iv, NBS, AIBN, *hv*, CCl_4, reflux, 2 h; v, NaOH, Bu_4NHSO_4, H_2O, reflux, 12 h; vi, HCl, H_2O–EtOH, reflux, 2 h.



Scheme 5 *Reagents and conditions*: i, cat. $Pd(PPh_3)_4$, $NaHCO_3$, Glyme, H_2O, reflux, 5 h; ii, NaOH, H_2O, reflux, 4 h; iii, HCl, H_2O, reflux, 2 h; iv, $(COCl)_2$, 25 °C, 1 h; v, HNR^1R^2, DMF, 80 °C, 4 h.

purity (>99%) was additionally checked by HPLC (Merck-Hitachi, RP-18, CH_2Cl_2–methanol 1:1).

Microanalyses were performed using an LECO CHNS-932 elemental analyzer. 2,5-Dibromotoluene (Acros), *N*-bromosuccinimide (Merck), oxalyl chloride (Lancaster), osmium tetroxide (Berlin Chemie), *N*-methylmorpholine *N*-oxide solution (Aldrich), 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (Aldrich), (*R*)-(−)-4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (Aldrich), 3-aminopropane-1,2-diol (Merck), 1-amino-1-deoxy-D-glucitol (Fluka), 1-deoxy-1-methylamino-D-glucitol (Acros) and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (Aldrich) were used as obtained. 2-Allyloxyethanol, phenylboronic acids,[24] 4-(7-hydroxy-2,5-dioxaheptyl)-2,2-dimethyl-1,3-dioxolane,[25] 4-(10-hydroxy-2,5,8-trioxadecyl)-2,2-dimethyl-1,3-dioxolane,[25] 4-(9-hydroxynonyl)-2,2-dimethyl-1,3-dioxolane,[26] bromomethyl-substituted 4,4″-didecyloxy-*p*-terphenyls **37**[15], **39**[18] and **40**[18] and methyl 2,5-bis(4-decyloxyphenyl)benzoate **14**[15] were obtained according to the procedures described in the corresponding references. Transition temperatures were measured 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, the transition enthalpies are collected in Table 1). Because some of the compounds are very hygroscopic, the samples were dried prior to investigation either *in vacuo* over phosphorus pentoxide for 48 h or by heating for 1 min to a temperature of approximately 150 °C. Afterwards the samples were immediately sealed and investigated.

3.2. Synthesis of the terphenyl derivatives 1 and 3

3.2.1. 4-(2,5-Dibromobenzyloxymethyl)-2,2-dimethyl-1,3-dioxolane 36. A solution of 2,5-dibromotoluene (20 mmol, 5 g) and *N*-bromosuccinimide (24 mmol, 4.27 g) in dry tetrachloromethane (50 ml) was placed in a quartz flask and heated to the boiling point. AIBN (50 mg) was added and the refluxing mixture was irradiated with UV light (366 nm). After 2 h the mixture was cooled to room temperature and the succinimide formed was filtered off. The solvent was removed *in vacuo* and the residue was purified by crystallization from ethanol. Yield:

Table 1 Phase transition enthalpies[a]

Compound		ΔH/kJ mol^{-1}						
1b	K–Iso	43.2			S_A–Iso	1.2		
1c	K–S_A	37.2			S_A–Iso	3.8		
1d	K–S_A	50.5			S_A–Iso	4.4		
1e	K–S_A	55.5			S_A–Iso	6.1		
1f	K–S_A	66.2			S_A–Iso	6.8		
1g	K–S_A	60.7			S_A–Iso	7.6		
1h	K–S_A	70.7			S_A–Iso	8.0		
2	K–Iso	60.1					N–Iso	3.4
3b	K–S_A	30.8			S_A–Iso	3.7		
5	K–S_A	29.2			S_A–Iso	9.0		
6	K–Iso	24.7			S_A–Iso	2.7		
9	K–S_A	49.1			S_A–N	0.8	N–Iso	1.4
10	K–S_A	51.5			S_A–Iso	6.7		
11	K–S_A	42.9			S_A–Iso	7.8		
12	K–S_C	12.1			S_C–S_A–Iso	9.2		
13	K–S_A	35.7			S_A–Iso	8.6		
17	K–S_A	71.4			S_A–Iso	6.3		
18	K–S_A	74.6			S_A–Iso	5.0		
19	K–S_A	47.3			S_A–Iso	3.3		
20	K–S_A	25.5			S_A–Iso	1.6		
22	K–Iso	28.3			S_A–Iso	2.3		
29b	K–Iso	45.2	Col_r–S_A	1.2	S_A–Iso	0.5		
29c	K–Iso	43.2	Col_r–Iso	1.9				
30b	K–Iso	49.3			S_A–Iso	0.7		
32	K–Iso	51.8						
33a	K–Iso	61.6			S_A–N	0.4	N–Iso	1.0
33b	K–Iso	0.8			S_A–N–Iso	0.9		
33c	K–Iso	42.1			S_A–N	0.1	N–Iso	0.4
34a	K–S_A	40.0			S_A–Iso	5.7		
34b	K–S_A	23.6			S_A–Iso	2.7		
34c	K–S_A	36.7			S_A–Iso	1.0		

[a]Abbreviations: K = crystalline solid, N = nematic phase, S_A = smectic A phase, S_C = smectic C phase, Col_r = rectangular columnar mesophase, Iso = isotropic liquid.

60%; mp 89 °C; δ_H(200 MHz, acetone, J/Hz) 4.69 (s, 2H, $PhCH_2Br$), 7.45 (dd, J 8.5, 2.4, 1H, H-Ar), 7.60 (d, J 8.5, 1H, H-Ar), 7.82 (d, J 2.4, 1H, H-Ar). The 2,5-dibromobenzyl bromide obtained in this way was used without further purification for the next step.

In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, Bu_4NHSO_4 (30 mg) was added to a mixture consisting of 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (0.1 mol, 13.2 g), 2,5-dibromobenzyl bromide (0.01 mol, 3.3 g) and 50% aq. NaOH (15 ml) under argon atmosphere. The mixture was stirred rapidly at 60 °C for 15 h. After cooling 50 ml water and 50 ml diethyl ether were added. The organic phase was separated and the aqueous phase was extracted three times with diethyl ether (100 ml). The combined organic phases were dried with Na_2SO_4 and afterwards, the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, chloroform). Yield: 42%; yellow oil; δ_H(500 MHz, $CDCl_3$, J/Hz) 1.37 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 3.57 (dd, J 10.0, 5.1, 1H, $PhCH_2OCH_AH_B$), 3.64 (dd, J 10.0, 5.6, 1H, $PhCH_2OCH_AH_B$), 3.78 (dd, J 8.3, 6.3, 1H, OCH_AH_B), 4.08 (dd, J 8.3, 6.4, 1H, OCH_AH_B), 4.31–4.35 (m, 1H, C*H*O), 4.57 (m, 2H, $PhCH_2O$), 7.25 (dd, J 8.3, 2.4, 1H, H-Ar), 7.36 (d, J 8.3, 1H, H-Ar), 7.62 (d, J 2.4, 1H, H-Ar).

3.2.3. General procedure for the Pd-catalyzed cross-coupling reactions. In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, $Pd(PPh_3)_4$ (0.03 mmol, 35 mg, 3 mol%) was added under an argon atmosphere to a mixture consisting of the appropriate dibromobenzene derivative (1 mmol), the boronic acid (2.4 mmol), benzene (30 ml), ethanol (30 ml) and 2 M Na_2CO_3 solution (30 ml). The mixture was stirred at reflux temperature for 4 h. After cooling the solvent was evaporated and the residue dissolved in diethyl ether (30 ml) and water (30 ml). The organic phase was separated and the aqueous phase was extracted twice with diethyl ether (50 ml). The combined organic phases were washed with brine and dried with Na_2SO_4. The solvent was removed *in vacuo* and the products obtained were purified by column chromatography (silica gel, chloroform).

4-[2,5-Bis(4-decyloxyphenyl)benzyloxymethyl]-2,2-dimethyl-1,3-dioxolane. δ_H(200 MHz, $CDCl_3$, J/Hz) 0.87 (t, J 6.7, 6H, CH_3), 1.18–1.27 (m, 28H, CH_2), 1.34 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.73–1.86 (m, 4H, OCH_2CH_2), 3.42 (dd, J 9.8, 5.8, 1H, $PhCH_2OCH_AH_B$), 3.53 (dd, J 9.7, 5.5, 1H, $PhCH_2OCH_AH_B$), 3.71 (dd, J 8.3, 6.3, 1H, OCH_AH_B), 3.96–4.20 (m, 5H, OCH_AH_B, $PhOCH_2$), 4.23–4.29 (m, 1H, C*H*O), 4.50 (s, 2H, $PhCH_2O$), 6.93 (d, J 8.7, 2H, H-Ar), 6.96 (d, J 8.7, 2H, H-Ar), 7.26–7.28 (m, 2H, H-Ar), 7.29 (d, J 8.7, 1H, H-Ar), 7.48–7.53 (m, 1H, H-Ar), 7.55 (d, J 8.7, 2H, H-Ar), 7.70 (d, J 1.8, 1H, H-Ar).

3.2.4. Deprotection of the 1,2-diol groups. The 2,2-dimethyl-1,3-dioxolane derivatives obtained by the cross-coupling reactions were used, without further purification, for deprotection. The appropriate 2,2-dimethyl-1,3-dioxolane derivative (1 mmol) was dissolved in ethanol (50 ml) and 10% hydrochloric acid (10 ml) was added. Then, the mixture was heated under reflux for 2 h. After cooling the solvent was evaporated and 50 ml water and 50 ml diethyl ether were added to the residue. The aqueous phase was extracted three times with diethyl ether (30 ml). Afterwards, the combined organic phases were washed with saturated $NaHCO_3$ solution and water, and dried with Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified by column chromatography and recrystallization.

5-[2,5-Bis(4-ethoxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1a***. Synthesized from **36** and 4-ethoxyphenylboronic acid. Crystallized from light petroleum (60–80 °C). Yield: 46%; transitions/°C: K 124 (N 58) Iso; elemental analysis (%): found (calc. for $C_{26}H_{30}O_5$): C, 73.82 (73.91); H, 7.29 (7.16); δ_H(200 MHz, $CDCl_3$, J/Hz) 1.43 (2t, J 6.9, 6H, CH_3), 1.76 (s, broad, 2H, OH), 3.4–3.7 (m, 4H, OCH_2), 3.75–3.9 [m, 1H, C*H*(OH)], 4.06 (t, J 6.8, 2H, $PhOCH_2$), 4.09 (t, J 7.0, 2H, $PhOCH_2$), 4.49 (s, 2H, $PhCH_2O$), 6.93 (d, J 8.5, 2H, H-Ar), 6.98 (d, J 8.6, 2H, H-Ar), 7.3–7.35 (m, 3H, H-Ar), 7.5–7.6 (m, 3H, H-Ar), 7.63 (d, J 1.8, 1H, H-Ar); m/z (%) 422 ($[M]^+$, 100).

5-[2,5-Bis(4-hexyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1b***. Synthesized from **36** and 4-hexyloxyphenylboronic acid. Crystallized from n-hexane. Yield: 44%; transitions/°C: K 80 (S_A 71) Iso; elemental analysis (%): found (calc. for $C_{34}H_{46}O_5$): C, 75.73 (76.37); H, 8.83 (8.67); δ_H(200 MHz, $CDCl_3$, J/Hz) 0.91 (t, J 6.3, 6H, CH_3), 1.21–1.58 (m, 12H, CH_2), 1.69–1.88 (m, 4H, OCH_2CH_2), 1.95 (dd, 1H, CH_2OH), 2.42 [d, 1H, CH(O*H*)], 3.45–3.68 (m, 4H, OCH_2), 3.74–3.86 [m, 1H, C*H*(OH)], 3.99 (t, J 6.2, 4H, $PhOCH_2$), 4.49 (s, 2H, $PhCH_2O$), 6.91 (d, J 8.5, 2H, H-Ar), 6.96 (d, J 8.6, 2H, H-Ar), 7.29 (d, J 8.5, 2H, H-Ar), 7.31 (d, J 8.3, 1H, H-Ar), 7.49–7.59 (m, 3H, H-Ar), 7.62 (d, J 1.8, 1H, H-Ar); m/z (%) 534 ($[M]^+$, 100).

5-[2,5-Bis(4-octyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1c***. Synthesized from **36** (1 mmol, 380 mg) and 4-octyloxyphenylboronic acid (2.4 mmol, 600 mg). Crystallized from light petroleum (60–80 °C) and afterwards from methanol. Yield: 35%; transitions/°C: K 79 S_A 102 Iso; elemental analysis (%): found (calc. for $C_{38}H_{54}O_5$): C, 77.19 (77.25); H, 9.03 (9.21); δ_H(200 MHz, $CDCl_3$, J/Hz) 0.88 (t, J 6.6, 6H, CH_3), 1.29–1.37 (m, 16H, CH_2), 1.43–1.48 (m, 4H, $OCH_2CH_2CH_2$), 1.76–1.83 (m, 4H, OCH_2CH_2), 3.48–3.68 (m, 4H, OCH_2), 3.80–3.89 [m, 1H, C*H*(OH)], 3.99 (t, J 6.5, 4H, $PhOCH_2$), 4.50 (s, 2H, $PhCH_2O$), 6.93–6.98 (m, 4H, H-Ar), 7.28 (d, J 8.4, 2H, H-

Ar), 7.31 (d, *J* 8.0, 1H, H-Ar), 7.51–7.53 (m, 1H, H-Ar), 7.54 (d, *J* 8.6, 2H, H-Ar), 7.64 (d, *J* 1.6, 1H, H-Ar).

5-[2,5-Bis(4-nonyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1d***. Synthesized from **36** (1 mmol, 380 mg) and 4-nonyloxyphenylboronic acid (2.4 mmol, 632 mg). Crystallized from light petroleum (60–80 °C). Yield: 32%; transitions/°C: K 82 S_A 106 Iso; elemental analysis (%): found (calc. for $C_{40}H_{58}O_5$): C, 77.56 (77.63); H, 9.53 (9.45); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.86 (t, *J* 6.4, 6H, CH_3), 1.27–1.34 (m, 20H, CH_2), 1.42–1.47 (m, 4H, $OCH_2CH_2CH_2$), 1.75–1.82 (m, 4H, OCH_2CH_2), 3.44–3.67 (m, 4H, OCH_2), 3.80–3.85 [m, 1H, C*H*(OH)], 3.98 (t, *J* 6.6, 4H, $PhOCH_2$), 4.50 (s, 2H, $PhCH_2O$), 6.92–6.97 (m, 4H, H-Ar), 7.26–7.31 (m, 3H, H-Ar), 7.49–7.54 (m, 3H, H-Ar), 7.63 (d, *J* 2.0, 1H, H-Ar).

5-[2,5-Bis(4-decyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1e***. Synthesized from **36** and 4-decyloxyphenylboronic acid. Crystallized from n-hexane. Yield: 54%; transitions/°C: K 83 S_A 114 Iso; elemental analysis (%): found (calc. for $C_{42}H_{62}O_5$): C, 77.74 (77.98); H, 9.85 (9.66); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.18–1.58 (m, 28H, CH_2), 1.71–1.89 (m, 4H, OCH_2CH_2), 3.43–3.72 (m, 4H, OCH_2), 3.77–3.91 [m, 1H, C*H*(OH)], 3.99 (t, *J* 6.5, 4H, $PhOCH_2$), 4.50 (s, 2H, $PhCH_2O$), 6.92 (d, *J* 8.6, 2H, H-Ar), 6.96 (d, *J* 8.7, 2H, H-Ar), 7.29 (d, *J* 8.5, 2H, H-Ar), 7.33 (d, *J* 8.2, 1H, H-Ar), 7.4–4.5 (m, 1H, H-Ar), 7.55 (d, *J* 8.8, 2H, H-Ar), 7.64 (d, *J* 1.8, 1H, H-Ar); δ_C(125 MHz, $CDCl_3$) 14.09 (CH_3), 22.67, 26.08, 26.10, 29.32, 29.41, 29.56, 29.60, 31.91 (CH_2), 64.08 (CH_2OH), 68.15 ($PhOCH_2$), 68.17 ($PhOCH_2$), 70.53 [$OCH_2CH(OH)$], 71.80 [$OCH_2CH(OH)$], 72.03 ($PhCH_2O$), 114.26, 114.90, 126.19, 127.60, 128.05, 130.16, 130.68, 132.67, 132.92, 135.22, 139.81, 140.14, 158.57, 158.89 (C-Ar); *m*/*z* (%) 646 ([M]$^+$, 100).

5-[2,5-Bis(4-undecyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1f***. Synthesized from **36** (1 mmol, 380 mg) and 4-undecyloxyphenylboronic acid (2.4 mmol, 701 mg). Crystallized from light petroleum (60–80 °C). Yield: 39%; transitions/°C: K 89 S_A 114 Iso; elemental analysis (%): found (calc. for $C_{44}H_{66}O_5$): C, 78.46 (78.24); H, 9.63 (9.86); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.86 (t, *J* 6.5, 6H, CH_3), 1.26–1.46 (m, 32H, CH_2), 1.76–1.83 (m, 4H, OCH_2CH_2), 3.43–3.71 (m, 4H, OCH_2), 3.79–3.86 [m, 1H, C*H*(OH)], 3.99 (t, *J* 6.5, 4H, $PhOCH_2$), 4.50 (s, 2H, $PhCH_2O$), 6.94 (d, *J* 8.6, 2H, H-Ar), 6.96 (d, *J* 8.8, 2H, H-Ar), 7.26–7.33 (m, 3H, H-Ar), 7.49–7.56 (m, 3H, H-Ar), 7.63 (d, *J* 2.0, 1H, H-Ar).

5-[2,5-Bis(4-dodecyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1g***. Synthesized from **36** and 4-dodecyloxyphenylboronic acid. Crystallized first from light petroleum (60–80 °C) and afterwards from methanol. Yield: 47%; transitions/°C: K 86 S_A 116 Iso; δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.6, 6H, CH_3), 1.27–1.55 (m, 36H, CH_2), 1.77–1.84 (m, 4H, OCH_2CH_2), 1.99 (br s, 2H, OH), 3.42–3.75 (m, 4H, OCH_2), 3.76–3.94 [m, 1H, C*H*(OH)], 3.99 (t, *J* 6.6, 4H, $PhOCH_2$), 4.50 (s, 2H, $PhCH_2O$), 6.9–7.0 (m, 4H, H-Ar), 7.27–7.39 (m, 3H, H-Ar), 7.5–7.7 (m, 4H, H-Ar); *m*/*z* (%) 702 ([M]$^+$, 100).

5-[2,5-Bis(4-tetradecyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***1h***. Synthesized from **36** and 4-tetradecyloxyphenylboronic acid. Crystallized from ethanol. Yield: 48%; transitions/°C: K 95 S_A 118 Iso; elemental analysis (%): found (calc. for $C_{50}H_{78}O_5$): C, 78.82 (79.09); H, 10.35 (10.36); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.4, 6H, CH_3), 1.1–1.6 (m, 42H, CH_2), 1.7–1.9 (m, 4H, OCH_2CH_2), 3.37–3.73 (m, 4H, OCH_2), 3.78–3.91 [m, 1H, C*H*(OH)], 3.99 (t, *J* 6.3, 4H, $PhOCH_2$), 4.50 (s, 2H, $PhCH_2O$), 6.93 (d, *J* 8.4, 2H, H-Ar), 6.96 (d, *J* 8.6, 2H, H-Ar), 7.29 (d, *J* 8.3, 2H, H-Ar), 7.31 (d, *J* 8.2, 1H, H-Ar), 7.47–7.56 (m, 3H, H-Ar), 7.63 (d, *J* 1.8, 1H, H-Ar); *m*/*z* (%) 758 ([M]$^+$, 100).

5-[2,5-Bis(4-propylphenyl)phenyl]-4-oxapentane-1,2-diol ***3a***. Synthesized from **36** and 4-propylphenylboronic acid. Crystallized from n-hexane. Yield: 37%; mp 60 °C; elemental analysis (%): found (calc. for $C_{28}H_{34}O_3$): C, 79.72 (80.35); H, 7.96 (8.19); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.97 (t, *J* 7.2, 3H, CH_3), 0.98 (t, *J* 7.2, 3H, CH_3), 1.59–1.78 (m, 4H, CH_2), 2.62 (t, *J* 7.5, 4H, $PhCH_2$), 3.4–3.7 (m, 4H, CH_2O), 3.7–3.9 [m, 1H, C*H*(OH)], 4.52 (s, 2H, $PhCH_2O$), 7.20–7.31 (m, 7H, H-Ar), 7.52–7.59 (m, 3H, H-Ar), 7.62 (d, *J* 2.0, 1H, H-Ar); *m*/*z* (%) 418 ([M]$^+$, 100).

5-[2,5-Bis(4-undecylphenyl)phenyl]-4-oxapentane-1,2-diol ***3b***. Synthesized from **36** and 4-undecylphenylboronic acid. Crystallized from n-hexane. Yield: 46%; transitions/°C: K 63 S_A 78 Iso; elemental analysis (%): found (calc. for $C_{44}H_{66}O_3$): C, 81.98 (82.19); H, 10.52 (10.35); δ_H(250 MHz, $CDCl_3$, *J*/Hz) 0.71 (t, *J* 6.5, 6H, CH_3), 1.0–1.3 (m, 32H, CH_2), 1.5–1.6 (m, 4H, CH_2), 1.73 (dd, *J* 4.0, 1H, CH_2OH), 2.34 [d, *J* 5.0, 1H, CH(O*H*)], 2.47 (t, *J* 6.4, 4H, $PhCH_2$), 3.3–3.6 (m, 4H, OCH_2), 3.6–3.7 [m, 1H, C*H*(OH)], 4.37 (s, 2H, $PhCH_2O$), 7.1–7.45 (m, 10H, H-Ar), 7.51 (d, *J* 1.4, 1H, H-Ar).

3.3. 5-{2,5-Bis[4-[4-decyloxyphenyl)phenyl]phenyl}-4-oxapentane-1,2-diol 5

Synthesized from **36** (1 mmol, 380 mg) and 4-(4-decyloxyphenyl)phenylboronic acid (2.4 mmol, 850 mg) according to procedures 3.2.3 and 3.2.4. Crystallized from n-hexane–ethyl acetate. Yield: 43%; transitions/°C: K 152 S_A 258 Iso; elemental analysis (%): found (calc. for $C_{54}H_{70}O_5$): C, 80.92 (81.16); H, 8.98 (8.83); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.88 (t, *J* 6.4, 6H, CH_3), 1.2–1.6 (m, 28H, CH_2), 1.7–1.9 (m, 4H, OCH_2CH_2), 1.94 (dd, *J* 4.0, 1H, CH_2OH), 2.43 [d, *J* 5.0, 1H, CH(O*H*)], 3.5–3.77 (m, 4H, OCH_2), 3.8–3.95 [m, 1H, C*H*(OH)], 4.00 (t, *J* 6.5, 4H, $PhOCH_2$), 4.57 (s, 2H, $PhCH_2O$), 6.98 (d, *J* 8.8, 4H, H-Ar), 7.4–7.7 (m, 14H, H-Ar), 7.76 (d, *J* 1.7, 1H, H-Ar); *m*/*z* (%) 798 ([M]$^+$, 100).

3.4. Synthesis of the diols (*S*)-1e, 4, 6, 7, 11, 13, 29b,c, 31, 34b,c, 35a,b

3.4.1. General procedure for the synthesis of benzyl ethers. In a two-necked flask equipped with a reflux condenser and a magnetic stirring bar, Bu_4NHSO_4 (5 mg) and 50% aq. NaOH (3 ml) were added to a solution of the alcohol (15 mmol) and the benzyl bromide (1.5 mmol) in 10 ml toluene under argon atmosphere. The mixture was stirred violently at 60 °C for 15 h. After cooling 30 ml water and 30 ml diethyl ether were added. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried with Na_2SO_4 and afterwards the solvent was removed *in vacuo*. The residue was purified by column chromatography.

3.4.2. Deprotection of the 1,2-diol group. The 2,2-dimethyl-1,3-dioxolane derivatives obtained were used, without further purification, for deprotection as described in 3.2.4.

(*S*)-5-[2,5-Bis(4-decyloxyphenyl)phenyl]-4-oxapentane-1,2-diol (*S*)-1e. Synthesized from (*R*)-(−)-4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and **37**. Eluent: chloroform–methanol (10 : 1). Crystallized from n-hexane. Yield: 28%; transitions/°C: K 83 S_A 114 Iso; elemental analysis (%): found (calc. for $C_{42}H_{62}O_5$): C, 77.86 (77.96); H, 9.70 (9.67); $[\alpha]_{589}^{25}$ +1.9, $[\alpha]_{436}^{25}$ +4.9 (*c* 1.0, $CHCl_3$); all other analytical data correspond to those given for *rac*-**1e**.

5-[3,5-Bis(4-decyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***4***. Synthesized from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and 3,5-bis(4-decyloxyphenyl)benzyl bromide.[20] Eluent: chloroform–methanol (10:1). Crystallized from n-hexane–ethyl acetate. Yield: 43%; mp 67 °C; elemental analysis (%): found (calc. for $C_{42}H_{62}O_5$): C, 77.88 (77.98); H, 9.78 (9.66); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.2–1.5 (m, 28H, CH_2), 1.7–1.8 (m, 4H, OCH_2CH_2), 2.06 (br s, 1H, CH_2OH), 2.59 [br s, 1H, CH(O*H*)], 3.58–3.68 (m, 3H, CH_2OH, OCH_AH_B), 3.72 (dd, *J* 11.3, 3.8, 1H, OCH_AH_B), 3.92 [m, 1H, CH(OH)], 3.99 (t, *J* 6.5, 4H, $PhOCH_2$), 4.64 (s, 2H, $PhCH_2O$), 6.96 (d, *J* 8.6, 4H, H-Ar), 7.41 (d, *J* 1.6, 2H, H-Ar), 7.53 (d, *J* 8.7, 4H, H-Ar), 7.64 (d, *J* 1.6, 1H, H-Ar); *m*/*z* (%) 646 ($[M]^+$, 100).

5-[5-Decyloxy-2-(4-decyloxyphenyl)phenyl]-4-oxapentane-1,2-diol ***6***. Synthesized from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and 5-decyloxy-2-(4-decyloxyphenyl)benzylbromide.[18] Eluent: chloroform–methanol (10:0.5). Crystallized from methanol. Yield: 20%; transitions/°C: K 43 (S_A 28) Iso; elemental analysis (%): found (calc. for $C_{36}H_{58}O_5$): C, 75.58 (75.75); H, 10.37 (10.24); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.86 (t, *J* 6.5, 6H, CH_3), 1.2–1.4 (m, 24H, CH_2), 1.4–1.5 (m, 4H, $OCH_2CH_2CH_2$), 1.7–1.8 [m, 4H, OCH_2CH_2), 1.96 (dd, *J* 6.0, 6.0, 1H, CH_2OH), 2.43 [d, *J* 5.1 1H, CH(O*H*)], 3.43 (dd, *J* 9.6, 6.2, 1H, OCH_AH_B), 3.48 (dd, *J* 9.5, 3.9 1H, OCH_AH_B), 3.54–3.6 (m, 1H, CH_AH_BOH), 3.62–3.69 (m, 1H, CH_AH_BOH), 3.78–3.85 [m, 1H, CH(OH)], 3.96 (t, *J* 6.5, 2H, $PhOCH_2$), 3.97 (t, *J* 6.5, 2H, $PhOCH_2$), 4.41 (s, 2H, $PhCH_2O$), 6.86 (dd, *J* 8.6, 2.7, 1H, H-Ar), 6.91 (d, *J* 8.8, 2H, H-Ar), 6.99 (d, *J* 2.4, 1H, H-Ar), 7.16 (d, *J* 8.6, 1H, H-Ar), 7.19 (d, *J* 8.8, 2H, H-Ar); δ_C(125 MHz, $CDCl_3$) 14.08 (CH_3), 22.67, 26.10, 29.32, 29.35, 29.42, 29.56, 29.59, 31.90 (CH_2), 64.10 (CH_2OH), 68.14 ($PhOCH_2$), 68.16 ($PhOCH_2$), 70.51 [$OCH_2CH(OH)$], 71.68 [$OCH_2CH(OH)$], 71.99 ($PhCH_2O$), 113.87, 114.18, 114.45, 115.03, 130.24, 131.23, 132.77, 134.0, 136.18, 158.30, 158.39 (C-Ar); *m*/*z* (%) 570 ($[M]^+$, 100).

5-(2,5-Didecyloxphenyl)-4-oxapentane-1,2-diol ***7***. Synthesized from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and 2,5-didecyloxybenzyl bromide.[18] Eluent: chloroform–methanol (10:0.5). Crystallized from n-pentane. Yield: 34%; mp 42 °C; elemental analysis (%): found (calc. for $C_{30}H_{54}O_5$): C, 72.65 (72.83); H, 11.34 (11.00); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.85 (t, *J* 6.4, 6H, CH_3), 1.1–1.5 (m, 28H, CH_2), 1.7–1.8 (m, 4H, OCH_2CH_2), 2.18 (br s, 1H, CH_2OH), 2.76 [br s, 1H, CH(O*H*)], 3.5–3.7 [m, 5H, OCH_2, CH(OH)], 3.87 (t, *J* 6.5, 2H, $PhOCH_2$), 3.89 (t, *J* 6.6, 2H, $PhOCH_2$), 4.50 (d, *J* 11.9, 1H, $PhCH_AH_BO$), 4.57 (d, *J* 12.1, 1H, $PhCH_AH_BO$), 6.75 (s, 1H, H-Ar), 6.76 (s, 1H, H-Ar), 6.87 (s, 1H, H-Ar); *m*/*z* (%) 494 ($[M]^+$, 100).

5-{5-Decyloxy-2-[4-(4-decyloxyphenyl)phenyl]phenyl}-4-oxapentane-1,2-diol ***11***. Synthesized from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and **39**. Eluent: chloroform–methanol (10:0.5). Crystallized from n-hexane. Yield: 23%; transitions/°C: K 86 S_A 114 Iso; elemental analysis (%): found (calc. for $C_{42}H_{62}O_5$): C, 77.83 (77.98); H, 9.79 (9.66); δ_H (200 MHz, $CDCl_3$, *J*/Hz) 0.88 (t, *J* 6.5, 6H, CH_3), 1.2–1.6 (m, 28H, CH_2), 1.75–1.84 (m, 4H, OCH_2CH_2), 1.92 (dd, *J* 6.0, 6.0, 1H, CH_2OH), 2.41 [d, *J* 5.1, 1H, CH(O*H*)], 3.44–3.52 (m, 2H, OCH_2), 3.55–3.60 (m, 1H, CH_AH_BOH), 3.62–3.68 (m, 1H, CH_AH_BOH), 3.79–3.85 [m, 1H, CH(OH)], 3.98 (t, *J* 6.5, 2H, $PhOCH_2$), 3.99 (t, *J* 6.5, 2H, $PhOCH_2$), 4.47 (s, 2H, $PhCH_2O$), 6.89 (dd, *J* 8.6, 2.6, 1H, H-Ar), 6.96 (d, *J* 8.8, 2H, H-Ar), 7.08 (d, *J* 2.4, 1H, H-Ar), 7.22 (d, *J* 8.8, 1H, H-Ar), 7.34 (d, *J* 8.1, 2H, H-Ar), 7.52–7.59 (2d, 4H, H-Ar); δ_C(50 MHz, $CDCl_3$) 14.09 (CH_3), 22.65, 26.05, 29.30, 29.39, 29.55, 31.87 (CH_2), 64.02 (CH_2OH), 68.10 ($PhOCH_2$), 70.47 [$OCH_2CH(OH)$], 71.64 [$OCH_2CH(OH)$], 71.99 ($PhCH_2O$), 113.90, 114.84, 115.12, 126.37, 128.01, 129.60, 131.21, 132.94, 133.87, 136.13, 138.87, 139.43, 158.61, 158.83 (C-Ar); *m*/*z* (%) 646 ($[M]^+$, 100).

5-{2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]phenyl}-4-oxapentane-1,2-diol ***13***. Synthesized from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and **40**. Eluent: chloroform–methanol (10:1). Crystallized from n-hexane. Yield: 21%; transitions/°C: K 75 S_A 144 Iso; elemental analysis (%): found (calc. for $C_{42}H_{62}O_5$): C, 77.69 (77.98); H, 9.82 (9.66); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.88 (t, *J* 6.5, 6H, CH_3), 1.2–1.4 (m, 24H, CH_2), 1.4–1.5 (m, 4H, $OCH_2CH_2CH_2$), 1.75–1.85 (m, 4H, OCH_2CH_2), 2.14 (br s, 1H, CH_2OH), 2.72 [br s, 1H, CH(O*H*)], 3.6–3.8 (m, 4H, OCH_2), 3.88–3.95 [m, 1H, CH(OH)], 3.99 (t, *J* 6.6, 2H, $PhOCH_2$), 4.02 (t, *J* 6.6, 2H, $PhOCH_2$), 4.62 (d, *J* 12.0, 1H, $PhCH_AH_BO$), 4.66 (d, *J* 12.0, 2H, $PhCH_AH_BO$), 6.93 (d, *J* 8.5, 1H, H-Ar) 6.96 (d, *J* 8.7, 2H, H-Ar), 7.2–7.6 (m, 3H, H-Ar), 7.59 (s, 5H, H-Ar); δ_C(125 MHz, $CDCl_3$) 14.07 (CH_3), 22.66, 26.07, 26.11, 29.27, 29.31, 29.38, 29.41, 29.58, 29.60, 31.90, (CH_2), 64.27 (CH_2OH), 68.18 ($PhOCH_2$), 68.42 ($PhOCH_2$), 68.95 [$OCH_2CH(OH)$], 70.50 [$OCH_2CH(OH)$], 72.26 ($PhCH_2O$), 111.77, 114.89, 126.52, 126.99, 127.45, 127.93, 127.97, 133.04, 133.08, 138.95, 139.30, 156.49, 158.80 (C-Ar); *m*/*z* (%) 646 ($[M]^+$, 100).

11-[2,5-Bis(4-decyloxyphenyl)phenyl]-4,7,10-trioxaundecane-1,2-diol ***29b***. Synthesized from 4-(7-hydroxy-2,5-dioxaheptyl)-2,2-dimethyl-1,3-dioxolane and **37**. Eluent: chloroform–methanol (10:0.3). Yield: 17%; transitions/°C: K 54 (Col_r 40 S_A 48) Iso; elemental analysis (%): found (calc. for $C_{46}H_{70}O_7$): C, 75.04 (75.16); H, 9.86 (9.60); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.7, 6H, CH_3), 1.17–1.55 (m, 28H, CH_2), 1.7–1.9 (m, 4H, OCH_2CH_2), 2.3 (br s, 2H, OH), 3.45–3.66 (m, 12H, OCH_2), 3.74–3.82 [m 1H, CH(OH)], 3.98 (t, *J* 6.5, 4H, $PhOCH_2$), 4.48 (s, 2H, $PhCH_2O$), 6.92 (d, *J* 8.7, 2H, H-Ar), 6.96 (d, *J* 8.7, 2H, H-Ar), 7.29 (d, *J* 8.0, 2H, H-Ar), 7.31 (d, 1H, *J* 8.7, H-Ar), 7.50 (dd, *J* 8.0, 2.0, 1H, H-Ar), 7.57 (d, *J* 8.8, 2H, H-Ar), 7.72 (d, *J* 1.8, 1H, H-Ar); δ_C(125 MHz, $CDCl_3$) 14.07 (CH_3), 22.65, 26.07, 26.09, 29.30, 29.32, 29.34, 29.41, 29.55, 29.57, 30.84, 31.88, (CH_2), 63.91 (CH_2OH), 68.11 ($PhOCH_2$), 68.15 ($PhOCH_2$), 69.62, 70.49, 70.53, 70.57, 70.81, [$OCH_2CH(OH)$, OCH_2], 71.28 [$OCH_2CH(OH)$], 73.00 ($PhCH_2O$), 114.16, 114.82, 125.85, 127.53, 128.05, 130.34, 130.46, 132.72, 133.12, 135.60, 139.63, 139.99, 158.46, 158.79 (C-Ar); *m*/*z* (%) 734 ($[M]^+$, 100).

14-[2,5-Bis(4-decyloxyphenyl)phenyl]-4,7,10,13-tetraoxatetradecane-1,2-diol ***29c***. Synthesized from 4-(10-hydroxy-2,5,8-trioxadecyl)-2,2-dimethyl-1,3-dioxolane and **37**. Eluent: chloroform–methanol (10:0.3). Yield: 16%; transitions/°C: K 45 (Col_r 40) Iso; elemental analysis (%): found (calc. for $C_{48}H_{74}O_8$): C, 73.56 (74.00); H, 9.53 (9.57); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.7, 6H, CH_3), 1.27–1.45 (m, 28H, CH_2), 1.76–1.83 (m, 4H, OCH_2CH_2), 3.50–3.62 (m, 16H, OCH_2), 3.71–3.87 [m, 1H, CH(OH)], 3.98 (t, *J* 6.5, 4H, $PhOCH_2$), 4.49 (s, 2H, $PhCH_2O$), 6.93 (d, *J* 8.5, 2H, H-Ar), 6.96 (d, *J* 8.6, 2H, H-Ar), 7.26–7.33 (m, 3H, H-Ar), 7.49 (dd, *J* 8.7, 1.7, 1H, H-Ar), 7.55 (d, *J* 8.7, 2H, H-Ar), 7.71 (d, *J* 1.7, 1H, H-Ar); *m*/*z* (%) 778 ($[M]^+$, 100).

13-[2,5-Bis(4-decyloxyphenyl)phenyl]-12-oxatridecane-1,2-diol ***31***. Synthesized from 4-(9-hydroxynonyl)-2,2-dimethyl-1,3-dioxolane and **37**. Eluent: chloroform–methanol (10:1). Crystallized from n-hexane. Yield: 21%; transitions/°C: K 54 (N 30) Iso; elemental analysis (%): found (calc. for $C_{50}H_{78}O_5$): C, 78.86 (79.11); H, 10.74 (10.36); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.88 (t, *J* 6.5, 6H, CH_3), 1.24–1.4 (m, 34H, CH_2), 1.4–1.62 (m, 8H, CH_2), 1.77–1.85 (m, 6H, OCH_2CH_2), 3.43 (t, *J* 6.5, 2H, $PhCH_2OCH_2$), 3.38–3.46 [m, 1H, CH_AH_BOH],

3.61–3.73, [m, 2H, CH_AH_BOH, C*H*(OH)], 4.02 (t, *J* 6.5, 2H, $PhOCH_2$), 4.04 (t, *J* 6.5, 2H, $PhOCH_2$), 4.42 (s, 2H, $PhCH_2O$), 6.94 (d, *J* 8.5, 2H, H-Ar), 6.97 (d, *J* 8.6, 2H, H-Ar), 7.29–7.35 (m, 3H, H-Ar), 7.50 (dd, *J* 8.7, 1.7, 1H, H-Ar), 7.56 (d, *J* 8.7, 2H, H-Ar), 7.71 (d, *J* 1.8, 1H, H-Ar); *m/z* (%) 758 ($[M]^+$, 100).

11-{2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]phenyl}-4,7,10-trioxaundecane-1,2-diol ***34b***. Synthesized from 4-(7-hydroxy-2,5-dioxaheptyl)-2,2-dimethyl-1,3-dioxolane and **40**. Eluent: chloroform–methanol (10:0.5). Yield: 32%; transitions/°C: K 36 S_A 97 Iso; δ_H(400 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.4, 6H, CH_3), 1.27–1.36 (m, 24H, CH_2), 1.42–1.49 (m, 4H, $OCH_2CH_2CH_2$), 1.75–1.83 (m, 4H, OCH_2CH_2), 2.28 (br s, 2H, OH), 3.50–3.71 (m, 12H, OCH_2), 3.78–3.83 [m, 1H, C*H*(OH)], 3.99 (t, *J* 6.6, 2H, $PhOCH_2$), 4.00 (t, *J* 6.4, 2H, $PhOCH_2$), 4.66 (s, 2H, $PhCH_2O$), 6.90 (d, *J* 8.4, 1H, H-Ar), 6.96 (d, *J* 8.8, 2H, H-Ar), 7.48 (dd, *J* 8.4, 2.3, 1H, H-Ar), 7.54 (d, *J* 8.6, 2H, H-Ar), 7.57–7.62 (m, 4H, H-Ar), 7.68 (d, *J* 2.3, 1H, H-Ar); *m/z* (%) 734 ($[M]^+$, 74), 660 (79).

14-{2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]phenyl}-4,7,10,13-tetraoxatetradecane-1,2-diol ***34c***. Synthesized from 4-(10-hydroxy-2,5,8-trioxadecyl)-2,2-dimethyl-1,3-dioxolane and **40**. Eluent: chloroform–methanol (10:0.3). Yield: 27%; transitions/°C: K 45 S_A 72 Iso; δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.4, 6H, CH_3), 1.27–1.55 (m, 28H, CH_2), 1.70–1.85 (m, 4H, OCH_2CH_2), 3.5–3.7 [m, 17H, OCH_2, C*H*(OH)], 3.99 (t, *J* 6.4, 4H, $PhOCH_2$), 4.66 (s, 2H, $PhCH_2O$), 6.90 (d, *J* 8.6, 1H, H-Ar), 6.96 (d, *J* 8.6, 2H, H-Ar), 7.4–7.7 (m, 8H, H-Ar); *m/z* (%) 778 ($[M]^+$, 100).

8-{2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]phenyl}-7-oxaoctane-1,2-diol ***35a***. Synthesized from 4-(4-hydroxybutyl)-2,2-dimethyl-1,3-dioxolane and **40**. Eluent: chloroform–methanol (10:0.2). Yield: 37%; transitions/°C: K 75 S_A 114 Iso; δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.88 (t, *J* 6.6, 6H, CH_3), 1.2–1.9 (m, 38H, CH_2), 3.39 (dd, *J* 10.8, 7.6, 1H, CH_AH_BOH), 3.5–3.7 [m, 4H, CH_AH_BOH, C*H*(OH), CH_2O], 3.99 (t, *J* 6.6, 2H, $PhOCH_2$), 4.00 (t, *J* 6.5, 2H, $PhOCH_2$), 4.59 (s, 2H, $PhCH_2O$), 6.90 (d, *J* 8.6, 1H, H-Ar), 6.96 (d, *J* 8.8, 2H, H-Ar), 7.47 (dd, *J* 8.4, 2.4, 1H, H-Ar), 7.5–7.65 (m, 6H, H-Ar), 7.64 (d, 2.3, 1H, H-Ar); *m/z* (%) 688 ($[M]^+$, 100).

13-{2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]phenyl}-12-oxatridecane-1,2-diol ***35b***. Synthesized from 4-(9-hydroxynonyl)-2,2-dimethyl-1,3-dioxolane and **40**. Crystallized from light petroleum (60–80 °C). Yield: 17%; mp 110–112 °C; elemental analysis (%): found (calc. for $C_{50}H_{78}O_5$): C, 78.87 (79.11); H, 10.53 (10.36); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.89 (t, *J* 6.8, 6H, CH_3), 1.29–1.40 (m, 44H, CH_2), 1.74–1.85 (m, 4H, OCH_2CH_2), 3.36–3.67 [m, 5H, C*H*(OH), OCH_2], 4.01 (t, *J* 6.6, 2H, $PhOCH_2$), 4.02 (t, *J* 6.5, 2H, $PhOCH_2$), 4.61 (s, 2H, $PhCH_2O$), 6.92 (d, *J* 8.6, 1H, H-Ar), 6.98 (d, *J* 8.8, 2H, H-Ar), 7.47–7.65 (m, 4H, H-Ar), 7.68 (d, 2.3, 1H, H-Ar); *m/z* (%) 758 ($[M]^+$, 18), 556 (100).

3.5. Synthesis of the oligoethylene glycol ethers 30

These compounds were obtained by etherification of appropriate benzyl bromides with triethylene glycol and tetraethylene glycol respectively, according to procedure 3.4.1.

11-[2,5-Bis(4-decyloxyphenyl)phenyl]-4,7,10-trioxaundecanol 30a. Synthesized from triethylene glycol and **37**. Eluent: chloroform–methanol (10:0.1). Yield: 18%; transitions/°C: K 61 (S_A 52) Iso; δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.26–1.55 (m, 28H, CH_2), 1.72–1.86 (m, 4H, OCH_2CH_2), 3.53–3.69 (m, 12H, OCH_2), 3.98 (t, *J* 6.5, 4H, $PhOCH_2$), 4.48 (s, 2H, $PhCH_2O$), 6.93 (d, *J* 8.5, 2H, H-Ar), 6.95 (d, *J* 8.6, 2H, H-Ar), 7.30 (d, *J* 8.0, 2H, H-Ar), 7.31 (d, *J* 8.6, 1H, H-Ar), 7.52 (dd, *J* 8.1, 1.7, 1H, H-Ar), 7.55 (d, *J* 8.7, 2H, H-Ar), 7.72 (d, *J* 1.7, 1H, H-Ar); *m/z* (%) 704 ($[M]^+$, 67), 556 (59).

14-[2,5-Bis(4-decyloxyphenyl)phenyl]-4,7,10,13-tetraoxatetradecanol 30b. Synthesized from tetraethylene glycol and **37**. Eluent: chloroform–methanol (10:0.5). Crystallized from n-hexane. Yield: 25%; transitions/°C: K 44 (S_A 31) Iso; elemental analysis (%): found (calc. for $C_{47}H_{72}O_7$): C, 75.08 (75.36); H, 9.76 (9.69); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.91 (t, *J* 6.4, 6H, CH_3), 1.2–1.6 (m, 28H, CH_2), 1.75–1.92 (m, 4H, OCH_2CH_2), 3.54–3.78 (m, 16H, OCH_2), 4.01 (t, *J* 6.5, 4H, $PhOCH_2$), 4.52 (s, 2H, $PhCH_2O$), 6.93 (d, *J* 8.5, 2H, H-Ar), 6.96 (d, *J* 8.6, 2H, H-Ar), 7.28 (d, *J* 8.5, 2H, H-Ar), 7.31 (d, *J* 8.6, 1H, H-Ar), 7.5–7.6 (m, 3H, H-Ar), 7.74 (d, *J* 1.7, 1H, H-Ar); *m/z* (%) 748 ($[M]^+$, 68), 704 (27).

3.6. Synthesis of the *p*-terphenyl derivatives 29a and 34a

At first the appropriate bromomethyl substituted 4,4″-didecyloxy-*p*-terphenyl derivatives **37** and **40** were etherified according to procedure 3.4.1 with 2-allyloxyethanol to give the allyl ether. The allyl ethers were used without further purification for the dihydroxylation reaction.

3.6.1. Procedure for the dihydroxylation. The appropriate allyl ether (1 mmol, 657 mg) was added to a solution of *N*-methylmorpholine *N*-oxide (1.4 mmol, 0.15 ml of 60% aq. solution) in acetone (20 ml). Osmium tetroxide (0.05 ml of 0.01 M solution in *tert*-butyl alcohol) was added and the resulting mixture was stirred for 24 h at room temperature. After this time starting materials could no longer be detected and the mixture was worked up as follows: sodium hydrogen sulfite (4 ml saturated solution) was added and the resulting slurry was vigorously stirred at room temperature for 30 min. Afterwards, the solid were filtered off, the residue was extracted three times with ethyl acetate (30 ml) and the combined organic phases were washed with 10% H_2SO_4, water and brine. After drying with Na_2SO_4 the solvent was evaporated and the crude products were purified by column chromatography.

8-[2,5-Bis(4-decyloxyphenyl)phenyl]-4,7-dioxaoctane-1,2-diol ***29a***. Synthesized from 2-allyloxyethanol and **37**, followed by dihydroxylation. Eluent: chloroform–methanol (10:0.3). Yield: 10%; transitions/°C: K 66 S_A 73 Iso; δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.7, 6H, CH_3), 1.24–1.74 (m, 28H, CH_2), 1.76–1.83 (m, 4H, OCH_2CH_2), 3.5–3.7 (m, 8H, OCH_2), 3.7–3.9 [m, 1H, C*H*(OH)], 3.98 (t, *J* 6.5, 4H, $PhOCH_2$), 4.49 (s, 2H, $PhCH_2O$), 6.93 (d, *J* 8.6, 2H, H-Ar), 6.96 (d, *J* 8.7, 2H, H-Ar), 7.27–7.51 (m, 3H, H-Ar), 7.51 (d, *J* 8.8, 1H, H-Ar), 7.55 (d, *J* 8.7, 2H, H-Ar), 7.70 (d, *J* 1.7, 1H, H-Ar); *m/z* (%) 690 ($[M]^+$, 100).

8-{2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]phenyl}-4,7-dioxaoctane-1,2-diol ***34a***. Synthesized from 2-allyloxyethanol and **40**, followed by dihydroxylation. Eluent: chloroform–methanol (10:0.5). Yield: 30%; transitions/°C: K 58 S_A 121 Iso; elemental analysis (%): found (calc. for $C_{44}H_{66}O_6$): C, 76.20 (76.48); H, 9.89 (9.63); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.6, 6H, CH_3), 1.2–1.6 (m, 28H, CH_2), 1.7–1.9 (m, 4H, OCH_2CH_2), 3.5–3.75 (m, 8H, OCH_2), 3.8–3.9 [m, 1H, C*H*(OH)], 3.98 (t, *J* 6.6, 2H, $PhOCH_2$), 4.00 (t, *J* 6.4, 2H, $PhOCH_2$), 4.66 (s, 2H, $PhCH_2O$), 6.90 (d, *J* 8.4, 1H, H-Ar), 6.96 (d, *J* 8.8, 2H, H-Ar), 7.4–7.6 (m, 7H, H-Ar), 7.65 (d, *J* 2.2, 1H, H-Ar); *m/z* (%) 690 ($[M]^+$, 100).

3.7. 2,5-Bis(4-decyloxyphenyl)benzyl(triethyl)ammonium bromide 28

In a three-necked flask equipped with a magnetic stirring bar and a dropping funnel **37** (1.25 mmol, 800 mg) was dissolved in dry acetonitrile (70 ml) at 50 °C under argon atmosphere. Dry triethylamine (30 ml) was added dropwise while stirring. The reaction mixture was stirred under reflux for 15 h. After cooling to room temperature the solvent was evaporated and the residue dissolved in chloroform (100 ml). The organic phase was washed several times with water and dried with $CaCl_2$. The solvent was removed *in vacuo* and the crude product obtained was purified by column chromatography (Silica gel, chloroform–methanol 10:2) followed by recrystallization from ethyl acetate. Yield: 35%; mp 140 °C; elemental analysis (%): found (calc. for $C_{45}H_{70}O_2NBr$): C, 72.96 (73.34); H, 9.26 (9.57); Br, 10.53 (10.84); N, 1.96 (1.90); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.86 (t, *J* 6.6, 6H, CH_3), 1.14 (t, *J* 6.4, 9H, NCH_2CH_3), 1.18–1.57 (m, 28H, CH_2), 1.7–1.9 (m, 4H, $OCH_2CH_2CH_2$), 3.15–3.35 (m, 6H, NCH_2CH_3), 3.97 (t, *J* 6.5, 4H, $PhOCH_2$), 4.94 (s, 2H, $PhCH_2N$), 6.94 (d, *J* 8.5, 2H, H-Ar), 6.99 (d, *J* 8.6, 2H, H-Ar), 7.21 (d, *J* 8.4, 2H, H-Ar), 7.35 (d, *J* 8.0, 1H, H-Ar), 7.56 (d, *J* 8.5, 2H, H-Ar), 7.65 (d, *J* 8.7, 1H, H-Ar), 7.87 (s, 1H, H-Ar).

3.8. Sodium 2,5-bis(4-decyloxyphenyl)benzoate 27

Methyl 2,5-bis(4-decyloxyphenyl)benzoate **14** (1 mmol, 601 mg) was added to a stirred solution prepared from ethanol (50 ml) and NaOH (0.25 mol, 10 g) and heated 4 h under reflux. After termination of the reaction the solvent was removed *in vacuo* and 50 ml water were added. The aqueous phase was extracted three times with chloroform (50 ml). The combined organic phases were washed several times with water and brine and afterwards dried with calcium chloride. After evaporation of the solvent the residue was recrystallized from ethyl acetate. Yield: 86%; mp 216–218 °C; elemental analysis (%): found (calc. for $C_{39}H_{53}O_4Na$): C, 77.25 (76.94); H, 8.85 (8.77); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.85 (t, *J* 6.4, 6H, CH_3), 1.1–1.8 (m, 28H, CH_2), 1.9–2.2 (m, 4H, OCH_2CH_2), 3.56 (t, *J* 6.3, 4H, $PhOCH_2$), 6.55 (d, *J* 8.3, 2H, H-Ar), 6.75 (d, *J* 8.5, 2H, H-Ar), 7.1–7.2 (m, 3H, H-Ar), 7.4–7.5 (m, 3H, H-Ar), 7.91 (s, 1H, H-Ar).

3.9. 2,5-Bis(4-decyloxyphenyl)benzoic acid 25

Compound **27** (10 mmol, 6.1 g) was dissolved in ethanol (250 ml). Concentrated hydrochloric acid (100 ml) was added while stirring and the mixture was heated under reflux for 2 h. After cooling, water (250 ml) was added dropwise and the mixture was extracted three times with diethyl ether (150 ml). The combined organic phases were washed several times with aq. $NaHCO_3$ solution and then with water. After drying with Na_2SO_4 the solvent was removed *in vacuo*. The crude product was purified by recrystallization from a mixture of n-hexane and ethyl acetate. Yield: 80%; transitions/°C: K 151 (S_A 125) Iso; elemental analysis (%): found (calc. for $C_{39}H_{54}O_4$): C, 79.67 (79.82); H, 9.46 (9.27); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.1–1.6 (m, 28H, CH_2), 1.7–1.9 (m, 4H, OCH_2CH_2), 3.96 (t, *J* 6.5, 2H, $PhOCH_2$), 3.99 (t, *J* 6.4, 2H, $PhOCH_2$), 6.90 (d, *J* 8.4, 2H, H-Ar), 6.96 (d, *J* 8.5, 2H, H-Ar), 7.29 (d, *J* 8.5, 2H, H-Ar), 7.38 (d, *J* 8.4, 1H, H-Ar), 7.55 (d, *J* 8.7, 2H, H-Ar), 7.69 (dd, *J* 8.6, 1.4, 1H, H-Ar), 8.09 (d, *J* 1.2, 1H, H-Ar); *m/z* (%) 586 ($[M]^+$, 100).

3.10. 2,5-Bis(4-decyloxyphenyl)benzoyl chloride 26

Oxalyl chloride (2.5 mmol, 460 mg) was added slowly with a syringe to a solution of **25** (0.25 mmol, 150 mg) in dry dichloromethane (10 ml) under argon atmosphere at room temperature. The reaction mixture was stirred for one hour. The solvent and excess oxalyl chloride were evaporated and the yellowish oil obtained was crystallized from n-hexane. Yield: 92%; transitions/°C: K 58 (N 40) Iso; elemental analysis (%): found (calc. for $C_{39}H_{53}O_3Cl$): C, 77.45 (77.39); H, 8.57 (8.83); Cl, 5.64 (5.86); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.88 (t, *J* 6.5, 6H, CH_3), 1.26–1.41 (m, 28H, CH_2), 1.67–1.78 (m, 4H, OCH_2CH_2), 3.81 (t, *J* 6.4, 2H, $PhOCH_2$), 4.00 (t, *J* 6.5, 2H, $PhOCH_2$), 6.87 (d, *J* 8.5, 2H, H-Ar), 6.92 (d, *J* 8.5, 2H, H-Ar), 7.29 (d, *J* 8.5, 2H, H-Ar), 7.30–7.32 (m, 1H, H-Ar), 7.49 (dd, *J* 8.7, 1.7, 1H, H-Ar), 7.53 (d, *J* 8.6, 2H, H-Ar), 7.75 (d, *J* 1.2, 1H, H-Ar).

3.11. Synthesis of the 2,5-bis(4-decyloxyphenyl)benzamides 15–24

In a three-necked flask equipped with a magnetic stirring bar the appropriate amine (1,5 mmol) was dissolved in dry DMF (30 ml) under argon atmosphere. A solution of **26** (0.5 mmol, 300 mg) in toluene (20 ml) was slowly added dropwise to this stirred mixture at room temperature. The mixture was stirred several hours at 80 °C, until the reaction was complete (TLC). After the solvent was removed *in vacuo* the residue was dissolved in diethyl ether (100 ml) and the organic phase was washed first with 10% hydrochloric acid (40 ml) and afterwards with water (50 ml). The organic phase was dried with sodium sulfate. Then the solvent was evaporated and the crude product obtained was purified by flash column chromatography followed by recrystallization.

2,5-Bis(4-decyloxyphenyl)benzamide 15. Synthesized by introduction of ammonia into a solution of **26** in DMF at room temperature. Eluent: chloroform–methanol (10:1). Crystallized from ethyl acetate. Yield: 65%; mp 184 °C; elemental analysis (%): found (calc. for $C_{39}H_{55}O_3N$): C, 79.99 (79.95); H, 9.21 (9.46); N, 2.04 (2.39); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.7, 6H, CH_3), 1.2–1.5 (m, 28H, CH_2), 1.75–1.84 (m, 4H, OCH_2CH_2), 3.97 (t, *J* 6.8, 2H, $PhOCH_2$), 3.99 (t, *J* 6.7, 2H, $PhOCH_2$), 5.28 (br s, 1H, NH), 5.44 (br s, 1H, NH), 6.94 (d, *J* 8.6, 2H, H-Ar), 6.97 (d, *J* 8.5, 2H, H-Ar), 7.35 (d, *J* 7.8, 1H, H-Ar), 7.38 (d, *J* 8.8, 2H, H-Ar), 7.56 (d, *J* 8.8, 2H, H-Ar), 7.65 (dd, *J* 8.1, 2.1, 1H, H-Ar), 7.96 (d, *J* 2.0, 1H, H-Ar); *m/z* (%) 585 ($[M]^+$, 100).

2,5-Bis(4-decyloxyphenyl)benzoylaminoethane 16. Synthesized from ethylamine and **26**. Eluent: chloroform–methanol (10:0.5). Crystallized from methanol. Yield: 84%; mp 111 °C; elemental analysis (%): found (calc. for $C_{41}H_{59}O_3N$): C, 79.98 (80.21); H, 9.37 (9.69); N, 2.04 (2.28); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 7.1, 9H, CH_3), 1.2–1.5 (m, 28H, CH_2), 1.75–1.83 (m, 4H, OCH_2CH_2), 3.21 (dq, 2H, $NHCH_2$), 3.96 (t, *J* 6.8, 2H, $PhOCH_2$), 3.98 (t, *J* 6.7, 2H, $PhOCH_2$), 5.19 (t, *J* 5.6, 1H, NH), 6.93 (d, *J* 8.7, 2H, H-Ar), 6.95 (d, *J* 8.7, 2H, H-Ar), 7.34 (d, *J* 8.8, 2H, H-Ar), 7.36 (d, *J* 8.7, 1H, H-Ar), 7.55 (d, *J* 8.7, 2H, H-Ar), 7.61 (dd, *J* 8.0, 2.0, 1H, H-Ar), 7.87 (d, *J* 1.9, 1H, H-Ar); *m/z* (%) 613 ($[M]^+$, 100).

2,5-Bis(4-decyloxyphenyl)benzohydrazide 17. Synthesized by adding hydrazine hydrate (100%) to a solution of **14** in n-butanol and stirring at reflux temperature for 10 h. Crystallized from ethanol. Yield: 83%; transitions/°C: K 98 S_A 131 Iso; elemental analysis (%): found (calc. for $C_{39}H_{56}O_3N_2$): C, 77.78 (77.96); H, 9.76 (9.39); N, 4.91 (4.66); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.7, 6H, CH_3), 1.22–1.51 (m, 28H, CH_2), 1.75–1.83 (m, 4H, OCH_2CH_2), 3.8–4.0 (br s, 2H, NH_2), 3.97 (t, *J* 6.8, 2H, $PhOCH_2$), 3.99 (t, *J* 6.7, 2H, $PhOCH_2$), 6.53 (br s, 1H, CONH), 6.93 (d, *J* 8.7, 2H, H-Ar), 6.96 (d, *J* 8.7, 2H, H-Ar), 7.31 (d, *J* 8.6, 2H, H-Ar), 7.38 (d, *J* 8.1, 1H, H-Ar), 7.54 (d, *J* 8.5, 2H, H-Ar), 7.64 (dd, *J* 8.1, 1.9, 1H, H-Ar), 7.83 (d, *J* 2.0, 1H, H-Ar); *m/z* (%) 600 ($[M]^+$, 8), 567 (26), 466 (100).

2-[2,5-Bis(4-decyloxyphenyl)benzoylamino]ethanol 18. Synthesized from 2-aminoethanol and **26**. Eluent: chloroform–methanol (10:1). Crystallized from n-hexane–ethyl acetate. Yield: 87%; transitions/°C: K 118 S_A 131 Iso; elemental analysis (%): found (calc. for $C_{41}H_{59}O_4N$): C, 77.99 (78.18); H, 9.37 (9.44); N, 2.04 (2.22); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.23–1.50 (m, 28H, CH_2), 1.77–1.82 (m, 4H, OCH_2CH_2), 3.26 (dt, *J* 10.2, 5.5, 2H, $NHCH_2$), 3.50 (t, *J* 5.1, 2H, CH_2OH), 3.97 (t, *J* 6.7, 2H, $PhOCH_2$), 3.99 (t, *J* 6.7, 2H, $PhOCH_2$), 5.68 (t, *J* 6.0, 1H, NH), 6.94 (dd, *J* 8.8, 2.1, 2H, H-Ar), 6.96 (2d, 4H, H-Ar), 7.37 (d, *J* 8.7, 3H, H-Ar), 7.55 (d, *J* 8.0, 2H, H-Ar), 7.63 (dd, *J* 8.0, 2.0, 1H, H-Ar), 7.86 (d, *J* 2.0, 1H, H-Ar); *m/z* (%) 629 ($[M]^+$, 100).

3-[2,5-Bis(4-decyloxyphenyl)benzoylamino]propane-1,2-diol 19. Synthesized from 3-aminopropane-1,2-diol and **26**. Eluent: ethyl acetate. Crystallized from n-hexane–ethyl acetate. Yield: 90%; transitions/°C: K 115 S_A 142 Iso; elemental analysis (%): found (calc. for $C_{42}H_{61}O_5N$): C, 76.19 (76.43); H, 9.21 (9.32); N, 2.04 (2.12); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.22–1.50 (m, 28H, CH_2), 1.74–1.85 (m, 4H, OCH_2CH_2), 3.21–3.27 (m, 1H, $NHCH_AH_B$), 3.32–3.37 (m, 1H, $NHCH_AH_B$), 3.40 (dd, *J* 11,2, 4.8, 1H, CH_AH_BOH), 4.35 (dd, *J* 11,4, 4.5, 1H, CH_AH_BOH), 3.55–3.59 [m, 1H, CH(OH)], 3.97 (t, *J* 6.7, 2H, $PhOCH_2$), 3.99 (t, *J* 6.7, 2H, $PhOCH_2$), 5.72 (dd, *J* 6.0, 6.0, 1H, NH), 6.93 (d, *J* 8.5, 2H, H-Ar), 6.95 (d, *J* 8.7, 2H, H-Ar), 7.33 (d, *J* 8.7, 2H, H-Ar), 7.35 (d, *J* 8.0, 1H, H-Ar), 7.54 (d, *J* 8.7, 2H, H-Ar), 7.63 (dd, *J* 8.0, 2.0, 1H, H-Ar), 7.86 (d, *J* 2.0, 1H, H-Ar); δ_C(125 MHz, $CDCl_3$) 14.11 (CH_3), 22.68, 26.04, 29.24, 29.28, 29.32, 29.41, 29.56, 29.58, 31.89 (CH_2), 42.70 ($NHCH_2$), 63.63 (CH_2OH), 68.13 ($PhOCH_2$), 68.23 ($PhOCH_2$), 70.89 [CH(OH)CH_2OH], 114.74, 114.91, 126.97, 128.01, 128.45, 129.92, 130.78, 131.84, 134.95, 137.31, 139.94, 159.12 (C-Ar), 171.58 (CO); *m/z* (%) 659 ($[M]^+$, 100).

***N*-[2,5-Bis(4-decyloxyphenyl)benzoyl]-1-deoxy-1-methylamino-D-glucitol 20.** Synthesized from 1-deoxy-1-methylamino-D-glucitol and **26**. Eluent: chloroform–methanol (10:2). Crystallized from n-pentane. Yield: 90%; mp 87 °C; elemental analysis (%): found (calc. for $C_{46}H_{69}O_8N$): C, 71.98 (72.31); H, 9.37 (9.10); N, 1.74 (1.83); $[\alpha]_D^{30}$ 0.9 (*c* 1.05, $CHCl_3$); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.86 (t, *J* 6.1, 6H, CH_3), 1.21–1.48 (m, 28H, CH_2), 1.71–1.82 (m, 4H, OCH_2CH_2), 2.47 (s, 3H, NCH_3), 3.2–4.95 [m, 8H, CH(OH), CH_2O, CH_2N], 3.94 (t, *J* 6.7, 2H, $PhOCH_2$), 3.96 (t, *J* 6.7, 2H, $PhOCH_2$), 6.93 (2d, 4H, H-Ar), 7.33 (d, *J* 8.6, 2H, H-Ar), 7.38 (d, *J* 8.1, 1H, H-Ar), 7.51 (d, *J* 8.6, 3H, H-Ar), 7.59 (dd, *J* 8.2, 1.8, 1H, H-Ar); *m/z* (%) 763 ($[M]^+$, 18), 599 (28), 586 (23), 569 (100).

1-[2,5-Bis(4-decyloxyphenyl)benzoylamino]-1-deoxy-D-glucitol 21. Synthesized from 1-amino-1-deoxy-D-glucitol and **26**. Eluent: chloroform–methanol (10:2). Crystallized from n-hexane–ethyl acetate. Yield: 76%; transitions/°C: K 112 S_A 147 Iso; elemental analysis (%): found (calc. for $C_{45}H_{67}O_8N$): C, 71.71 (72.06); H, 9.22 (9.00); N, 1.59 (1.87); $[\alpha]_D^{25}$ −0.1 (*c* 1.09, $CHCl_3$); δ_H(200 MHz, DMSO, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.21–1.52 (m, 28H, CH_2), 1.74–1.83 (m, 4H, OCH_2CH_2), 3.2–3.7 [m, 8H, CH(OH), CH_2O, CH_2N], 3.98 (t, *J* 6.7, 2H, $PhOCH_2$), 3.99 (t, *J* 6.7, 2H, $PhOCH_2$), 4.1–4.4 (m, 3H, OH), 4.48 (d, *J* 4.7, 1H, OH), 4.77 (d, *J* 4.5, 1H, OH), 6.93 (d, *J* 8.7, 2H, H-Ar), 6.99 (d, *J* 8.8, 2H, H-Ar), 7.34 (d, *J* 8.6, 2H, H-Ar), 7.38 (d, *J* 8.1, 1H, H-Ar), 7.62 (m, 4H, H-Ar), 8.19 (dd, *J* 5.4, 5.4, 1H, NH); *m/z* (%) 749 ($[M]^+$, 68), 627 (21), 586 (83), 569 (100).

3-[2,5-Bis(4-decyloxyphenyl)benzoyl]-3-azapentane-1,5-diol 22. Synthesized from diethanolamine and **26**. Eluent: chloroform–methanol (10:1). Crystallized from n-hexane–ethyl acetate. Yield: 70%; transitions/°C: K 110 (S_A 97) Iso; elemental analysis (%): found (calc. for $C_{43}H_{63}O_5N$): C, 76.43 (76.63); H, 9.32 (9.42); N, 2.04 (2.08); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.21–1.50 (m, 28H, CH_2), 1.74–1.83 (m, 4H, OCH_2CH_2), 2.8–3.9 (m, 8H, CH_2N, CH_2O), 3.96 (t, *J* 6.7, 2H, $PhOCH_2$), 3.98 (t, *J* 6.7, 2H, $PhOCH_2$), 6.92 (d, *J* 8.8, 2H, H-Ar), 6.95 (d, *J* 8.7, 2H, H-Ar), 7.39 (d, *J* 8.7, 1H, H-Ar), 7.43 (d, *J* 8.7, 2H, H-Ar), 7.53 (d, *J* 8.8, 2H, H-Ar), 7.55 (d, *J* 1.8, 1H, H-Ar), 7.61 (dd, *J* 8.1, 1.8, 1H, H-Ar); *m/z* (%) 674 ($[M+1]^+$, 100).

4-[2,5-Bis(4-decyloxyphenyl)benzoyl]morpholine 23. Synthesized from morpholine and **26**. Eluent: ethyl acetate. Crystallized from n-hexane–ethyl acetate. Yield: 81%; mp 96 °C; elemental analysis (%): found (calc. for $C_{43}H_{61}O_4N$): C, 78.69 (78.74); H, 9.51 (9.37); N, 2.08 (2.14); δ_H(500 MHz, $CDCl_3$, *J*/Hz) 0.87 (t, *J* 6.5, 6H, CH_3), 1.24–1.51 (m, 28H, CH_2), 1.71–1.87 (m, 4H, OCH_2CH_2), 2.49–3.75 (m, 8H, CH_2N, CH_2O), 3.99 (t, *J* 6.7, 4H, $PhOCH_2$), 6.97 (2d, 4H, H-Ar), 7.40 (d, *J* 8.9, 2H, H-Ar), 7.5–7.7 (m, 5H, H-Ar); *m/z* (%) 655 ($[M]^+$, 80), 429 (27).

16-[2,5-Bis(4-decyloxyphenyl)benzoyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane 24. Synthesized from 1,4,7,10,13-pentaoxa-16-azacyclooctadecane and **26**. Eluent: ethyl acetate. Crystallized from n-hexane. Yield: 72%; mp 73 °C; elemental analysis (%): found (calc. for $C_{51}H_{77}O_8N$): C, 73.29 (73.61); H, 9.57 (9.33); N, 1.61 (1.68); δ_H(200 MHz, $CDCl_3$, *J*/Hz) 0.86 (t, *J* 6.4, 6H, CH_3), 1.24–1.56 (m, 28H, CH_2), 1.69–1.85 (m, 4H, OCH_2CH_2), 3.1–3.8 (m, 24H, NCH_2, OCH_2), 3.94 (t, *J* 6.7, 2H, $PhOCH_2$), 3.98 (t, *J* 6.7, 2H, $PhOCH_2$), 6.87 (d, *J* 8.7, 2H, H-Ar), 6.94 (d, *J* 8.8, 2H, H-Ar), 7.3–7.6 (m, 7H, H-Ar); *m/z* (%) 831 ($[M]^+$, 100).

4. Results and discussion

4.1. Facial amphiphiles with lateral propane-2,3-diol groups

The glycerol ether **1e** was the first compound investigated.[27] It exhibits an enantiotropic smectic A phase. A comparison of the diol **1** with compound **2**[27] carrying a lateral alkyl substituent of comparable size (Fig. 2) indicates a significant mesophase stabilizing influence of the two hydroxy groups. Furthermore, it is obvious that the laterally attached hydrogen bonding group increases the structural order, which means that the layered smectic A phase is stabilized with respect to the nematic phase of the nonamphiphilic compound **2**. Contrary to smectic phases of conventional amphiphiles and

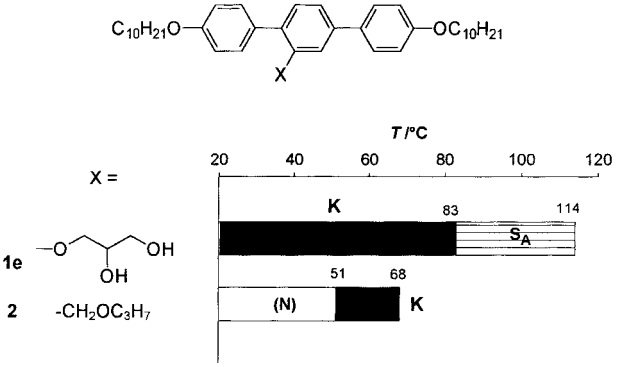


Fig. 2 Comparison of the mesomorphic properties of the laterally substituted compounds **1e** and **2**.[27] The existence regions of the phases are displayed as bars. Black areas indicate the solid crystalline state and hatched or blank areas correspond to liquid crystalline phases. If the liquid crystalline phase appears below the melting point, these are monotropic (metastable) mesophases which are given in brackets. The numbers above the bars indicate the phase transition temperatures. Abbreviations: K = crystalline solid, N = nematic Phase, S_A = smectic A phase.

amphiphiles containing terminally connected rigid units, which usually form bilayer structures, the smectic phase of **1e** presents a monolayer structure. The fixation of the molecules in the single-layers should be provided by attractive hydrogen bonding[28] between their hydroxy groups and probably also by hydrogen bonding between the hydroxy groups and the aromatic π-systems. Furthermore, the hydroxy groups significantly increase the polarity in the region of the rigid cores and thus favor micro-segregation of these regions from the lipophilic alkyl chains.[29] Thus, the smectic layer structure is stabilized by the attractive forces provided by hydrogen bonding and by micro-segregation.

The propane-2,3-diol group incorporates a stereogenic center. Remarkably, however, no measurable influence of chirality on the mesomorphic properties has been found. Both the racemic compound **1e** and the optically active compound (*S*)-**1e** (K 83 S_A 114 Iso) have identical melting and clearing temperatures. Therefore all other compounds described in this paper have been prepared only as racemic mixtures.

The dependence of the mesomorphic properties on the length of the terminal chains is shown in Fig. 3. With the exception of the nematic ethoxy substituted compound **1a** all other synthesized *p*-terphenyl derivatives **1** display smectic A phases. Remarkably, the mesophase stability significantly increases on elongation of the terminal lipophilic chains.

Also the quinquaphenyl derivative **5** and the biphenyl derivative **6** exhibit S_A phases. The corresponding methyl substituted biphenyl derivative **8**, carrying the much smaller methyl group, exhibits a monotropic nematic phase with a significantly lower clearing temperature than the S_A phase of **6**. This again shows the stabilizing influence of the lateral diol group. However, compound **7**, incorporating only a single benzene ring, is a non-mesomorphic compound. This shows that the amphiphilic structure alone does not cause the liquid crystallinity in this class of compounds. Mesomorphic properties are also lost if the linear *p*-terphenyl rigid core is replaced by an angular *m*-terphenyl central unit (compound **4**). This is in accordance with the behavior of conventional calamitic liquid crystals. The mesophase destabilization on replacing the alkoxy substituents by alkyl groups (compounds **3**) is also analogous to nonamphiphilic calamitic mesogens.

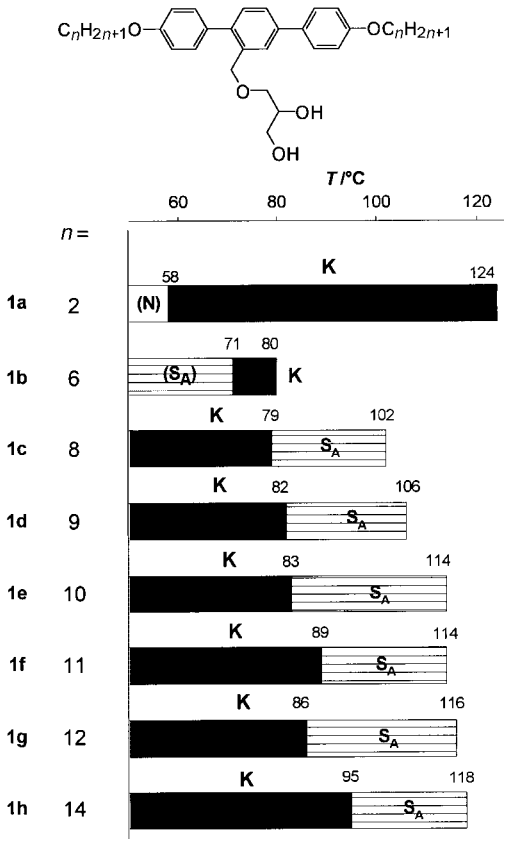
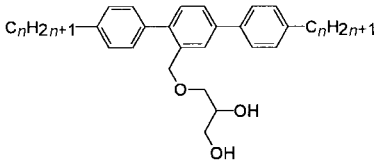
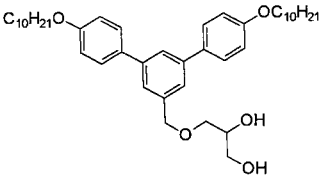
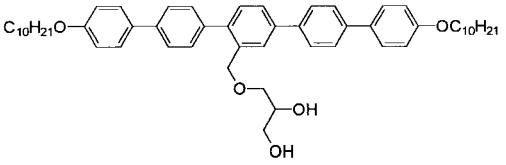
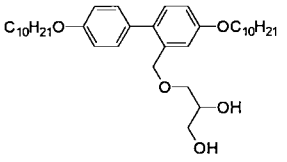


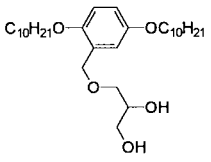
Fig. 3 Mesomorphic properties of the compounds **1** as a function of the length of the terminal chains.

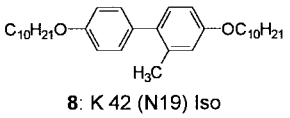












4.2. Influence of the position of the diol group

In Fig. 4 the dependence of the mesomorphic properties on the position of the 4,5-dihydroxy-2-oxapentyl group is compared with the influence of a methyl group in the same positions. For the diol derivatives **1e**, **11** and **13** the order of mesophase stability (**1e** ~ **11** < **13**) is principally the same as for the methyl substituted molecules (**9**[15] ~ **10**[18] < **12**[18]). However, the S_C phases of the methyl substituted derivatives are completely replaced by smectic A phases. Furthermore it seems that the mesophase stabilizing effect of the lateral diol group is largest for the centrally substituted compound **1e** and it decreases on migration of the lateral group to the terminal end of the rigid core. Thus, a mesophase stabilization in comparison with the corresponding methyl substituted compounds is observed only for the 2′-substituted compound, whereas the clearing temperature of the diol **13** with its polar group in the 3-position is significantly lower than that of the corresponding 3-methyl derivative **12**. Probably two different reasons are responsible for this effect. At first the mesophase destabilizing influence of lateral substituents depends on their

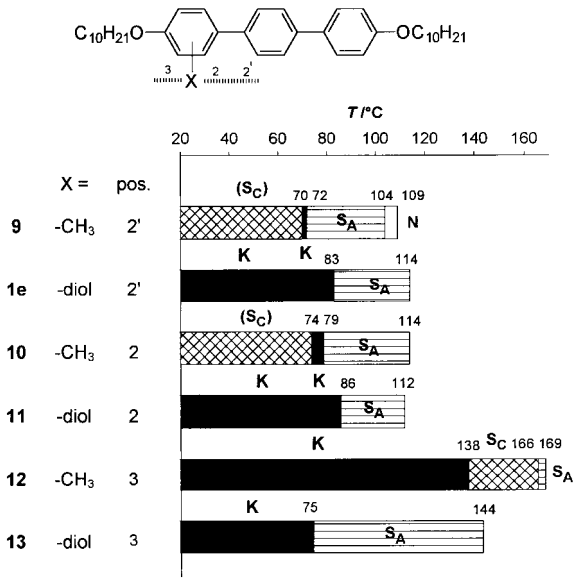


Fig. 4 Influence of the position of the lateral groups on the liquid crystalline behavior.

position at the rigid core. Those in central positions have a more pronounced destabilizing influence than those in more peripheral positions.[1–3,5,18] The reason may be that the lateral substituents in a central position are forced to be located between the rigid *p*-terphenyl cores, whereas those in a peripheral position can be expelled more easily into the region of the flexible terminal alkyl chains. This would be more favorable for lipophilic substituents, like the methyl group, than for polar hydrophilic substituents which are incompatible with the alkyl groups. This second effect could be responsible for the destabilization of the smectic layers of the 3-substituted diol derivative **13** with respect to the methyl substituted compound **12**.

Remarkably, for all diol substituted compounds, no S_C phase was found even on supercooling the samples. It should be mentioned here that this phenomenon is often observed in systems of calamitic molecules with strong attractive forces between their rigid cores, especially in donor–acceptor systems.[30] For example, S_A phases can be exclusively induced in mixed systems of calamitic molecules with donor and acceptor properties[30] and in mixed systems consisting of calamitic mesogens and TNF.[31] Steric effects should also contribute to the loss of S_C phases. The large lateral substituents disfavor tilting, because this would further enlarge the lateral cross-section and additionally disturb the packing of the alkyl chains.

4.3. Variation of the lateral groups

A wide variety of different polar groups has been checked. In Fig. 5 the molecules with lateral amide groups are compared with the methyl carboxylate **14**[15,27] which has exclusively a nematic phase. The amide **15** and the *N*-ethyl amide **16** are high melting crystalline solids which rapidly crystallize on cooling. Therefore no liquid crystalline phases can be observed. However if one additional proton donating functional group (OH or NH_2) is introduced into the lateral group, then liquid crystalline properties can be found. Both the hydrazide **17** and the 2-hydroxyethylamide **18** form S_A phases with significantly higher mesophase stability than the ester compound **14**.[27] Furthermore, with an increasing number of hydroxy groups in the lateral chain the mesophase stability of the S_A phase rises (compounds **18**, **19** and **20** in Fig. 5). Remarkably, the mesophase stability increases despite the fact that the lateral groups are enlarged simultaneously. This means that the mesophase stabilization provided by the additional hydrogen

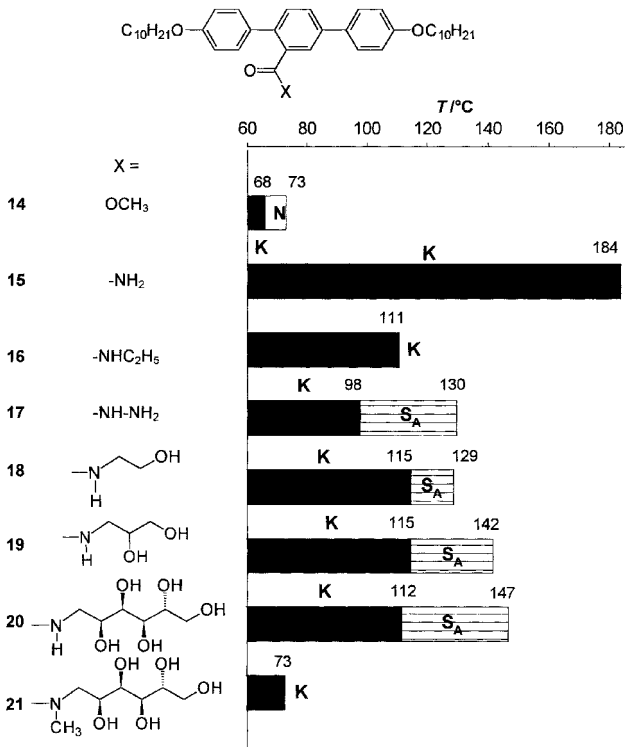


Fig. 5 Properties of 4,4″-didecyloxyterphenyl derivatives with lateral amide groups.

bonding is larger than the mesophase destabilizing effect due to unfavorable steric interactions from increasing the size of the substituents by additional CH_2OH groups. It is especially remarkable that the acylated aminosugar **20**[27] exhibits the most stable smectic phase of all compounds compared in Fig. 5. This compound represents an entirely new type of mesogenic carbohydrate derivative, which combines a rigid rod-like core laterally connected with a polyhydroxy unit. It seems, however, that this class of compounds is very sensitive to slight changes of the molecular structure. The *N*-methyl amide **21**, for example, in which the NH group of **20** is replaced by a NCH_3 group, is a non-mesogenic solid. It seems that the NH group plays an important role as a proton donor group in the mesophase stabilization of this class of compounds. Likewise, comparison of the ether **1e** with the related amide **19** reveals a mesophase stabilization of 28 K following replacement of the CH_2O group by a CONH group. However, the mesophase destabilization on introduction of the *N*-methyl

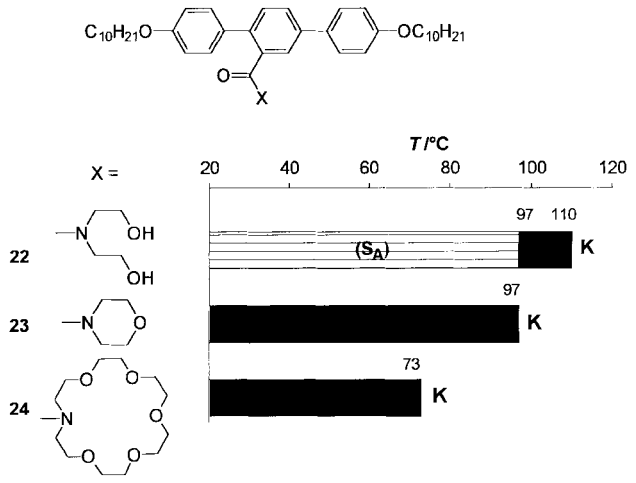


Fig. 6 Comparison of the mesomorphic properties of the amides **22**, **23** and **24**.

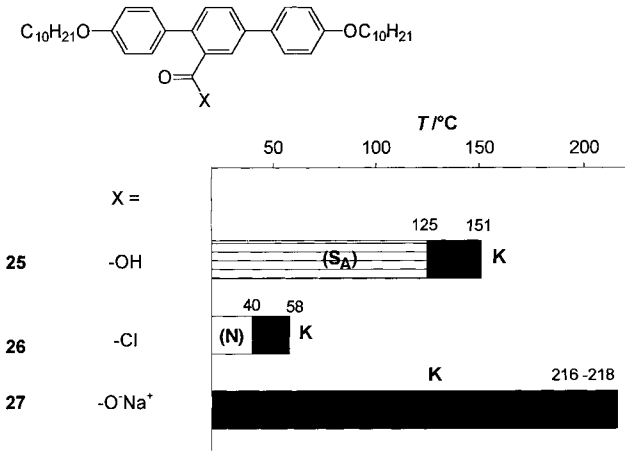
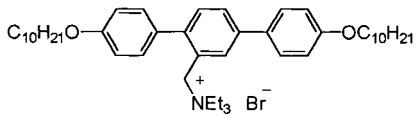


Fig. 7 Comparison of the phase transition temperatures of the carboxylic acid **25**,[27] the corresponding acid chloride **26**[27] and the sodium carboxylate **27**.

group is much larger. Therefore, the complete loss of mesogenic properties for compound **21** could not be explained by the diminished degree of hydrogen bonding alone. Changes in the molecular conformation can probably also contribute to this effect.

Compounds with polar lateral groups without the possibility of forming hydrogen bonds are in most cases non-mesomorphic. This is obvious from a comparison of the diol **22** with the morpholide **23**, which is the cyclic analogue of the diol **22** without hydroxy groups (Fig. 6). The azacrown compound **24** is also a crystalline solid.

Intermolecular hydrogen bonding is also important in carboxylic acids which are known to form dimers.[32] In Fig. 7 the carboxylic acid **25**[27] is compared with its acid chloride **26**.[27] Again the carboxylic acid **25**, *i.e.* the compound which is able to form hydrogen bonding, displays the higher mesophase



28: K 140 Iso

stability. The ionic amphiphiles, the carboxylate **27** (Fig. 7) as well as the quaternary ammonium salt **28** are high melting solids without detectable thermotropic liquid crystalline properties.

4.4. Polyether amphiphiles

In order to further clarify the relation between molecular structure and liquid crystalline behavior we have decoupled the lateral *rac*-propane-2,3-diol unit from the rigid *p*-terphenyl core *via* hydrophilic polyether chains.[12] The phase transition temperatures of these compounds are collected in Fig. 8. The clearing temperatures as well as the melting temperatures decrease significantly with increasing length of the oligo(oxyethylene) spacer which connects the propane-2,3-diol group to the rigid core. The clearing temperatures are more depressed per spacer length increment than the melting temperatures. This results in monotropic mesophases for compounds **29b** and **29c** with longer oligo(oxyethylene) spacers. However they can easily be supercooled. The diol **1e** and the ethylene glycol derivative **29a** form a smectic A phase as the only mesophase. On cooling of compound **29b** a transition from the S_A phase to a columnar mesophase occurs at 40 °C. As shown in Fig. 9 the transition to the columnar phase can be seen in the polarizing microscope by the formation of a spherulitic texture in the homeotropically aligned S_A phase.

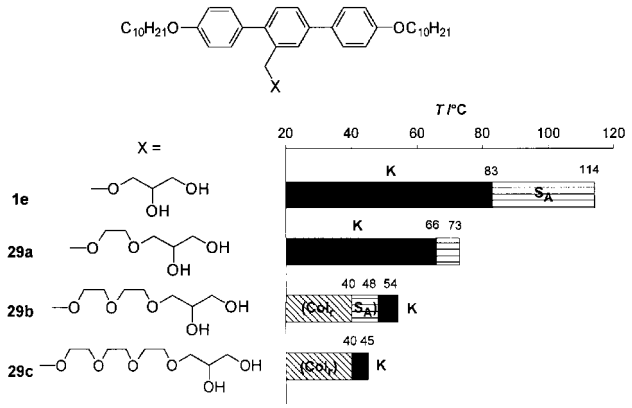


Fig. 8 Influence of the length of the lateral polyether chain on the mesomorphic properties of 2′-substituted 4,4″-didecyloxyterphenyl derivatives[12] (Col_r = rectangular columnar mesophase).

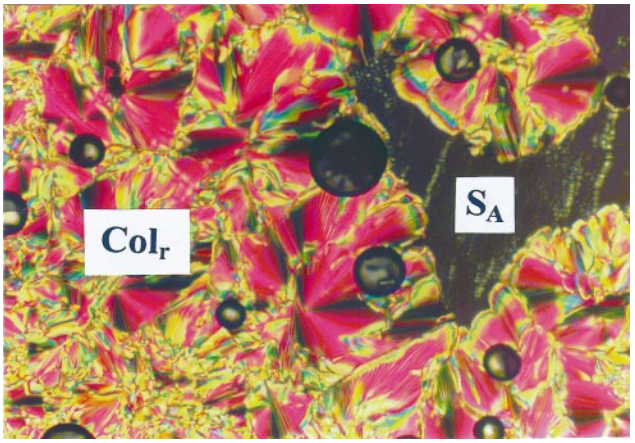


Fig. 9 Optical photomicrograph of the texture of compound **29b** between crossed polarizers at 40 °C. The Col_r phase (spherulitic texture at the left hand side) is growing out of the homeotropically aligned domains of the S_A phase while cooling. Small regions of the homeotropically aligned S_A phase with some oily streaks can still be seen at the right-hand side.

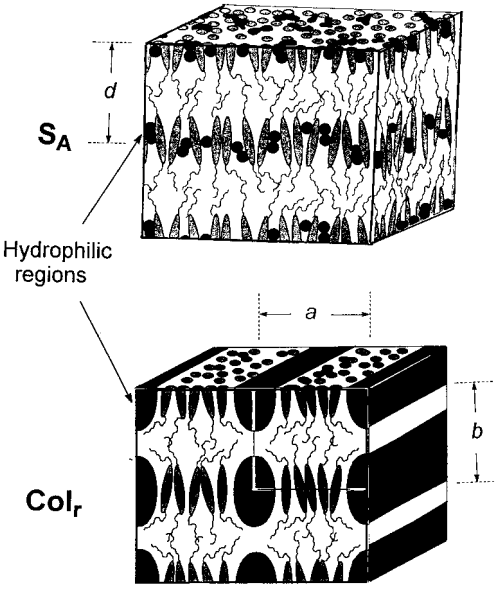


Fig. 10 Schematic illustration of the S_A phase and a possible ribbon arrangement for the rectangular columnar phases (Col_r) of compounds **29b** and **29c**.[12] The black areas represent the phase separated regions of the polar groups. The polar groups of the molecules in the middle of the ribbons cross over the neighboring calamitic terphenyl units.

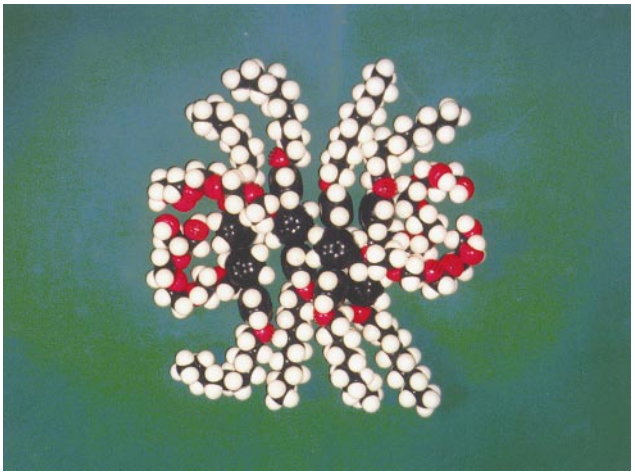


Fig. 11 CPK model showing a possible arrangement of the molecules **29c** in the cross-section of a ribbon.

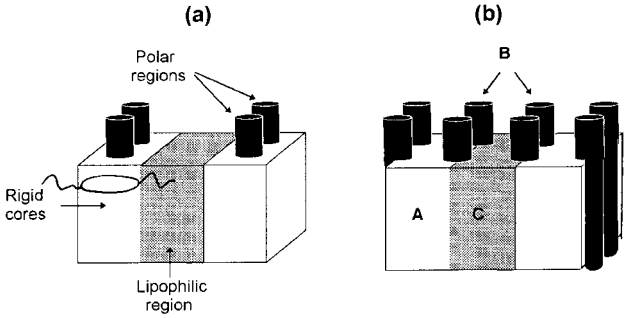


Fig. 12 Schematic representation of the lamellae-cylinder structures of (a) the Col_r phases of compounds **29b** and **29c** and (b) of a microphase segregated linear ABC triblock copolymers.[33,34]

From the X-ray diffraction pattern and taking into account the molecular dimensions a rectangular columnar structure was suggested for this mesophase.[12] Compound **29c** with a longer polyether chain exhibits exclusively the (monotropic) rectangular columnar mesophase (Col_r). For these columnar phases a ribbon structure as shown in Fig. 10 was proposed.[12] According to this model, the flexible and polar polyether chains should segregate from the rigid cores into separate domains and thus give rise to a collapse of the smectic layers into ribbons which can be regarded as small band like segments of these layers. The ribbons should consist of parallel rigid *p*-terphenyl cores laterally separated by the hydrophilic domains of the lateral groups. The alkyl chains are molten and fill up the space between the ribbons in the other dimension. From the obtained lattice parameter it was calculated that between four and five molecules should be arranged in the cross-section of the ribbons.[12] Therefore, the polar lateral groups of the molecules in the middle of these ribbons must cross over the neighboring calamitic terphenyl units in order to become incorporated into the polar regions. In Fig. 11 the CPK models of four molecules of the tris(oxyethylene) derivative **29c** are placed side by side as they would be arranged in the cross-section of the ribbons. It shows that indeed the lateral groups of the molecules in the middle are sufficiently long to reach the polar regions. Therefore, we propose that, in addition to a certain polarity and size, a sufficient length of the polar groups is also an important prerequisite for columnar mesophase formation in this class of compounds.

The proposed ribbon model seems reasonable, because it enables the segregation of polar and lipophilic units into separate regions whereby the parallel organization of the rod-like molecules is maintained. In respect of the local order within the ribbons, the columnar phase can be regarded as a modulated smectic phase, but in comparison to most other modulated phases the lateral diameter of the ribbons is rather small. Alternatively, this ribbon structure can be described as an alternating structure of two types of lamellae. One type consists of alkyl chains and the second type is composed of ribbons of rigid *p*-terphenyl units laterally separated by cylinders containing the hydrophilic groups [see Fig. 12(*a*)]. This model is related to that suggested for supermolecular structures which have recently been found in triblock copolymers consisting of three linearly combined flexible blocks [see Fig. 12(*b*)].[33] Here, beside other superstructures, lamellae with cylinders at the lamella interfaces have been found.[34] Indeed, the molecules described here can be regarded as low molecular weight three-block compounds composed of three different and incompatible blocks: the rigid cores, the flexible and lipophilic alkyl chains and the flexible but polar polyether chains. In contrast to linear triblock copolymers, the Y-shaped block molecules described here have the cylinders located within one of the distinct layers instead of being located at their interface. There are at least two reasons for their position within the layer of the rigid cores. At first, this organization is provided by the fixation of the polar groups in a central lateral position. Additionally, the rigidity of central rod-like block reduces the number of possible conformations and thus

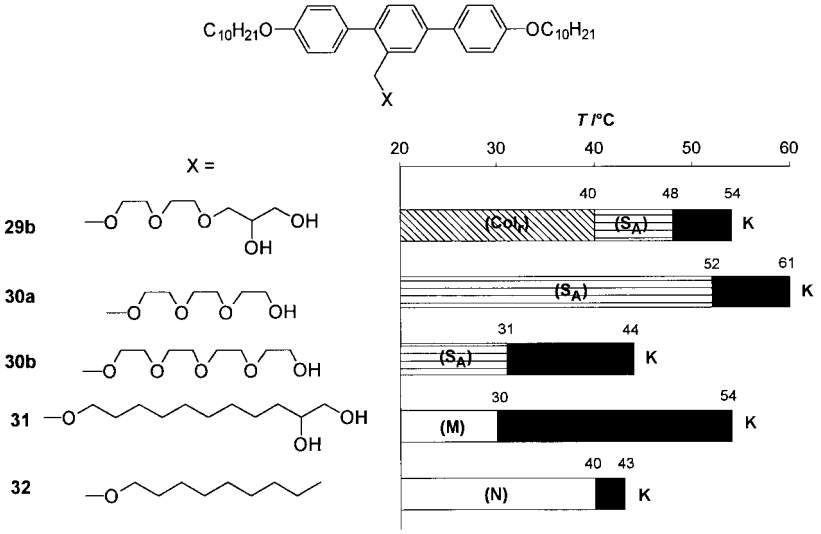


Fig. 13 Influence of the structure of the lateral group on the mesomorphic properties of the 2′-substituted *p*-terphenyl derivatives (M = unknown mesophase with schlieren texture).

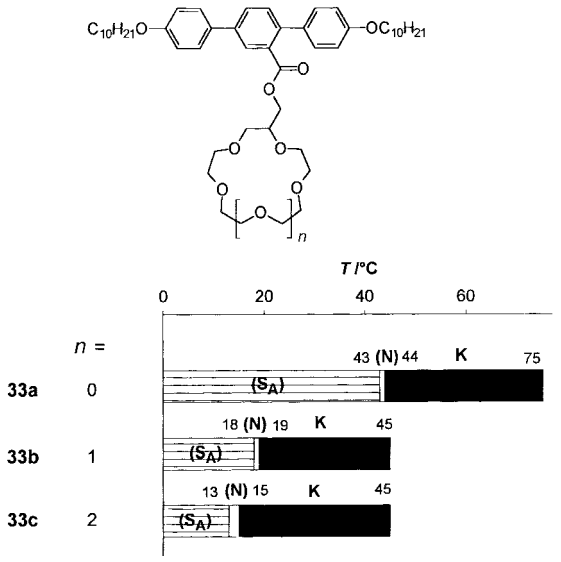


Fig. 14 Influence of the size of laterally attached crown units on the mesomorphic properties of the facial amphiphiles.

inhibits the organization of the molecules in a conventional inverted hexagonal columnar mesophase as known for flexible double chain amphiphiles and taper shaped molecules.[35]

In order to further evaluate the structural requirements which are responsible for the occurrence of columnar mesophases, compound **32** with a lateral alkyl chain, compound **31** with a 1,2-diol unit coupled *via* a hydrophobic alkyl spacer, and two oligo(oxyethylene) ethers without diol units (compounds **30**) were investigated. As shown in Fig. 13 the columnar phase is replaced by a smectic A phase if one of the hydroxy groups in the polar group is removed (compounds **30**). A nematic phase is found if the polyether chain is replaced by a lipophilic alkyl chain (compound **32**). If a diol group is attached to the end of the lateral alkyl group (compound **31**) a monotropic mesophase with a schlieren texture is observed. Because compound **31** rapidly crystallizes we were not able to differentiate between an S_C phase and a nematic phase. Nevertheless, these structural variations show that a sufficient number of hydrogen bonding sites (diols *vs.* simple alcohols) providing sufficiently strong attractive interactions between the rigid cores, and also a certain polarity of the lateral substituents (polyether chains instead of alkyl chains), are both necessary for the occurrence of columnar mesophases.

4.5. Crown ether derivatives

The crown compounds **33a**–**c**[36] (Fig. 14) represent closed analogues of compounds **29** and **30**. Because of the absence of proton donor groups they lack the possibility of hydrogen bonding. As mentioned in the introduction, such large lateral groups usually suppress smectic phases and give rise to nematic phases. Also the laterally alkyl-substituted terphenyl derivatives **2** (see Fig. 2) and **32** (Fig. 13) have exclusively nematic phases. No smectic phase can be observed on cooling compound **32** until crystallization sets in at 15 °C. The crown compounds **33**, however, have an S_A–N dimorphism in contrast to the alkyl substituted compounds **2** and **32**. This means that layer structures are preferred by these polyethers. Probably the polar crown ether groups can force micro-segregation between the central regions consisting of the rigid cores and the crown ether units from the terminal lipophilic alkyl chains. Thus, in the crown compounds the steric disturbance of the lateral groups is in competition with the layer stabilizing effect provided by micro-segregation.[37]

4.6. Influence of the position of the polyether chain

As mentioned above the 3-substituted diol **13** has a significantly higher smectic mesophase stability than the corresponding 2′-substituted molecule **1e** (see Fig. 4). Also the 3-substituted polyether compounds **34** (Fig. 15) have enhanced clearing temperatures in comparison to the 2′-substituted analogues **29** (Fig. 8). Remarkably however, only S_A phases and no columnar mesophases could be detected for the diols **34b** and **34c** with long polyether chains in the peripheral 3-position at the rigid core. It seems that the formation of columnar mesophases is bound to a very special molecular structure and it is favored by a central attachment of the polar group.

Also in the series of 3-substituted compounds the polyether chains were replaced by alkyl chains (see Fig. 15). Compound **35a** in which one ether oxygen in the lateral chain of **34a** is replaced by a CH_2 group has a slightly decreased mesophase stability. No mesomorphic properties can be found for compound **35b** in which the diol group is decoupled by a long

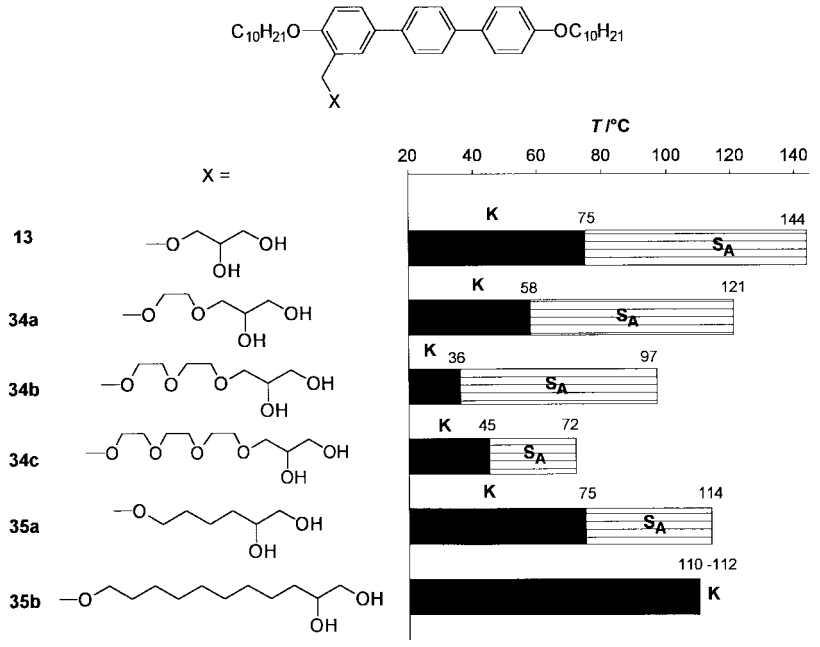


Fig. 15 Influence of the structure of the lateral group on the mesomorphic properties of 3-substituted 2,2″-didecyloxyterphenyl derivatives.

alkyl spacer. This could be due to the poor supercoolability of this compound (85 °C).

5. Conclusions

The investigations have shown that—depending on the molecular structure—facial amphiphiles can form monolayer S_A phases and columnar mesophases. Micro-segregation and cohesive forces provided by hydrogen bonding stabilize a parallel layer-like arrangement of the calamitic molecules. If the polar groups are hydrogen bonding functional groups, their mesophase stability can be higher than that of related compounds with smaller lateral substituents. However, the stabilization of layered mesophases is in competition with the disturbance provided by the space filling of these substituents. Furthermore, in many cases (*e.g.* ionic amphiphiles) the high melting temperatures and the poor supercoolability of the materials prevents potential (monotropic) mesophases from being observed.

In cases of compounds with rather large, flexible and polar lateral substituents fixed to the center of the rigid terphenyl unit (compounds **29b** and **29c**, see Fig. 8) columnar mesophases can be found. These columnar phases should represent ribbon phases resulting from the collapse of the smectic layers. The lateral polyether chains are incompatible with the rigid and lipophilic *p*-terphenyl units and segregate from them into separate cylindrical domains which interrupt the smectic layers. These molecules can be regarded as block molecules composed of three different and incompatible molecular parts. It could be expected that the design of novel types of low molecular weight block compounds consisting of three or even more different and incompatible molecular parts connected *via* different topologies might provide interesting new liquid crystalline materials.[37,38]

Finally, it should be mentioned that all compounds with hydrophilic lateral groups can form lyotropic mesophase, as will be reported in a separate paper.[13]

Acknowledgments

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6. References

1 K. J. Toyne, *Crit. Rep. Appl. Chem.*, 1987, **22**, 28.
2 G. W. Gray, M. Hird and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1991, **195**, 221.
3 M. Hird, K. J. Toyne, P. Hindmarsh, J. C. Jones and V. Minter, *Mol. Cryst. Liq. Cryst.*, 1995, **260**, 227.
4 W. Weissflog and D. Demus, *Cryst. Res. Technol.*, 1983, **18**, K21.
5 W. Weissflog, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, vol. 2b, p. 863.
6 G. W. Gray, *J. Chem. Soc.*, 1955, 236.
7 A. Jacobi and W. Weissflog, *Liq. Cryst.*, 1997, **22**, 107.
8 (*a*) G. J. T. Tiddy, *Phys. Rep.*, 1988, **57**, 1; (*b*) J. M. Seddon and R. H. Templer, in *Handbook of Biological Physics*, ed. R. Lipowsky and E. Sackmann, Elsevier, Amsterdam, 1995, vol. 1, p. 97.
9 J. A. Schröter, R. Plehnert, C. Tschierske, S. Katholy, D. Janietz, F. Penacorada and L. Brehmer, *Langmuir*, 1997, **13**, 796.
10 C. Tschierske, *Progr. Polym. Sci.*, 1996, **21**, 775.
11 C. Tschierske, J. A. Schröter, N. Lindner, C. Sauer, S. Diele, R. Festag, M. Wittenberg and J.-H. Wendorff, Dabrowski and J. Zielinski, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1998, **3319**, 8.
12 F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, M. Wittenberg and J. H. Wendorff, *Adv. Mater.*, 1997, **9**, 564.
13 J. A. Schröter, C. Tschierske, M. Wittenberg and J.-H. Wendorff, *J. Am. Chem. Soc.*, in the press.
14 (*a*) N. Miyaura, K. Yamada and A. Suzuki, *Tetrahedron Lett.*, 1979, 3437; (*b*) M. Hird, G. W. Gray and K. J. Toyne, *Mol. Cryst. Liq. Cryst. Lett.*, 1991, **206**, 187; (*c*) M. Hird, G. W. Gray and K. J. Toyne, *Liq. Cryst.*, 1994, **16**, 625.
15 J. Andersch and C. Tschierske, *Liq. Cryst.*, 1996, **31**, 51.
16 C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, 1938, **60**, 1908.
17 V. van Rheenen, R. C. Kelley and D. F. Cha, *Tetrahedron Lett.*, 1976, 1973.
18 J. Andersch, C. Tschierske, S. Diele and D. Lose, *J. Mater. Chem.*, 1996, **6**, 1297.
19 Obtained by NBS bromination of 5-decyloxy-2-(4-decyloxyphenyl)toluene, which was prepared by Suzuki coupling of 2-bromo-5-decyloxytoluene with 1 equiv. of 4-decyloxyphenylboronic acid analogous to the synthesis of **39** (Scheme 4) (ref. 18).
20 Obtained by NBS bromination of 3,5-bis(4-decyloxyphenyl)toluene, which was prepared by Suzuki coupling of 3,5-dibromotoluene with 2 equiv. of 4-decyloxyphenylboronic acid, analogous to the synthesis of 2,5-bis(4-decyloxyphenyl)benzyl bromide (ref. 15).
21 R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, 1920, **42**, 599.
22 R. Plehnert, J. A. Schröter and C. Tschierske, *Langmuir*, 1998, **14**, 5245.
23 J. Goerdeler, *Houben-Weyl, Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1958, vol. 11/2, p. 591.
24 M. Hird, A. J. Seed, K. J. Toyne, J. W. Goodby, G. W. Gray and D. G. McDonnell, *J. Mater. Chem.*, 1993, **3**, 851.
25 F. Hentrich, C. Tschierske, S. Diele and C. Sauer, *J. Mater. Chem.*, 1994, **4**, 1547.
26 D. Landini, F. Montanari and F. Rolla, *Synthesis*, 1979, 134.
27 F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, R. Kleppinger and J. H. Wendorff, *Angew. Chem.*, 1995, **107**, 1780; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1631.
28 Although the mesophase stabilization by hydrogen bonding is well documented for calamitic molecules with terminal hydrogen bonding (ref. 10, 32) and for taper-shaped polyhydroxy compounds [ref. 35(*c*),(*d*)], the mesophase stabilization by a laterally attached diol group is rather surprising. The formation of an S_A phase for a compound with laterally attached hydroxy groups was only reported for some inositol ethers (K. Praefcke and D. Blunk, *Liq. Cryst.*, 1993, **14**, 1181; K. Praefcke, D. Blunk and J. Hempel, *Mol. Cryst. Liq. Cryst.*, 1994, **243**, 323.)
29 C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.
30 (*a*) K. Praefcke and D. Singer, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 2b, p. 945; (*b*) R. Dabrowski and K. Czuprynski, in *Modern Topics in Liquid Crystals*, ed. A. Buka, World Scientific, 1993, p. 124.
31 (*a*) B. Neumann, D. Joachimi and C. Tschierske, *Liq. Cryst.*, 1997, **22**, 509; (*b*) R. Lunkwitz, B. Neumann and C. Tschierske, *Liq. Cryst.*, 1998, **25**, 403.
32 C. M. Paleos and D. Tsiourvas, *Angew. Chem.*, 1995, **107**, 1839.
33 W. Zheng and Z.-G. Wang, *Macromolecules*, 1995, **28**, 7215.
34 C. Auschra and R. Stadler, *Macromolecules*, 1993, **26**, 2171.
35 (*a*) A. Eckert, B. Kohne and K. Praefcke, *Z. Naturforsch.*, 1988, **43b**, 878; (*b*) K. Praefcke, B. Kohne, A. Eckert and J. Hempel, *Z. Naturforsch.*, 1990, **45b**, 1084; (*c*) K. Praefcke, P. Marquardt, B. Kohne and W. Stephan, *J. Carbohydr. Chem.*, 1991, **10**, 539; (*d*) G. Lattermann and G. Staufer, *Liq. Cryst.*, 1989, **4**, 347; (*e*) K. Borisch, S. Diele, P. Göring, H. Müller and C. Tschierske, *Liq. Cryst.*, 1997, **22**, 427; (*f*) V. Percec, J. Heck, G. Johansson, D. Tomazos, M. Kawasumi and G. Ungar, *J. Macromol. Sci., Pure Appl. Chem.*, 1994, **A31**, 1031; (*g*) V. Percec, G. Johannson, J. Heck, G. Ungar and S. V. Batty, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1411.
36 J. A. Schröter, C. Tschierske, M. Wittenberg and J. H. Wendorff, *Angew. Chem.*, 1997, **109**, 1160; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1119.
37 C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.
38 Block molecules can also incorporate perfluorinated segments [*e.g.* polyphilic molecules: F. Tournilhac, L. Bosio, J.-F. Nicoud and J. Simon, *J. Chem. Phys. Lett.*, 1988, **145**, 452; L. M. Blinov, T. A. Lobko, B. I. Ostrovskii, S. N. Sulianov and F. G. Tournilhac, *J. Phys. II*, 1993, **3**, 1121) or oligosiloxane units (M. Ibn-Elhaj, A. Skoulios, D. Guillon, J. Newton, P. Hodge and H. J. Coles, *Liq. Cryst.*, 1995, **19**, 373; J. Newton, H. Coles, P. Hodge and J. Hannington, *J. Mater. Chem.*, 1994, **4**, 869).

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