Monodisperse Linear Liquid Crystalline Polyethers *via* a Repetitive 2^n Geometric Growth Algorithm

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ABSTRACT: A simple and general stepwise procedure for the synthesis of linear monodisperse liquid crystalline (LC) polyethers with degrees of polymerization (DPs) up to 33 (M_n = 15 090) is presented. The particular examples used for this demonstration are based on the conformationally flexible mesogen 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB) and flexible spacers containing 10 methylenic units. The synthetic algorithm employed is exemplified by two synthetic pathways and is based on the repetition of a synthetic cycle consisting of either five or three synthetic steps. After each cycle the molecular weight is doubled. The method is very versatile, as it allows the synthesis of a large library of compounds. Linear monodisperse oligomers with DP = 1, 2, 4, 16, 17, and 33 and with a variety of chain ends were synthesized. The dependence of the phase behavior of these oligomers on the nature of their chain ends and on their DP was investigated. The mesophase stability and range increase continuously with DP. The effect of chain ends on the phase behavior decreases with DP with the following trend on the stabilization on the nematic phase of these polyethers: Bn (i.e., benzyl) > $(CH_2)_{10}OH$ > $(CH_2)_{10}Br$ ∼ $(CH_2)_{10}OMs$ > $(CH_2)_8CH{=}CH_2$ ∼ $(CH_2)_9CH_3$ > THP (i.e., tetrahydropyranyl) > OH.

Introduction

In 1988 we introduced the concept of main chain liquid crystalline (LC) polyethers based on conformational isomerism.[1,2] Since then, LC polyethers based on conformational isomerism have contributed to the elucidation of some of the most fundamental problems of the field of main chain LC polymers (LCPs). Thus, this concept has been used to generate models for linear LCPs which exhibit one[1−3a] and two uniaxial nematic,[3b] smectic,[3c,d] and columnar hexagonal[3e−g] phases. These LCPs were used to investigate chain conformation by 1-D and 2-D ^{2}H-NMR[4a−c] and SANS experiments,[4d] structure and dynamics of disclinations by electron microscopy,[4e] viscoelastic and chain conformation properties by dynamic light scattering,[4f−k] rheology,[4l] and electrorheology.[4m]

The same concept was exploited for the elaboration of LC polyethers with more complex architecture such as macrocyclics,[5] hyperbranched compounds,[6] and dendrimers.[7]

Recently we have demonstrated that macrocyclic LCPs exhibit various dependencies between structure, phase behavior, and properties, that are not encountered in their linear homologues.[5b,e,f] The investigation of these dependencies requires a convenient synthetic method able to provide access to both linear and cyclic monodisperse LCPs with a broad range of molecular weights. The most convenient method for the generation of macrocyclic LCPs in quantities sufficient for structural and physical investigations is the cyclization of the corresponding oligomeric α,ω-bisphenol with an α,ω-dibromoalkane.[5c] So far we have synthetized *via* a stepwise method linear monodisperse regioirregular oligomers up to tetramer[8] and cyclics up to pentamer.[5c] LC cyclics up to decamer were synthesized in extremely small quantities by a one-pot procedure followed by chromatographic separation.[5e] Linear LC oligomers up to the tetramer were also reported from other laboratories.[9] The synthesis of large linear oligomers was hampered in the case of polyesters by their limited solubility[9] and by the large number of reaction steps required for their preparation in the case of polyethers.[8]

A review on the synthetic strategies used in the preparation of various classes of oligomers reveals that one of the most efficient preparative methods is based on a repetitive 2^n geometric growth approach.[10] This strategy was recently used in the synthesis of monodisperse paraffins,[11a] oligo(phenylacetylene)s,[11b] oligo(thiophene)s,[11c] oligo(phenylene)s,[11d] and other classes of oligomers.[11c] A modified version of this synthetic method is extensively employed in the synthesis of dendrimers.[12]

The goal of this paper is to report the elaboration of a synthetic method for the preparation of linear monodisperse LC oligoethers and polyethers *via* a repetitive 2^n geometric growth approach. The particular examples used to demonstrate this method are regioirregular oligoethers and polyethers based on 1-(4-hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB).[3a,8] The synthesis and characterization of linear monodisperse oligomers and polymers with a degree of polymerization (DP) up to 33 (M_n = 15 090) will be reported in this publication.

Results and Discussion

Synthesis of Linear TPB Oligomers. The generic principle of the repetitive stepwise synthetic algorithm used is outlined in Scheme 1. This strategy is based on the repetition of the synthetic cycle described below. The first cycle starts with a difunctional monomer (M) containing two reactive chain ends (X and Y) in a protected form, such as X_p and respectively Y_p (*i.e.* $X_p{-}M{-}Y_p$). X_p and Y_p are orthogonal protecting groups (*i.e.* one can be cleaved without affecting the other). On one side of the synthetic cycle, X_p is deprotected and refunctionalized to form $X{-}M{-}Y_p$. On the other, Y_p is deprotected and refunctionalized to form $X_p{-}M{-}Y$. The synthetic cycle is closed by reacting $X_p{-}M{-}Y$ with $X{-}M{-}Y_p$ to form $X_p{-}M{-}M{-}Y_p$. Repetition of the same steps affords $X_p{-}M{-}M{-}M{-}M{-}Y_p$ after the second cycle, $X_p{-}[M]_8{-}Y_p$ after the third cycle, $X_p{-}[M]_{16}{-}Y_p$

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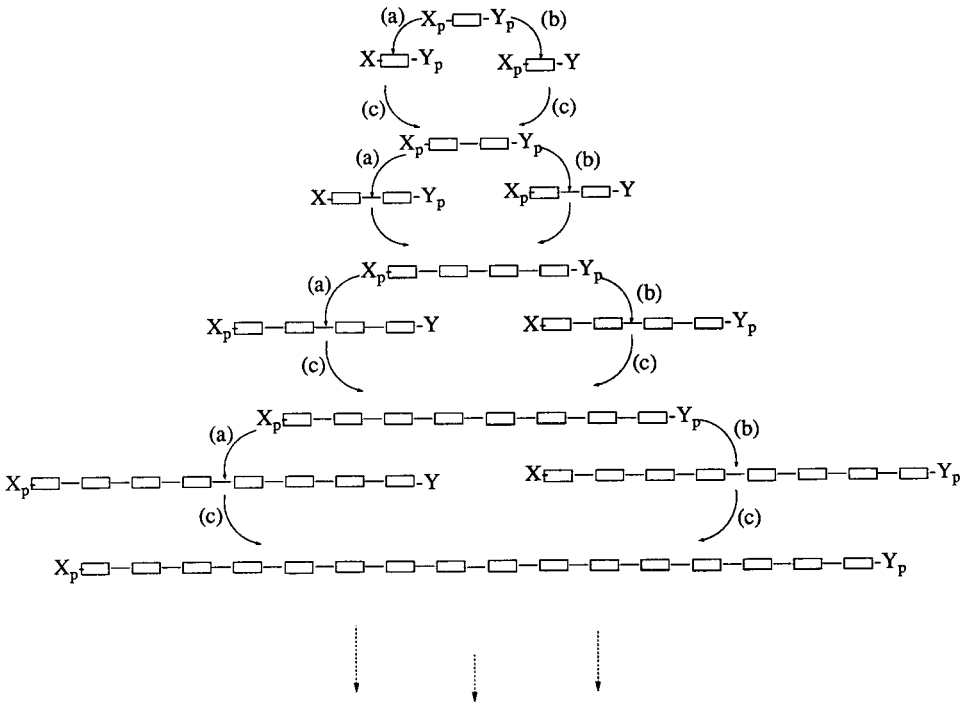
Scheme 1. Generic Synthetic 2^n Growth Algorithm



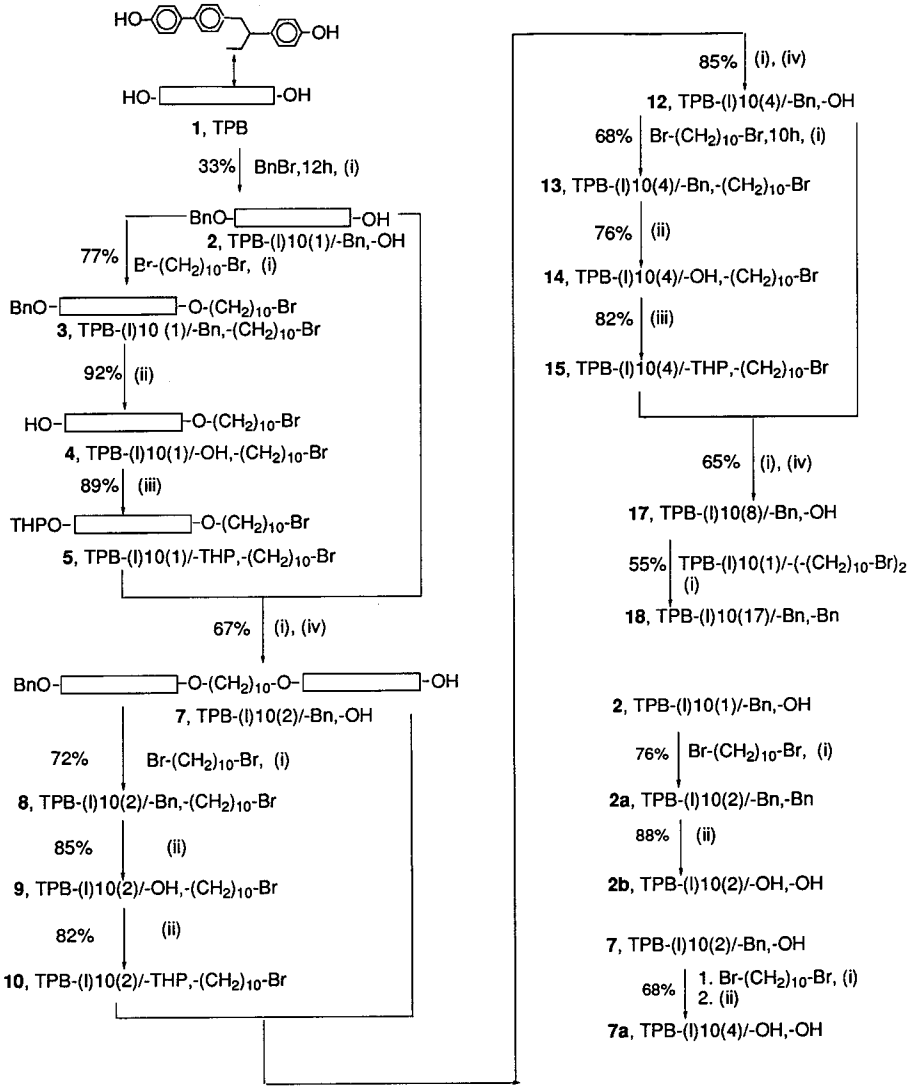
(a) = deprotection and refunctionalization of Xp
(b) = deprotection and refunctionalization of Yp
(c) = coupling of X with Y.

after the fourth cycle, $X_p-[M]_{32}-Y_p$ after the fifth cycle, and so on (*i.e.* 2^n after *n* cycles). After each synthetic cycle the molecular weight of the oligomer or polymer is therefore doubled.

This algorithm is illustrated by two different synthetic pathways which are detailed in Schemes 2 and 3. In Scheme 2 X_p = OBn, Y_p = OTHP, X = OH, and Y = $O(CH_2)_{10}Br$ whereas in Scheme 3 X_p = OBn, Y_p = $O(CH_2)_{10}OH$, X = OH, and Y = $O(CH_2)_{10}OMs$. In both cases the starting material is the regioirregular mixture of the benzyl ether (Bn) monoprotected TPB, TPB-(l)-10(1)/-OH,-Bn (**2**), which was prepared in 33% yield by the monoetherification of TPB with benzyl bromide followed by purification by column chromatography (Al_2O_3, CH_2Cl_2/MeOH = 10/1) and recrystallization (MeOH). The ratio between the two regioisomers (*i.e.* protected on the monophenyl side or on the biphenyl side of the TPB unit) was 30:70. In the first reaction scheme (Scheme 2), the phenol group was subsequently alkylated with an excees of 1,10-dibromodecane to form TPB-(l)10(1)/Bn,-$(CH_2)_{10}$-Br (**3**) in 77% yield after purification by column chromatography (SiO_2, acetone/hexane = 1/30). The benzyl ether protecting group was removed under mild conditions by hydrogenolysis using Pd/C as catalyst to afford TPB-(l)10(1)/OH,-$(CH_2)_{10}$-Br (**4**) in 92% yield after recrystallization (hexane/toluene = 1/10). The resulting new phenol group was protected as the THP ether to form TPB-(l)10(1)/THP,-$(CH_2)_{10}$-Br (**5**) in 89% yield after purification by column chromatography (SiO_2, EtOAc/hexanes = 1/30). The last step of the first synthetic cycle from Scheme 2 consisted in the coupling of **5** with **2**, which afforded TPB-(l)10-(2)/-THP,-Bn. The protecting THP group was subsequently cleaved under mild acidic conditions (CH_3-COOH) to form TPB-(l)10(2)/-OH,-Bn (**7**) in 67% overall yield for both steps after chromatographic separation (SiO_2 EtOAc/hexanes = 1/5). The same reaction steps were repeated for the second and third cycles and the corresponding tetramer TPB-(l)10(4)/-OH,-Bn (**12**) and octamer TPB-(l)10(8)/-OH,-Bn (**17**) were obtained in 85% and respectively 65% isolated yield following purification by column chromatography (SiO_2, EtOAc/hexanes = 1/10 and respectively SiO_2, EtOAc/hexanes = 1/2). TPB-(l)10(8)/-OH,-Bn was then dimerized *via* its alkylation in a 2:1 ratio with 1-(4-((bromodecyl)oxy)-4′-biphenylyl)-2-(4′-((bromodecyl)oxy)phenyl)butane (*i.e.* TPB-(l)10(1)/(-$(CH_2)_{10}Br)_2$) to form TPB-(l)10(17)/-Bn,-Bn (**18**), which was isolated in 55% yield after purification by column chromatography (SiO_2, EtOAc/hexanes = 1/1). In Scheme 2 each synthetic cycle consists of five synthetic steps. However, this pathway offers the possibility of synthesizing oligomers with a variety of different chain ends as well as oligomers with the same chain ends. This is also exemplified in Scheme 2 by the synthesis of the symmetrical dimer TPB-(l)-10(2)/-OH,-OH (**2b**), which was obtained by the dimerization of TPB-(l)10(1)/-Bn,-OH (**2**) in the presence of 1,10-dibromodecane to form TPB-(l)-10(2)/-Bn,-Bn (**2a**, 76% yield after chromatographic separation, SiO_2, EtOAc/hexanes = 1/5) followed by cleavage of the benzyl ether groups (88% yield, SiO_2, EtOAc/hexanes = 1/5) and by the similar synthesis of a symmetrical tetramer, TPB-(l)-10(4)/-OH,OH (**7a**) from TPB-(l)10(2)/-Bn,-OH (**7**) (68% combined yield for both steps after purification by column chromatography, SiO_2, EtOAc/hexanes = 1/2).

A faster procedure, involving a shorter synthetic cycle consisting of only three synthetic steps is presented in Scheme 3. The starting material was again TPB-(l)10-(1)/-Bn,-OH (**2**), which was alkylated with 1-bromodecanol (**20**) to form TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$-OH (**21**), which was isolated in 64% yield after a combination of column chromatography (SiO_2, CH_2Cl_2) and recrystallization (hexanes). In the first cycle, the benzyl ether group was cleaved as before, yielding TPB-(l)10(1)/-OH,-

Scheme 2. 2^n Synthetic Algorithm Based on a Five-Step Synthetic Cycle

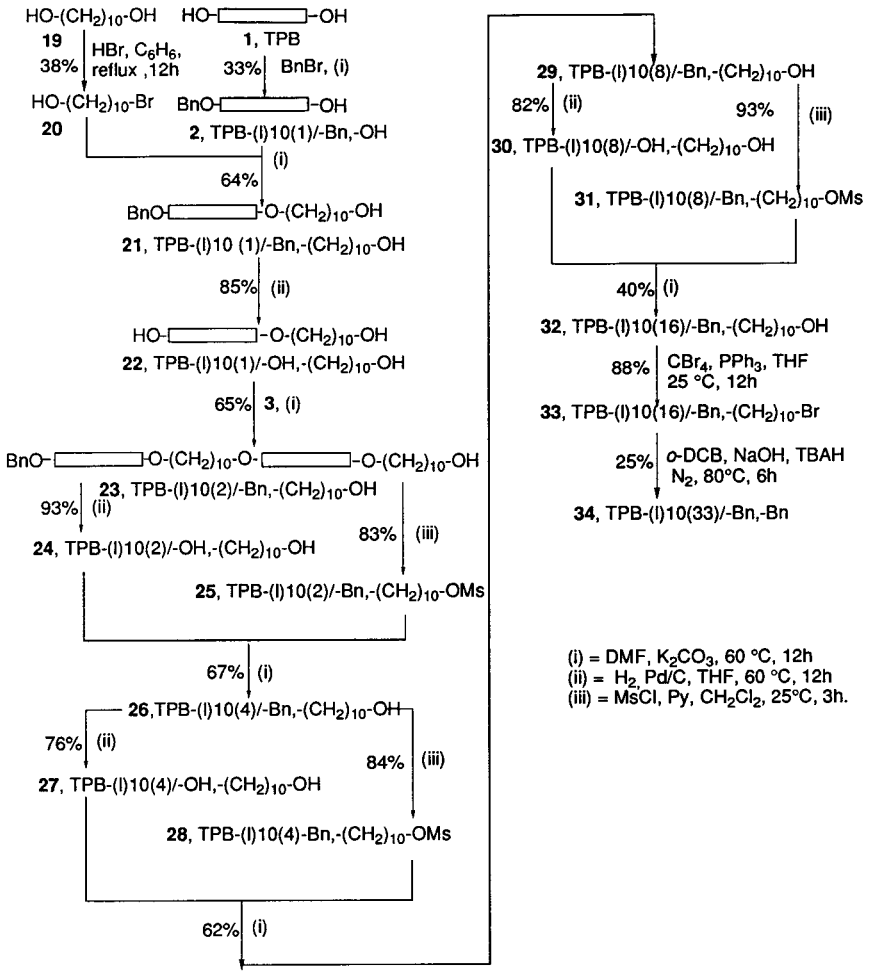


(i) = DMF, K_2CO_3, 60 °C,10h, N_2; (ii) = Pd/C, H_2, THF, 60 °C,10h
(iii) = DHP, DPTS, CH_2Cl_2, 25 °C, 2h ; (iv) = HOAc, THF, H_2O, 60 °C, 6h.

$(CH_2)_{10}$-OH (**22**) in 85% isolated yield after purification by column chromatography (SiO_2, MeOH) and recrystallization (hexanes/toluene = 1/1). **22** was then alkylated in the last step of the first cycle with TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$-Br (**3**) to form the TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$-OH dimer (**23**), which was isolated in 65% yield after chromatographic purification (SiO_2, EtOAc/hexanes = 1/2). On one side of the second cycle the benzyl ether group was cleaved to form TPB-(l)10(2)/-OH,-$(CH_2)_{10}$-OH (**24**) (93% yield, SiO_2, CH_2Cl_2), while on the other side the CH_2OH group was converted to the corresponding mesylate in TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$-OMs (**25**) (83% yield, after precipitation from CH_2Cl_2 into MeOH and recrystallization from hexanes). Coupling of **24** with **25** afforded the TPB-(l)10(4)/-Bn,-$(CH_2)_{10}$-OH tetramer (**26**) (67% yield after chromatographic purification, SiO_2, EtOAc/hexanes = 1/3). The same synthetic steps were repeated in the third and fourth cycles to yield the corresponding octamer TPB-(l)10(8)/-Bn,-$(CH_2)_{10}$-OH (**29**) (62% yield after purification by column chromatograpy, SiO_2, CH_2Cl_2/hexanes = 7/1, and precipitation from CH_2Cl_2 into acetone) and respectively the 16-mer TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$-OH (**32**) in 40% yield (after purification by column chromatography, SiO_2, CH_2Cl_2/hexanes = 3/1, and precipitation from CH_2Cl_2 into a CH_2Cl_2/acetone = 1.5/1 mixture). The alcohol group of **32** was then brominated with CBr_4/PPh_3 to the corresponding TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$-Br (**33**) (88% yield after precipitation from CH_2Cl_2 into a CH_2Cl_2/acetone = 1.5/1 mixture). Dimerization of **33** *via* the alkylation of **1** (**33**:**1** = 2:1) under phase transfer catalyzed conditions afforded the linear 33-mer TPB-(l)10(33)/-Bn,-Bn (**34**) in 25% isolated yield by a combination of column (SiO_2, CH_2Cl_2/hexanes = 1.5/1) and preparative thin layer chromatography (SiO_2, CH_2Cl_2/hexanes = 2/1).

Figure 1a presents selected GPC traces of the compounds in this series with DP = 1, 2, 4, 8, 16, and 33 while Figure 1b plots the dependence of the molecular weights determined by GPC versus the corresponding absolute values. Due to the presence of rigid units in the main chain, the hydrodynamic volume of these linear structures is larger than that of the polystyrene standards of similar molecular weight that were used for the calibration of the GPC instrument. Therefore, the experimental molecular weights determined by GPC

Scheme 3. 2^n Synthetic Algorithm Based on a Three-Step Synthetic Cycle



calibrated with polystyrene standards are as expected higher than the absolute values. The overestimation of the molecular weight ranges from a factor of 1.2 for DP = 1 to 1.57 for DP = 4 and respectively to 1.82 for DP = 33. Nonetheless the plot from Figure 1b can serve as a molecular weight calibration curve for similar compounds in this series. This effect was also observed for several other series of oligomers.[11b−f] The absolute calibration, log M_w versus V_e, of this series of oligomers is presented in Figure 1c.

Phase Behavior of Linear Oligomers. The phase behavior of all compounds is summarized in Table 1 while Figure 2 presents some selected DSC traces. The phase behavior of these oligomers will be discussed in terms of the influence of the DP and of the nature of chain ends on the mesophase stability (*i.e.* T_{ni} or T_{in}), the mesophase range (*i.e.* $T_{in}-T_g$), the degree of supercooling of the isotropization temperature (*i.e.* $\Delta T_i = T_{ni} - T_{in}$), and its corresponding enthalpy and entropy changes. Previous discussions on these experimental[8] and theoretical[13] dependencies are available.

Monomers. The dependence of the phase transition temperatures of the monomers in this series on the nature of their chain ends is shown in Figure 3a (data from their first and second heating DSC scans) and Figure 3b (data from their first cooling DSC scans). On the first heating scan all monomers display only crystalline meltings. The relative order of their melting temperatures, which is maintained on all heating scans, is shown in Figure 3a. Taking into account the subsequent cooling and reheating DSC scans, three types of monomers can be distinguished: (a) monomers that display only crystalline phases [TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$-OH > TPB-(l)10(1)/-OH,-$(CH_2)_{10}$-OH > TPB-(l)10(1)/-(-$(CH_2)_9$-$CH_3)_2$ > TPB-(l)10(1)/-(-$(CH_2)_8$-CH=$CH_2)_2$]; (b) monomers that display a monotropic nematic phase [TPB-(l)10(1)/-(-$(CH_2)_{10}$-OH)$_2$ > TPB-(l)10(1)/-(-$(CH_2)_{10}$-Br)$_2$]; (c) monomers that display an apparent enantiotropic nematic phase (*i.e.*, on the time scale of the DSC experiment it is enantiotropic; however, under equilibrium conditions it is monotropic). On the second heating DSC scan this nematic phase is followed by recrystallization and melting: TPB-(l)10(1)/-OH,-OH > TPB-(l)10(1)/-Bn,-OH > TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$-Br >TPB-(l)10(1)/-OH,-$(CH_2)_9$-CH_3 > TPB-(l)10(1)/-OH,-$(CH_2)_8$-CH=CH_2 > TPB-(l)10(1)/-THP,-$(CH_2)_{10}$-Br. An average degree of supercooling of approximately 7.3 °C is observed for the nematic phase of these monomers. TPB-(l)10(1)/-OH,-$(CH_2)_{10}$-Br exhibits only a glass transition on the first cooling and second heating DSC scans. The difference between the maximum and the minimum transition temperatures of the monomers is 117 °C on the first heating scan, 91 °C on the first cooling scan, and 170 °C on the second heating DSC scan. The transition temperatures and the breadth of the mesophase are therefore strongly dependent on the type of substituent present on the chain end of the TPB mesogenic unit (*i.e.* aromatic > aliphatic) as well as on the type of functional group on the aliphatic chain end (OH >> Br > CH_3 ~ CH=CH_2). Higher transition temperatures are therefore observed for the monomers containing free phenol groups (that promote network formation by H bonding)[14b] or benzyl ether groups (that increase molecular rigidity). Substitution by long alkyl

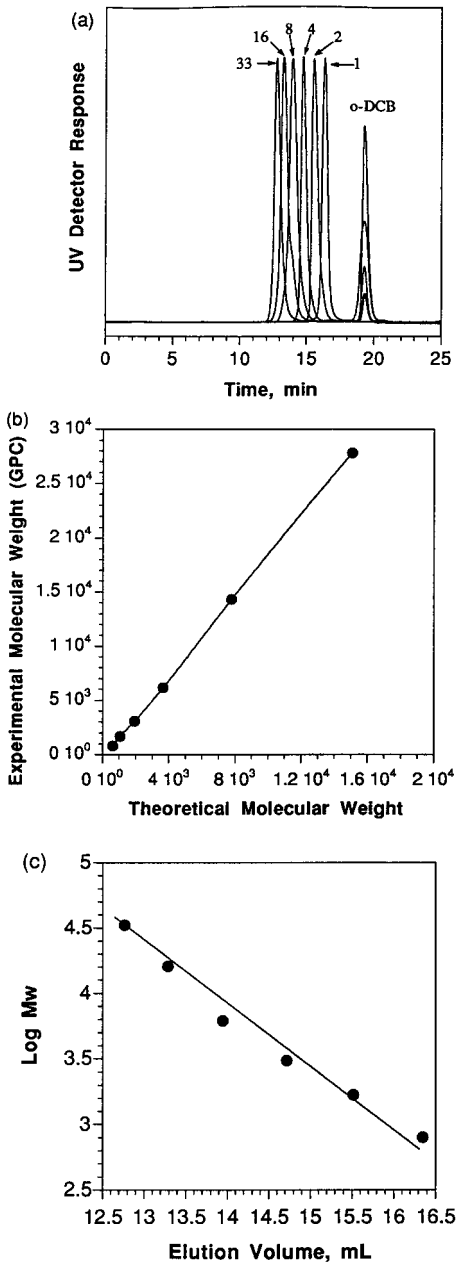


Figure 1. (a) Selected GPC traces of TPB-(l)10(*z*), $z = 1$, 2, 3, 4, 8, 16, 33. (b) Dependence of the molecular weight determined by GPC versus the calculated molecular weight. (c) Dependence of log M_w on elution volume.

chains depresses the isotropization temperature as well as the glass transition.

The order of the mesophase range of the monomers is shown in Figure 3b as a function of their chain end structure. The widest mesophase is generated by those substituents which maximize T_{ni} and minimize T_g.

The average axial ratio (L/d, where L is the end to end molecular distance calculated in all cases assuming the *anti* conformation of the mesogen and an *all-trans* conformation of the CH_2 units of the fully extended spacer and d is the average molecular diameter) of the monomers ranges from 1.46 for TPB-(l)10(1)/-OH,-OH to 2.70 for TPB-(l)10(1)/-OH,-$(CH_2)_{10}$-OH and, respectively, 3.93 for TPB-(l)10(1)/-(-$(CH_2)_{10}$-Br)$_2$. This explains the poor mesogenic character of this series of monomers and, consequently, their rather high rate of crystallization.

Dimers. The dependence of the phase transition temperatures of the dimers on the nature of their chain ends is shown in Figure 4a (data from the first and second heating DSC scans) and Figure 4b (data from the first cooling DSC scan). On the first heating DSC scan all dimers display only crystalline meltings. A graphical representation of this dependence is provided in Figure 4a. With the exception of symmetrically substituted TPB-(l)10(2)/-(-$(CH_2)_{10}$-Br)$_2$, TPB-(l)10(2)/-(-$(CH_2)_9$-CH_3)$_2$, and TPB-(l)10(2)/-(-$(CH_2)_8$-CH=CH_2)$_2$, the trend in isotropization temperatures is similar to the trend observed for the corresponding monomers.

On cooling, a nematic phase is displayed by all dimers. This nematic phase is followed by either a crystalline phase or a glass transition. The decreasing order of the mesophase stability of these compounds is shown in Figure 4b. This order is in most cases reversed versus the corresponding order of the isotropization temperatures from the first heating scan. The strongest effect is seen for TPB-(l)10(2)/-OH,OH, which unlike TPB-(l)-10(1)/-OH,OH displays now the lowest transition temperature in the series.

The dependence of the transition temperatures of the dimers, determined from their second heating DSC scan, on the nature of their chain ends is shown in Figure 4a. Almost half of the dimers in this series display only crystalline meltings preceded by a glass transition. For these monotropic dimers the trend in the melting temperatures from the first heating scan is also maintained on the second heating scan. The other dimers display only a nematic phase in addition to T_g. This nematic phase is therefore enantiotropic. In the case of TPB-(l)10(2)/-Bn,-Bn and TPB-(l)10(2)/-(-$(CH_2)_8$-CH=CH_2)$_2$, however, the nematic phase is followed by recrystallization and subsequent melting. The trend for the nematic to isotropic transition temperature is as follows: TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$-OMs > TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$-Br > TPB-(l)10(2)/-Bn,-OH > TPB-(l)10(2)/-THP,-$(CH_2)_{10}$-Br > TPB-(l)10(2)/-OH,-$(CH_2)_{10}$-Br ~ TPB-(l)10(2)/-OH,-OH. The effect of the chain ends is similar with that observed from the cooling scan; *i.e.*, alkyl chains depress the isotropization temperature and T_g while free phenol groups depress T_{ni} but increase T_g. Consequently, they generate the least stable and the narrowest mesophases. The presence of the benzyl ether group increases the stabilitity of the mesophase by enhancing the rigidity of the TPB unit to which it is attached.

In terms of mesophase range, the trend is shown in Figure 4b. This order parallels the one observed for the case of monomers. The breadth of the mesophase is controlled by both the isotropic to nematic (T_{in}, *i.e.* mesophase stability) and the nematic to crystalline (T_{nk}) or nematic to glassy (T_{ng}) transition temperatures. Higher isotropization temperatures are observed for dimers containing two benzyl ether groups or a benzyl ether group and an alkyl chain (OH > OMs > Br and Bn > THP) or two alkyl chains (OH > CH_3 > Br > CH=CH_2). Dimers containing free phenol groups have lower transition temperatures. The dimers that display a crystalline phase in addition to the nematic phase are typically symmetrically disubstituted with alkyl chains. The narrowest mesophase is observed for TPB-(l)10(2)/-OH,-OH, which has both the lowest T_{in} and the highest T_g. This effect is due to H-bonding network formation between the phenol groups and is also encountered in higher oligomers with this type of chain ends. We have previously observed a similar behavior in a related system.[14] The average supercooling of the nematic

Table 1. Characterization of TPB-(l)10(z)/X,Y (z = 1, 2, 3, 4, 8, 16, 17, 33; X or Y = OH, Bn, THP, $(CH_2)_{10}OH$, $(CH_2)_{10}OMs$, $(CH_2)_{10}Br$, $(CH_2)_9CH_3$, $(CH_2)_8CH{=}CH_2$) and of TPB-10(l)

		transition temperatures (°C) and corresponding enthalpy changes (kcal/mru) in parentheses	
entry	compound	first heating (first line) and second heating (second line)	first cooling
1	TPB-(l)10(1)/-OH,-OH (**1**)	k 119 (0.60) k 155 (7.24) i g 47 n 77 (−2.43) k 121 (1.82) k 126 (−3.42) k 155 (6.54) i	i 68 (0.65) n 39 g
2	TPB-(l)10(1)/-OH,-Bn (**2**)	k 137 (6.92) i g 24 n 61 (−4.07) k 135 (6.98) k 145 (1.74) i	i 61 (1.94) n 17 g
3	TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$Br (**3**)	k 79 (12.92) i g −15 n 29 (−11.53) k 74 (11.02) i	i 22 (1.12) n −24 g
4	TPB-(l)10(1)/-OH,-$(CH_2)_{10}$Br (**4**)	k 72 (7.18) i g −15 i	i −23 g
5	TPB-(l)10(1)/-THP,-$(CH_2)_{10}$Br (**5**)	k 88 (14.07) i g −19 n −4 (0.99) i 38 k (−10.08) k 76 (10.18) k 83 (0.4) i	i −13 (1.03) n −27 g
6	TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$OH (**21**)	k 106 (5.94) i k 108 (5.66) i	i 65 (5.72) k
7	TPB-(l)10(1)/-OH,-$(CH_2)_{10}$OH (**22**)	k 92 (11.60) i k 70 (1.81) k 82 (2.40) k 91 (2.53) i	i 16 (3.84) k
8	TPB-(l)10(1)/-OH/-$(CH_2)_9$-CH_3[a]	k 82 (11.2) i g 5 n 18 (0.58) i 20 (−3.11) k 42 (−3.88) k 80 (9.32) i	i 12 (1.48) n −5 g
9	TPB-(l)10(1)/-OH/-$(CH_2)_8$-$CH{=}CH_2$[a]	k 83 (9.33) i g 0 n 8 (1.06) i 11 k 19 k 38 (−6.54) k 80 k 85 (9.06) i	i −1 (0.67) n −11 g
10	TPB-(l)10(1)/-(-$(CH_2)_8$-$CH{=}CH_2$)$_2$[a]	k 49 (9.82) i k 31 k 38 (6.43) i	i 10 (5.86) k
11	TPB-(l)10(1)/-(-$(CH_2)_{10}$-OH)$_2$[a]	k 70 (11.8) k 84 (0.34) i k 52 k 58 (−3.01) k 85 (6.35) i	i 60 (2.06) n 35 (2.32) k
12	TPB-(l)10(1)/-(-$(CH_2)_{10}$-Br)$_2$[a]	k 57 (9.69) i k 13 k 31 (3.04) k 54 (8.27) i	i 13 (0.65) n −16 k
13	TPB-(l)10(1)/-(-$(CH_2)_9$-CH_3)$_2$[a]	k 58 (12.01) i k 46 (−0.37) k 59 (11.06) i	i 23 k 19 k 12 (8.57)
14	TPB-(l)10(2)/-Bn,-OH (**7**)	k 108 (6.22) i g 31 n 53 (1.51) i	i 44 (1.50) n 23 g
15	TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$Br (**8**)	k 74 (6.86) i g 0 n 60 (2.04) i	i 53 (1.93) n −8 g
16	TPB-(l)10(2)/-OH,-$(CH_2)_{10}$Br (**9**)	k 42 (2.84) i g −2 n 40 (1.81) i	i 30 (1.78) n −10 g
17	TPB-(l)10(2)/-THP,-$(CH_2)_{10}$Br (**10**)	k 52 (0.47) k 67 (3.34) k 83 (2.87) i g 7 n 51 (1.92) i	i 42 (1.85) n −1 g
18	TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$OH (**23**)	k 82 (2.48) k 90 (1.91) k 110 (2.99) i g 14 k 32 (−1.62) k 52 (1.12) k 76 (−0.61) k 110 (0.69) i	i 68 (1.91) n 6 g
19	TPB-(l)10(2)/-OH,-$(CH_2)_{10}$OH (**24**)	k 99 (9.91) i g 11 k 32 (−0.83) k 48 (−0.69) k 70 (1.30) k 90 (5.32) i	i 56 (2.66) n 45 (0.69) k 10 g
20	TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$OMs	k 80 (3.01) k 103 (4.06) k 111 (1.14) i g 5 k 30 (0.90) n 64 (1.67) i	i 57 (1.54) n 11 (0.53) k 2 g
21	TPB-(l)10(2)/-(-$(CH_2)_9$-CH_3)$_2$[a]	g 47 k 52 k 68 k 82 k 98 (7.75) i k 8 k 31 (−3.16) k 69 k 94 (6.85) i	i 58 (1.65) n 26 (1.23) k 0 (0.37) g
22	TPB-(l)10(2)/-(-$(CH_2)_8$-$CH{=}CH_2$)$_2$[a]	k 52 k 69 k 81 k 90 (8.53) i g −9 n 8 (−4.10) k 60 k 89 (5.86) i	i 50 (1.25) n 18 (0.15) k 6 g
23	TPB-(l)10(2)/-(-$(CH_2)_{10}$-OH)$_2$[a]	k 54 k 92 (7.38) i k 62 (−0.79) k 81 k 90 (5.75) i	i 68 (2.48) n 48 (1.90) k
24	TPB-(l)10(2)/-(-$(CH_2)_{10}$-Br)$_2$[a]	k 83 k 98 k 113 (8.00) i g 16 (−0.46) k 82 k 112 (8.68) i	i 51 (1.13) n 35 (3.59) k
25	TPB-(l)10(2)/-Bn,-Bn (**2a**)	k 110 k 116 k 126 (6.15) i g 27 n 76 (1.74) i 80 k 82 (−0.62) k 116 k 126 (1.21) i	i 69 (1.82) n 20 g
26	TPB-(l)10(2)/-OH,-OH (**2b**)	k 55 (3.32) k 117 (1.45) i g 26 n 40 (0.52) i	i 27 (0.41) n 18 g
27	TPB′-(l)10(3)/-Bn,-Bn[b]	k 98 (5.50) k 105 (0.89) i g 28 n 85 (2.80) i	i 75 (2.72) n 22 g
28	TPB′-(l)10(3)/-OH,-OH[b]	g 40 k 101 (2.10) k 115 (2.90) i g 41 n 59 (1.51) i	i 48 (1.58) n 32 g
29	TPB-(l)10(3)/-(-$(CH_2)_9$-CH_3)$_2$[a]	k 84 k 88 (6.17) i g 10 n 78 (2.31) i	i 70 (2.25) n 2 g
30	TPB′-(l)10(3)/-(-$(CH_2)_{10}$-Br)$_2$[b]	g 6 k 37 (1.06) k 71 (3.98) i g 5 n 70 (2.62) i	i 59 (2.53) n −5 g
31	TPB-(l)10(4)/-Bn,OH (**12**)	k 81 (3.71) i g 36 n 80 (1.80) i	i 72 (1.77) n 29 g
32	TPB-(l)10(4)/-Bn,-$(CH_2)_{10}$Br (**13**)	k 94 (4.81) i g 22 n 84 (2.15) i	i 76 (2.12) n 14 g
33	TPB-(l)10(4)/-OH,-$(CH_2)_{10}$Br (**14**)	k 37 (1.45) k 61 (0.91) k 88 (1.51) i g 18 n 68 (1.82) i	i 62 (1.81) n 15 g
34	TPB-(l)10(4)/-THP,-$(CH_2)_{10}$Br (**15**)	k 27 (10.87) k 90 (4.60) i g 18 n 74 (2.11) i	i 67 (2.09) n 12 g
35	TPB-(l)10(4)/-Bn,-$(CH_2)_{10}$OH (**26**)	k 48 (1.15) k 85 (2.88) i g 21 n 86 (2.08) i	i 79 n (2.06) 16 g
36	TPB-(l)10(4)/-OH,-$(CH_2)_{10}$OH (**27**)	k 101 (6.71) i g 24 n 86 (2.10) i	i 78 (2.09) n 20 g
37	TPB-(l)10(4)/-Bn,-$(CH_2)_{10}$OMs (**28**)	k 52 (0.84) k 82 (2.52) i g 17 n 81 (1.85) i	i 75 (1.88) n 12 g

Table 1 (Continued)

entry	compound	transition temperatures (°C) and corresponding enthalpy changes (kcal/mru) in parentheses: first heating (first line) and second heating (second line)	first cooling
38	TPB-(l)10(4)/-(-$(CH_2)_9$-$CH_3)_2$[a]	k 77 k 85 k 90 (5.19) i g 15 n 85 (2.35) i	i 78 (2.31) n 9 g
39	TPB-(l)10(4)/-OH, OH (**7a**)	k 107 (6.36) i g 43 n 70 (1.59) i	i 60 (1.63) n 34 g
40	TPB-(l)10(8)/-Bn,-OH (**17**)	k 94 (2.91) k 110 (0.36) i g 37 n 96 (2.09) i	i 86 (2.11) n 31 g
41	TPB-(l)10(8)/-Bn,-$(CH_2)_{10}$OH (**29**)	g 33 k 56 (0.67) k 100 (2.22) i g 31 n 100 (2.44) i	i 91 (2.52) n 24 g
42	TPB-(l)10(8)/-OH,-$(CH_2)_{10}$OH (**30**)	k 90 (2.62) i g 29 n 91 (2.23) i	i 82 (2.14) n 21 g
43	TPB-(l)10(8)/-Bn,-$(CH_2)_{10}$OMs (**31**)	k 94 (2.86) i g 30 n (2.65) 94 i	i 86 (2.59) n 22 g
44	TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$OH (**32**)	k 106 (2.85) i g 36 n 103 (2.46) i	i 94 (2.69) n 28 g
45	TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$Br (**33**)	g 40 k 55 (1.24) k 102 (2.34) i g 35 n 102 (2.49) i	i 93 (2.44) n 27 g
46	TPB-(l)10(17)/-Bn,-Bn (**18**)	k 109 (2.51) i g 36 n 103 (2.22) i	i 92 (2.29) n 26 g
47	TPB-(l)10(33)/-Bn,-Bn (**34**)	k 107 (3.27) i g 39 n 107 (2.80) i	i 94 n (2.79) 31 g
48	TPB-(l)10[c] (M_n = 37 700)	g 42 k 48 n 112 (2.54) i g 43 n 112 (2.54) i	i 96 (2.61) n 35 g

[a] Reference 8. [b] Reference 5c. [c] Reference 3a.

phase of the enantiotropic dimers is 8.6 °C and is not significantly affected by the nature of the chain ends, with the exception of TPB-(l)10(2)/-OH,-OH, for which $T_{ni} - T_{in}$ = 13 °C. Again, network formation *via* H bonding does not allow for a fast alignment of the mesogens[14] and, consequently, the supercooling is increased. This is a kinetic effect which also explains why this dimer and, as described later, the higher oligomers with these chain ends, on their first heating DSC scan, display the highest isotropization temperature in their series whereas, on the subsequent heating and cooling scans, they display the lowest isotropization temperature in their series. This shows that on the time scale of the DSC experiment (first cooling and second heating) the network does not have the time to reorganize to its original extent that was displayed on the first heating scan. Free alcohol OH groups do however stabilize the nematic mesophase *via* H bonding by comparion with other substituents at the end of the aliphatic chain ends.

The difference between the maximum and the minimum transition temperatures of the dimers in this series is 84 °C on the first heating scan, 47 °C on the first cooling scan, and 86 °C on the second heating DSC scan. While these differences are smaller than the corresponding values for the monomers, they demonstrate that the chain ends still have a considerable effect on the transition temperatures at DP = 2.

The axial ratios vary from 4.16 for TPB-(l)10(2)/-OH,-OH to 5.09 for TPB-(l)10(2)/-OH,-$(CH_2)_{10}$-OH and respectively 6.63 for TPB-(l)10(2)/-(-$(CH_2)_{10}$-Br)$_2$. These values are within the range of the theoretical minimum axial ratio that stabilizes a thermotropic nematic phase[15] and explain why the dimers have better mesogenic ability than the monomers. Nonetheless, they also maintain a high crystallization ability.

Trimers. The dependence of the phase transition temperatures and the corresponding mesophase range of the trimers on the nature of their chain ends is plotted in Figure 5. On the first heating DSC scan all trimers display crystalline meltings, showing a trend similar to that observed for the corresponding dimers. On cooling and subsequent reheating, an enantiotropic nematic phase was observed in all cases, with the following order of the isotropization temperature: TPB′-(l)10(3)/-Bn,-Bn > TPB-(l)10(3)/-(-$(CH_2)_9$-$CH_3)_2$ > TPB′-(l)10(3)/-(-$(CH_2)_{10}$-Br)$_2$ > TPB′-(l)10(3)/-OH,OH. This order is similar to that observed for the corresponding dimers. T_{in} and T_g are depressed by the presence of long alkyl chains while free phenol groups depress T_{in} but increase T_g. Therefore, in terms of mesophase width (Figure 5), the order is again consistent with the order observed for the dimers. The average supercooling of the nematic phase of the trimers is 10 °C. The difference between the maximum and the minimum transition temperatures of the trimers in this series is 44 °C on the first heating scan, 27 °C on the first cooling scan, and 26 °C on the second heating DSC scan. These values are roughly half of those of the corresponding dimers but still demonstrate a strong effect of the chain ends on the phase transition temperatures at DP = 3. The axial ratios continue to increase from 6.75 for TPB-(l)10(3)/-OH,-OH to 8.93 for TPB-(l)10(3)/-(-$(CH_2)_{10}$-Br)$_2$, which is consistent with the continous increase in the stability and range of the nematic mesophase.

Tetramers. The dependence of the phase transition temperatures and the corresponding mesophase range of the tetramers on the nature of their chain ends is plotted in Figure 6. On the first heating DSC scan all tetramers display only crystalline meltings. On second and subsequent heating and cooling scans an apparent enantiotropic nematic phase was observed for all tetramers. The order of their isotropization parallels the correponding order of the dimers. The corresponding mesophase breadth is shown in Figure 6. The width of the mesophase parallels to a certain extent the stability of the mesophase. The average degree of supercooling of the nematic phase displayed by these tetramers is 7.4 °C. The difference between the maximum and the minimum transition temperatures of the tetramers in this series is 26 °C on the first heating scan, 18 °C on the first cooling scan, and 18 °C on the second heating DSC scan. The values are approximately half of the ones for the corresponding trimers but still show a large effect of the chain ends on the phase transition temperatures at DP = 4. The axial ratios vary from 9.19 for TPB-(l)10(4)/-OH,-OH to 10.19 for TPB-(l)10(4)/-OH,-

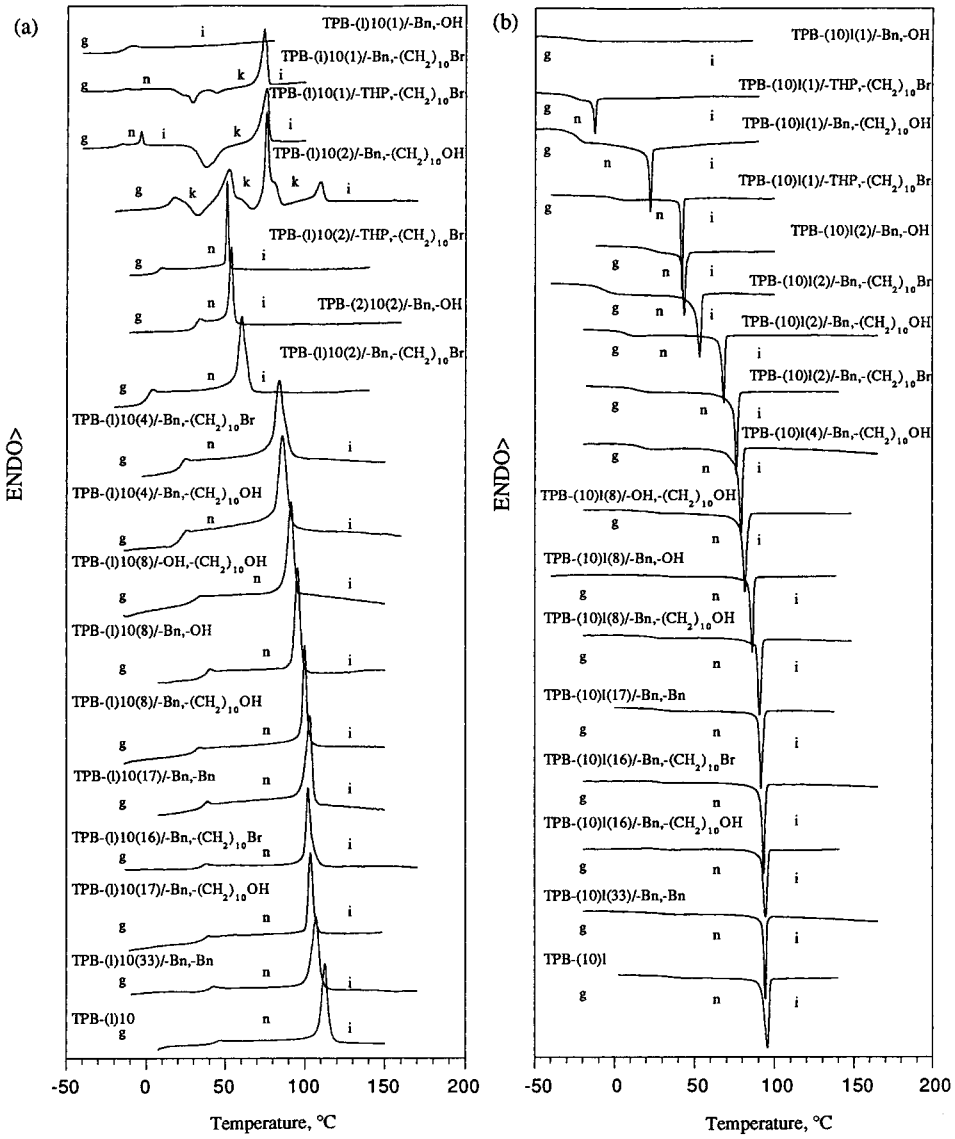


Figure 2. Selected DSC traces of the TPB-(l)10 series: (a) second heating scan; (b) first cooling scan.

$(CH_2)_{10}$-Br and respectively to 11.40 for TPB-(l)10(4)/-$(-(CH_2)_9-CH_3)_2$.

Octamers. The dependence of the transition temperatures and the corresponding mesophase range of the octamers on their chain ends is shown in Figure 7. All octamers display a crystalline melting on their first heating scan. An apparent enantiotropic nematic phase is observed on second and subsequent heating and cooling scans, and the trend in the isotropization temperatures is as follows: TPB-(l)10(8)/-Bn,-$(CH_2)_{10}$-OH > TPB-(l)10(8)/-Bn,-$(CH_2)_{10}$-OMs ~ TPB-(l)10(8)/-Bn,-OH > TPB-(l)10(8)/-OH,-$(CH_2)_{10}$-OH. The order of the corresponding mesophase widths (Figure 7) parallels the order of the isotropization tempereatures. The average supercooling of the nematic phase is 9 °C. The difference between the maximum and the minimum transition temperatures of the octamers is 20 °C on the first heating scan, 9 °C on the first cooling scan, and 9 °C on the second heating DSC scan. These values are approximately half the ones for the corresponding tetramers and show that the effect of chain ends on the phase transitions is beginning to weaken at DP = 8. The average axial ratio for the octamers is 20.36.

16/17-Mers. All 16/17-mers are crystalline on the first heating scan with the folowing order of the melting temperatures: TPB-(l)10(17)/-Bn,-Bn > TPB-(l)10(16)/-Bn,-OH > TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$-Br. On second and subsequent heating and cooling scans they display an enantiotropic nematic phase (Figure 8). The differences between the transition temperatures of these compounds are within 1 °C of each other. The average mesophase range is about 66 °C, and the average supercooling of the nematic phase is 9.6 °C. The effect of chain ends on the transition temperatures at this range of DPs becomes very small. The average axial ratio is 40.8 for the 16-mers and 42.2 for the 17-mer.

33-Mer. The oligomer with DP = 33 is crystalline on the first heating. TPB-(l)10(33)/-Bn,-Bn displays an apparent enantiotropic nematic phase on second and subsequent heating and cooling scans (Figure 8) and has a mesophase range of about 66 °C with a supercooling of 13 °C. Its average axial ratio is 61.64.

General Trends in the Phase Behavior of TPB-(l)10(*z*) (*z* = 1, 2, 3, 4, 8, 16, 33). The influence of DP on the phase behavior is summarized in Figure 9. Figure 9a plots the dependence of the average values of the isotropic to nematic and glass transition temperatures and of the associated mesophase range on DP. These temperatures increase abruptly up to DP = 8 toward a plateau trend after DP = 16. While the monomers show a high rate of crystallization on all DSC scans, the dimers are the last in this series to display

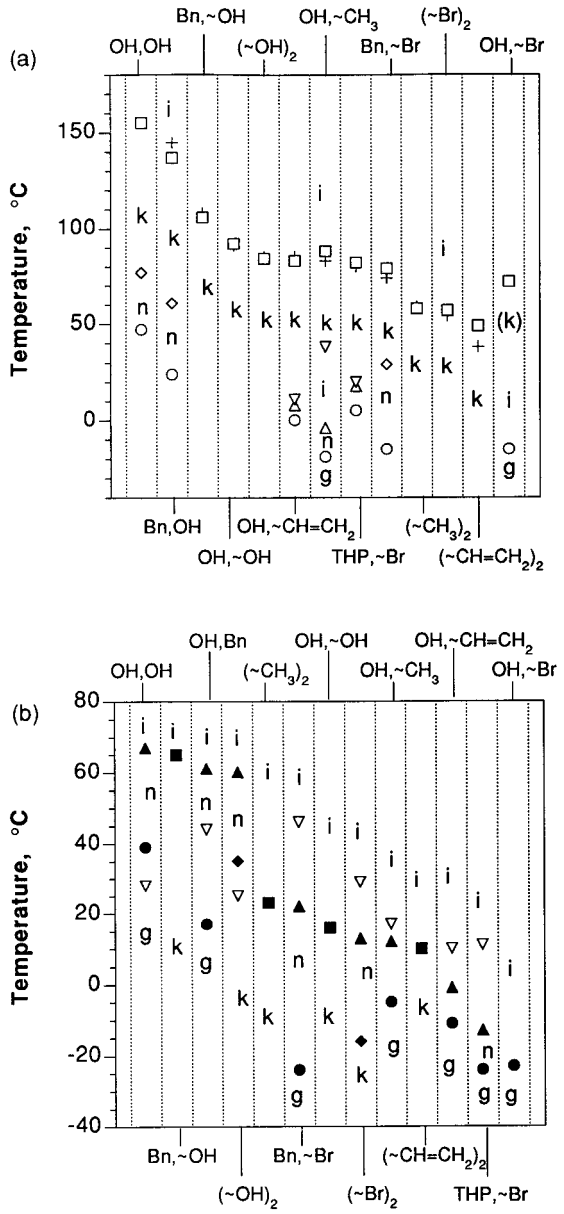


Figure 3. (a) Dependence of the phase transition temperatures of TPB-(l)10(1) on the nature of their chain ends. Data from the first heating (□, T_{ki}) and second heating (+, T_{ki}; △, T_{ni}; ▽, T_{ik}; ◇, T_{nk}; ○, T_g) DSC scans. (b) Dependence of the phase transition temperatures and of the mesophase ranges of TPB-(l)10(1) on the nature of their chain ends. Data from the first cooling DSC scan (▲, T_{in}; ■, T_{ik}; ◆, T_{nk}; ●, T_g; ▽, $T_{in} - T_g$ or $T_{in} - T_{nk}$).

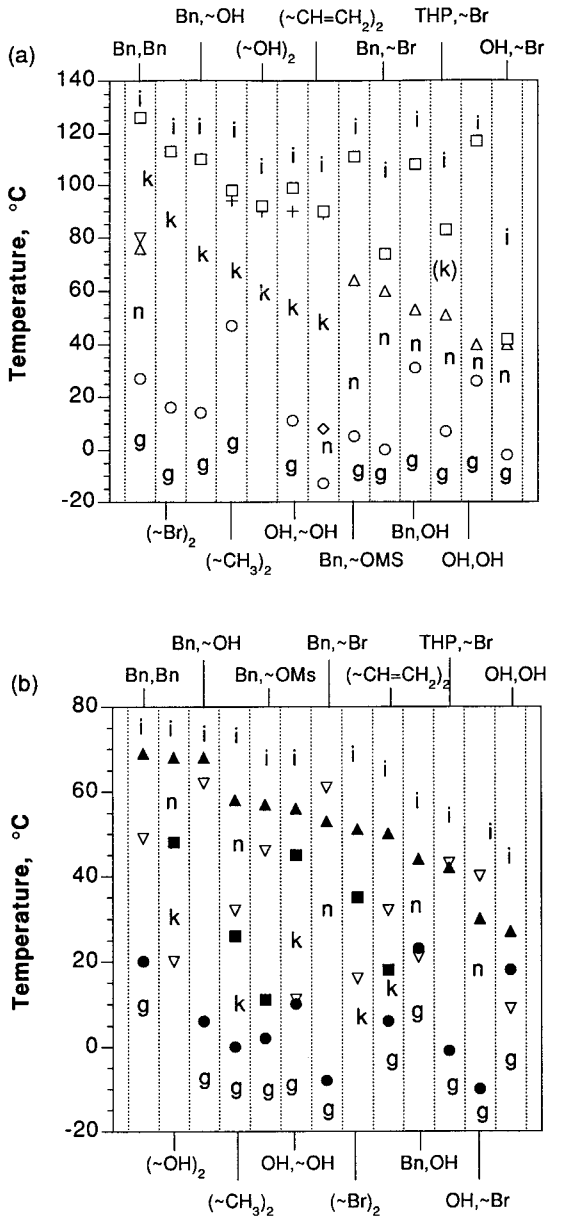


Figure 4. (a) Dependence of the phase transition temperatures of TPB-(l)10(2) on the nature of their chain ends. Data from the first heating (□, T_{ki}) and second heating (+, T_{ki}; △, T_{ni}; ▽, T_{ik}; ◇, T_{nk}; ○, T_g) DSC scans. (b) Dependence of the phase transition temperatures and correponding mesophase ranges of TPB-(l)10(2) on the nature of their chain ends. Data from the first cooling DSC scan (▲, T_{in}; ■, T_{ik}; ◆, T_{nk}; ●, T_g; ▽, $T_{in} - T_g$ or $T_{in} - T_{nk}$).

crystallization and melting after the first heating scan. From this DP on, all compounds display a crystalline melting only on the first heating scan and a nematic mesophase on the first and subsequent cooling scans and respectively the second and subsequent heating DSC scans. The kinetically controlled crystalline phase observed on the first heating scan is replaced by an apparent enantiotropic nematic phase on the subsequent heating and cooling scans upon increasing DP. As predicted theoretically, increasing DP leads to a continous increase in the stability of the nematic phase.[13] A steep increase in the dependence of the average mesophase widths of these compounds on DP (Figure 9a) is also observed up to DP = 8 and, to a smaller extent, up to DP = 16. This trend parallels the trend in the isotropization temperatures. Figure 9b plots $1/T_i$ versus 1/DP. The linear dependence of $1/T_i$ vs 1/DP observed in this plot demonstrates the synthetic accuracy of this homologous series of oligomers.

Chain ends do affect phase behavior; however, their influence decreases with DP. This is clearly seen in Figure 9c, which plots the dependence of the difference between the maximum and the minimum isotropization temperatures within each series of oligomers versus DP. Very large differences are seen up to DP = 4 to DP = 8, followed by a leveling-off trend toward DP = 16. This is in agreement with the (hyperbolic) decrease in the volume fraction of the chain ends, which is inversely proportional to DP. The general trend observed on the effect of chain ends on the stabilization of the nematic phase is as follows: Bn > $(CH_2)_{10}OH$ > $(CH_2)_{10}Br$ ~ $(CH_2)_{10}OMs$ > $(CH_2)_8CH{=}CH_2$ ~ $(CH_2)_9CH_3$ > THP > OH. This order is the result of the contribution of the substituent to the axial ratio and the overall molecular

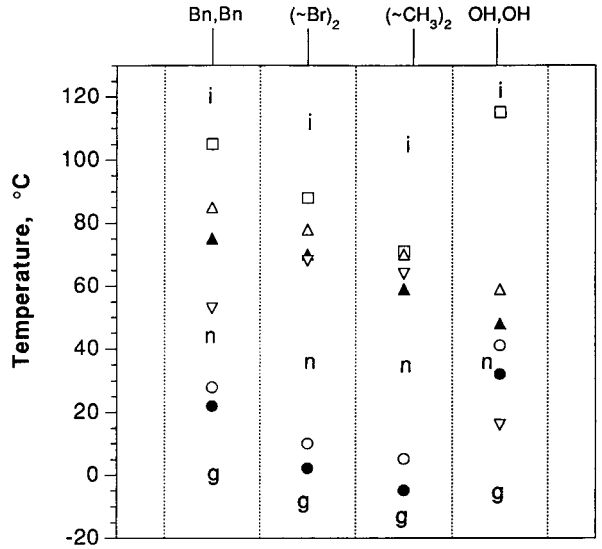


Figure 5. Dependence of the phase transition temperatures and of the corresponding mesophase range of TPB-(l)10(3) on the nature of their chain ends. Data from the first heating (□, T_{ki}), first cooling (▲, T_{in}; ●, T_g; ▽, $T_{in} - T_g$), = ▽ and second heating (△, T_{ni}; ○, T_g).

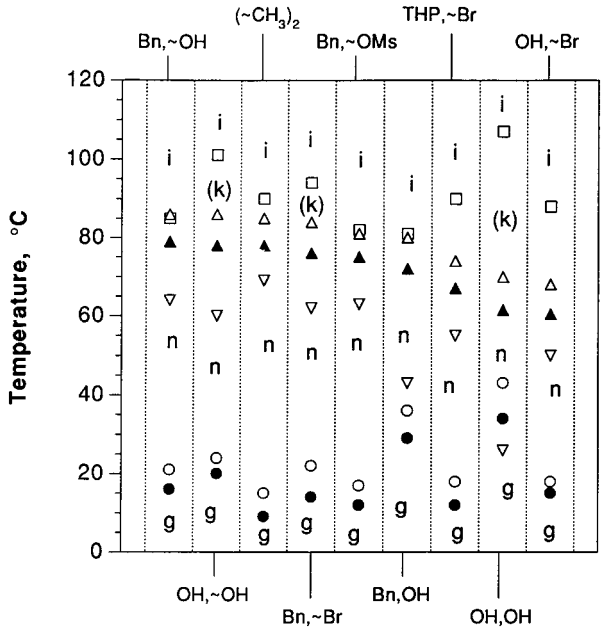


Figure 6. Dependence of the phase transition temperatures and of the mesophase range of TPB-(l)10(4) on the nature of their chain ends. Data from the first heating (□, T_{ki}), first cooling (▲, T_{in}; ●, T_g; ▽, $T_{in} - T_g$), and second heating (△, T_{ni}; ○, T_g) DSC scans.

rigidity (through their own rigidity, flexibility, and size) as well as to the intermolecular interactions between chains (through their H bonding capabilities or their dipole moment). These trends are consistent with literature data.[14,16] Therefore, while the phase transition temperatures are clearly molecular weight dependent, they can also be manipulated *via* an appropriate choice of chain ends especially at low to medium degrees of polymerization.

Figure 9d plots the dependence of the average values of the enthalpy and corresponding entropy changes at the isotropic to nematic transition on DP. A strong increase is observed for both parameters up to DP = 8, followed by a slower increase toward larger DPs. This trend parallels the trend in the dependence of the mesophase stability and range on DP and is consistent

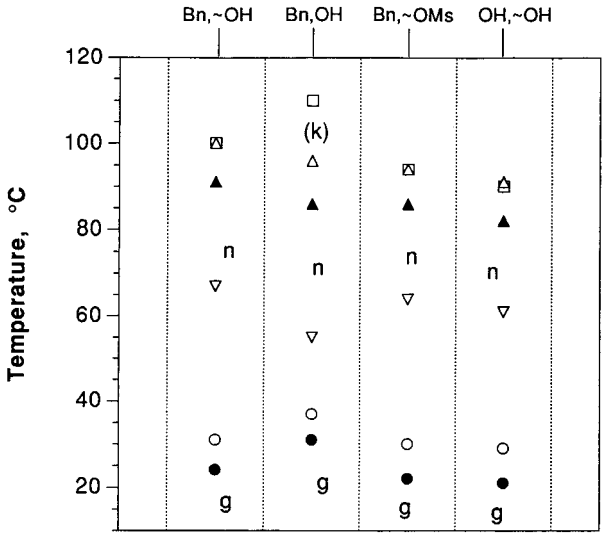


Figure 7. Dependence of the phase transition temperatures and of the mesophase range of TPB-(l)10(8) on the nature of their chain ends. Data from the first heating (□, T_{ki}), first cooling (▲, T_{in}; ●, T_g; ▽, $T_{in} - T_g$), and second heating (△, T_{ni}; ○, T_g) DSC scans.

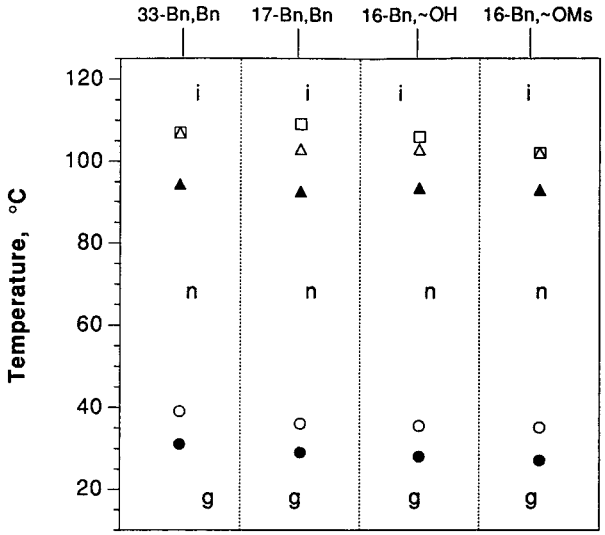


Figure 8. Dependence of the phase transition temperatures and of the mesophase range of TPB-(l)10(*z*) *z* = 16, 17, and 33, on the nature of their chain ends. Data from the first heating (□, T_{ki}), first cooling (▲, T_{in}; ●, T_g; ▽, $T_{in} - T_g$), and second heating (△, T_{ni}; ○, T_g) DSC scans.

with the continous increase of the order in the nematic phase, brought about by the continous increase in the cooperative allignment of the chains in the nematic phase with DP.

The rate of crystallization both from solution and melt states of these oligomers decreases continuously with increasing molecular weight. Melting and crystallization processes are observed for almost all monomers and for certain dimers on all heating and cooling DSC scans. From DP = 2 on, a melting transition is seen only on the first heating DSC scan. Extensive annealing is required to crystallize these oligomers from their nematic phase. Therefore, the nematic mesophase of all these compounds is only monotropic even if it can be observed both on heating and cooling DSC scans. The dependence of this melting temperature on DP is summarized in Figure 9d. Typical nematic textures were displayed by all oligomers in this series. Consistent with the increase in viscosity that accompanies the increase in molecular weight, the rate of texture forma-

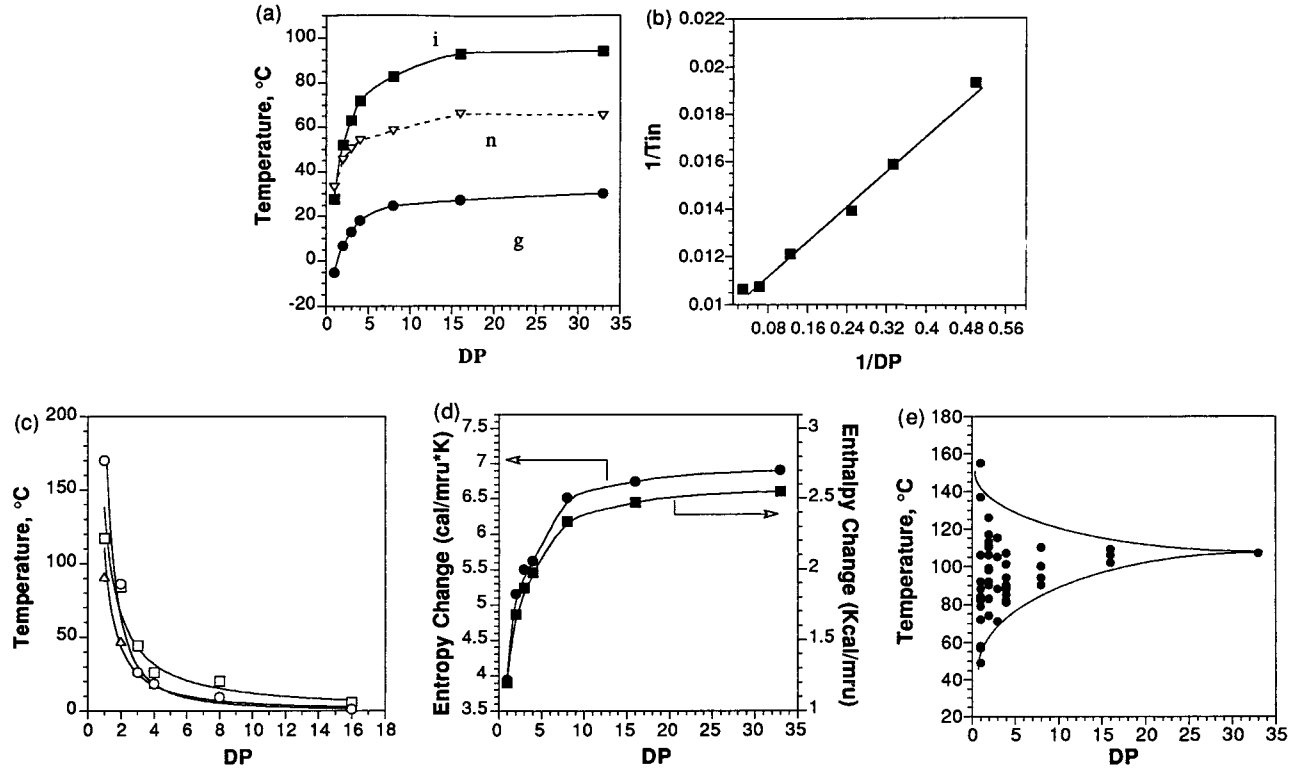


Figure 9. (a) The dependence of the average isotropic to nematic (■, T_{in}) and glass (●, T_{gn}) transition temperatures and of the corresponding average mesophase widths (▽, $T_{in} - T_g$) on DP. Data from the first cooling DSC scan. (b) Dependence of $1/T_i$ versus 1/DP. (c) Dependence of the difference between the maximum and the minimum isotropization temperatures within each series of oligomers on DP. Data from the first heating (□, $T_{max} - T_{min}$), first cooling (△, $T_{max} - T_{min}$), and second heating (○, $T_{max} - T_{min}$) DSC scans. (d) Dependence of the average enthalpy (■, ΔH) and entropy (●, ΔS) changes at the isotropic to nematic transition. Data from the first cooling DSC scan. (e) Dependence of the melting temperature of the TPB-(l)10(*z*) oligomers on DP. Data from the first heating DSC scan.

tion decreases and a longer annealing time is necessary for texture development. Consequently, prolonged annealing times for the compounds with DP = 16 or 33 lead only to very fine nematic textures.

Conclusions

A simple and general stepwise procedure for the synthesis of linear monodisperse LC polyethers was presented. The synthetic algorithm used was exemplified by two synthetic pathways and is based on the repetition of a synthetic cycle consisting of either five or three synthetic steps. After each cycle the molecular weight is doubled. A library of linear monodisperse LC oligomers with a variety of chain ends was generated, and the dependence of the phase behavior of these compounds on their DP and on the nature of their chain ends was discussed. While the general trends in the dependence of the phase behavior on molecular weight are consistent with our previous results for fractionated polyethers based on the same repeat unit,[8] the method presented herein is synthetically superior and very versatile, since it allows the synthesis of linear oligomers of precise dimensions and with an absolute control over their chain ends. Combinations of various steps in Schemes 1−3 provide easy access to oligomers with any desired DP. In each synthetic cycle, an A-B type of monomer can be generated and used directly in cyclization experiments or can be employed as a building block for more complicated LC architectures.

Experimental Section

Materials. 3,4-Dihydro-2*H*-pyran (DHP), 1,10-dibromodecane, tetrabutylammonium hydrogen sulfate (TBAH), HBr (48% in H_2O), CH_3SO_2Cl, (Aldrich), Pd(5%)/C (Lancaster), and benzyl bromide (BnBr, Fluka) were used as received. *N*,*N*-Dimethylformamide (DMF) was dried over CaH_2. 1-(4-Hydroxy-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (TPB),[3a] 1-(4-((bromodecyl)oxy)-4′-biphenylyl)-2-(4-((bromodecyl)oxy)-phenyl)butane (TPB-(l)10(1)/-(-$(CH_2)_{10}Br)_2$),[8] and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)[17] were synthesized as previously described. Column chromatography SiO_2 (40 μm, J. T. Baker) and basic Al_2O_3 (50−200 μm, Acros), thin layer chromatography (TLC) SiO_2 sheets with fluorescent indicator (Kodak-13181), preparative SiO_2 chromatographic plates with fluorescent indicator (Whatman, PLK5F), and all other chemicals were commercially available and were used as received.

Techniques. A Varian Gemini 200 NMR spectrometer was used to record the ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra at 20 °C. TMS was used as internal standard. Relative molecular weights and purities were determined on a Perkin-Elmer Series 10-LC GPC/HPLC instrument, equipped with a LC-100 column oven, a Nelson Analytical 900 Series data station, and a UV detector. The measurements were done using THF as solvent (1 mL/min, 40 °C) and two PL gel columns of 5×10^2 and 10^4 Å. A calibration plot constructed with polystyrene standards was used for the determination of the relative molecular weights. Purities were determined with the same instrument. The purity of all compounds was also supported by TLC. GC analyses were performed on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and a 3% SP-2250 column. Elemental analysis was performed by Galbraith Laboratories. A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) calibrated with In and Zn standards and equipped with a TAC7/DX thermal analysis controller was used to record the first-order thermal transition temperatures, which were read at the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures were measured as the middle of the change in heat capacity. The scanning rate was

20 °C/min in all cases. All heating and cooling scans were perfectly reproducible after the first heating scan. An Olympus BX40 optical polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to analyze the anisotropic textures. Molecular modeling and measurements of molecular dimensions were performed on a Silicon Graphics Indy workstation using the MacroModel software (version 5, from Columbia University) with the MM3 force field for energy minimization.

Synthesis of 1-(4-(Benzyloxy)-4′-biphenylyl)-2-(4-hydroxyphenyl)butane (2, *i.e.* TPB-(l)10(1)/-Bn,-OH, a mixture of constitutional isomers). To a stirred mixture of TPB (33 g, 0.1 mol) and K_2CO_3 (22 g, 0.16 mol) in DMF (200 mL) was added BnBr (17.1 g, 0.1 mol) dropwise over 1 h at 60 °C under N_2. After 12 h, DMF was distilled and NaOH (10%, 200 mL) was added. The mixture was extracted with Et_2O (4×, 200 mL). The organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. The solvent was evaporated and the product purified by column chromatography (Al_2O_3, $CHCl_3/CH_3OH$ = 10/1) followed by recrystallization from MeOH to yield 14 g (33%) of **2** (mp (DSC) 137 °C). The ratio of the two constitutional isomers (*i.e.* protected on the monophenyl side and respectively on the biphenyl side, determined by ^{1}H-NMR from the integration of the $C_6H_5CH_2C_6H_4CH(Et)$ and $C_6H_5CH_2C_6H_4C_6H_4$ singlets) was 30:70. Purity (HPLC) 99%. Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.90. Found: C, 85.30; H, 6.85. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 0.76 (t, 3H, CH_3, J = 6.96 Hz), 1.74 (m, 2H, CH_2CH_3), 2.67 (m, 1H, $CH_2CH(Et)$), 2.85 (d, 2H, $CH_2CH(Et)$, J = 7.27 Hz), 5.01 and 5.08 (s, 2H, $C_6H_4OCH_2C_6H_5$), 6.70 (d, 1H, *ortho* to Bn on the monophenyl, J = 8.36 Hz), 6.83 (d, 1H, *ortho* to OH on the monophenyl, J = 8.52 Hz), 6.92 (d, 1H, *ortho* to OH on the biphenyl, J = 8.42 Hz), 7.03 (m, 5H; 1H *ortho* to Bn on the biphenyl, 2H *ortho* to $CH_2CH(Et)$ on the biphenyl, 1H *meta* to OH on the monophenyl), 7.39 (m, 9H; 2H *meta* to $CH_2CH(Et)$ on the biphenyl, 2H *meta* to OH and Bn on the biphenyl and 5H of the Bn group). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm) 12.09 (CH_3), 28.51 (CH_3CH_2), 48.12 ($CH_2CH(Et)$), 70.11 ($C_6H_5CH_2O$), 114.60 (*ortho* to Bn on the monophenyl), 115.04 (*ortho* to Bn on the monophenyl), 115.13 (*ortho* to OH on the biphenyl), 115.58 (*ortho* to OH on the OH on the biphenyl), 126.23 (*meta* to $CH_2CH(Et)$ on the biphenyl), 127.53 (*meta* to Bn on the biphenyl), 127.9 (*meta* to Bn on the monophenyl and *meta* to CH_2O on C_6H_5), 128.16 (*ortho* to CH_2O on C_6H_5), 128.56 (*meta* to OH on the monophenyl), 128.85 (*para* to CH_2 on C_6H_5), 129.53 (*ortho* to CH_2CH on the biphenyl), 133.83 (*para* to Bn on the biphenyl), 133.94 (*para* to OH on the biphenyl), 137.04 (*para* to $CH_2CH(Et)$ on the biphenyl), 137.44 (*para* to Bn on the monophenyl), 138.06 (*ipso* to $CH_2CH(Et)$ on the biphenyl), 139.45 (*ipso* to CH_2O on Bn), 153.53 (*ipso* to OH on the monophenyl), 154.84 (*ipso* to OH on the biphenyl), 157.56 (*ipso* to Bn on the monophenyl), 158.12 (*ipso* to Bn on the biphenyl).

Synthesis of 1,10-Bis[(4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxy]decane (2a, *i.e.* TPB-(l)10-(2)/-Bn,-Bn, a mixture of constitutional isomers). A mixture of **2** (0.5 g, 1.25 mmol), DMF (20 mL), 1,10-dibromodecane (0.18 g, 0.6 mmol), and K_2CO_3 (1.73 g, 12.5 mmol) was stirred at 80 °C under N_2 for 10 h. CH_2Cl_2 (50 mL) and H_2O (50 mL) were added, and the organic phase was washed with H_2O, dilute HCl, and H_2O and was dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatography (SiO_2, EtOAc/hexanes = 1/10) to yield 0.44 g (76%) of **2a**. Purity (HPLC) 98.7%. Thermal transitions are repoted in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.78 (t, 6H, CH_3, J = 7.18 Hz), 1.34, (m, 12H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$), 1.81 (m, 8H; 4H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$), 2.68 (m, 2H, $CH_2CH(Et)$), 2.86 (d, 4H, $CH_2CH(Et)$, J = 6.99 Hz), 3.98 (m, 4H, CH_2CH_2OPh), 5.04 and 5.11 (s, 4H, $CH_2C_6H_5$), 6.82 (d, 4H, *ortho* to OCH_2 on the monophenyl, J = 7.89 Hz), 6.91 (d, 4H, *ortho* to OCH_2 on the monophenyl, J = 8.80 Hz), 7.01 (d, 4H, *meta* to OCH_2 on the monophenyl, J = 8.26 Hz), 7.08 (d, 4H, *ortho* to $CH_2CH(Et)$, J = 8.14 Hz), 7.40 (4H, *meta* to OCH_2 on the monophenyl, J = 8.20 Hz), 7.45 (d, 4H, *meta* to CH_2O on the biphenyl, J = 8.65 Hz), 7.50 (m, 10H, C_6H_5).

Synthesis of 1,10-Bis[(4-(1-ethyl-2-(4-hydroxy-4′-biphenylyl)ethyl)phenyl)oxy]decane (2b, *i.e.* TPB-(l)10(2)/-OH,-OH, a mixture of constitutional isomers). A mixture of **2a** (0.40 g, 0.42 mmol) Pd/C (40 mg), and THF (20 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 at 60 °C for 10 h. The solution was filtered, and the solvent was evaporated. The product was purified by column chromatography (SiO_2, EtOAc/hexanes = 1/5) to yield 0.29 g (88%) of **2b**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.78 (t, 6H, CH_3, J = 6.81 Hz), 1.34 (m, 12H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$), 1.82 (m, 8H; 4H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$), 2.67 (m, 2H, $CH_2CH(Et)$), 2.86 (d, 4H, $CH_2CH(Et)$, J = 6.94 Hz), 3.97 (m, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$), 6.74 (d, 2H, *ortho* to OH on the monophenyl, J = 8.61 Hz), 6.81 (d, 2H, *ortho* to OH on the biphenyl, J = 8.71 Hz), 6.87 (d, 2H, *ortho* to OCH_2 on the monophenyl, J = 8.59 Hz), 6.94 (d, 2H, *ortho* to OCH_2 on the biphenyl, J = 8.72 Hz), 6.99 (d, 4H, *meta* to O on the monophenyl, J = 8.66 Hz), 7.07 (d, 4H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.18 Hz), 7.39 (d, 4H, *meta* to $CH_2CH(Et)$ on the biphenyl, J = 8.25 Hz), 7.48 (d, 4H, *meta* to O on the biphenyl, J = 8.58 Hz).

Synthesis of 1-(4-(Benzyloxy)-4′-biphenylyl)-2-(4-((bromodecyl)oxy)phenyl)butane (3, *i.e.* TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$Br, a mixture of constitutional isomers). A mixture of **2** (5.98 g, 14.66 mmol), $Br(CH_2)_{10}Br$ (21.91 g, 73.32 mmol), K_2CO_3 (12.15 g, 87.96 mmol), and EtOH (100 mL) was stirred at 80 °C under N_2 for 10 h. $CHCl_3$ (100 mL) was added, and the organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. Excess $Br(CH_2)_{10}Br$ was distilled and the product purified by column chromatography (SiO_2, acetone/hexane = 1/30) to yield 7.08 g (77%) of **3**. Purity (HPLC) 98.9%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.79 (t, 3H, CH_3, J = 6.8 Hz), 1.34 (m, 12H, $O(CH_2)_2(CH_2)_6(CH_2)_2Br$), 1.82 (m, 6H; 2H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$), 2.67 (m, 1H, $CH_2CH(Et)$), 2.86 (d, 2H, $CH_2CH(Et)$, J = 6.96 Hz), 3.42 (t, 2H, CH_2Br, J = 6.84 Hz), 3.97 (m, 2H, CH_2CH_2OPh), 5.04 and 5.11 (s, 2H, $CH_2C_6H_5$), 6.83 (d, 1H, *ortho* to OCH_2CH_2 on the monophenyl, J = 7.87 Hz), 6.87 (d, 1H, *ortho* to Bn on the monophenyl, J = 8.8 Hz), 6.97 (d, 2H, *meta* to -OCH_2- on the monophenyl, J = 8.54 Hz), 7.09 (d, 2H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.34 Hz), 7.45 (m, 9H; 2H, *meta* to CH_2O on the biphenyl, 2H *meta* to $CH_2CH(Et)$ on the biphenyl, and 5H of the Bn group). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.12 (CH_3), 26.07−29.35 ($BrCH_2(CH_2)_7(CH_2)_2O$ and CH_2CH_3), 32.83 ($OCH_2CH_2(CH_2)_8Br$), 33.86 (CH_2Br), 43.23 ($CH_2CH(Et)$), 48.88 ($CH_2CH(Et)$), 67.01 ($C_6H_4OCH_2CH_2$), 70.06 ($C_6H_5CH_2OC_6H_4$), 114.20 (*ortho* to OCH_2CH_2 on the monophenyl), 114.58 (*ortho* to Bn on the monophenyl), 114.75 (*ortho* to OCH_2 on the biphenyl), 115.12 (*ortho* to Bn on the biphenyl), 126.25 (*meta* to $CH_2CH(Et)$ on the biphenyl), 127.47 (*ortho* to OCH_2 on C_6H_5), 127.54 (*meta* to CH_2O on C_6H_5), 128.63 (*meta* to Bn on the biphenyl), 128.70 (*para* to CH_2O on C_6H_5), 133.48 (*para* to Bn on the biphenyl), 136.91 (*para* to $CH_2CH(Et)$ on the biphenyl), 137.30 (*ipso* to CH(Et) on the monophenyl), 138.20 (*ipso* to OCH_2 on C_6H_5), 139.77 (*ipso* to $CH_2CH(Et)$ on the biphenyl), 157.03 (*ipso* to $O(CH_2)_{10}$ on the monphenyl), 157.40 (*ipso* to $O(CH_2)_{10}$ on the biphenyl), 158.17 (*ipso* to Bn on the biphenyl), 158.53 (*ipso* to Bn on the biphenyl).

Synthesis of 1-(4-Hydroxy-4′-biphenylyl)-2-(4-((bromodecyl)oxy)phenyl)butane (4, *i.e.* TPB-(l)10(1)/-OH, -$(CH_2)_{10}$Br, a mixture of constitutional isomers). A mixture of **3** (6.94 g, 11.07 mmol), Pd/C (0.6 g), and THF (100 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 for 12 h. The solution was filtered and the product recrystallized from hexane/toluene = 1/10 to yield 5.47 g (92%) of **4**. Purity (HPLC) 98%. Mp (DSC) 72 °C. Thermal transitions are repoted in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 3H, CH_3, J = 7.28 Hz), 1.31 (m, 12H, $O(CH_2)(CH_2)_6(CH_2)_2Br$), 1.77 (m, 6H; 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$, 2H, CH_2CH_3), 2.68 (m, 1H, $CH_2CH(Et)$), 2.87 (d, 2H, $CH_2CH(Et)$, J = 7.37 Hz), 3.41 (t, 2H, CH_2Br, J = 6.84 Hz), 3.95 (m, 2H, $CH_2CH_2OC_6H_4$), 6.80 (d, 2H, *ortho* to OCH_2 on the biphenyl, J = 8.76 Hz), 6.88 (d, 2H, *ortho* to OH on the biphenyl, J = 8.71 Hz), 6.98 (d, 2H, *meta* to OCH_2 on the

monophenyl, J = 8.56 Hz), 7.02 (d, 2H, *ortho* to CH_2CH(Et) on the biphenyl, J = 8.11 Hz), 7.38 (d, 2H, *meta* to CH_2CH-(Et) on the biphenyl, J = 8.16 Hz), 7.45 (d, 2H, *meta* to OH, J = 8.44 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.22 (CH_3), 26.16−29.45 ($BrCH_2(CH_2)_7(CH_2)_2O$ and CH_2CH_3), 32.92 (CH_2-CH_2O), 34.13 (CH_2Br), 43.32 (CH_2CH(Et)), 48.95 (CH_2CH(Et)), 68.07 ($C_6H_4OCH_2CH_2$), 68.07 ($C_6H_4OCH_2CH_2$), 114.32 (*ortho* to OCH_2 on the monophenyl), 114.85 (*ortho* to CH_2O on the biphenyl), 115.13 (*ortho* to OH on the monophenyl), 115.68 (*ortho* to OH on the biphenyl), 133.96 (*para* to OH on the biphenyl), 137.05 (*para* to CH_2CH(Et) on on the biphenyl), 138.13 (*ipso* to CH_2CH(Et) on the monophenyl), 139.65 (*ipso* to CH_2CH(Et) on the biphenyl), 154.95 (*ipso* to OH on the biphenyl), 157.43 (*ipso* to OCH_2CH_2 on the monophenyl).

Synthesis of 1-(4-(Tetrahydropyranyloxy)-4′-biphenyl-yl)-2-(4-((bromodecyl)oxy)phenyl)butane (5, *i.e.* TPB-(l)-10(1)/-THP,-$(CH_2)_{10}$Br, a mixture of constitutional isomers). A solution of **4** (5.38 g, 10.02 mmol), DHP (1.26 g, 15 mmol), and DPTS (0.147 g, 0.5 mmol) in dry CH_2Cl_2 (150 mL) was stirred at 25 °C under N_2 for 2 h. The organic phase was washed with H_2O, dilute $NaHCO_3$, and H_2O and was dried over $MgSO_4$. Purification by column chromatography (SiO_2, EtOAc/hexanes = 1/30) afforded 5.54 g (89%) of **5**. Purity (HPLC) 98.9%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 3H, CH_3, J = 7.32 Hz), 1.31 (m, 12H, $O(CH_2)_2(CH_2)_6(CH_2)_2$), 1.62 (m, 12H; 2H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$, 6H, $OCHCH_2(CH_2)_3$ of the THP group, 2.65 (m, 1H, CH_2CH(Et)), 2.87 (d, 2H, CH_2CH(Et), J = 7.29 Hz), 3.41 (t, 2H, CH_2Br, J = 6.88 Hz), 3.65 (m, 1H, $OCHOCH_2(CH_2)_3$ of THP), 3.95 (m, 3H; 2H, $(CH_2)_9CH_2OC_6H_4$, 1H, $OCHOCH_2(CH_2)_3$), 5.38 and 5.46 (m, 1H, OC*H*O on the monophenyl and the biphenyl), 6.81 (d, 2H, *ortho* to O−THP on the monphenyl, J = 8.4 Hz), 6.94 (d, 2H, *meta* to O−THP on the monophenyl, J = 8.7 Hz), 7.03 (d, 2H, *ortho* to OCH_2CH_2 on the biphenyl, J = 7.8 Hz), 7.09 (d, 2H, *ortho* to CH_2CH(Et) on the biphenyl, J = 8.14 Hz), 7.39 (d, 2H, *meta* to OCH_2CH_2 on the biphenyl, J = 7.8 Hz), 7.48 (d, 2H, *meta* to CH_2CH(Et) on the biphenyl, J = 8.42 Hz). ^{13}CNMR ($CDCl_3$, TMS, δ, ppm): 11.97 (CH_3), 18.64 (OCH_2-CH_2CH_2 on THP), 25.09 (OCH_2CH_2 on THP), 25.92−29.21 $O(CH_2)_2(CH_2)_7CH_2Br$ and CH_2CH_3), 30.23 ($O(CH_2)_3CH_2$ of THP), 32.66 ($CH_2CH_2(CH_2)_8Br$), 43.07 (CH_2CH(Et)), 48.66 (CH_2CH(Et)), 61.78 ($OCH_2(CH_2)_3$ on THP), 67.67 (Br-$(CH_2)_9CH_2O$), 96.22 (OCHO on THP), 114.03 (*ortho* to THP on the monophenyl), 114.56 (*ortho* to THP on the biphenyl), 116.08 (*ortho* to $Br(CH_2)_{10}O$ on the monophenyl), 116.55 (*ortho* to $Br(CH_2)_{10}O$ on the biphenyl), 126.10 (*meta* to CH_2CH(Et) on the monophenyl), 127.59 (*ortho* to THP on the monophenyl), 128.43 (*ortho* to CH_2CH(Et) on the biphenyl), 129.35 (*meta* to $Br(CH_2)_{10}O$ on the biphenyl), 134.32 (*para* to $Br(CH_2)_{10}O$ on the biphenyl), 136.64 (*para* to CH_2CH(Et) on the biphenyl), 137.95 (*ipso* to CH_2CH(Et) on the monophenyl), 139.30 (*ipso* to CH_2CH(Et) on the biphenyl), 155.08 (*ipso* to $Br(CH_2)_{10}O$ on the monophenyl), 156.27 (*ipso* to $Br(CH_2)_{10}O$ on the biphenyl), 157.24 (*ipso* to O−THP on the monophenyl), 158.33 (*ipso* to O−THP on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-((4-(2-ethyl-2-(4-hydroxyphenyl)ethyl)-4′-biphenylyl)oxy)decane (7, *i.e.* TPB-(l)10(2)/-Bn,-OH, a mixture of constitutional isomers). A mixture of **5** (5.44 g, 8.76 mmol), **2** (3.41 g, 8.34 mmol), K_2CO_3 (5.8 g, 42 mmol), and DMF (70 mL) was stirred under N_2 at 60 °C for 10 h and then was diluted with CH_2Cl_2 (100 mL), and the organic phase was separated and washed with H_2O, dilute HCl, and H_2O. The solvent was evaporated, and the THP protecting group of the resulting TPB-(l)10(2)/-Bn,THP (**6**) was cleaved in the presence of HOAc (60 mL), THF (30 mL), and H_2O (15 mL) while the mixture was stirred at 60 °C for 6 h.[18] CH_2Cl_2 (150 mL) was added, and the organic phase was washed with H_2O, dilute $NaHCO_3$, and H_2O and dried over $MgSO_4$. Purification by column chromatograpy (SiO_2, EtOAC/hexanes = 1/5) afforded 4.83 g (67%) of **7**. Purity (HPLC) 98.9%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 6H, CH_3, J = 7.04 Hz), 1.31 (m, 12H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$), 1.69 (m, 8H; 4H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$), 2.71 (m, 2H, CH_2CH(Et)), 2.88 (d, 4H, CH_2CH(Et), J = 7.32 Hz), 3.99 (m, 4H, $OCH_2(CH_2)_8CH_2O$), 4.54 and 4.73 (s, 1H O*H*), 5.04 and 5.11 (s, 2H, $C_6H_5CH_2O$), 6.74 (d, 2H, *ortho* to OH on the monophenyl, J = 8.54 Hz), 6.81 (d, 2H, *ortho* to OCH_2 on the monophenyl, J = 8.68 Hz), 6.88 (d, 2H, *ortho* to OH on the biphenyl, J = 8.72 Hz), 6.95 (d, 2H, *ortho* to OCH_2 on the biphenyl, J = 8.9 Hz), 7.04 (d, 4H, *meta* to OH and OCH_2 on the monophenyl, J = 7.34 Hz), 7.08 (d, 4H, *ortho* to CH_2CH-(Et) on the biphenyl, J = 7.81 Hz), 7.42 (m, 13H; 8H, *meta* to OCH_2 and *meta* to CH_2CH(Et) on the biphenyl, 5H of the Bn group). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.13 (CH_3), 26.07−29.38 ($OCH_2(CH_2)_8CH_2O$ and CH_2CH_3), 43.23 (CH_2CH(Et)), 48.85 (CH_2CH(Et)), 67.95 ($OCH_2(CH_2)_8CH_2O$), 70.09 ($C_6H_5CH_2O$), 114.20 and 115.74 (*ortho* to OCH_2 and OH on the monophenyl), 115.05 and 115.56 (*ortho* to OCH_2 and OH on the biphenyl), 126.23 (*meta* to CH_2CH(Et) on the biphenyl), 127.47−127.78 (*ortho* and *para* to CH_2O on the Bn), 127.90 (*ortho* to OCH_2 on the monophenyl), 129.53 (*meta* to OCH_2 on the biphenyl), 133.93 (*para* to CH_2O on the biphenyl), 136.92 (*para* to CH_2CH(Et) on the biphenyl), 139.53−140.12 (*ipso* to CH_2CH(Et) on the biphenyl and *ipso* to CH_2O on Bn), 157.32 (*ipso* to O on the monophenyl), 158.09 (*ipso* to O on the biphenyl).

Synthesis of 1,10-Bis[(4-(1-ethyl-2-((((4-(1-ethyl-2-(4-hydroxy-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl))ethyl)phenyl)oxy]decane (7a, *i.e.* TPB-(l)10(4)/-OH,-OH, a mixture of constitutional isomers). A mixture of **7** (0.12 g, 0.14 mmol), $Br(CH_2)_{10}Br$ (0.3 g, 1.11 mmol), K_2CO_3 (0.18 g, 1.31 mmol), and DMF (15 mL) was stirred under N_2 at 60 °C for 10 h and then was precipitated in H_2O and was extracted with CH_2Cl_2 (3×, 50 mL). The organic phase was washed with H_2O, dilute HCl, and H_2O and was dried over $MgSO_4$. The solution was concentrated on a rotatory evaporator. Pd/C (30 mg) and THF (15 mL) were then added, and the mixture was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 at 60 °C for 10 h. The solution was filtered, the solvent was evaporated, and the product was purified by column chromatography (SiO_2, EtOAc/hexanes = 1/2) to yield 80 mg (68%) of **7a**. Purity (HPLC) 98.8%. Thermal transitions are repoted in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.78 (t, 12H, CH_3, J = 6.85 Hz), 1.34 (m, 36H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$), 1.82 (m, 20H; 8H, CH_2CH_3, 12H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$), 2.67 (m, 4H, CH_2CH(Et)), 2.86 (d, 8H, CH_2CH(Et), J = 6.92 Hz), 3.98 (m, 12H, $OCH_2CH_2(CH_2)_6$-CH_2CH_2O), 6.74 (d, 2H, *ortho* to OH on the monophenyl, J = 8.68 Hz), 6.82 (d, 2H, *ortho* to OH on the biphenyl, J = 8.77 Hz), 6.88 (d, 6H, *ortho* to OCH_2 on the monophenyl, J = 8.52 Hz), 6.94 (d, 6H, *ortho* to OCH_2 on the biphenyl, J = 8.75 Hz), 6.99 (d, 8H, *meta* to O on the monophenyl, J = 8.72 Hz), 7.07 (d, 8H, ortho to CH_2CH(Et) on the biphenyl, J = 8.22 Hz), 7.40 (d, 8H, *meta* to CH_2CH(Et) on the biphenyl, J = 8.28 Hz), 7.48 (d, 8H, *meta* to O on the biphenyl, J = 8.62 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.08 (CH_3), 26.09−29.56 (CH_2CH_3 and $OCH_2(CH_2)_8CH_2O$), 43.22 (CH_2CH(Et)), 48.86 (CH_2CH(Et)), 67.81 (OCH_2CH_2), 114.18−114.58 (*ortho* to O on the monophenyl), 115.07−115.49 (*ortho* to O on the biphenyl), 126.12 (*meta* to CH_2CH(Et) on the biphenyl), 128.59 (*ortho* to CH_2CH(Et) on the monophenyl), 128.79 (*ortho* to CH_2CH(Et) on the biphenyl), 129.45 (*meta* to CH_2O on the biphenyl), 133.19 (*para* to O on the biphenyl), 136.83 (*para* to CH_2CH(Et) on the biphenyl), 136.82 (*ipso* to CH_2CH(Et) on biphenyl), 157.55 (*ipso* to O on the monophenyl), 158.46 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-((bromodecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (8, *i.e.* TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$Br, a mixture of constitutional isomers). A mixture of **7** (3.15 g, 3.65 mmol), $Br(CH_2)_{10}Br$ (5.48 g, 18.25 mmol), K_2CO_3 (4.96 g, 36.5 mmol), and DMF (50 mL) was stirred at 70 °C under N_2 for 8 h and then was diluted with CH_2Cl_2 (40 mL) and H_2O (40 mL). The organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. Excess $Br(CH_2)_{10}Br$ was distilled, and the product was purified by column chromatography (SiO_2, EtOAc/hexanes = 1/10) to yield 2.85 g (72%) of **8**. Purity (HPLC) 99%. Anal. Calcd for $C_{71}H_{87}O_4Br$: C, 78.64; H, 8.08. Found: C, 78.65; H, 7.86. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 6H, CH_3, J = 7.24 Hz), 1.33

(m, 24H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$), 1.76 (m 12H; 4H CH_2CH_3, 8H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$ and $OCH_2CH_2(CH_2)_6CH_2CH_2Br$), 2.66 (m, 2H, $CH_2CH(Et)$), 2.86 (d, 4H, $CH_2CH(Et)$), 3.41 (t, 2H, CH_2Br, J = 6.88 Hz), 5.04 and 5.11 (s, 2H, $C_6H_5CH_2O$), 6.81 (d, 4H, *ortho* to OCH_2 on the monophenyl, J = 8.42 Hz), 6.94 (d, 4H, *ortho* to OCH_2, J = 8.81 Hz), 7.03 (d, 4H, *meta* to OCH_2 on the monophenyl, J = 8.18 Hz), 7.07 (d, 4H, *ortho* to $CH_2CH(Et)$, J = 7.97 Hz), 7.39 (m, 8H; 4H *meta* to $CH_2CH(Et)$ on the biphenyl, 2H, *ortho* to CH_2O on the Bn, 2H, *meta* to CH_2O on the Bn), 7.48 (m, 5H; 4H *meta* to OCH_2 on the biphenyl, 1H, *para* to CH_2O on Bn). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.12 (CH_3), 26.06−29.38 ($OCH_2CH_2(CH_2)_6CH_2CH_2O$ and CH_2CH_3), 32.81 (OCH_2CH_2), 33.98 (CH_2Br), 43.23 ($CH_2CH(Et)$), 48.85 ($CH_2CH(Et)$), 67.96 (OCH_2CH_2), 70.02 ($C_6H_5CH_2O$) 114.16 (*ortho* to CH_2O on the monophenyl), 114.71 (*ortho* to CH_2O on the biphenyl), 126.22 (*meta* to $CH_2CH(Et)$ on the biphenyl), 127.52 (*ortho* to CH_2 on Bn), 127.64 (*meta* to OCH_2 on the monophenyl), 128.61 (*ortho* to $CH_2CH(Et)$ on the biphenyl), 129.52 (*meta* to CH_2O on the biphenyl), 133.44 (*para* to CH_2O on the biphenyl), 136.88 (*ipso* to $CH_2CH(Et)$ on the biphenyl), 138.16 (*ipso* to $CH_2CH(Et)$ on the monophenyl), 139.44 (*ipso* to CH_2O on C_6H_5), 157.38 (*ipso* to CH_2O on the monophenyl), 158.47 (*ipso* to CH_2O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-hydroxy-4′-biphenylyl)-ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-((bromodecyl)oxy)-phenyl)ethyl)-4′-biphenylyl)decane (9, *i.e.* TPB-(l)10(2)/-OH,-$(CH_2)_{10}$Br, a mixture of constitutional isomers). A mixture of **8** (2.63 g, 2.43 mmol), Pd/C (0.2 g), and THF (40 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 at 60 °C for 10 h. CH_2Cl_2 was added and the solution filtered. The product was purified by column chromatography (SiO_2, EtOAc/hexanes = 1/5) to yield 2.05 g (85%) of **9**. Purity (HPLC) 98.8%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.76 (t, 6H, CH_3, J = 7.24 Hz), 1.32 (m, 24H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$ and $O(CH_2)_2(CH_2)_6(CH_2)_2Br$), 1.73 (m, 12; 4H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$), 2.67 (m, 2H, $CH_2CH(Et)$), 2.87 (d, 4H, $CH_2CH(Et)$, J = 7.87 Hz), 3.41 (t, 2H, CH_2Br, J = 6.95 Hz), 3.95 (m, 6H, OCH_2CH_2), 4.58 and 4.79 (s, 1H, OH), 6.74 (d, 2H, *ortho* to OH on the monophenyl, J = 8.61 Hz), 6.82 (d, 2H *ortho* to OCH_2 on the monophenyl, J = 8.21 Hz), 6.88 (d, 2H, *ortho* to OH on the biphenyl, J = 8.76 Hz), 6.94 (d, 2H, *ortho* to OCH_2 on the biphenyl, J = 8.81 Hz), 7.03 (d, 4H, *meta* to O on the monophenyl, J = 7.88 Hz), 7.07 (d, 4H, *ortho* to $CH_2CH(Et)$, on the biphenyl, J = 8.05 Hz), 7.42 (d, 4H, *meta* to $CH_2CH(Et)$ on the biphenyl, J = 8.28 Hz), 7.48 (d, 4H, *meta* to O on the biphenyl, J = 8.72 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.11 (CH_3), 26.06−29.38 ($OCH_2CH_2(CH_2)_6CH_2CH_2O$, CH_2CH_3), 30.82 (OCH_2CH_2), 32.67 (CH_2Br), 43.22 ($CH_2CH(Et)$), 48.86 ($CH_2CH(Et)$), 67.93 (OCH_2CH_2 on the monophenyl), 68.06 (OCH_2CH_2 on the biphenyl), 114.17 (*ortho* to O on the monophenyl), 114.71 (*ortho* to O on the biphenyl), 126.31 (*meta* to ($CH_2CH(Et)$ on the biphenyl), 127.85 (*meta* to O on the monophenyl), 128.61 (*ortho* to $CH_2CH(Et)$ on the biphenyl), 129.52 (*meta* to O on the biphenyl), 133.89 (*para* to O on the biphenyl), 137.08 (*para* to $CH_2CH(Et)$ on the biphenyl), 139.22 (*ipso* to $CH_2CH(Et)$ on the monophenyl), 139.88 (*ipso* to $CH_2CH(Et)$ on the bipheny), 155.02 (*ipso* to O on the monophenyl), 157.63 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-(tetrahydropyranyloxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-((bromodecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (10, *i.e.* TPB-(l)10(2)/-THP,-$(CH_2)_{10}$Br, a mixture of constitutional isomers). A solution on **9** (1.91 g, 1.92 mmol), DHP (0.24 g, 2.87 mmol), and DPTS (28 mg, 0.1 mmol) in dry CH_2Cl_2 (20 mL) was stirred at 25 °C for 3 h. The organic phase was washed with H_2O, dilute $NaHCO_3$, and H_2O and dried over $MgSO_4$. Purification by column chromatography (SiO_2, EtOAc/hexanes = 1/15) afforded 1.7 g (82%) of **10**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.79 (t, 6H, CH_3, J = 7.24 Hz), 1.33 (m, 24 H; 24H $O(CH_2)_2(CH_2)_6(CH_2)_2O$ and $O(CH_2)_2(CH_2)_6(CH_2)_2Br$), 1.79 (m, 18H; 4H, CH_2CH_3, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$, 4H, $OCH_2CH_2(CH_2)_6CH_2CH_2Br$, 6H, $OCHOCH_2(CH_2)_3$ of THP), 2.70 (m, 2H, $CH_2CH(Et)$), 2.89 (d, 4H, $CH_2CH(Et)$, J = 7.04 Hz), 3.42 (t, 2H, CH_2Br, J = 6.82 Hz), 3.66 (m, 1H, $OCHOCH_2CH_2$ of THP), 3.97 (m, 7H; 6H, $C_6H_4OCH_2CH_2$, 1H, $OCHOCH_2CH_2$ of THP), 5.39−5.47 (m, 1H, $OCHOCH_2$ of THP), 6.83 (d, 4H, *ortho* to O on the monophenyl, J = 8.51 Hz), 6.95 (d, 4H, *ortho* to O on the biphenyl, J = 8.76 Hz), 7.06 (d, 4H, *meta* to O on the monophenyl, J = 8.14 Hz), 7.10 (d, 4H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.68 Hz), 7.42 (d, 4H, *meta* to $CH_2CH(Et)$ on the biphenyl, J = 8.75 Hz), 7.50 (d, 4H, *meta* to O on the biphenyl, J = 8.65 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.08 (CH_3), 18.86 ($OCHOCH_2CH_2CH_2$ of THP), 25.20 ($OCHOCH_2CH_2CH_2$ of THP), 26.04−29.22 ($OCH_2CH_2(CH_2)_6CH_2CH_2O$ and CH_2CH_3), 30.35 ($OCHOCH_2CH_2CH_2CH_2$ of THP), 32.78 ($OCH_2CH_2(CH_2)_6CH_2CH_2O$ and $OCH_2CH_2(CH_2)_6CH_2CH_2Br$), 33.35 ($CH_2Br$), 43.21 ($CH_2CH(Et)$), 48.41 ($CH_2CH(Et)$), 62.07 ($OCHOCH_2CH_2$ of THP), 67.94 ($C_6H_4OCH_2CH_2O$, 96.48 (OCHO of THP), 114.26 (*ortho* to OCH_2 on the monophenyl), 114.68 (*ortho* to OCHO on the monophenyl), 116.15 (*ortho* to OCH_2 on the biphenyl), 116.65 (*ortho* to OCHO on the biphenyl), 126.19 (*meta* to $CH_2CH(Et)$ on the biphenyl), 127.80 (*meta* to OCH_2 on the monophenyl), 128.57 (*ortho* to $CH_2CH(Et)$ on the biphenyl), 129.49 (*meta* to OCH_2 on the monophenyl), 133.42 (*meta* to OCH_2 on the biphenyl), 138.12 (*ipso* to $CH_2CH(Et)$ on the monophenyl), 139.45 (*ipso* to $CH_2CH(Et)$ on the biphenyl), 157.35 (*ipso* to OCH_2 on the monophenyl), 158.44 (*ipso* to OCH_2 on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-hydroxyphenyl)ethyl)-4′-biphenylyl)oxadecyl)-oxy)phenyl)ethyl)-4′-biphenylyl)decane (12, *i.e.* TPB-(l)-10(4)/-Bn,-OH, a mixture of constitutional isomers). A mixture of **10** (1.51 g, 1.40 mmol), **7** (1.19 g, 1.41 mmol), K_2CO_3, (1.38 g, 10 mmol), and DMF (40 mL) was stirred under N_2 at 60 °C for 12 h and then was diluted with CH_2Cl_2 (50 mL), and the organic phase was washed with H_2O, dilute HCl, and H_2O. The solvent was evaporated, and the THP group of the resulting TPB(l)10(4)/-Bn,THP (**11**) was cleaved with HOAc (40 mL) in a mixture of THF (20 mL) and H_2O (10 mL) at 60 °C for 3 h. More CH_2Cl_2 (50 mL) was added, and the organic phase was washed with H_2O, dilute $NaHCO_3$, and H_2O and then was dried over $MgSO_4$. Purification by column chromatography (SiO_2, EtOAc/hexanes = 1/10) afforded 2.12 g (85%) of **12**. Purity (HPLC) 98.5%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, CH_3, J = 7.34 Hz), 1.34 (m, 36H, $O(CH_2)_2(CH_2)_6(CH_2)_2O$), 1.77 (m, 20H; 8H, CH_2CH_3, 12H, $OCH_2CH_2(CH_2)_6CH_2CH_2O$), 2.67 (m, 4H, $CH_2CH(Et)$), 2.87 (d, 8H, $CH_2CH(Et)$, J = 7.04 Hz), 4.54 and 4.78 (s, 1H, OH), 5.03 and 5.11 (s, 2H, $C_6H_5CH_2O$), 6.73 (d, 2H, *ortho* to OH, J = 8.05 Hz), 6.81 (d, 6H, *ortho* to OCH_2 on the monophenyl, J = 8.17 Hz), 6.94 (d, 8H, *ortho* to OCH_2 on the biphenyl, J = 8.76 Hz), 7.03 (d, 8H, *ortho* to O on the monophenyl, J = 8.44 Hz), 7.08 (d, 8H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.06 Hz), 7.40 (d, 8H, *meta* to $CH_2CH(Et)$, J = 8.14 Hz), 7.51 (m, 13H; 8H *meta* to O on the biphenyl, 5H of C_6H_5). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.05 (CH_3), 26.02−29.43 (CH_2CH_3 and $OCH_2(CH_2)_8CH_2O$), 43.18 ($CH_2CH(Et)$), 48.75 ($CH_2CH(Et)$), 67.87 (OCH_2CH_2), 70.02 ($C_6H_5CH_2O$), 114.12−114.66 (*ortho* to OH and OCH_2 on the monophenyl), 115.03−115.48 (*ortho* to OH and OCH_2 on the biphenyl), 126.18 (*meta* to $CH_2CH(Et)$ on the biphenyl), 127.41−128.55 (*ortho* and *para* to CH_2O on Bn), 128.55 (*ortho* to $CH_2CH(Et)$ on the monophenyl), 128.81 (*ortho* to $CH_2CH(Et)$ on the biphenyl), 129.48 (*meta* to CH_2O on the biphenyl), 133.19 (*para* to BnO on the biphenyl), 136.88 (*para* to $CH_2CH(Et)$ on the biphenyl), 136.88−140.10 (*ipso* to $CH_2CH(Et)$ and *ipso* to CH_2O on Bn), 157.51 (*ipso* to O on the monophenyl), 158.44 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((bromodecyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (13, *i.e.* TPB-(l)10-(4)/-Bn,-$(CH_2)_{10}$Br, a mixture of constitutional isomers). A mixture of **12** (0.93 g, 0.52 mmol), $Br(CH_2)_{10}Br$

(1.05 g, 3.5 mmol), K_2CO_3 (0.7 g, 5 mmol), and DMF (l5 mL) was stirred under N_2 at 60 °C. CH_2Cl_2 (50 mL) was added, and the organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. Excess $Br(CH_2)_{10}Br$ was distilled, and the product was purified by column chromatography (SiO_2, EtOAc/hexane = 1/10) to yield 0.71 g (68%) of **13**. Purity (HPLC) 98%. Anal. Calcd for $C_{135}H_{167}O_8Br$: C, 8.35; H, 8.55. Found: C, 81.41; H, 8.90. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, CH_3, J = 7.24 Hz), 1.33 (m, 48H, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$O), 1.77 (m, 24H; 8H, CH_2CH$_3$, 16H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O and OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$Br), 2.67 (m, 4H, CH$_2$CH(Et)), 2.88 (d, 8H, CH_2CH(Et), J = 7.14 Hz), 3.40 (t, 2H, CH_2Br, J = 7.89 Hz), 3.96 (m, 14H, OCH_2(CH$_2$)$_8$CH_2O), 5.04 and 5.11 (s, 2H, C$_6$H$_5$CH_2O), 6.80 (d, 8H, *ortho* to O on the monophenyl, J = 8.60 Hz), 6.93 (d, 8H, *ortho* to O on the biphenyl, J = 8.80 Hz), 7.03 (d, 8H, *meta* to O on the monophenyl, J = 8.08 Hz), 7.07 (d, 8H, *ortho* to CH$_2$CH(Et) on the biphenyl, J = 8.06 Hz), 7.39 (d, 8H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.16 Hz), 7.48 (d, 8H, *meta* to O on the biphenyl, J = 8.76 Hz), 7.46−7.51 (m, 5H, OCH$_2$C$_6$$H_5$). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.10 (*C*H$_3$), 26.09−29.42 (O(CH$_2$)$_2$(*C*H$_2$)$_6$(CH$_2$)$_2$O and *C*H$_2$-CH$_3$), 32.85 (OCH$_2$*C*H$_2$), 34.02 (*C*H$_2$Br), 43.24 (*C*H$_2$CH(Et)), 48.86 (CH$_2$*C*H(Et)), 67.98 (C$_6$H$_4$O*C*H$_2$CH$_2$), 70.04 (C$_6$H$_5$*C*H$_2$O), 114.81 (*ortho* to O on the monophenyl), 114.75 (*ortho* to O on the biphenyl), 126.26 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.58−127.80 (*ortho* and *para* to CH$_2$O on Bn), 127.68 (*meta* to O on the monophenyl), 128.65 (*ortho* to CH$_2$CH(Et) on the biphenyl), 129.53 (*meta* to O on the biphenyl), 133.49 (*para* to O on the biphenyl), 136.96 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.18 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.46 (*ipso* to CH$_2$ on C$_6$H$_5$), 157.45 (*ipso* to O on the monophenyl), 158.48 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-hydroxy-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)-ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((bromodecyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (14, *i.e.* TPB-(l)10(4)/-OH,-(CH$_2$)$_{10}$Br, a mixture of constitutional isomers). A mixture of **13** (0.86 g, 0.43 mmol), Pd/C (10 mg), and THF (20 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 at 60 °C for 12 h. CH_2Cl_2 (50 mL) was added, the solution was filtered, and the solvent was distilled. Purification by column chromatograpy (SiO_2, EtOAc/hexanes = 1/2) afforded 0.62 g (76%) of **14**. Purity (HPLC) 98.2%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, CH_3, J = 7.28 Hz), 1.33 (m, 48H, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$O, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$Br), 1.77 (m, 24H; 8H, CH_2CH$_3$, 16H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O and OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$Br), 2.67 (m, 4H, CH$_2$CH(Et)), 2.88 (d, 8H, CH_2CH(Et), J = 7.18 Hz), 3.40 (t, 2H, CH_2Br, J = 7.86 Hz), 3.97 (m, 14H, OCH_2(CH$_2$)$_8$CH_2O), 4.74 (s, 1H, OH), 6.81 (d, 8H, *ortho* to O on the monophenyl, J = 8.64 Hz), 6.94 (d, 8H, *ortho* to O on the biphenyl, J = 8.81 Hz), 7.04 (d, 8H, *meta* to O on the monophenyl, J = 8.05 Hz), 7.08 (d, 8H, *ortho* to CH$_2$CH(Et), J = 7.96 Hz), 7.40 (d, 8H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.26 Hz), 7.49 (d, 8H, *meta* to O on the biphenyl, J = 8.58 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.09 (*C*H$_3$), 26.10−29.45 (O(CH$_2$)$_2$(*C*H$_2$)$_6$(CH$_2$)$_2$O and *C*H$_2$CH$_3$), 32.88 (OCH$_2$*C*H$_2$), 34.05 (*C*H$_2$Br), 43.21 (*C*H$_2$CH(Et)), 48.82 (CH$_2$*C*H(Et)), 67.94 (C$_6$H$_4$O*C*H$_2$CH$_2$), 114.78 (*ortho* to O on the monophenyl), 114.72 (*ortho* to O on the biphenyl), 126.29 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.67 (*meta* to O on the monophenyl), 128.64 (*ortho* to CH$_2$CH(Et) on the biphenyl), 129.51 (*meta* to O on the biphenyl), 133.51 (*para* to O on the biphenyl), 136.98 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.19 (*ipso* to CH$_2$CH(Et) on the monophenyl), 157.42 (*ipso* to O on the monophenyl), 158.47 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-(tetrahydropyranyloxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((bromodecyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)-decane (15, *i.e.* TPB-(l)10(4)/-THP,-(CH$_2$)$_{10}$Br, a mixture of constitutional isomers). A mixture of **14** (0.47 g, 0.25 mmol), DHP (0.06 g, 0.75 mmol), DPTS (4 mg, 0.01 mmol), and dry CH_2Cl_2 (15 mL) was stirred at 25 °C for 3 h. The solvent was evaporated, and the product was purified by column chromatography (SiO_2, EtOAc/hexanes = 1/5) to yield 0.4 g (82%) of **15**. Purity (HPLC) 98.6%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, CH_3, J = 7.35 Hz), 1.33 (m, 48H, O(CH$_2$)$_2$(CH_2)$_6$-(CH$_2$)$_2$O and O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$Br), 1.78 (m, 30H; 8H, CH_2-CH$_3$, 16H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O and OCH$_2$CH_2(CH$_2$)$_6$CH_2-CH$_2$Br, 6H, OCHOCH$_2$(CH_2)$_3$ of THP), 2.67 (m, 4H, CH$_2$CH(Et)), 2.88 (d, 8H, CH_2CH(Et), J = 7.21 Hz), 3.41 (t, 2H, CH_2Br, J = 7.69 Hz), 3.98 (m, 15 H, OCH_2(CH$_2$)$_8$CH_2O, 1H, OCHOCH_2-(CH$_2$)$_3$ of THP), 5.38−5.50 (m, 1H, OCHO of THP), 6.81 (d, 8H, *ortho* to O on the monophenyl, J = 8.64 Hz), 6.94 (d, 8H, *ortho* to O on the biphenyl, J = 8.82 Hz), 7.03 (d, 8H, *meta* to O on the monophenyl, J = 8.15 Hz), 7.07 (d, 8H, *ortho* to CH$_2$-CH(Et), J = 8.14 Hz), 7.39 (d, 8H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.22 Hz), 7.48 (d, 8H, *meta* to O on the biphenyl, J = 8.69 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.10 (*C*H$_3$), 18.82 (OCHOCH$_2$CH$_2$*C*H$_2$ of THP), 25.24 (OCHOCH$_2$*C*H$_2$CH$_2$ of THP), 26.01−29.28 (OCH$_2$CH$_2$(*C*H$_2$)$_6$CH$_2$CH$_2$O and *C*H$_2$-CH$_3$), 30.37 (OCHOCH$_2$CH$_2$CH$_2$*C*H$_2$ of THP), 32.80 (OCH$_2$*C*H$_2$-(CH$_2$)$_6$*C*H$_2$CH$_2$O and OCH$_2$*C*H$_2$(CH$_2$)$_6$*C*H$_2$CH$_2$Br), 33.33 (*C*H$_2$-Br), 43.24 (*C*H$_2$CH(Et)), 48.45 (CH$_2$*C*H(Et)), 62.02 (OCHOC*H*$_2$-CH$_2$ of THP), 67.92 (C$_6$H$_4$O*C*H$_2$CH$_2$O, 96.45 (O*C*HO of THP), 114.22 (*ortho* to OCH$_2$ on the monophenyl), 114.69 (*ortho* to OCHO on the monophenyl), 116.17 (*ortho* to OCH$_2$ on the biphenyl), 116.64 (*ortho* to OCHO on the biphenyl), 126.18 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.83 (*meta* to OCH$_2$ on the monophenyl), 128.51 (*ortho* to CH$_2$CH(Et) on the biphenyl), 129.52 (*meta* to OCH$_2$ on the monophenyl), 133.44 (*meta* to OCH$_2$ on the biphenyl), 138.19 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.57 (*ipso* to CH$_2$CH(Et) on the biphenyl), 157.40 (*ipso* to OCH$_2$ on the monophenyl), 158.52 (*ipso* to OCH$_2$ on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-((((4-(1-ethyl-2-(4-(((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)-ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)-oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-((((4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((bromodecyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)-phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl-4′-biphenylyl)-decane (17, *i.e.* TPB-(l)10(8)/-Bn,-OH, a mixture of constitutional isomers). A mixture of **12** (0.28 g, 0.16 mmol), **15** (0.32 g, 0.16 mmol), K_2CO_3 (0.10 g, 0.8 mmol), and DMF (20 mL) was stirred under N_2 at 60 °C for 12 h and then was diluted with H_2O (80 mL) and CH_2Cl_2 (80 mL). The organic phase was washed with H_2O, dilute HCl, and H_2O. The solvent was evaporated, and the THP group on the resulting TPB-(l)10(8)/-Bn,THP (**16**) was cleaved by HOAc (20 mL) in a mixture of THF (10 mL) and H_2O (5 mL) while the mixture was stirred at 60 °C for 5 h. The organic phase was washed with H_2O, dilute $NaHCO_3$, and H_2O and dried over $MgSO_4$. Purification by column chromatography (SiO_2, EtOAc/hexanes = 1/2) afforded 0.35 g (65%) of **17**. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 24 H, CH_3, J = 7.46 Hz), 1.33 (m, 84H, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$O), 1.77 (m, 44H; 16H, CH_2CH$_3$, 28H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O), 2.67 (m, 8H, CH$_2$CH(Et)), 2.88 (d, 16H, CH_2CH(Et), J = 7.24 Hz), 3.97 (m, 28H, OCH_2(CH$_2$)$_8$CH_2O), 5.04 and 5.11 (s, 2H, CH_2C$_6$H$_5$), 6.81 (d, 16H, *ortho* to O on the monophenyl, J = 8.42 Hz), 6.94 (d, 16H, *ortho* to O on the biphenyl, J = 8.80 Hz), 7.04 (d, 16H, *meta* to O on the monophenyl, J = 8.24 Hz), 7.08 (d, 16H, *ortho* to CH$_2$CH(Et), J = 8.16 Hz), 7.40 (d, 16H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.16 Hz), 7.42 (m, 5H, C$_6$H$_5$CH$_2$), 7.49 (d, 16H, *meta* to O on the biphenyl, J = 8.52 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): (12.11, *C*H$_3$), 26.11−29.48 (*C*H$_2$CH$_3$ and OCH$_2$(*C*H$_2$)$_8$CH$_2$O), 43.25 (*C*H$_2$CH-(Et)), 48.80 (CH$_2$*C*H(Et)), 67.84 (O*C*H$_2$CH$_2$), 70.04 (C$_6$H$_5$*C*H$_2$O), 114.55 (*ortho* to O on the monophenyl), 115.30 (*ortho* to O on the biphenyl), 126.24 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.66 (*C*$_6$H$_5$), 128.68 (*ortho* to CH$_2$CH(Et) on the monophenyl), 128.75 (*ortho* to CH$_2$CH(Et) on the biphenyl), 129.54 (*meta* to CH$_2$O on the biphenyl), 133.08 (*para* to O on the biphenyl), 136.65 (*para* to CH$_2$CH(Et) on the biphenyl), 136.81−140.12

(*ipso* to $CH_2CH(Et)$ and *ipso* to CH_2O on Bn), 157.55 (*ipso* to O on the monophenyl), 158.41 (*ipso* to O on the biphenyl).

Synthesis of TPB-(l)10(17)/-Bn,-Bn (18). A mixture of **17** (0.14 g, 0.041 mmol), TPB-(l)10(1)/-(-$(CH_2)_{10}Br)_2$ (0.015 g, 0.02 mmol), K_2CO_3 (0.05, 0.4 mmol), and DMF (15 mL) was stirred at 60 °C under N_2 for 12 h. CH_2Cl_2 (50 mL) was added, and the mixture was washed with H_2O, dilute HCl, and H_2O and then was dried over $MgSO_4$. Purification by column chromatogtraphy (SiO_2, EtOAc/hexanes = 1/1) afforded 85 mg (55%) of **18**. Purity (HPLC) 99%. Anal. Calcd for $C_{548}H_{674}O_{34}$: C, 84.32; H, 8.70. Found: C, 84.19; H, 8.50. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 51H, C*H*$_3$, J = 7.46 Hz), 1.33 (m, 84H, O$(CH_2)_2$(C*H*$_2$)$_6$$(CH_2)_2$O), 1.77 (m, 98H; 34H, C*H*$_2$CH$_3$, 64H, OCH$_2$C*H*$_2$$(CH_2)_6$C*H*$_2CH_2$O), 2.67 (m, 17H, CH$_2$C*H*(Et)), 2.88 (d, 34H, C*H*$_2$CH(Et), J = 7.29 Hz), 3.97 (m, 64H, OC*H*$_2$-$(CH_2)_8$C*H*$_2$O), 5.01 and 5.04 (s, 4H, C_6H_5C*H*$_2$O), 6.81 (d, 34H, *ortho* to O on the monophenyl, J = 8.35 Hz), 6.94 (d, 34H, *ortho* to O on the biphenyl, J = 8.55 Hz), 7.04 (d, 34H, *meta* to O on the monophenyl, J = 8.18 Hz), 7.08 (d, 34H, *ortho* to CH_2CH-(Et), J = 8.25 Hz), 7.40 (d, 34H, *meta* to CH_2CH(Et) on the biphenyl, J = 8.35 Hz), 7.42 (m, 10H, $C_6H_5CH_2$), 7.49 (d, 34H, *meta* to O on the biphenyl, J = 8.48 Hz).

Synthesis of 1-Bromodecanol (20). A mixture of 1,10-dihydroxydecane (**19**) (44 g, 0.22 mol), HBr (48%, 12.5 mL), and C_6H_6 (200 mL) was stirred at reflux for 12h in a 500 mL one-neck flask equipped with a condenser and a Dean-Stark apparatus.[19] The organic phase was washed with H_2O, dilute $NaHCO_3$, and H_2O and dried over $MgSO_4$. The solvent was distilled and the product purified by column chromatography (SiO_2, hexanes, then CH_2Cl_2) and distillation to yield 20.26 g (38%) of **5**. Purity (GC) 99%. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.3 (m, 12H, Br$(CH_2)_2$(C*H*$_2$)$_6$$(CH_2)_2$OH), 1.56 (m, 2H, C*H*$_2CH_2$Br), 1.85 (m, 2H, C*H*$_2CH_2$OH), 3.41 (t, 3H, C*H*$_2$Br, J = 6.88 Hz), 3.64 (t, 2H, C*H*$_2$OH, J = 6.60 Hz).

Synthesis of 1-(4-(Benzyloxy)-4′-biphenylyl)-2-(4-((hydroxydecyl)oxy)phenyl)butane (21, *i.e.* TPB-(l)10(1)/-Bn,-$(CH_2)_{10}$OH, a mixture of constitutional isomers). To a stirred mixture of **2** (13.9 g, 34.3 mmol), K_2CO_3 (8.21 g, 60 mmol), and DMF (200 mL) was added dropwise a solution of **20** (12.5 g, 5.21 mmol) in DMF (20 mL) at 60 °C under N_2. After 12 h the reaction mixture was poured into H_2O, acidified, and extracted with CH_2Cl_2 (3×, 200 mL). The organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was distilled, and the product was purified by column chromatography (SiO_2, CH_2Cl_2) followed by recrystallization from hexanes to yield 13.4 g (64%) of **21**. Mp (DSC) 107 °C. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.79 (t, 3H, C*H*$_3$, J = 6.75 Hz), 1.34 (m, 12H, O$(CH_2)_2$(C*H*$_2$)$_6$$(CH_2)_2$OH), 1.82 (m, 6H; 2H, C*H*$_2$CH$_3$, 4H, OCH$_2$C*H*$_2$$(CH_2)_6$C*H*$_2CH_2$OH), 2.67 (m, 1H, CH$_2$C*H*(Et), J = 7.35 Hz), 2.86 (d, 2H, C*H*$_2$CH(Et), J = 6.98 Hz), 3.64 (t, 2H, C*H*$_2$OH, J = 6.88 Hz), 3.97 (m, 2H, CH$_2$C*H*$_2$OPh), 5.04 and 5.11 (s, 2H, C*H*$_2$$C_6H_5$), 6.82 (d, 1H, *ortho* to OCH$_2$CH$_2$ on the monophenyl, J = 7.88 Hz), 6.87 (d, 1H, *ortho* to Bn on the monophenyl, J = 8.78 Hz), 6.97 (d, 2H, *meta* to OCH$_2$ on the monophenyl, J = 8.55 Hz), 7.09 (d, 2H, *ortho* to CH_2CH(Et) on the biphenyl, J = 8.34 Hz), 7.45 (m, 9H; 2H, *meta* to CH_2O on the biphenyl, 2H, *meta* to CH_2CH(Et) on the biphenyl, and 5H of the Bn group). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.11 (*C*H$_3$), 26.11−29.33 (HOCH$_2$(*C*H$_2$)$_7$$(CH_2)_2$O and *C*H$_2CH_3$), 32.88 (OCH$_2$*C*H$_2$$(CH_2)_8$OH), 43.23 (*C*H$_2$CH(Et)), 48.88 (CH$_2$*C*H(Et)), 63.01 (*C*H$_2$OH), 67.02 ($C_6H_4$O*C*H$_2CH_2$), 70.09 ($C_6H_5$*C*H$_2$-$OC_6H_4$), 114.23 (*ortho* to OCH$_2$CH$_2$ on the monophenyl), 114.60 (*ortho* to Bn on the monophenyl), 114.72 (*ortho* to OCH$_2$ on the biphenyl), 115.14 (*ortho* to Bn on the biphenyl), 126.28 (*meta* to CH_2CH(Et) on the biphenyl), 127.49 (*ortho* to OCH$_2$ on C_6H_5), 127.58 (*meta* to CH_2O on C_6H_5), 128.69 (*meta* to Bn on the biphenyl), 128.75 (*para* to CH_2O on C_6H_5), 133.51 (*para* to Bn on the biphenyl), 136.93 (*para* to CH_2CH(Et) on the biphenyl), 137.32 (*ipso* to CH(Et) on the monophenyl), 138.20 (*ipso* to OCH$_2$ on C_6H_5), 139.79 (*ipso* to CH_2CH(Et) on the biphenyl), 157.08 (*ipso* to O$(CH_2)_{10}$ on the monphenyl), 157.37 (*ipso* to O$(CH_2)_{10}$ on the biphenyl), 158.19 (*ipso* to Bn on the biphenyl), 158.57 (*ipso* to Bn on the biphenyl).

Synthesis of 1-(4-(Benzyloxy)-4′-biphenylyl)-2-(4-((hydroxydecyl)oxy)phenyl)butane (22, *i.e.* TPB-(l)10(1)/-OH,-$(CH_2)_{10}$OH, a mixture of constitutional isomers). A mixture of **21** (6.5 g, 10.3 mmol), Pd/C (0.6 g), and THF (100 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under an H_2 atmosphere at 60 °C for 12 h. The solution was filtered, and the product was purified by flash column chromatography (SiO_2, MeOH) and recrystallized from hexane/toluene (1/1) to yield 4.03 g (85%) of **22**. Purity (HPLC) 99%. Mp (DSC) 91 °C. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 3H, CH$_3$, J = 7.28 Hz), 1.31 (m, 12H, O(CH$_2$)(C*H*$_2$)$_6$$(CH_2)_2$OH), 1.77 (m, 6H; 4H, OCH$_2$C*H*$_2$(C*H*$_2$)$_6$C*H*$_2$CH$_2$OH, 2H, C*H*$_2$CH$_3$), 2.68 (m, 1H, CH$_2$C*H*(Et)), 2.87 (d, 2H, C*H*$_2$CH(Et), J = 7.37 Hz), 3.64 (t, 2H, C*H*$_2$OH, J = 6.88 Hz), 3.95 (m, 2H, CH$_2$C*H*$_2$OC_6H_4), 6.80 (d, 2H, *ortho* to OCH$_2$ on the biphenyl, J = 8.76 Hz), 6.88 (d, 2H, *ortho* to OH on the biphenyl, J = 8.71 Hz), 6.99 (d, 2H, *meta* to OCH$_2$ on the monophenyl, J = 8.56 Hz), 7.01 (d, 2H, *ortho* to CH_2CH(Et) on the biphenyl, J = 8.11 Hz), 7.38 (d, 2H, *meta* to CH_2CH(Et) on the biphenyl, J = 8.18 Hz), 7.45 (d, 2H, *meta* to OH, J = 8.48 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.25 (*C*H$_3$), 26.19−29.48 (HOCH$_2$(*C*H$_2$)$_7$$(CH_2)_2$O and *C*H$_2CH_3$), 32.95 (*C*H$_2CH_2$O), 43.37 (*C*H$_2$CH(Et)), 48.96 (CH$_2$*C*H(Et)), 63.15 (*C*H$_2$OH), 68.09 ($C_6H_4OCH_2CH_2$), 68.07 ($C_6H_4OCH_2CH_2$), 114.36 (*ortho* to OCH$_2$ on the monophenyl), 114.84 (*ortho* to CH_2O on the biphenyl), 115.14 (*ortho* to OH on the monophenyl), 115.69 (*ortho* to OH on the biphenyl), 133.93 (*para* to OH on the biphenyl), 137.07 (*para* to CH_2CH-(Et) on the biphenyl), 138.15 (*ipso* to CH_2CH(Et) on the monophenyl), 139.66 (*ipso* to CH_2CH(Et) on the biphenyl), 154.92 (*ipso* to OH on the biphenyl), 157.39 (*ipso* to OCH$_2$CH$_2$ on the monophenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-((hydroxydecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (23, *i.e.* TPB-(l)10(2)/-Bn,-$(CH_2)_{10}$OH, a mixture of constitutional isomers). A mixture of **22** (4.18 g, 8.82 mmol), **3** (5.32 g, 8.48 mmol), K_2CO_3 (1.46 g, 10.6 mmol), and DMF (100 mL) was stirred under N_2 at 60 °C for 12 h and then was diluted with CH_2Cl_2 (300 mL), and the organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatograpy (SiO_2, EtOAc/hexanes = 1/2) to yield 5.43 g (65%) of **23**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 6H, C*H*$_3$, J = 7.24 Hz), 1.33 (m, 24H, O$(CH_2)_2$(C*H*$_2$)$_6$$(CH_2)_2$O), 1.76 (m 12H; 4H C*H*$_2CH_3$, 8H, OCH$_2$C*H*$_2$$(CH_2)_6$C*H*$_2CH_2$O), 2.68 (m, 2H, CH$_2$C*H*(Et)), 2.86 (d, 4H, C*H*$_2$CH(Et), J = 7.27 Hz), 3.64 (t, 2H, C*H*$_2$OH, J = 6.42 Hz), 3.96 (m, 6H, OC*H*$_2$-$(CH_2)_8$C*H*$_2$O), 5.04 and 5.11 (s, 2H, C_6H_5C*H*$_2$O), 6.79 (d, 4H, *ortho* to OCH$_2$ on the monophenyl, J = 8.42 Hz), 6.95 (d, 4H, *ortho* to OCH$_2$, J = 8.78 Hz), 7.04 (d, 4H, *meta* to O on the monophenyl, J = 8.35 Hz), 7.08 (d, 4H, *ortho* to C*H*$_2$CH(Et), J = 8.10 Hz), 7.40 (m, 8H; 4H *meta* to C*H*$_2$CH(Et) on the biphenyl, 2H, *ortho* to CH_2O on the Bn, 2H, *meta* to CH_2O on the Bn), 7.48 (m, 5H; 4H, *meta* to OCH$_2$ on the biphenyl, 1H, *para* to CH_2O on Bn). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.14 (*C*H$_3$), 26.25−29.45 (OCH$_2$CH$_2$$(CH_2)_6CH_2CH_2$O and *C*H$_2CH_3$), 32.85 (OCH$_2$*C*H$_2$), 43.27 (*C*H$_2$CH(Et)), 48.92 (CH$_2$*C*H(Et)), 63.10 (*C*H$_2$OH), 67.98 (O*C*H$_2CH_2$), 70.09 ($C_6H_5$*C*H$_2$O) 114.18 (*ortho* to CH_2O on the monophenyl), 114.75 (*ortho* to CH_2O on the biphenyl), 126.28 (*meta* to CH_2CH(Et) on the biphenyl), 127.48 (*ortho* to CH_2 on Bn), 127.55 (*meta* to OCH$_2$ on the monophenyl), 128.63 (*ortho* to CH_2CH(Et) on the biphenyl), 129.48 (*meta* to CH_2O on the biphenyl), 133.38 (*para* to CH_2O on the biphenyl), 136.88 (*ipso* to CH_2CH(Et) on the biphenyl), 138.08 (*ipso* to CH_2CH(Et) on the monophenyl), 139.45 (*ipso* to CH_2O on C_6H_5), 157.45 (*ipso* to CH_2O on the monophenyl), 158.51 (*ipso* to CH_2O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-hydroxy-4′-biphenylyl)-ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-((hydroxydecyl)-oxy)phenyl)ethyl)-4′-biphenylyl)decane (24, *i.e.* TPB-(l)-10(2)/-OH,-$(CH_2)_{10}$OH, a mixture of constitutional isomers). A mixture of **23** (2.7 g, 2.64 mmol), Pd/C (0.3 g), and THF (80 mL) was repeatedly vacuumed, flushed with H_2, and then stirred under an H_2 atmosphere at 60 °C for 12 h. The

solution was filtered, the solvent was evaporated, and the product was purified by column chromatography (SiO_2, CH_2Cl_2) to yield 2.3 g (93%) of **24**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.76 (t, 6H, C*H*$_3$, $J = 7.28$ Hz), 1.32 (m, 24H, O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O), 1.72 (m, 12; 4H, C*H*$_2$CH$_3$, 8H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.67 (m, 2H, CH$_2$C*H*(Et)), 2.87 (d, 4H, C*H*$_2$CH(Et), $J = 7.86$ Hz), 3.65 (t, 2H, C*H*$_2$OH, $J = 6.86$ Hz), 3.96 (m, 6H, OC*H*$_2$CH$_2$), 4.58 and 4.79 (s, 1H, O*H*), 6.74 (d, 2H, *ortho* to OH on the monophenyl, $J = 8.62$ Hz), 6.82 (d, 2H *ortho* to OCH$_2$ on the monophenyl, $J = 8.21$ Hz), 6.88 (d, 2H, *ortho* to OH on the biphenyl, $J = 8.69$ Hz), 6.94 (d, 2H, *ortho* to OCH$_2$ on the biphenyl, $J = 8.81$ Hz), 7.03 (d, 4H, *meta* to O on the monophenyl, $J = 7.86$ Hz), 7.07 (d, 4H, *ortho* to CH$_2$C*H*(Et), on the biphenyl, $J = 8.05$ Hz), 7.42 (d, 4H, *meta* to CH$_2$C*H*(Et) on the biphenyl, $J = 8.28$ Hz), 7.48 (d, 4H, *meta* to O on the biphenyl, $J = 8.72$ Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.15 (*C*H$_3$), 26.08−29.40 (OCH$_2$CH$_2$(*C*H$_2$)$_6$CH$_2$CH$_2$O, *C*H$_2$CH$_3$), 30.85 (OCH$_2$*C*H$_2$), 43.25 (CH$_2$*C*H(Et)), 48.93 (*C*H$_2$CH(Et)), 63.18 (*C*H$_2$OH), 67.94 (O*C*H$_2$CH$_2$ on the monophenyl), 68.15 (O*C*H$_2$CH$_2$ on the biphenyl), 114.21 (*ortho* to O on the monophenyl), 114.68 (*ortho* to O on the biphenyl), 126.28 (*meta* to (CH$_2$CH(Et) on the biphenyl), 127.66 (*meta* to O on the monophenyl), 128.47 (*ortho* to CH$_2$CH(Et) on the biphenyl), 129.38 (*meta* to O on the biphenyl), 133.66 (*para* to O on the biphenyl), 137.11 (*para* to CH$_2$CH(Et) on the biphenyl), 139.18 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.74 (*ipso* to CH$_2$CH(Et) on the bipheny), 155.05 (*ipso* to O on the monophenyl), 157.86 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((methanesulfonyloxy)decyl)oxy)phenyl))ethyl)-4′-biphenylyl)decane (25, *i.e.* TPB-(l)10(2)/-Bn,-(CH$_2$)$_{10}$OMs, a mixture of constitutional isomers). To a solution of **23** (2.7 g, 2.64 mmol) in CH_2Cl_2/Py (1/1, 100 mL) was added dropwise a solution of methanesulfonyl choride in pyridine (20 mL) at 0 °C. The reaction mixture was allowed to stir for 3 h at 25 °C and then was acidified, washed with H_2O, and dried over $MgSO_4$. The solvent was evaporated, and the product was precipitated in MeOH, filtered, dried, and then recrystallized from hexanes to yield 2.4 g (83%) of **25**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 6H, C*H*$_3$, $J = 7.26$ Hz), 1.33 (m, 24H, O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O), 1.77 (m 12H; 4H C*H*$_2$CH$_3$, 8H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.68 (m, 2H, CH$_2$C*H*(Et)), 2.86 (d, 4H, C*H*$_2$CH(Et), $J = 7.29$ Hz), 3.01 (s, 3H, SO$_2$C*H*$_3$), 3.96 (m, 6H, OC*H*$_2$(CH$_2$)$_8$C*H*$_2$O), 4.22 (t, 2H, C*H*$_2$OMs, $J = 6.60$ Hz), 5.04 and 5.11 (s, 2H, C$_6$H$_5$C*H*$_2$O), 6.79 (d, 4H, *ortho* to OCH$_2$ on the monophenyl, $J = 8.45$ Hz), 6.95 (d, 4H, *ortho* to OCH$_2$, $J = 8.76$ Hz), 7.04 (d, 4H, *meta* to O on the monophenyl, $J = 8.38$ Hz), 7.08 (d, 4H, *ortho* to C*H*$_2$CH(Et), $J = 8.15$ Hz), 7.40 (m, 8H; 4H *meta* to C*H*$_2$CH(Et) on the biphenyl, 2H, *ortho* to CH$_2$O on the Bn, 2H, *meta* to CH$_2$O on the Bn), 7.48 (m, 5H; 4H *meta* to OCH$_2$ on the biphenyl, 1H, *para* to CH$_2$O on Bn). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.18 (*C*H$_3$), 26.55−29.88 (OCH$_2$CH$_2$(*C*H$_2$)$_6$CH$_2$CH$_2$O and *C*H$_2$CH$_3$), 32.88 (OCH$_2$*C*H$_2$), 38.79 (OSO$_2$*C*H$_3$), 43.54 (*C*H$_2$CH(Et)), 48.68 (CH$_2$*C*H(Et)), 67.84 (O*C*H$_2$CH$_2$), 70.12 (C$_6$H$_5$*C*H$_2$O), 83.22 (*C*H$_2$OSO$_2$CH$_3$), 114.21 (*ortho* to CH$_2$O on the monophenyl), 114.75 (*ortho* to CH$_2$O on the biphenyl), 126.36 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.77 (*ortho* to CH$_2$ on Bn), 127.44 (*meta* to OCH$_2$ on the monophenyl), 128.29 (*ortho* to CH$_2$CH(Et) the biphenyl), 129.55 (*meta* to CH$_2$O on the biphenyl), 133.41 (*para* to CH$_2$O on the biphenyl), 136.75 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.12 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.52 (*ipso* to CH$_2$O on C$_6$H$_5$), 157.48 (*ipso* to CH$_2$O on the monophenyl), 158.52 (*ipso* to CH$_2$O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((hydroxydecyl)oxy)phenyl)ethyl)-4′-biphenylyl)-oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (26, *i.e.* TPB-(l)10(4)/-Bn,-(CH$_2$)$_{10}$OH, a mixture of constitutional isomers). A mixture of **24** (2.29 g, 2.46 mmol), **25** (1.82 g, 2.64 mmol), K_2CO_3 (1.7 mmol, 7.8 mmol), and DMF (75 mL) was stirred under N_2 at 60 °C for 14 h and then poured into H_2O (300 mL), acidified (10% HCl, 100 mL), and extracted with CH_2Cl_2 (3×, 200 mL). The organic phase was washed with H_2O and dried over $MgSO_4$, and the solvent was evaporated. Purification by column chromatography (SiO_2, EtOAc/hexanes, 1/3) followed by recrystallization from hexanes afforded 2.12 g (67%) of **26**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, C*H*$_3$, $J = 7.28$ Hz), 1.33 (m, 48H, O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O), 1.77 (m, 24H; 8H, C*H*$_2$CH$_3$, 16H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.67 (m, 4H, CH$_2$C*H*(Et)), 2.88 (d, 8H, C*H*$_2$CH(Et), $J = 7.18$ Hz), 3.63 (t, 2H, C*H*$_2$OH, $J = 6.88$ Hz), 3.96 (m, 14H, OC*H*$_2$(CH$_2$)$_8$C*H*$_2$O), 5.04 and 5.11 (s, 2H, C$_6$H$_5$C*H*$_2$O), 6.80 (d, 8H, *ortho* to O on the monophenyl, $J = 8.68$ Hz), 6.93 (d, 8H, *ortho* to O on the biphenyl, $J = 8.85$ Hz), 7.04 (d, 8H, *meta* to O on the monophenyl, $J = 8.06$ Hz), 7.07 (d, 8H, *ortho* to CH$_2$CH(Et) on the biphenyl, $J = 8.08$ Hz), 7.40 (d, 8H, *meta* to CH$_2$CH(Et) on the biphenyl, $J = 8.20$ Hz), 7.49 (d, 8H, *meta* to O on the biphenyl, $J = 8.76$ Hz), 7.40−7.51 (m, 5H, OCH$_2$C$_6$*H*$_5$). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.15 (*C*H$_3$), 26.12−29.69 (O(CH$_2$)$_2$(*C*H$_2$)$_6$(CH$_2$)$_2$O and *C*H$_2$CH$_3$), 32.88 (OCH$_2$*C*H$_2$), 43.24 (*C*H$_2$CH(Et)), 48.86 (CH$_2$*C*H(Et)), 63.24 (*C*H$_2$OH), 68.10 (C$_6$H$_4$O*C*H$_2$CH$_2$), 70.11 (C$_6$H$_5$*C*H$_2$O), 114.88 (*ortho* to O on the monophenyl), 114.68 (*ortho* to O on the biphenyl), 126.34 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.55−127.81 (*ortho* and *para* to CH$_2$O on Bn), 126.22 (*meta* to O on the monophenyl), 127.93 (*ortho* to CH$_2$CH(Et) on the biphenyl), 128.87 (*meta* to O on the biphenyl), 133.49 (*para* to O on the biphenyl), 136.96 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.18 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.46 (*ipso* to CH$_2$ on C$_6$H$_5$), 157.45 (*ipso* to O on the monophenyl), 158.48 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-hydroxy-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)-ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((hydroxydecyl)oxy)phenyl)ethyl)-4′-biphenylyl)-oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (27, *i.e.* TPB-(l)10(4)/-OH,-(CH$_2$)$_{10}$OH, a mixture of constitutional isomers). A mixture of **26** (1 g, 0.51 mmol), Pd/C (0.2 g), and THF (50 mL) was repeatedly vacuumed and flushed with H_2 and then was stirred under an H_2 atmosphere at 60 °C for 12 h. The solution was filtered, the solvent was evaporated, and the product was purified by flash column chromatography (SiO_2, EtOAc/hexanes 1/2) to yield 0.7 g (76%) of **27**. Purity (HPLC) 98.9%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, C*H*$_3$, $J = 7.28$ Hz), 1.33 (m, 48H, O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O), 1.77 (m, 24H; 8H, C*H*$_2$CH$_3$, 16H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.67 (m, 4H, CH$_2$C*H*(Et)), 2.88 (d, 8H, C*H*$_2$CH(Et), $J = 7.18$ Hz), 3.64 (t, 2H, C*H*$_2$OH, $J = 6.85$ Hz), 3.96 (m, 14 H, OC*H*$_2$(CH$_2$)$_8$C*H*$_2$O), 6.80 (d, 8H, *ortho* to O on the monophenyl, $J = 8.74$ Hz), 6.93 (d, 8H, *ortho* to O on the biphenyl, $J = 8.66$ Hz), 7.04 (d, 8H, *meta* to O on the monophenyl, $J = 8.10$ Hz), 7.07 (d, 8H, *ortho* to CH$_2$CH(Et) on the biphenyl, $J = 8.12$ Hz), 7.40 (d, 8H, *meta* to CH$_2$CH(Et) on the biphenyl, $J = 8.15$ Hz), 7.49 (d, 8H, *meta* to O on the biphenyl, $J = 8.76$ Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.18 (*C*H$_3$), 26.21−29.80 (O(CH$_2$)$_2$(*C*H$_2$)$_6$(CH$_2$)$_2$O and *C*H$_2$CH$_3$), 32.52 (OCH$_2$*C*H$_2$), 43.78 (*C*H$_2$CH(Et)), 48.22 (CH$_2$*C*H(Et)), 63.24 (*C*H$_2$OH), 68.10 (C$_6$H$_4$O*C*H$_2$CH$_2$), 114.54 (*ortho* to O on the monophenyl), 114.21 (*ortho* to O on the biphenyl), 126.18 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.18 (*meta* to O on the monophenyl), 127.99 (*ortho* to CH$_2$CH(Et) on the biphenyl), 128.55 (*meta* to O on the biphenyl), 133.25 (*para* to O on the biphenyl), 136.84 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.22 (*ipso* to CH$_2$CH(Et) on the monophenyl), 157.28 (*ipso* to O on the monophenyl), 158.67 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-(((methanesulfonyloxy)decyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)-decane (28, *i.e.* TPB-(l)10(4)/-Bn,-(CH$_2$)$_{10}$OMs, a mixture of constitutional isomers). To a solution of **26** (0.95 g, 0.49 mmol) in Py/CH_2Cl_2 (50 mL, 1/3) was added dropwise a solution of MsCl (0.11 g, 1 mmol) in Py (10 mL) under N_2 at 0 °C, and the mixture was stirred for 3 h at 25 °C and then was poured into H_2O, acidified, and extracted with CH_2Cl_2 (3×, 100

mL). The organic phase was washed with H_2O, dried over $MgSO_4$, concentrated on a rotary evaporator, and precipitated into MeOH. The precipitate was filtered and dried to yield 0.83 g (84%) of **28**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 12H, CH_3, J = 7.28 Hz), 1.33 (m, 48H, O(CH_2)$_2$(CH_2)$_6$(CH_2)$_2$O), 1.77 (m 12H; 8H CH_2CH$_3$, 16H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O), 2.68 (m, 4H, CH$_2$CH(Et)), 2.86 (d, 8H, CH_2CH(Et), J = 7.31 Hz), 3.01 (s, 3H, SO$_2$CH_3), 3.96 (m, 14H, OCH_2(CH$_2$)$_8$CH_2O), 4.22 (t, 2H, CH_2OMs, J = 6.64 Hz), 5.04 and 5.11 (s, 2H, C$_6$H$_5$CH_2O), 6.80 (d, 8H, *ortho* to O on the monophenyl, J = 8.51 Hz), 6.94 (d, 8H, *ortho* to O on the biphenyl, J = 8.26 Hz), 7.04 (d, 8H, *meta* to O on the monophenyl, J = 8.08 Hz), 7.08 (d, 8H, *ortho* to CH$_2$CH(Et) on the biphenyl, J = 8.12 Hz), 7.40 (d, 8H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.05 Hz), 7.50 (d, 8H, *meta* to O on the biphenyl, J = 8.25 Hz), 7.40−7.51 (m, 5H, OCH$_2$C$_6$H$_5$). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.22 (*C*H$_3$), 26.21−29.66 (OCH$_2$CH$_2$(*C*H$_2$)$_6$CH$_2$CH$_2$O and *C*H$_2$CH$_3$), 32.55 (OCH$_2$*C*H$_2$), 38.55 (OSO$_2$*C*H$_3$), 43.33 (*C*H$_2$CH(Et)), 48.87 (CH$_2$*C*H(Et)), 67.85 (O*C*H$_2$CH$_2$), 70.12 (C$_6$H$_5$*C*H$_2$O), 114.11 (*ortho* to CH$_2$O on the monophenyl), 114.63 (*ortho* to CH$_2$O on the biphenyl), 126.25 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.36 (*ortho* to CH$_2$ on Bn), 127.45 (*meta* to OCH$_2$ on the monophenyl), 128.29 (*ortho* to CH$_2$CH(Et) on the biphenyl), 129.58 (*meta* to CH$_2$O on the biphenyl), 133.34 (*para* to CH$_2$O on the biphenyl), 136.75 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.14 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.52 (*ipso* to CH$_2$O on C$_6$H$_5$), 157.28 (*ipso* to CH$_2$O on the monophenyl), 158.48 (*ipso* to CH$_2$O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-((((4-(1-ethyl-2-(4-(((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)-ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)-oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-((((4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((hydroxy-decyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)-phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)-decane (29, i.e. TPB-(l)10(8)/-Bn,-(CH$_2$)$_{10}$-OH, a mixture of constitutional isomers). A mixture of **27** (0.65 g, 0.35 mol), **28** (0.79 g, 0.39 mmol), K_2CO_3 (0.2 g, 1.45 mmol), and DMF (30 mL) was stirred at 60 °C under N_2 for 16 h and then was poured into H_2O, acidified, and extracted with CH_2Cl_2 (3×, 100 mL). The organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatography (SiO_2, CH_2Cl_2/hexanes 7/1) followed by precipitation from CH_2Cl_2 in acetone. The resulting solid was filtered and dried to yield 0.81 g (62%) of **29**. Purity (HPLC) 99%. Anal. Calcd for $C_{263}H_{328}O_{17}$: C, 83.98; H, 8.79. Found: C, 84.18; H, 8.82. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 24H, CH_3, J = 7.32 Hz), 1.33 (m, 96H, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$O), 1.78 (m, 46H; 16H, CH_2CH$_3$, 30H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O), 2.67 (m, 8H, CH$_2$CH(Et)), 2.88 (d, 16H, CH_2CH(Et), J = 7.11 Hz), 3.64 (t, 2H, CH_2OH, J = 6.28 Hz), 3.96 (m, 30H, OCH_2(CH$_2$)$_8$CH_2O), 5.04 and 5.11 (s, 2H, C$_6$H$_5$CH_2O), 6.80 (d, 16H, *ortho* to O on the monophenyl, J = 8.55 Hz), 6.94 (d, 16H, *ortho* to O on the biphenyl, J = 8.32 Hz), 7.04 (d, 16H, *meta* to O on the monophenyl, J = 8.08 Hz), 7.07 (d, 16H, *ortho* to CH$_2$CH(Et) on the biphenyl, J = 8.05 Hz), 7.40 (d, 16H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.16 Hz), 7.49 (d, 16H, *meta* to O on the biphenyl, J = 8.48 Hz), 7.40−7.51 (m, 5H, OCH$_2$C$_6$H$_5$). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.08 (*C*H$_3$), 25.78−29.21 (O(CH$_2$)$_2$(*C*H$_2$)$_6$(CH$_2$)$_2$O and *C*H$_2$CH$_3$), 32.28 (OCH$_2$*C*H$_2$), 42.86 (*C*H$_2$CH(Et)), 47.69 (CH$_2$*C*H(Et)), 63.45 (*C*H$_2$OH), 68.48 (C$_6$H$_4$O*C*H$_2$CH$_2$), 70.41 (C$_6$H$_5$*C*H$_2$O), 114.55 (*ortho* to O on the monophenyl), 114.70 (*ortho* to O on the biphenyl), 126.55 (*meta* to CH$_2$CH(Et) on the biphenyl), 127.22−127.93 (*ortho* and *para* to CH$_2$O on Bn), 126.52 (*meta* to O on the monophenyl), 127.52 (*ortho* to CH$_2$CH(Et) on the biphenyl), 128.48 (*meta* to O on the biphenyl), 133.21 (*para* to O on the biphenyl), 136.74 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.05 (*ipso* to CH$_2$CH(Et) on the monophenyl), 139.28 (*ipso* to CH$_2$ on C$_6$H$_5$), 157.11 (*ipso* to O on the monophenyl), 158.21 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-((((4-(1-ethyl-2-((((4-(1-ethyl-2-(4-(((4-(1-ethyl-2-(4-hydroxy-4′-biphenylyl)ethyl)-phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxa-decyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-((((4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((hydroxy-decyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)-phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-2-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)decane (30, i.e. TPB-(l)10(8)/-HO,-(CH$_2$)$_{10}$-OH, a mixture of constitutional isomers). A mixture of **29** (0.4 g, 0.1 mmol), Pd/C (0.08 g), and THF (25 mL) was repeatedly vacuumed and flushed with H_2 and then stirred under H_2 at 60 °C for 12 h. The solution was filtered, the solvent was evaporated, and the product was purified by column chromatography (SiO_2, CH_2Cl_2) followed by precipitation in acetone. The resulting solid was filtered and dried to yield 0.32 g (82%) of **30**. Purity (HPLC) 98.8%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 24H, CH_3, J = 7.48 Hz), 1.33 (m, 96H, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$O), 1.78 (m, 46H; 16H, CH_2CH$_3$, 30H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O), 2.67 (m, 8H, CH$_2$CH(Et)), 2.88 (d, 16H, CH_2CH(Et), J = 7.11 Hz), 3.64 (t, 2H, CH_2OH, J = 6.36 Hz), 3.97 (m, 30H, OCH_2(CH$_2$)$_8$CH_2O), 6.80 (d, 16H, *ortho* to O on the monophenyl, J = 8.42 Hz), 6.94 (d, 16H, *ortho* to O on the biphenyl, J = 8.28 Hz), 7.04 (d, 16H, *meta* to O on the monophenyl, J = 8.10 Hz), 7.07 (d, 16H, *ortho* to CH$_2$CH(Et) on the biphenyl, J = 8.12 Hz), 7.40 (d, 16H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.24 Hz), 7.49 (d, 16H, *meta* to O on the biphenyl, J = 8.48 Hz). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.14 (*C*H$_3$), 25.55−29.35 (O(CH$_2$)$_2$(*C*H$_2$)$_6$(CH$_2$)$_2$O and *C*H$_2$CH$_3$), 32.24 (OCH$_2$*C*H$_2$), 42.47 (*C*H$_2$CH(Et)), 47.88 (CH$_2$*C*H(Et)), 63.21 (*C*H$_2$OH), 68.48 (C$_6$H$_4$O*C*H$_2$CH$_2$), 114.28 (*ortho* to O on the monophenyl), 114.74 (*ortho* to O on the biphenyl), 126.26 (*meta* to CH$_2$CH(Et) on the biphenyl), 126.41 (*meta* to O on the monophenyl), 127.24 (*ortho* to CH$_2$CH(Et) on the biphenyl), 128.53 (*meta* to O on the biphenyl), 133.34 (*para* to O on the biphenyl), 136.55 (*ipso* to CH$_2$CH(Et) on the biphenyl), 138.17 (*ipso* to CH$_2$CH(Et) on the monophenyl), 157.04 (*ipso* to O on the monophenyl), 158.28 (*ipso* to O on the biphenyl).

Synthesis of 1-((4-(1-Ethyl-2-(4-((((1-ethyl-2-(4-((((1-ethyl-2-(4-(((4-(1-ethyl-2-(4-(benzyloxy)-4′-biphenylyl)eth-yl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)ox-adecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxadecyl)oxy)-4′-biphenylyl)ethyl)phenyl)oxy)-10-(4-(2-ethyl-2-(4-(((4-(2-ethyl-2-((((4-(2-ethyl-2-(4-(((4-(2-ethyl-2-(4-((hydroxy-decyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)-phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)oxadecyl)oxy)phenyl)ethyl)-4′-biphenylyl)-decane (31, i.e. TPB-(l)10(8)/-Bn,-(CH$_2$)$_{10}$-OMs, a mixture of constitutional isomers). To a solution of **29** (0.4 g, 0.1 mmol) in CH_2Cl_2/Py (3/11, 40 mL) was added dropwise a solution of MsCl (61 mg, 0.5 mmol) in Py (5 mL) under N_2 at 0 °C, and the mixture was stirred at 25 °C for 4 h. $H_2$0 (100 mL) and CH_2Cl_2 were then added, and the organic phase was washed with H_2O, dilute HCl, and H_2O and was dried over $MgSO_4$. The solution was concentrated and precipitated into acetone. The resulting solid was filtered and dried to yield 0.39 g (93%) of **31**. Purity (HPLC) 98.9%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 24H, CH_3, J = 7.20 Hz), 1.33 (m, 96H, O(CH$_2$)$_2$(CH_2)$_6$(CH$_2$)$_2$O), 1.77 (m, 40H; 16H, CH_2CH$_3$, 32H, OCH$_2$CH_2(CH$_2$)$_6$CH_2CH$_2$O), 2.68 (m, 8H, CH$_2$CH(Et)), 2.86 (d, 16H, CH_2CH(Et), J = 7.24 Hz), 3.01 (s, 3H, SO$_2$CH_3), 3.96 (m, 30H, OCH_2(CH$_2$)$_8$CH_2O), 4.22 (t, 2H, CH_2OMs, J = 6.58 Hz), 5.04 and 5.11 (s, 2H, C$_6$H$_5$CH_2O), 6.80 (d, 16H, *ortho* to O on the monophenyl, J = 8.48 Hz), 6.94 (d, 16H, *ortho* to O on the biphenyl, J = 8.18 Hz), 7.04 (d, 16H, *meta* to O on the monophenyl, J = 8.12 Hz), 7.08 (d, 16H, *ortho* to CH$_2$CH(Et) on the biphenyl, J = 8.14 Hz), 7.40 (d, 16H, *meta* to CH$_2$CH(Et) on the biphenyl, J = 8.08 Hz), 7.50 (d, 16H, *meta* to O on the biphenyl, J = 8.25 Hz), 7.41−7.52 (m, 5H, OCH$_2$C$_6$H$_5$). ^{13}C-NMR ($CDCl_3$, TMS, δ, ppm): 12.12 (*C*H$_3$), 26.36−29.68 (OCH$_2$CH$_2$(*C*H$_2$)$_6$CH$_2$CH$_2$O and *C*H$_2$CH$_3$), 32.75 (OCH$_2$*C*H$_2$), 38.32 (OSO$_2$*C*H$_3$), 43.38 (*C*H$_2$CH(Et)), 49.13 (CH$_2$*C*H(Et)), 68.05 (O*C*H$_2$CH$_2$), 70.11 (C$_6$H$_5$*C*H$_2$O), 114.05 (*ortho* to CH$_2$O on the

monophenyl), 114.14 (*ortho* to CH_2O on the biphenyl), 126.18 (*meta* to $CH_2CH(Et)$ on the biphenyl), 127.52 (*ortho* to CH_2 on Bn), 127.61 (*meta* to OCH_2 on the monophenyl), 128.75 (*ortho* to $CH_2CH(Et)$ on the biphenyl), 129.52 (*meta* to CH_2O on the biphenyl), 133.45 (*para* to CH_2O on the biphenyl), 136.96 (*ipso* to $CH_2CH(Et)$ on the biphenyl), 138.11 (*ipso* to $CH_2CH(Et)$ on the monophenyl), 139.33 (*ipso* to CH_2O on C_6H_5), 157.26 (*ipso* to CH_2O on the monophenyl), 158.58 (*ipso* to CH_2O on the biphenyl).

Synthesis of TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$-OH (32). A mixture of **30** (0.32 g, 0.085 mmol), **31** (0.39 g, 0.09 mmol), K_2CO_3 (0.15 g, 1.08 mmol), and DMF (50 mL) was stirred at 60 °C under N_2 for 18 h and then was poured into H_2O (100 mL), acidified (dilute HCl, 50 mL), and extracted with CH_2Cl_2 (3×, 75 mL). The organic phase was washed with H_2O and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatograpy (SiO_2, CH_2Cl_2/hexanes 3/1) followed by successive precipitation from CH_2Cl_2 into MeOH and then into an acetone/CH_2Cl_2 (1.5/1) mixture. The resulting solid was filtered and dried to yield 0.25 g (40%) of **32**. Purity (HPLC) 98.9%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 48H, C*H*$_3$, J = 7.26 Hz), 1.33 (m, 192H, O(C*H*$_2$)$_2$(C*H*$_2$)$_6$(C*H*$_2$)$_2$O), 1.78 (m, 96H; 32H, C*H*$_2$CH$_3$, 64H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.67 (m, 16H, CH$_2$C*H*(Et)), 2.88 (d, 32H, C*H*$_2$CH(Et), J = 7.24 Hz), 3.64 (t, 2H, C*H*$_2$OH, J = 6.32 Hz), 3.96 (m, 62H, OC*H*$_2$(CH$_2$)$_8$C*H*$_2$O), 5.04 and 5.11 (s, 2H, C_6H_5C*H*$_2$O), 6.80 (d, 32H, *ortho* to O on the monophenyl, J = 8.21 Hz), 6.94 (d, 32H, *ortho* to O on the biphenyl, J = 8.22 Hz), 7.04 (d, 32H, *meta* to O on the monophenyl, J = 8.14 Hz), 7.07 (d, 32H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.08 Hz), 7.40 (d, 32H, *meta* to $CH_2CH(Et)$ on the biphenyl, J = 8.12 Hz), 7.49 (d, 16H, *meta* to O on the biphenyl, J = 8.36 Hz), 7.40−7.51 (m, 5H, $OCH_2C_6H_5$).

Synthesis of TPB-(l)10(16)/-Bn,-$(CH_2)_{10}$Br (33). To a mixture of **32** (0.2 g, 0.027 mmol) and CBr_4 (90 mg) in THF (20 mL) was added dropwise a solution of PPh_3 (71 mg, 0.27 mmol) in THF (5 mL) at 0 °C and then the reaction mixture was stirred at room temperature for 12 h. H_2O (100 mL) and CH_2Cl_2 (100 mL) were added, and the organic phase was washed with H_2O, dilute HCl, and H_2O and dried over $MgSO_4$. The solvent was evaporated, and the product was purified by successive precipitations from CH_2Cl_2 first into MeOH then into an acetone/CH_2Cl_2 (1.5/1) mixture. The resulting solid was filtered and dried to yield 0.18 g (88%) of **33**. Purity (HPLC) 98.8%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 48H, C*H*$_3$, J = 7.33 Hz), 1.33 (m, 192H, O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O), 1.78 (m, 96H; 32H, C*H*$_2$CH$_3$, 64H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.67 (m, 16H, CH$_2$C*H*(Et)), 2.88 (d, 32H, C*H*$_2$CH(Et), J = 7.19 Hz), 3.41 (t, 2H, C*H*$_2$Br, J = 6.58 Hz), 3.96 (m, 62H, OC*H*$_2$(CH$_2$)$_8$C*H*$_2$O), 5.04 and 5.11 (s, 2H, C_6H_5C*H*$_2$O), 6.80 (d, 32H, *ortho* to O on the monophenyl, J = 8.18 Hz), 6.94 (d, 32H, *ortho* to O on the biphenyl, J = 8.48 Hz), 7.04 (d, 32H, *meta* to O on the monophenyl, J = 8.18 Hz), 7.07 (d, 32H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.16 Hz), 7.40 (d, 32H, *meta* to $CH_2CH(Et)$ on the biphenyl, J = 8.24 Hz), 7.49 (d, 32H, *meta* to O on the biphenyl, J = 8.28 Hz), 7.40−7.51 (m, 5H, $OCH_2C_6H_5$).

Synthesis of TPB-(l)10(33)/-Bn,-Bn (34). A mixture of **33** (175 mg, 0.023 mmol), **1** (3.65 mg, 0.014 mmol), TBAH (1.5 mg, 0.005 mmol), *o*-DCB (0.3 mL), and NaOH (10N, 0.3 mL) was stirred under N_2 at 80 °C for 6 h. CH_2Cl_2 (50 mL) and H_2O (50 mL) were added, and the organic phase was washed with H_2O and dilute HCl and was dried over $MgSO_4$. After purification by column chromatography (SiO_2, CH_2Cl_2/hexanes = 1.5/1) followed by a series of preparative TLC plates (SiO_2, CH_2Cl_2/hexanes = 2/1) the product was precipitated from CH_2Cl_2: first into MeOH and then into acetone. The resulting solid was filtered and dried to yield 43 mg (25%) of **34**. Purity (HPLC) 99%. Thermal transitions are reported in Table 1. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.77 (t, 99H, C*H*$_3$, J = 7.28 Hz), 1.33 (m, 384H, O(CH$_2$)$_2$(C*H*$_2$)$_6$(CH$_2$)$_2$O), 1.78 (m, 194H; 66H, C*H*$_2$CH$_3$, 128H, OCH$_2$C*H*$_2$(CH$_2$)$_6$C*H*$_2$CH$_2$O), 2.67 (m, 33H, CH$_2$C*H*(Et)), 2.88 (d, 66H, C*H*$_2$CH(Et), J = 7.25 Hz), 3.96 (m, 128H, OC*H*$_2$(CH$_2$)$_8$C*H*$_2$O), 5.04 and 5.11 (s, 4H, C_6H_5C*H*$_2$O), 6.80 (d, 66H, *ortho* to O on the monophenyl, J = 8.20 Hz), 6.94 (d, 66H, *ortho* to O on the biphenyl, J = 8.52 Hz), 7.04 (d, 66H, *meta* to O on the monophenyl, J = 8.22 Hz), 7.07 (d, 66H, *ortho* to $CH_2CH(Et)$ on the biphenyl, J = 8.08 Hz), 7.40 (d, 66H, *meta* to $CH_2CH(Et)$ on the biphenyl, J = 8.28 Hz), 7.49 (d, 66H, *meta* to O on the biphenyl, J = 8.32 Hz), 7.40−7.51 (m, 10H, $OCH_2C_6H_5$).

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